

Effect of Delayed Addition of TEA on the Performance of Cement with Different Sulfate Carriers

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Abstract. *Concrete 3D printing is one promising technique used for future construction. However, a bottleneck limiting this technology's rapid development and practical application is the conflicting requirements for concrete properties before and after printing. Hence, the application of the accelerator and a deep understating of its working mechanism is becoming more and more important. As one commonly used accelerator, triethanolamine (TEA) has the advantage of low dosage and high efficiency to reach a fast setting. However, it is still unclear how the delayed addition of TEA affects the performance of cementitious materials. Besides, it is found that the different types and combinations of sulfate carriers can significantly affect the performance of TEA on cement hydration. However, the combined effect of different sulfate carriers and different addition times of TEA on the hydration process of cement paste is also unclear. The effect of different TEA addition times on the hydration and setting performance of cement pastes containing different types and combinations of sulfate carriers were thoroughly investigated in this study. It is found that, depending on the types of sulfate carriers inside, the different addition times of TEA can significantly affect the hydration and setting performance of cement paste. Specifically, to artificial cement (ArC) prepared with hemihydrate (HH), the different TEA addition times do not affect the setting performance of cement paste. To ArC with the two sulfate carriers of anhydrite (AH) and HH, a flash setting was observed when the TEA was added simultaneously. However, a delayed addition of TEA for just 5 min can make the setting performance back to normal. To ArC with only AH, a longer addition time of 15 min is needed to eliminate the flash setting behavior. This phenomenon could be originated from the competed interaction of sulfate ions released from sulfate carriers and TEA with the aluminate phase contained in the clinker.*

Keywords: *Triethanolamine; Addition time; Cement hydration; Setting performance*

1 Introduction

Concrete 3D printing is one promising technique used for future construction with the outstanding advantages of labor-saving, high efficiency, and strong structural designability [1, 2]. However, a bottleneck limiting this technology's rapid development and practical application is the conflicting requirements for concrete properties before and after printing [3]. Prior to printing, 3D printing concrete needs to remain high flowability to achieve satisfied pumpability and printability. However, after printing out of the concrete, a fast setting and rapid hardening performance of the concrete is desired to reach the requirement on the buildability of 3D printing concrete, which can prevent the collapse of the built structure. Many methods

have been developed to achieve the set-on-demand concrete to realize such a rapid transformation, the application of accelerators is the most developed approach and they can be added to the printed concrete by the two following methods: 1) mixing simultaneously with retarder during concrete preparation [4]; 2) mixing after concrete preparation at the print head by a second pipe [5].

Regarding the first method, all of the chemicals, including the retarder and accelerator, are mixed with the concrete from the beginning. The hydration of cement was first retarded to ensure pumpability and printability. Then the accelerator takes the leading role to achieve buildability [6]. Regarding the second method, the concrete was first prepared and pumped without the accelerator, which ensures the pumpability. After that, the accelerator was added and mixed with the prepared concrete just before printing it out. Compared to the first method, the second one can significantly reduce the sensitivity during concrete printing and enhance the robustness of the printed concrete. Hence, this method is regarded to be more promising for the wide application of concrete 3D printing in the future.

Triethanolamine (TEA) is one commonly used accelerator. Many of our previous studies have shown that the addition of TEA leads to the fast setting of cement paste with a quite low dosage compared to that of aluminum sulfate (~5 wt.% for aluminum sulfate and 0.5 wt.% for TEA), which is believed to be caused by the accelerated reaction of aluminate phase (mainly C_3A and C_4AF) due to the strong complexing ability of TEA with the aluminate and iron ions [7]. Hence, in order to avoid the flash setting during concrete 3D printing, it is reasonable to add the TEA into the well mixed concrete later, namely the delayed addition of TEA should be used. Actually, many literatures have reported the significant effect of different addition methods on the performance of chemical admixtures, especially for superplasticizer [8]. It is commonly accepted that the delayed addition of superplasticizer can improve its dispersing ability with less adsorption amount, which is believed to be caused by the less consumption of superplasticizer by the formed hydration products [9]. However, even though TEA has been applied in concrete in many studies [10], it is still unclear how the different addition methods of TEA can affect the properties of cement paste. Besides, in our former publication [7], it is found that the different types and combinations of sulfate carriers can greatly affect the performance of TEA on cement hydration. Considering the huge effect of sulfate carriers, another question is what is the combined effect of different sulfate carriers and different addition methods of TEA on the hydration process of cement.

