OPTIMIZATION OF THE HYDRATION BEHAVIOR OF ACCELERATED CEMENT PASTES BY COLLOIDAL SILICA

OPTIMIERUNG DES HYDRATATIONSVERHALTENS BESCHLEUNIGTER ZEMENTPASTEN DURCH KOLLOIDALE KIESELSÄURE

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This work presents the characterization of the hydration behavior of cement pastes containing colloidal silica and accelerators for sprayed concrete. Cement pastes were characterized by isothermal calorimetry and scanning electron microscopy. Results showed that colloidal silica accelerated alite hydration and could also control accelerated C_3A reactions, reducing the early formation of AFm phases. The conclusions derived from this study indicate a possible synergistic effect between colloidal silica and accelerator in accelerating alite hydration and avoiding undersulfated C_3A reactions, which may lead to higher mechanical strength at early ages.

In dieser Studie wurde das Hydratationsverhaltens von Zementleimen, denen Kieselsole (kolloidale Lösungen von amorphem Siliziumdioxid) und Beschleunigern für Spritzbeton zugesetzt wurden, untersucht. Die Zementleime wurde durch isotherme Kalorimetrie und Rasterelektronenmikroskopie charakterisiert. Die Ergebnisse zeigen, dass kolloidales Siliziumdioxid einerseits die Alithydratation beschleunigte und andererseits durch die Vermeidung von untersulfatisierten C_3A-Reaktionen die frühe Bildung von AFm-Phasen verringert wurde. Die aus dieser Studie abgeleiteten Schlussfolgerungen weisen auf einen möglichen synergistischen Effekt zwischen kolloidalem Siliziumdioxid und Beschleuniger hin. Dieser Effekt könnte zu einer erheblichen Steigerung der Frühfestigkeit im jungen Spritzbeton führen.

1. Introduction

Sprayed concrete is a construction method widely employed for structural support of tunnels and mines [1]. For the stabilization of the tunnel excavation front, a fast development of mechanical strength at early ages is required [2], which is achieved by using cement contents around 400 kg/m^3 and accelerator dosages from 5 to 10% by cement weight [3,4]. CEM I is the most common cement used for sprayed concrete production due to its fast hydration kinetics at early ages [5].

Accelerators lead to a fast setting immediately after spraying [6–8]. Then, sprayed concrete may not eliminate the entrapped air during spraying, resulting in higher water accessible porosities when compared to conventional concrete [5,9]. In addition, the fast setting associated with the high pressure employed during application leads to aggregate rebound and turns the matrix heterogeneous mainly in the interface with the substrate [4].

The increase in porosity is common when alkaline accelerators are added in dosages above 0.18 mol of aluminate ions per cement kg [10,11]. Such accelerators deplete sulfate ions from the liquid phase quickly and accelerate C_3A reactions, resulting in a suppress of alite hydration [7,12]. Consequently, the compressive strength of sprayed concrete produced with alkaline accelerators tend to be 20% lower than concretes produced with alkali-free accelerators [9,13]. Moreover, when alkaline accelerators are employed, the matrix is more susceptible to deleterious processes caused by the ingress of aggressive agents due to the inclusion of aluminum from accelerator [11,14].

To overcome those limitations, the combined use of admixtures and mineral additions may promote a synergistic interaction and optimize the evolution of mechanical strength of the matrix. Admixtures composed by colloidal silica improve the rheological behavior of the fresh concrete and facilitate pumping and spraying operations [15]. In addition, these compounds accelerate alite hydration, increasing the rate of mechanical strength development at early ages [16,17]. Therefore, the use of colloidal silica may contribute to the reduction of accelerator dosage, minimizing the undesired effects that may be generated due to the incorporation of aluminum in the matrix.

In this context, the objective of this study is to evaluate how the combined use of colloidal silica and accelerators influence hydration kinetics and the microstructure of cement pastes. Hydration kinetics was evaluated by isothermal calorimetry and the microstructure of the matrix was analyzed by scanning electron microscopy. Results show a synergistic effect of the combined use of colloidal silica and accelerators, resulting in faster reaction rates than in systems produced without colloidal silica.

