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# Characterization of early-age hydration process of cement pastes based on impedance measurement

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## HIGHLIGHTS

- The hydration process of cement pastes is evaluated by XRD, FTIR and NCIM.
- Hydration behaviors are interpreted by FTIR, XRD and NCIM.
- Influences of mineral admixture and curing temperature are studied.
- Compressive strength and impedance data have a good linear relation.

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## ABSTRACT

This paper investigates the hydration process of cement pastes using an isothermal calorimetry, Fourier transforms infrared spectroscopy (FTIR), X-ray diffraction (XRD) analysis and non-contact impedance measurement (NCIM). The reliability of impedance data from NCIM is checked by classical Kramers–Kronig transformation. Hydration behaviors of pure cement paste in different stages (dissolution, competition and acceleration stages) are interpreted by FTIR, XRD and NCIM. Influences of water to cement ratios, fly ash, slag, silica fume and curing temperature are investigated by compressive strength test and NCIM. It is found that the compressive strength and impedance data have a good linear relationship.



## 1. Introduction

Cement-based materials are by far the most important building materials. More than 10 billion-ton of cement is produced each year [1]. The hydration of cement-based materials is the key issue in the practical applications, it usually involves in complex physical–chemical transformations, for instances, ion dissolving, hydration products generation and microstructure forming [2]. The calorimetric method traditionally provides an in-situ way to understand cement hydration. The mechanism and stages of hydration are interpreted and identified by heat liberation [3]. However, some drawbacks of this method were pointed out, such as inappropriate test conditions and over-simple theoretical assumption [3].

In this work, the hydration mechanisms of cement pastes is studied by Fourier transforms infrared spectroscopy (FTIR), X-ray diffraction (XRD) and non-contact impedance measurement (NCIM). It have been reported that NCIM has the potential to evaluate non-destructively the pore structure evolution of cement-based materials in-situ [4]. The reliability of impedance data from NCIM is checked via Kramers–Kronig transformation, which is widely used in electrical circuit analysis [5]. It is known that the mineral admixture (fly ash, slag and silica fume) and curing temperature have a great impact on the hydration of cement pastes [6–9]; this present work further studies the influences of different water to cement ratios, dosages of fly ash, slag, silica fume and curing temperature on the impedance response of hydrating cement pastes.

### 2. Experiments and methods

#### 2.1. Materials and mix proportion

In this study, ordinary Portland cement meeting the requirement of ASTM Type I and de-air water were used. Cement pastes with water to cement ratios (w/c) 0.3, 0.4 and 0.5 by mass were prepared in the environmental chamber with temperature

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(20 °C) and humidity (100%) and these pastes were noted as P3, P4 and P5. Besides, cement pastes with notations of P4F10, P4F20, were also prepared. P4F10 and P4F20 represented pastes having the water to binder ratio (w/b) of 0.4, in which 10% and 20% of cement were replaced by fly ash by mass under curing temperature 20 °C. Similar, P4S10 and P4S30 denoted that 10% and 30% of cement were replaced by slag and w/b ratio was 0.4; P4SF5 and P4SF10 with w/b ratio 0.4 represented that 5% and 10% of cement were replaced by silica fume. For different curing temperature cases, P4T10 and P4T30 were noted as cement pastes with w/c 0.4 under curing temperature 10 °C and 30 °C, respectively. These pastes were mixed in a planetary-type mixer at 45 rpm for 2 min first and then at 90 rpm for 2 min. The cement pastes were cured in the environmental chamber with relative humidity 100% for 3 days.

The chemical compositions of the cement, fly ash, slag and silica fume are given in Table 1.

The morphology of cement, fly ash, slag and silica fume is shown in Fig. 1.

### 2.2. Experimental tests

#### 2.2.1. Non-contact impedance measurement

The Non-Contact Impedance Measurement (NCIM) has been developed recently [10]. Its working mechanism and corresponding test procedure can be consulted in Ref. [4]. A series of resistor–capacitor and resistor–inductor series circuits have been used to inspect the accuracy of NCIM: the measured impedance responses can be perfectly coincident with the ones calculated by corresponding nominal values.

#### 2.2.2. Compressive strength test

The fresh cement pastes were cast into 4 cm × 4 cm × 4 cm molds for compressive strength tests at 1 day and 3 days. The tests were undertaken with a loading rate 1 kN/s.

#### 2.2.3. Heat evolution

The heat evolution of P4 was conducted using isothermal calorimetry. The fresh cement paste was injected into the glass ampoule of calorimetry via the syringe. The de-air water with the same weight as P4, was also injected into the other glass ampoule as a reference. The heat release of P4 was recorded continuously with hydration time in one day.

#### 2.2.4. Fourier transforms infrared spectroscopy

The hydration of P4 was stopped after particular periods of time by successively immersing the crushed pastes into ethyl alcohol and drying them in a vacuum chamber (with 20% relative humidity at 20 ± 2 °C) for 3 days. The Fourier transforms infrared spectroscopy (FTIR) was conducted in Vertex 70 Hyperion 100 and 16 scans were recorded to register each sample. The samples were prepared by mixing 1 mg of sample with 300 mg of potassium bromid. The scans were performed in the mid-infrared region at frequencies ranged from 4000 $cm^{-1}$ to 400 $cm^{-1}$.

