

Research Article

Use of Boron Compounds as Grinding Aids with Alcohol Amines and Their Effect on Portland Cement Setting Points

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Milling aids have been predominantly developed to increase the performance or grinding capacity of cement products, and alcohol amines have been used as grinding aids in cement grinding processes for many years. Moreover, the setting point of cement produced with grinding aids is most often changed. In this study, the effects of alkanolamines and boron compounds in different mixing amounts as grinding aids on the set point of cement were researched. Triethanolamine (TEA) and triiso-propanolamine (TIPA) were used as alkanolamines and boric acid (BA) and anhydrous borax (AHB) as the boron compounds. It is evident that BA with TEA had a small effect on the cement setting point where the former decreased the retarding effect of the latter, but BA had no effect with TIPA. AHB decreased the retarding effect of TEA but had no effect with TIPA on setting times. When the boron compounds were added to TEA, they accelerated the initial setting points of cement by 15 to 20 minutes and the final setting points by 25 to 30 minutes according to the amount of TEA used.

1. Introduction

A hydration reaction instantly starts when water is mixed with cement to form a paste that first begins to lose its plasticity and stiffens and then hardens [1]. The main phases, C_3A , C_3S , C_2S , and C_4AF , react quickly with water to produce a jell-like mixture that starts solidifying. The action of changing from a fluid state to a solid state is called setting which is the transformation process from the initial state (a scattered concentrated suspension) to the final state (a connected and strengthened system of particles). In practice, this transformation of cement and concrete is obtained by chemical reactions between cement particles and water (i.e., cement hydration) [2]. The typical setting of cement is associated with the hydration of alite (C_3S) and the formation of the calcium silicate hydrate (CSH) phase [3].

Cement as a slurry has fluidity just after mixing with water and can smoothly flow into a mold. The sulphoaluminates create interlocking crystals, and as the CSH starts to form, the generated network of solids causes the cement to set. The cement paste has no strength at this hydration stage and is also very friable. The required length of time for the initial setting can be determined by the amount of gypsum present in the cement. Hardening of the cement paste (the beginning of strength gain in other words) occurs after the formation of CSH, which starts some hours after mixing.

Accelerating chemical aids causes cement setting to accelerate according to one or more of the following mechanisms:

- (1) The ability to accelerate compounds to flocculate hydrophilic colloids, thereby resulting in a more permeable CSH surface layer through which water and ions can diffuse faster [4].
- (2) Accelerating the participation of compound ions in aluminate reactions, which form aluminate ion phases mostly when there is insufficient sulfate to react with C₃A. The monosulphate conversion of ettringite will not occur if free ions are available [5].
- (3) An increased calcium concentration causes quicker liquid supersaturation with respect to calcium hydroxide (Ca(OH)₂) concentration, while a lower

sulfate concentration will cause a slower formation of ettringite, which will shorten the initiation of (C_3A) aluminate hydration [6].

A retarding admixture retards the setting of concrete [7] by one or more of the following mechanisms:

- Adsorption of the retarding compound on the surface of cement particles, thereby forming a thin protective layer that slows down hydration.
- (2) Adsorption of the retarding admixture onto calcium hydroxide nuclei poisons their growth, which is essential for continued hydration of cement after the end of the induction period.
- (3) Formation of complexes with calcium ions in solution, which increases their solubility and discourages the creation of the calcium hydroxide nuclei referred to in (2).
- (4) Precipitation of insoluble derivatives of the retarding compounds formed by reaction with the highly alkaline aqueous solution around the cement particles forms a protective skin [8].

Alkanolamines are amines containing a single, double, or triple hydroxyalkyl group. They are frequently used as concrete admixtures and grinding aids. The action of triethanolamine (TEA) in the hydration of cement is not described explicitly in the literature since it has still not been concluded whether it is an accelerator or a retarder. Dodson [1] claimed that "The most popular addition rate of TEA is in the range of 0.010 to 0.25% on the weight of cement. The conclusions show that at a dosage of 0.02%, TEA acts as an accelerator, at 0.25% as a retarder, at 0.5 % as a severe retarder and 1.0% as a flash-set accelerator." Similar behavior was found by Ramachandran [2] when measuring the initial and final setting characteristics of Portland cement mortar mixed with 0-0.5% TEA. Other studies have shown that the most prominent feature of TEA is its ability to act as both a set retarder and a set accelerator depending on its dosage. TEA accelerates C₃A hydration as well as delays C₃S hydration [2, 3]. Jolicoeur et al. [9] used TEA amounts ranging from 0.02 to 0.15% in their study, and when 0.1% was used, a strong accelerator effect was observed due to the rapid hydration of C_3A (false setting). Heren and Olmez [10] investigated the hydration, and mechanical effects of ethanolamine oligomers added to the consistency water in varying amounts of 0.1 to 1%. They compared monoethanolamine, diethanolamine, and TEA at doses of 0.1 to 1.0% in white Portland cement and found no significant effect on the initial setting times at low doses but considerable retardation at higher doses for all three types. TEA is a weak base, and in the aqueous phase, it is mostly in the molecular state. Furthermore, it can chelate with specific metallic ions such as Fe^{3+} in highly alkaline media [11].