Hence, in this study, the effect of different TEA addition methods on the hydration and setting performance of cement pastes, which contains different types and combination of sulfate carriers, were investigated by using the combined techniques of calorimetry, in-situ X-ray diffraction (XRD), compressive strength. The results shown in this study from one aspect provide us guidance on the application of TEA as one accelerator used in concrete 3D printing. More importantly, it could further deepen our understanding of the interaction of TEA with the multi-phases contained in cement during the hydration process and build the bridge between the hydration process to the macro properties of cement paste.

2 Experiments and method

2.1 Materials

The block-shaped clinker provided by HeidelbergCement AG was used in this study and its mineralogical composition is shown in Table 1. A planetary ball mill (Pulverisette 5 of Fritsch GmbH) was used to grind the clinker into powder to a Blaine specific surface of 4300 ± 100 cm^2/g . The ground clinker powder was then mixed with different types of sulfate carriers to prepare the artificial cement (ArC), as shown in Table 2. Both the anhydrite (AH) and β -hemihydrate (HH) were provided by CASEA GmbH (Germany). To reach a homogenous distribution of the sulfate carriers inside the ArC. The ground clinker and sulfate carrier are mixed together in a sealed plastic bottle with 4 rubber balls inside to break the possible agglomeration for 3 days in an overhead shaker (REAX 20/12, Heidolph Instruments). Beside the prepared ArC, an industrial ordinary Portland cement (OPC, CEM I 42.5 R, HeidelbergCement, Heidelberg, Germany) which was made of the clinker above, was also used to test the effect of the addition method of TEA on the hydration and setting performance of cement paste.

Table 1. Mineralogical composition of the used clinker in this study (%)

| Alite | Belite | C ₃ A (orth.) | C ₃ A (cub.) | C ₄ AF | Calcite | Quartz | f-CaO | others | Sum |
|-------|--------|-----------------------------|----------------------------|-------------------|---------|--------|-------|--------|-------|
| 60.68 | 19.62 | 3.02 | 6.65 | 7.33 | 0.62 | 0.25 | 1.08 | 0.49 | 99.74 |

Table 2. Mineralogical composition of the used clinker in this study (%)

| Sample | Clinker (g) | Anhydrite (g) | β -Hemihydrate (g) | SO ₃ content (%) |
|-----------|-------------|---------------|-----------------------------|--------------------------------|
| OPC | 100 | 2.670 | 2.812 | 2.98 |
| ArC_AH | 100 | 5.340 | 0.000 | 2.98 |
| ArC_AH/HH | 100 | 2.670 | 5.612 | 2.98 |
| ArC_HH | 100 | 0.000 | 2.812 | 2.98 |

2.2 Preparation of cement pastes

The cement paste was prepared at a constant water-to-cement mass ratio (w/c) of 0.5. Two different addition methods of TEA were used, namely the simultaneous addition method (S-method) and the delayed addition method (D-method). To the S-method, 1.5 g TEA (corresponding to a TEA dosage of 0.5 wt.%) was first dissolved in 150 g DI water. Then the TEA solution was added to 300 g cement (or ArC samples) and mixed by using a hand mixer at the mixing speed of 950 rpm for 2 min to prepare the cement paste for the following experiments. For the preparation of cement paste by using the D-method, firstly 120 g DI water was added to 300 g cement (or ArC samples) and mixed at the same speed for 1 min. After standing still for a certain time (5 min, 10 min, 15 min, 30 min and 1 h), the TEA solution prepared from 30 g DI water and 1.5 g TEA was added into the cement paste within 10 s and mixed for another 1 min. Hence, a constant w/c ratio of 0.5 was kept in the D-method.