2. Further important information

2.1 Materials

Materials selected to execute the experimental program are described in Table 1. Cement composition is presented in a previous research [11]. Its specific surface area determined by BET was 1.16 m^2/g and insoluble residue determined according to [18] was 1.32% by cement weight (% bcw).

Tab. 1: Materials selected to the experimental program

Material	Type
Cement	CEM II/B-S 42.5R
Dispersing admixture	Polycarboxylate ether solution
Admixture based on silica	Colloidal silica suspension
Accelerators	Alkaline (sodium aluminate), alkali-free (aluminum sulfate)
Water	Deionized

Tab. 2: Properties of accelerators

Property	AF	AK
Solid content (%)	40.0	43.0
Specific weight (g/cm^3)	1.32	1.45
pH at 20 °C	2.5	13.0
Al_2O_3 content (%)	11.2	24.0
Sufate content (%)	23.0	-
Na_2O content (%)	-	19.0
Stabilizing agent	organic acid	-

Distilled water, a superplasticizer based on a polycarboxylate solution (34 % of solid content) and a suspension of colloidal silica (CS) containing 30% of solid content and a specific surface are of 305 m^2/g were used. In addition, pastes were prepared with two different accelerators, composed by an aluminum sulfate solution (alkali-free) and a sodium aluminate solution (alkaline). These accelerators are identified as AF and AK, respectively, and their properties are presented in Table 2.

2.2 Composition and preparation of cement pastes

Pastes were composed by a fixed water/cement (w/c) ratio equal to 0.45 and 0.3% of superplasticizer by cement weight (% bcw). Accelerator AF was used at 6.0 and 8.0% bcw, while accelerator AK was added at 2.0 and 4.0% bcw. The dosage of the colloidal silica suspension was equal to 1.0% bcw. Pastes were identified by '*CS content_accelerator type and dosage*'. Pastes with no admixture were identified as '*REF*' and pastes containing only the superplasticizer were identified as '*REF_SP*'.

The preparation of pastes consisted in mixing cement and water for 1 min using an IKA RW 20 agitator coupled with a R1342 4-bladed stirrer at 1500 rpm. Then, superplasticizer was added and the mixture was homogenized for 1 min at 1500 rpm. After that, the colloidal silica suspension was added and mixed for 1 min at 1500 rpm and the paste was transferred to a climatic chamber, where it was kept at 23ºC for 1 h. Finally, accelerators were added and the resulting mix was homogenized for 30 s at 1500 rpm.

The addition of accelerator 1 h after the initial mixing intends to reproduce the condition found in sprayed concrete in practice (notice that concretes must be transported to the worksite after mixing, where they are sprayed with accelerators). This procedure also contributes to a clearer assessment of the heat flow attributed to accelerator reaction, which otherwise would overlap with the heat released during the initial mixing of cement and water [10].

2.3 Test methods

2.3.1 Isothermal calorimetry

Isothermal calorimetry was performed at 23 ºC during 24 h with 8.0 g of cement paste, using a TAMAir isothermal calorimeter. This test was performed to analyze the hydration behavior of cement pastes of different compositions.

2.3.2 Scanning electron microscopy

Scanning electron microscopy was performed to analyze the microstructure of cement pastes 15 h after accelerator addition. Fracture surfaces of cement pastes were analyzed in a Quanta FEG 650 microscope at the voltage of 20 kV. Samples were dried by the solvent exchange method [19,20] and coated with carbon. Morphology of the precipitated hydrates was evaluated by secondary electron imaging and their chemical composition was assessed by energy dispersive X-ray analysis.

3. Results and discussion

3.1 Isothermal calorimetry

Figure 1 shows the heat flow curves of accelerated cement pastes from 0 to 24 h. Figure 1.a represents the heat flow curves of pastes produced with accelerator AF, while Figure 1.b depicts the curves of pastes produced with accelerator AK. Table 3 summarizes the characteristic points of the heat flow curves, determined according to [10].

