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# Differential analysis of AC impedance spectroscopy of cement-based materials considering CPE behavior

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## HIGHLIGHTS

- Cement-based materials.
- Differential impedance analysis.
- CPE behavior.
- Time constant.
- Impedance parameters.

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## ABSTRACT

A differential impedance analysis method considering constant phase element (CPE) was proposed for cement-based materials. Results indicated that the method is very accurate for the identification circuit of single capacitive loop. For series circuit of double capacitive loops, the method can accurately identify all impedance parameters when ratio ($q$) of the two time constants is large. For series and parallel circuits of double capacitive loops, even when $q$ is close to 1, number of the capacitive loop can be identified accurately. The method can selectively identify the variation, frequency range and frequency dependence of the impedance parameters of cement-based materials; it can also explain why when two capacitive loops exist in a Nyquist plot of cement-based materials, only one can be observed by the naked eye. The method is beneficial for establishing a reasonable equivalent circuit of impedance spectroscopy with a CPE behavior, especially when $q$ is very small.



## 1. Introduction

Since the first application of AC impedance spectroscopy (ACIS) for the study of cement-based materials [1], many ACIS studies of cement paste, mortar and concrete have been conducted. This interest has been generated because of the possibility of correlating the micro-structural properties of cement-based materials [2,3]. To obtain reasonable ACIS parameters that characterize the properties of cement-based materials, some equivalent circuits [2,4–8] have been proposed to interpret the ACIS of cement-based materials. A capacitive loop often occurs in the high frequency region of the Nyquist plot of an ACIS of cement-based materials. The capacitive loop is generally attributed to a response from the micro-pore network in the cement-based materials that are in a condition of excitation voltage [8]. In most cases, such a capacitive loop was simulated with the simple equivalent circuit $R_0(R_1C_1)$ [8,9].

However, in many situations, two capacitive loops were found in the cement-based materials, and equivalent circuit $R_0(R_1C_1)(R_2C_2)$ was used to interpret the ACIS results [8,10–14]. In addition, considering two capacitive loops from the angle of the conducting paths of the current, some equivalent circuits [15–17] have been proposed. However, the equivalent circuit proposed by Macphee et al. [15–17] may be complicated and difficult to apply. Song [8]

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proposed a new equivalent circuit that is easier to use; this circuit is based on the idea of the conducting paths of the current, and it has been used by many researchers [18–23]. Song's model suggests two capacitive loops; however, the first loop cannot be tested due to the very high frequency that would be needed [8]. Still, in many situations, two capacitive loops have been found [11,14,17,18,24–26], and in other situations, it was not possible to observe two capacitive loops with the naked eye [14,18]. Therefore, the identification of the number of capacitive loops (namely, number of the time constant) that are present in the high-frequency range of the impedance spectra is a key question [14]. However, the number of the time constant is very important to the application of an equivalent circuit for the interpretation of ACIS of cement-based materials.

Keddam et al. [14] suggested that there is a certain minimum number of time constants $R_iC_i$ that is necessary to properly reproduce the experimental data that is used. The feasibility of Keddam et al.'s suggestion [14] depends on whether the circuit is correct. Cabeza et al. [18] used a differential impedance analysis (DIA) method, as described in publications [27–29], to identify the number of time constants. Two time constants are found in the ACIS data that was obtained in the frequency range from 100 kHz to 15 MHz [18]; however, only one capacitive loop could be seen in this frequency range by the naked eye.

The main advantage of the DIA method is the lack of need for a preliminary working hypothesis or for the pre-construction of an operating model [27–29]. However, the DIA method, as proposed in publications [27–29], can only be used for the interpretation of the parameters of the ACIS involving no constant phase element, and for the identification of the number of time constants. In the ideal case, ACIS analysis of the Nyquist plot becomes a semicircle, the center of which lies on the real axis. However, this ideal response is rarely observed. For most materials, an inclined semicircle, the center of which is depressed below the real axis by an angle, is a more likely response. The depression of the angle is a common phenomenon in AC impedance studies [30]. Considerable error in estimating capacitance may sometimes be introduced by not taking the dispersion effects into account. This dispersion behavior usually may be described by a constant phase element (CPE) [31,32], and can be called as CPE behavior.