#### 2.2.5. X-ray diffraction analysis

X-ray diffraction (XRD) analysis was performed on samples described in FTIR section by PW18300 equipped with a graphite monochromator and Cu anode. The step side employed in this work was 0.02°, 1 s per step in the 5–70° $2\theta$ range.

### 2.3. Kramers–Kronig transformations

The reliability of impedance data of P3, P4 and P5 from NCIM is examined through Kramers–Kronig transformation [5,11]. Based on Kramers–Kronig transformation, real and imaginary parts of the impedance are correlated each other through Eq. (1) [12]:

$$Z^{//}(\omega,t) = \left(-\frac{2\omega}{\pi}\right)\int_0^\infty \frac{Z^{/}(x,t) - Z^{/}(\omega,t)}{x^2-\omega^2}dx \qquad (1)$$

where $\omega$ and $t$ are the given frequency and time, respectively; $Z^{/}(\omega, t)$ and $Z^{//}(\omega, t)$ are real and imaginary parts of impedance at $\omega$ and $t$; $x$ is the fitting angular frequency; $Z^{/}(x, t)$ is fitting real part.

In Eq. (1), the key to solve the approximation of Kramers–Kronig transformation in the finite integral is to obtain the term $Z^{/}(x, t)$. It can be accomplished by fitting a polynomial with three orders [13]:

$$Z^{/}(x,t) = a_0 + a_1x + a_2x^2 + a_3x^3 \qquad (2)$$

where $a_0$, $a_1$, $a_2$ and $a_3$ are fitting parameters.

## 3. Results and discussion

### 3.1. Reliability assessment via Kramers–Kronig transformation

Figs. 2–4 demonstrate experimental imaginary parts from the test measurement and calculated ones from Kramers–Kronig transformation from Eq. (1) and (2) for P3, P4 and P5. In Figs. 2–4, experimental and calculated imaginary parts exhibit the same trend and two typical features can be found in these figures, which proves that data sets from NCIM are reliable: (1) At the very beginning of hydration, the imaginary part from experimental test or Kramers–Kronig transformation is almost zero; while it increases as frequency and hydration time increase in subsequent hydration stage. (2) It is expected that values of imaginary part from NCIM is larger than those from the calculation of Kramers–Kronig transformation. Obviously, in the present Kramers–Kronig transformation, Eq. (1) must require such data set that covers an infinite frequency domain. Practically, none of data set satisfies this condition because of the intrinsic limitation of impedance measuring instruments itself [14]. Therefore, smaller calculated imaginary part from Kramers–Kronig transformation is unavoidably generated by evaluating the integral over finite bandwidth, rather than an infinite frequency bandwidth [14]. The further interpretation of configuration of impedance curves will be illustrated in the following subsection.

### 3.2. Hydration stages identification

Fig. 5 presents the resistivity curve and rate of resistivity curve for P4 from NCIM, according to Ref. [15]. Four hydration stages are identified from Fig. 5: (I) dissolution stage, (II) competition stage, (III) acceleration stage and (IV) deceleration stage [16], which is consistent with stages partition derived from heat flow curve in Fig. 6 [17]. In this work, the impedance response of stages I, II and III is preliminarily investigated from the view point of physical–chemical behaviors. Normally, the abbreviations used in this work are as follows [18]: C = CaO; S = $SiO_2$; A = $Al_2O_3$; H = $H_2O$; CH = $Ca(OH)_2$; $\overline{S} = SO_3$.

#### 3.2.1. Dissolution stage

In the dissolution stage, the current of the cement paste ($I$) is mainly associated with the applied voltage of signal ($E$) and the parameter ($\theta$) related to surface morphology of cement particles, according to Ref. [19]. $\Theta$ is the ratio of the surface that releases ions into the solution to the total surface area of cement particles. Accordingly, the increase in $\theta$ leads to the rising of current inside the cement paste [19]. The complete differential form of current can be written as:

**Table 1**
The chemical composition of cement, fly ash, slag and silica fume (wt%).

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cement | CaO | SiO4 | $SO_3$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $K_2O$ | $TiO_2$ | | | |
| wt% | 65.47 | 19.55 | 5.75 | 3.82 | 3.21 | 1.48 | 0.52 | 0.26 | | | |
| Fly ash | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_4$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ |
| wt% | 1.24 | 1.54 | 30.36 | 51.64 | 0.67 | 1.35 | 1.17 | 4.96 | 2.09 | 0.08 | 4.88 |
| slag | MgO | $Al_2O_3$ | $SiO_2$ | $SO_4$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | | |
| wt% | 8.12 | 13.84 | 34.16 | 3.53 | 0.63 | 37.86 | 1.01 | 0.52 | 0.34 | | |
| Silica fume | MgO | $SiO_2$ | $SO_4$ | $K_2O$ | CaO | MnO | $Fe_2O_3$ | | | | |
| wt% | 0.79 | 96.68 | 0.39 | 1.26 | 0.80 | 0.01 | 0.07 | | | | |