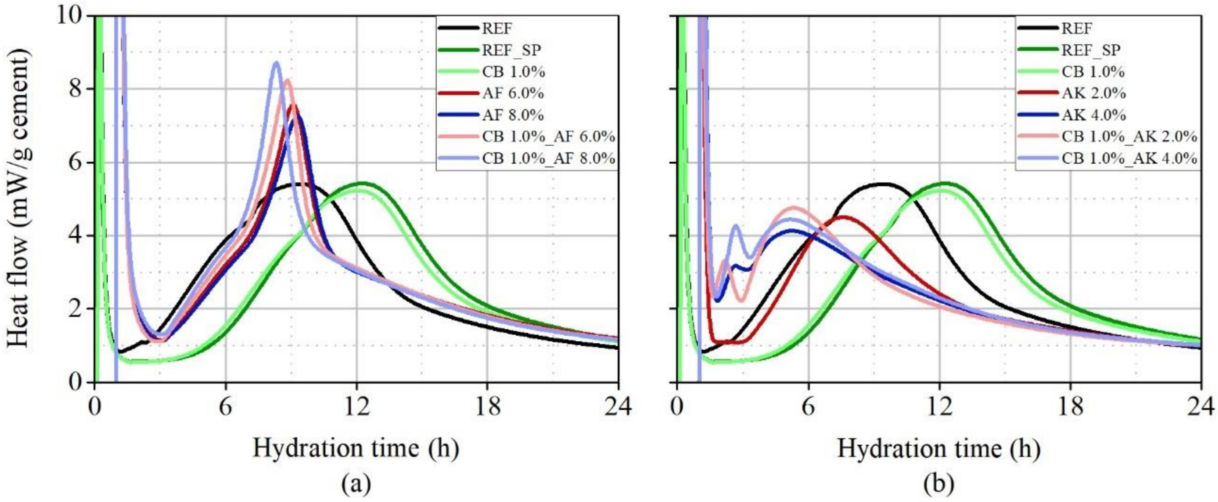


Figure 1: Heat flow curves from 0 to 24 h obtained with cement pastes produced with accelerator AF (a) and accelerator AK (b)

Tab. 3: Analysis of the heat flow curves obtained with the cement pastes

Paste	Induction period (h)	Slope acceleration (mW/g.h)	Maximum heat flow (mW)
REF	2.6	0.838	5.40
REF_SP	5.4	0.830	5.41
CB 1.0%	4.9	0.777	5.23
AF 6.0%	2.4	0.761	7.56
AF 8.0%	2.4	0.710	7.26
AK 2.0%	2.3	0.990	4.49
AK 4.0%	0.94	0.949	4.12
CB 1.0%_ AF 6.0%	2.2	0.830	8.22
CB 1.0%_ AF 8.0%	2.2	0.896	8,71
CB 1.0%_ AK 2.0%	0.73	1.71	4.75
CB 1.0%_ AK 2.0%	0.80	1.05	4.44

In Figure 1.a, it is possible to observe that paste REF_SP presents a longer induction period than paste REF due to the retarding effect of the superplasticizer. The addition of the colloidal silica suspension does not alter the hydration profile of the paste REF_SP significantly. In previous tests performed by the research group (not published), it seemed that colloidal silica agglomerated in pastes that did not contain accelerators. The formation of silica clusters prevents the formation of nucleation sites.

Comparing the curves of AF 6.0% and AF 8.0% with the curve of paste REF_SP, a clear influence of the accelerator may be observed. As expected, accelerators increase the overall hydration rate due to the consumption of calcium and sulfate ions from the liquid phase for the formation of aluminate hydrates. Therefore, induction periods are reduced significantly, and the maximum heat flow reached in the main hydration peak is greater when accelerators are employed.

