



# Comparison of the retarding mechanisms of zinc oxide and sucrose on cement hydration and interactions with supplementary cementitious materials



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## ABSTRACT

Sucrose and zinc oxide (ZnO) are effective cement hydration retarders. The goal of this study was to provide a new look into the ZnO cement hydration mechanism and to investigate impacts of various supplementary cementitious materials (SCMs) on retardation behavior of ZnO and sucrose. Changes in the pore solution composition and reaction kinetics were measured for cementitious systems with ZnO or sucrose that contained rice straw ash (RSA), wheat straw ash, silica fume, metakaolin, and fly ash. Among the SCMs used, RSA dramatically suppressed ZnO and sucrose retardation. Experimental results indicated that the mechanism by which ZnO retards hydration reaction could be nucleation and/or growth poisoning of C-S-H. Reduced retardation of paste samples containing RSA was attributed to the ability of RSA to provide nucleation sites for C-S-H precipitation. This study provides a better understanding of the interaction between SCMs and cement hydration retarders essential in predicting retarder-dose effects.

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## 1. Introduction

Chemical admixtures are added to concrete to modify and improve concrete properties. Retarders, as chemical admixtures, are used in concrete to increase the working time of the concrete, allowing for longer haul, placement, and finishing times. Sugars are well-known cement hydration retarders. Numerous researchers have studied the impact of sucrose (sugar) on cement retardation [1–5]. Although the mechanism by which sucrose delays cement hydration is not yet completely understood, several studies have proposed that sucrose retards cement hydration by slowing the formation of hydration products through poisoning nucleation sites for such products, e.g. calcium silicate hydrate (C-S-H) [3,6]. Sucrose does not prevent C-S-H growth permanently, though, because as the dissolution of cement continues, more ions enter the solution and more nucleation sites are produced. Eventually the number of these sites overcomes the poisoning abilities of the sucrose molecules. At this point, the hydration reactions proceed faster than the condition where no sucrose was added to the system. This has led sugars to be called “delayed accelerators” [7]. It has been pro-

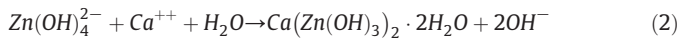
posed that the high calcium concentration in the pore solution is the reason for this fast hydration reaction following the retardation period [3].

Zinc oxide (ZnO) is another hydration retarder that has been considered for use in some applications [8,9]. The mechanism by which ZnO retards cement hydration is proposed to be different than that of the sucrose. Arliguie and Grandet [10,11] proposed that in the presence of zinc ions in the pore solution, an amorphous layer of zinc hydroxide (Zn(OH)<sub>2</sub>) is formed on the surface of anhydrous tricalcium silicate (C<sub>3</sub>S) phase in cement. They also showed that the zinc retards the hydration of tricalcium aluminate (C<sub>3</sub>A) if the amount of SO<sub>3</sub> in the system is more than 2.5%. They postulated that formation of the amorphous layer of zinc hydroxide on the surfaces of anhydrous cement grains isolates the cement particles from water and thus inhibits cement hydration. According to Arliguie and Grandet [10,11], once the concentrations of calcium and hydroxyl ions in the pore solution are high enough, the amorphous zinc hydroxide transforms into a crystalline calcium zinc hydroxide. Once this happens, the cement hydration reactions start again. Eqs. (1) and (2) show the suggested chemical reactions of ZnO in cement pore solution [8,12].



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Using Fourier transform infrared spectroscopy (FTIR), Yusuf et al. [13] showed that a crystalline phase of calcium zinc hydroxide was present in paste samples containing ZnO that were cured for 28 days. However, there is no experimental evidence for the presence of a zinc hydroxide layer around cement particles, so this theory for the mechanism of the retarding action of ZnO remains unconfirmed experimentally.

Supplementary cementitious materials (SCMs), such as silica fume, slag, and metakaolin, can have a major impact on cement hydration kinetics [14,15]. SCMs can have a dilution effect at early ages and/or a seeding effect [2,14,16]. When using SCMs in cementitious systems, typically the amount of cement in the system is reduced and replaced by the SCM, effectively diluting the amount of cement in the system. As a consequence, the effective water–cement ratio (w/c) is increased compared to a system without SCMs at the same water content. This provides more space for the hydration products, enabling the acceleration period of cement hydration to be extended because of additional space available for the reaction products to form [14]. This phenomenon is part of what is often called the “filler effect.” Another aspect of the filler effect results from enhanced nucleation resulting from seeding provided by SCMs. Because of the seeding effect, the induction period of cement hydration can be dramatically reduced and hydration rate can be increased during the early period [2,16]. The reduction in the induction period is due to C–S–H precipitating faster on the nucleation sites provided by the SCMs than on the surface of cement grains [2,16]. SCM surface area reactivity and “chemical affinity” [16] are the primary factors that determine the ability of SCMs to provide nucleation sites for C–S–H precipitation [2,16].

C–S–H can also form because of the pozzolanic reaction between the silica-containing SCM and calcium hydroxide dissolved in the pore solution [2]. The formation rate of this C–S–H depends on the rate of pozzolanic reaction, which is unique to each SCM. The pozzolanic reaction rate can be enhanced when the amorphous silica content and surface area of the SCM are increased [17,18].