2.3 Methods

The hydration process of cement paste with and without the addition of TEA mixing by two different methods was monitored by using a calorimeter (MC-CAL/100P, Calmetrix Inc, USA) over 7 days at a constant temperature of 20 °C. Vicat needle test (Toni Technik Toniset, Firma Zwick Roell) was used to measure the setting time of cement paste prepared in the same way as above according to EN 196-3. In-situ XRD measurements were conducted for samples. The radiation (Cu K α) was generated with 40 kV and 40 mA, filtered by Ni and measured by a PiXcel1D detector. The compressive strength of hardened cement paste prepared with the different TEA addition methods was measured after curing for 3 d, 7 d, and 28 d. A cubic mold with a dimension of 20mm \times 20mm \times 20mm was used for the preparation of the sample. For each curing age, 3 samples were measured and the average value was reported.

3 Results and discussion

3.1 Setting performance

The setting time of OPC and ArCs with different sulfate carriers was tested by using two TEA addition methods. To the samples without TEA (named reference), nearly no difference in the setting time can be found by using the two different water addition methods. Hence, only the data from the S-method of reference was shown. For the references of OPC and ArCs without the addition of TEA, a normal setting performance can be found for these samples with a decreasing setting time in the sequence of ArC_AH/HH > ArC_HH > ArC_AH \approx OPC.

Regarding the effect of TEA, as expected, the addition of 0.5 wt.% TEA can significantly reduce the setting time of OPC to a few minutes by using the S-method. However, the delayed addition of TEA not only eliminates the accelerated effect of TEA on the setting time, but also strongly postpones the setting time of the OPC from around 6 h of the reference to nearly 12 h of the sample with the dosage of 0.5 wt.%. ArC_AH/HH shows a similar phenomenon to that of OPC, but with a longer setting time for the sample by using the D-method. To the sample of ArC_HH, however, no flash setting behavior can be observed, regardless of the different TEA addition methods used. Furthermore, an increased setting time was observed for samples with the addition of TEA. Regarding the effect of the addition method on the setting of ArC_AH, a flash setting and rapid hardening of the cement paste can always be found in both samples by using the S-method and D-method. Besides, a slightly longer final setting time was found for the ArC_AH using the D-method than that with the S-method.

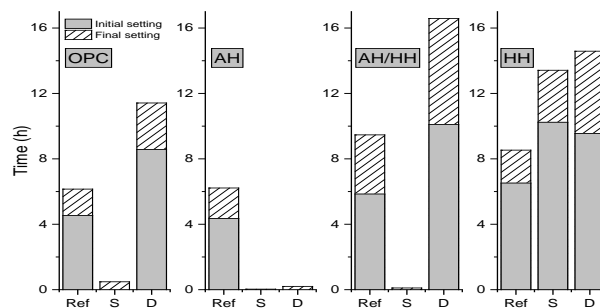


Figure 1. Initial and final setting time of OPC and ArCs.

3.2 Hydration process

In order to well understand the effect of TEA addition method on the varied setting performance of cement paste with different types of sulfate carriers, the hydration process was measured and the results are shown in Fig. 2. For the samples without the addition of TEA, the two water addition methods have nearly no effect on the hydration process. Regarding the sample with the addition of TEA by using S-method (as shown in Fig. 2), the longest prolonged induction period was found for the sample of OPC, followed by ArC_AH/HH, ArC_AH and ArC_HH. Again, the cement with the combined AH and HH inside (OPC and ArC_AH/HH) shows the longest induction period compared to that with a single type of sulfate carriers inside (namely ArC_HH and ArC_AH), which matches well with our previous results[9].

Comparing the two different addition methods, a greatly shortened induction period can be found for the samples of OPC, ArC_AH/HH and ArC_AH by using the D-method. It indicates that the strong retardation of silicate phase caused by the accelerated aluminatate phase is eliminated by the delayed addition of TEA. Besides, a peak shoulder after the main hydration peak can always be found for the samples prepared by using the D-method, which is not found for the samples with the S-method except that of ArC_HH. It indicates the delayed addition of TEA cannot promote the hydration of the aluminatate phase, which is normally the TEA did in the S-method. The heat flow does not show a big difference to the sample of ArC_HH, which is consistent with the setting performance observed in Fig. 1.