When colloidal silica is added to the paste, an additional accelerating effect is observed. Pastes CB 1.0%_AF 6.0% and CB 1.0%_AF 8.0% present shorter induction periods and faster reaction rates than pastes AF 6.0% and AF 8.0%, respectively. This occurs because colloidal silica particles act as nucleating sites for the precipitation of C-S-H, contributing to increase the hydration rate of alite.

In Figure 1.b, similar results were found when the alkaline accelerator was used. The addition of colloidal silica contributes to reduce induction periods due to the nucleation effect of silica particles. An interesting fact is that the peak corresponding to accelerated C_3A reactions, observed around 2 h in the heat flow curves, is more intense in pastes containing colloidal silica. In addition, the reaction rate of the following peak is higher when colloidal silica is employed. This analysis indicates that colloidal silica may also contribute to avoid C_3A reactions that suppress alite hydration.

In this sense, the combined interaction of colloidal silica and accelerator is beneficial to provide faster hydration rates, which are higher than when accelerators are used alone. Therefore, it is feasible to assume that the addition of colloidal silica may contribute to reduce accelerator dosage to obtain an equivalent hydration profile to systems containing accelerators at higher dosages. This approach may contribute to improve the durability of the matrix against chemical attacks, due to the reduced amount of aluminum incorporated in the matrix by accelerators.