SCMs can interact with chemical admixtures used in concrete, especially set modifying admixtures. Taylor-Lange et al. [19] studied the impact of ZnO retardation on paste samples with and without metakaolin as a 15% replacement of cement. They showed that the retarding action of ZnO was significantly decreased by the presence of the metakaolin and attributed this behavior to the amorphous nature of the metakaolin used [19]. To the best of our knowledge, the influence of other SCMs on the retarding action of ZnO as well as the impact of SCMs on retarding action of sucrose have not been investigated. Given the variety of SCMs, understanding the interaction between SCMs and cement hydration retarders is essential in predicting retarder-dose effects.

This paper investigated the retarding action of ZnO and sucrose on cement-based mixtures containing silica fume, rice straw ash, wheat straw ash, fly ash, or metakaolin SCMs. This study provides a better understanding of the mechanism(s) by which ZnO and sucrose retard cement hydration, leading to a better prediction of retarder dosage for various cementitious systems. Additionally, this work addresses whether or not the amorphous content of SCMs plays a role in decreasing retardation action of ZnO and sucrose.

## 2. Materials and methods

### 2.1. Materials

An ASTM C150 [20] Type I portland cement was used. The cement chemical composition, fineness, and potential composition calculated using the Bogue method outlined in ASTM C150 are shown in Table 1. Undensified silica fume, Dynapoz metakaolin, Class F fly ash, metakaolin, wheat straw ash, and rice straw ash were selected as the

**Table 1**  
Cement composition.

Chemical composition (%)		Bogue compounds (%)	
SiO <sub>2</sub>	19.66	C <sub>3</sub> S	60.17
Al <sub>2</sub> O <sub>3</sub>	4.71	C <sub>2</sub> S	10.97
Fe <sub>2</sub> O <sub>3</sub>	3.26	C <sub>3</sub> A	6.97
CaO	62.74	C <sub>4</sub> AF	9.92
MgO	2.32	Blaine fineness	
K <sub>2</sub> O	0.56	395 m <sup>2</sup> /Kg	
Na <sub>2</sub> O	0.12		
SO <sub>3</sub>	3.34		

SCMs for this study. Undensified silica fume was used to reduce agglomeration and to have higher surface area, compared to the commercially used densified silica fume. ACS grade zinc oxide and sucrose were used as hydration retarders.

In order to produce rice straw ash (RSA) and wheat straw ash (WSA) with high amorphous content, high surface area, and low loss on ignition (LOI), the biomass (wheat straw and rice straw) was pretreated with 0.1 N HCl (diluted from reagent grade HCl) at 80 °C. 250 g of biomass was immersed in 3100 ± 100 mL of 0.1 N HCl solution in a 4000 mL glass jar. The sample was stored undisturbed at a constant temperature of 80 °C for 24 h. The biomass was then rinsed twice, each time with 2500 mL of distilled water, and dried at 80 °C in an oven. To prepare the ash (WSA or RSA), a programmable electric muffle furnace was used to heat the biomass. 200 g of dried biomass was fired in each batch. A stainless steel cage with two wire mesh shelves was used to hold the biomass during burning, and a stainless steel pan was placed below the cage to catch any ash that fell through the mesh. Finally, the ash was ground for 1 h at 85 revolutions per minute (rpm) in a laboratory ball mill. WSA was prepared by burning the pretreated wheat straw at 650 °C for 1 h and is labeled as WSA650. Two types of RSA were prepared. RSA650 was obtained by burning pretreated rice straw at 650 °C for 1 h, and RSA500 was prepared by burning pretreated rice straw at 500 °C for 2 h. Chemical and physical properties of the SCMs are given in Table 2.

The following naming convention is used: OPC stands for a sample that does not contain any SCM; OPC + WSA650, OPC + RSA650, and OPC + RSA500 represent samples that contain 15% of WSA650, RSA650, and RSA500 replacement of cement, respectively. Similarly, OPC + MK, OPC + SF, and OPC + FA are samples that contain 15% of MK, SF, and FA replacement of cement, respectively. When ZnO or sucrose was used, it is indicated at the end of the sample name in parenthesis with the dosage, such as OPC + RSA500(0.15% ZnO).

### 2.2. Experimental methods

#### 2.2.1. Material characterization

Surface areas of samples were determined using BET nitrogen adsorption using a Micromeritics ASAP 2020 Surface Area and Porosimetry Analyzer. Samples were degassed before testing for 7 h to 24 h at 200–400 °C and at a pressure of 500 μm Hg or less.

**Table 2**  
Oxide composition and specific surface area of SCMs.

Sample ID	Chemical compositions (%)							BET surface area (m <sup>2</sup> /g)
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	
WSA-650	86.5	0.28	1.13	9.73	0.78	1.54	0.1	65
RSA-650	88.2	0.47	0.74	9.48	0.56	0.31	0.17	134
RSA-500	85.7	1.4	1.02	10.73	0.6	0.34	0.23	200
Silica fume (SF)	96.96	0.13	0.05	0.43	0.96	0.38	0.08	8.8
Fly ash (FA)	55.11	20.42	8.18	9.9	2.72	–	–	0.4
Metakaolin	53.77	44.1	0.6	0.16	0.01	0.3	0.12	7.5

Note: Low surface area of SF may be due to poor dispersion.

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