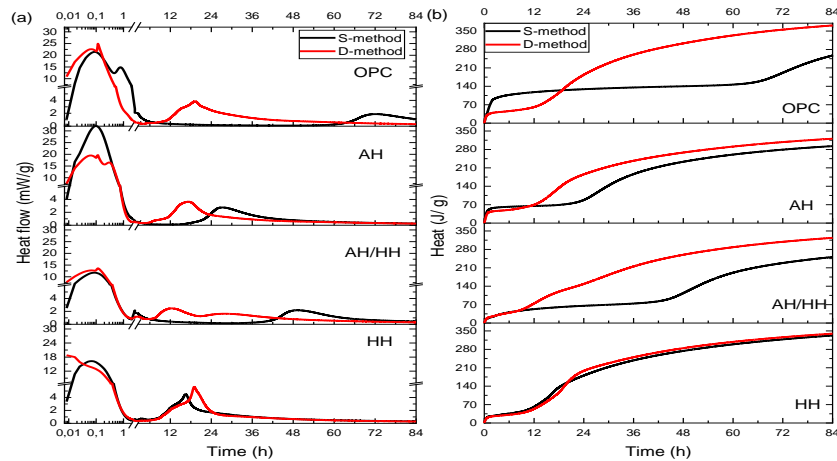


Figure 2. Effect of different sulfate carriers on the heat development of OPC and ArC pastes. (a) heat flow; (b) cumulative heat by excluding the value in the first hour

3.3 In-situ XRD

The results are shown in Fig. 3. For the OPC paste prepared with TEA using S-method, a large amount of AFt was found at the very beginning. Afterward, even though the precipitation of AFt was nearly stopped, a rapid dissolution of C₃A and anhydrite was observed within the first 6 h of hydration. Compared to the S-method, the delayed addition of TEA leads to higher intensity of C₃A and an initially lower but continuously increased intensity of AFt, which indicates the fast dissolution of C₃A was prohibited when the TEA was added just 5 min later.

Besides, the depletion time of anhydrite was extended to around 18 h, which was much longer than that prepared with the S-method.

Regarding the samples of ArC_AH prepared with S-method, a much decreased C_3A intensity at the beginning was observed compared to the sample of OPC with the same method. Afterward, the intensity of C_3A was nearly constant. The formation of AFt was quite fast in the first 3 h and then reduced to a lower speed. An obvious decrease in C_3S intensity was found after the hydration of 12 h, but the occurrence of CH was observed at around 18 h. For the samples prepared using the D-method, even though a similar trend was found for each phase to that prepared with S-method, a higher C_3A intensity was found compared to that with the D-method. To the samples of ArC_AH/HH with the different TEA addition methods, the trend in the dissolution of C_3A and anhydrite, as well as the formation of AFt, are similar to that of OPC and again the intensity of C_3A is higher when using D-method. Even though a nearly constant C_3S amount was observed for ArC_AH/HH with the S-method, a fast dissolution of C_3S starts to observe at around 6 h and the corresponding increased heat flow was found. Besides, the occurrence of CH was delayed to about 18 h. To the samples of ArC_HH, no sulfate carriers can be detected from the beginning, which indicates all of the sulfates are released from the sulfate carriers and then could stay in the bulk solution as free ions and/or be adsorbed on the surface of cement particles. Along with the gradual formation of AFt, the sulfate ions in the bulk solution are gradually consumed and the desorption of sulfate ions from the surface of cement particles was followed.