Some researchers [19,21,33–36] have found that a dispersion phenomenon exists in mortar and concrete. Many researchers [14,18,25,37,38] have found or discussed the dispersion phenomenon of cement paste, and certain other some researchers [30,39,40] have found the dispersion phenomenon of paste with mineral admixtures. Gu et al. [30,41] have analyzed the dispersion phenomenon and suggested that it is common to cement-based materials. In fact, when a dispersion phenomenon exists, the so-called time constant may be identified using the DIA method without considering CPE as a constant; however, it is difficult to identify the number of time constants using the DIA method when the CPE behavior exists. Although a secondary DIA is developed for the structural and parametric identification of dispersion behavior [42,43], it only recognizes the Warburg impedance and dispersion index $n$ of the Local Operating Model, which is not enough information for cement-based materials. Therefore, this study aims to develop a differential impedance analysis method for interpreting ACIS of cement-based materials that considers the CPE behavior.

## 2. Principles of the differential analysis of ACIS considering CPE behavior

### 2.1. Local scanning model with CPE behavior ($LOM_{CPE}$)

The method of the differential analysis of ACIS, as given in publications [27–29], is based on scanning with the so-called Local Operating Model ($LOM_C$), as plotted in Fig. 1a. When Stoynov et al. [27–29] proposed the DIA method, the CPE behavior was not included in the $LOM_C$ [44]. In the present study, a new LOM with CPE behavior ($LOM_{CPE}$) was used for the differential analysis of ACIS, as shown in Fig. 1b. The scanning procedure using $LOM_{CPE}$ is same as the procedure that used $LOM_C$ that is described in publication [43].

### 2.2. Parametric identification of the local scanning model with CPE behavior ($LOM_{CPE}$)

The calculation process of the parametric identification of the $LOM_{CPE}$ is given in Appendix A. The parametric identification results can be expressed as Eqs. (1)-(4):

$$R_s = Z_{re} - \frac{\frac{1}{R_p} + C_0\omega^n \cos\left(\frac{n\pi}{2}\right)}{\left(\frac{1}{R_p}\right)^2 + \frac{2}{R_p}C_0\omega^n \cos\left(\frac{n\pi}{2}\right) + (C_0\omega^n)^2} \quad (1)$$

$$C_0 = \frac{\omega^n \sin\left(\frac{n\pi}{2}\right)}{Z_{im}\left(\frac{1}{T^2} + \frac{2\omega^n \cos\left(\frac{n\pi}{2}\right)}{T} + \omega^{2n}\right)} \quad (2)$$

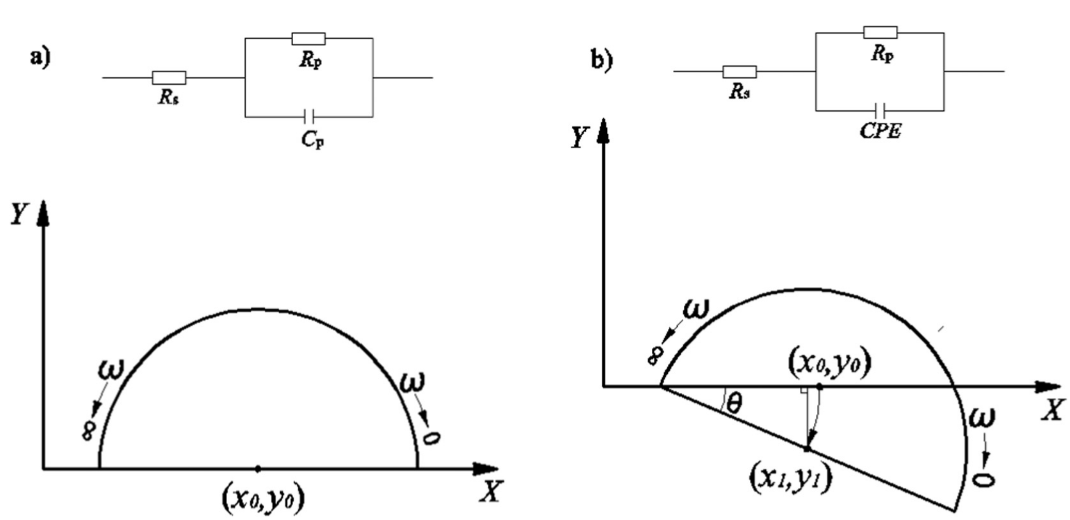


**Fig. 1.** Local scanning model (LOM) used for the differential method: a) LOM with capacitance element ($LOM_C$); b) LOM with CPE element ($LOM_{CPE}$).