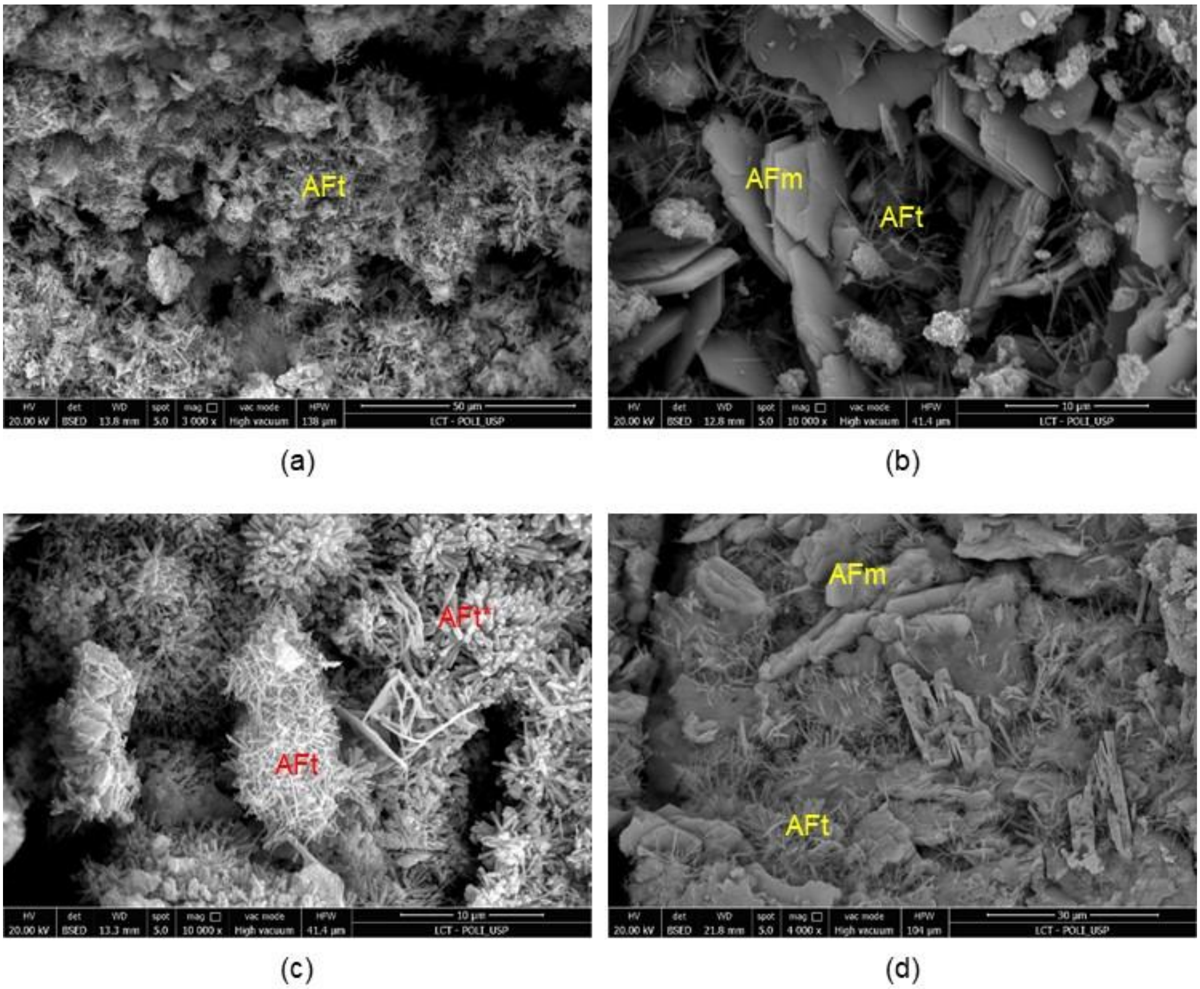
3.2 Scanning electron microscopy

Figure 2 presents SEM images obtained with cement pastes AF 8.0% (Figure 2.a) AK 4.0% (Figure 2.b), CB 1.0%_AF 8.0% (Figure 2.c) and CB 1.0%_AK 4.0% (Figure 2.d) 15 h after accelerator addition.

Figure 2.a, the precipitation of a large amount of acicular ettringite crystals may be observed in paste AF 8.0%. These crystals are formed due to the reaction of aluminum sulfate provided by accelerator with calcium and sulfate ions from the liquid phase and with aluminate phases from cement [10]. In Figure 2.b, the amount of ettringite crystals is lower and flat hexagonal plate-like crystals, composed mainly of AFm phases, may be found. This happens because the alkaline accelerator does not contain sulfate in its formulation, resulting in the conversion of ettringite to AFm phases by C_3A reactions [21].

In Figure 2.c, the morphology of ettringite crystals is different due to the use of colloidal silica (crystals identified by *AFt**). Crystals seem to be thicker and agglomerated in small clusters, which may be the result of the nucleation effect of silica particles. In Figure 2.d, the paste CB 1.0%_AK 4.0% seems to present a larger amount of ettringite crystals and lower contents of AFm phases than paste AK 4.0% (Figure 2.b). This result is beneficial because the early formation of AFm phases tend to reduce the mechanical strength of the matrix [9]. This observation is in line with the results of isothermal calorimetry.

In practice, the preparation of sprayed concrete using colloidal silica for real applications is not well known. In Brazil, laboratory-scale tests have been performed lately to propose novel admixtures for sprayed concrete production.



(a) (b)

(c) (d)

Figure 2: SEM images of cement pastes AF 8.0% (a) AK 4.0% (b), CB 1.0%_AF 8.0% (c) and CB 1.0%_AK 4.0% (d) 15 h after accelerator addition

4. Conclusions

The following conclusions may be derived from the results obtained in this experimental program:

- A synergistic effect of the combined use of colloidal silica and accelerators was observed, resulting in faster reaction rates than in systems produced without colloidal silica.
- Colloidal silica acts as nucleating sites for the precipitation of C-S-H, contributing to increase the hydration rate of alite. In addition, this compound may also contribute to avoid C3A reactions that suppress alite hydration, especially when alkaline accelerators are used.
- The morphology of ettringite crystals change when colloidal silica is used. Crystals seem to be thicker and agglomerated in small clusters in pastes produced with alkali-free accelerators.
- When alkaline accelerators are used, the amount of AFm phases formed by accelerator reaction is reduced.

- It is feasible to assume that the addition of colloidal silica may contribute to reduce accelerator dosage to obtain an equivalent hydration profile to systems containing only accelerators, normally employed at higher dosages.

5. References

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