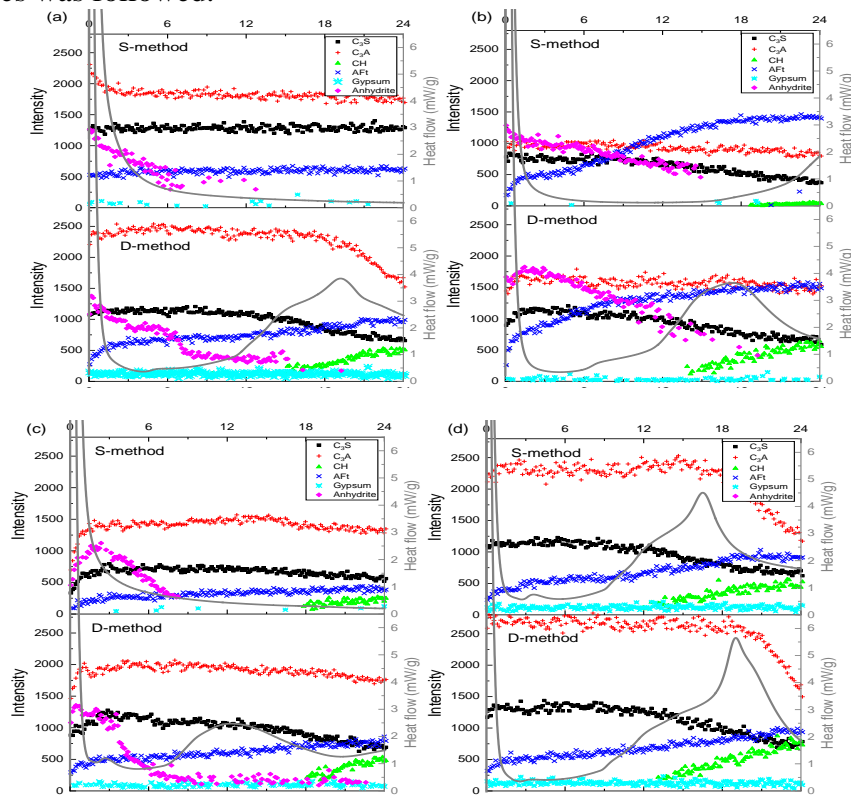


Figure 3. Combination of the characteristic XRD reflexes for several phases and the calorimetric curve along with the hydration of OPC and ArC pastes with different sulfate carriers as well as with the TEA dosage of 0.5 wt.%; (a) OPC; (b) ArC with AH; (c) ArC with AH and HH; (d) ArC with HH.

3.5 Compressive strength

The results are shown in Fig. 4. To OPC with the two addition methods of TEA, the OPC with D-method shows a much higher compressive strength at 3 d than that of the S-method. Along with the further hydration, the compressive strength of OPC with the two addition methods of TEA becomes nearly comparable. For ArCs with different sulfate carriers with the S-method, ArC_AH always shows the highest compressive strength before 7 d regardless of the addition of TEA or not, then followed by ArC_HH and ArC_AH/HH. However, at 28 days, the ArC_HH shows the highest strength followed by ArC_AH/HH and ArC_AH. It indicated that the presence of anhydrite favors the development of compressive strength at an early stage, while hemihydrate increases the compressive strength at 28 d.

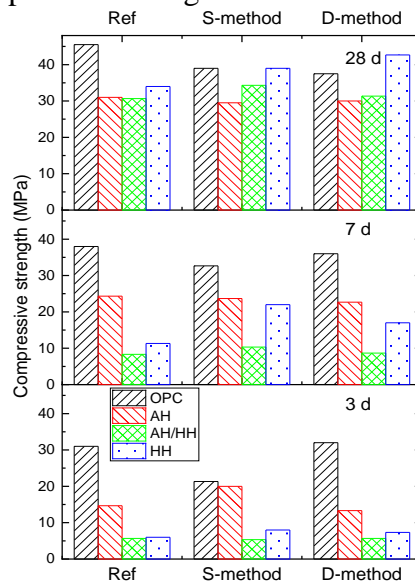


Figure 4. Compressive strength of OPC and ArC with different sulfates.

4 Conclusions

- Depending on the types of sulfate carriers inside, the different addition methods of TEA can greatly affect the hydration and setting performance of cement paste. Specifically, the applied simultaneous addition (S-method) and delayed addition (D-method) with an interval of 5 min of TEA lead to a flash setting of ArC_AH. However, a normal setting behavior can be found for ArC_AH with a prolonged delayed addition time of 15 min. It indicates not only the adsorption of sulfate ions on the surface of aluminat phases, but also the formation of AFt on the active surface of aluminat phase could play a vital role to passivate the fast reaction of aluminat phase, including C_3A and C_4AF .
- For the sample with both sulfate carriers inside (namely OPC and ArC_AH/HH), a flash setting was found in the S-method and a normal setting behavior was observed with the applied D-method. The flash setting performance with the used S-method could be

related to the loose structure of the formed AFt on the active site, which cannot hinder the accelerated dissolution of C_3A and C_4AF through the complexation of TEA. However, for the samples with the D-method, the interval allows the formation of dense structure to prohibit the acceleration effect of TEA on the aluminate phase.

- For ArC_HH, hemihydrate dissolves very fast at the beginning, more sulfate ions are released into the bulk solution. Hence, most of the active surface are adsorbed by the sulfate ions and the role of AFt on the passivation of C_3A become quite limited. Then the surface of aluminate phase is passivated and the TEA cannot promote the dissolution of the aluminate phases. Hence a normal setting behavior can always be found regardless of the addition method of TEA.

References

- du Plessis, A.J. Babafemi, S.C. Paul, B. Panda, J.P. Tran, C. Broeckhoven. (2021). *Biomimicry for 3D concrete printing: A review and perspective*, Additem.Manuf. 38 101823.
- Das, L. Reiter, S. Mantellato, R.J. Flatt. (2022). *Early-age rheology and hydration control of ternary binders for 3D printing applications*, Cem. Concr. Res. 162, 107004.
- Liu, Y. Chen, Y. Xiong, L. Jia, L. Ma, X. Wang, C. Chen, N. Banthia, Y. Zhang. (2022). *Influence of HPMC and SF on buildability of 3D printing foam concrete: From water state and flocculation point of view*, Compos. Part B: Eng. 242, 110075.
- M. Tramontin Souza, I. Maia Ferreira, E. Guzi de Moraes, L. Senff, S. Arcaro, J.R. Castro Pessôa. M. J. Ribeiro, A.P. Novaes de Oliveira. (2022). *Role of chemical admixtures on 3D printed Portland cement: Assessing rheology and buildability*, Constr. Build. Mater. 314, 125666.
- S. Bhattacharjee, M. Santhanam. (2022). *Investigation on the effect of alkali-free aluminium sulfate based accelerator on the fresh properties of 3D printable concrete*, Cem. Concr. Compos. 130, 104521.
- D.P. Bentz, S.Z. Jones, I.R. Bentz, M.A. Peltz. (2018). *Towards the formulation of robust and sustainable cementitious binders for 3-D additive construction by extrusion*, Constr. Build. Mater. 175, 215-224.
- T. Hirsch, Z. Lu, D. Stephan. (2021). *Effect of different sulphate carriers on Portland cement hydration in the presence of triethanolamine*, Constr. Build. Mater. 294, 123528.
- K.-C. Hsu, J.-J. Chiu, S.-D. Chen, Y.-C. Tseng. (1999). *Effect of addition time of a superplasticizer on cement adsorption and on concrete workability*, Cem. Concr. Compos. 21(5), 425-430.
- H. El-Didamony, M. Heikal, K.A. Khalil, S. Al-Masry. (2012). *Effect of delaying addition time of SMF superplasticizer on the physico-mechanical properties and durability of cement pastes*, Constr. Build. Mater. 35, 261-269.
- W. Feng, Y. Jin, D. Zheng, Y. Fang, Z. Dong, H. Cui. (2022). *Study of triethanolamine on regulating early strength of fly ash-based chemically foamed geopolymer*, Cem. Concr. Res. 162, 107005.
- H. Eldidamony, M. Heikal, I. Aiad, S. Al-Masry. (2013). *Behavior of delayed addition time of snf superplasticizer on microsilica-sulphate resisting cements*, Ceram. Silikaty. 57 (3), 232-242.
- M. Heikal, I. Aiad. (2008). *Influence of delaying addition time of superplasticizers on chemical process and properties of cement pastes*, Ceram. Silikaty. 52, 8-15.