Triisopropanolamine (TIPA) is a tertiary amine used in the cement industry as a grinding aid and in formulas of concrete. The addition of small amounts of TIPA can result in a significant increase in the strength of cement pastes at early and late ages [12]. Aggoun et al. [13] investigated the early strength and setting effects of TIPA-TEA-calcium nitrate mixture combinations in ordinary Portland cement and obtained necessary and promising results for both the setting and curing accelerator effects of the aminecalcium nitrate composition. The researcher found that TIPAs curing accelerator performance was higher than TEA regardless of cement type.

Katsiotia and coworkers [14] evaluated six commercial grinding additives used in the production of Portland cement (ground in a ball mill at the laboratory stage). They tested all cement mixtures for initial and final setting times, consistency of standard paste, flow of traditional mortar, and compressive strengths after 2, 7, and 28 days. They found slight decreases in the initial and final setting times in the cases of TEA-containing grinding aids based on C₃A reaction acceleration. However, they also found that the presence of TIPA as a grinding aid in cement mixtures increases the initial and final setting times by around 15%, acting as a retarder of hydration at early stages. The aim of the research by Allahverdi and Babasafari [15] was to interpret the effectiveness of TEA on the grindability and set and strength behavior of Portland cement in laboratory ball and vibrating disk mills when adding 0.06% amount by weight to the cement. They concluded that the addition of TEA increased both initial and final setting times and decreased the compressive strength at 3-, 7-, and 28-day curing ages in both ball and vibrating disk mill-ground cement.

Assaad and Issa [16] determined the effect of grinding aid (GA) additions on the variation of flow of cement pastes. Two types of GA were used in which the first one was aminebased GA composed of a mixture of TIPA and TEA and the second was glycol-based GA composed of DEG and MEG. The Blaine fineness or energy consumption (Ec) is set constant for the experiments. They found that the water demand was increasing continuously with GA concentration because of higher cement fineness at constant Ec. The setting times of cement reduced by increasing GA concentration with constant Ec. When Blaine was set fixed with higher GA concentrations, a gradual increase in setting times and a decreasing tendency in water demands were seemed.

In another research by Assaad [17], the scale effect of using grinding aids by comparing the results obtained from the closed-circuit tube mill to a laboratory-type mill was evaluated. Glycol and amine-based grinding aids were used in the study, and all grindings were realized for the fixed Blaine fineness. The results showed that cement mixtures ground in laboratory exhibited lightly reduction in water demand compared to those ground in an industrial tube mill. The setting times remained almost unchanged with some exceptions.

Boron compounds used in the study are products of Eti Maden. Turkey has the world's most massive boron deposits which are approximately 73% of world boron reserves [18]. Boric acid (H_3BO_3) with a 56.3–56.8% B_2O_3 and anhydrous borax (disodium tetraborate anhydrous, $Na_2B_4O_7$) with a 68.3–69.4% B_2O_3 are the available products of Eti Maden in the market.

Water-soluble sugars, sugar acids and salts, and borax and boric acid (BA) are known as set retarders [19]. However, in the study of Koyuncu and coworkers [20], sodium borax pentahydrate (Na₂B₄O₇·5H₂O) at a specific ratio was used in concrete as a replacement material for Portland cement. In the concrete specimens, it was observed from the results of the experiments that while adding borax increased the compressive strength and flexural strength, setting time, unit weight and workability decreased. Additionally, it has been observed in other studies that the cement paste made with boron-containing cement had an increased setting point both at the beginning and the final setting [21, 22]. Davraz [23] used boron-modified active belite cement, calcium aluminate cement, and Portland cement as binder materials in mortar mixtures. The researcher aimed to research the effects of the boron compounds on the hydration reactions of the different cement types and their effect on controllability. BA was used in the studies at ratios of 0.25-1.00% by weight of cement in mortar mixtures with Portland cement. It was found that by increasing the usage portion of B₂O₃, the retarding effect was enhanced and could be controlled by adding accelerator aids to the mixture. The best results were from sodium aluminate and a 1% BA mixture. The formation of calcium diborate (CBH₆) barrier layers on the particle surfaces could be delayed to reach the optimum setting times and strength at a convenient B₂O₃ concentration [23].

Sonoda and coworkers [24] used NMR spectroscopy to study the complex formation behavior between TEA and BA in aqueous solution and to determine the stoichiometric compositions, stability, and structures of the boron complexes. They discovered the formation of two kinds of 1:1 complexes in aqueous solutions: TEA-B and its hydrolysis product with a bicyclo [3,3,0] structure. Both of them had a tetrahedral structure of boron-nitrogen bonds around the boron atoms.

Generally, the concentration range of grinding aids added is from 50 to 500 ppm. After the grinding process, the additives might not be in their original chemical form any longer. Moreover, grinding aid composition might not only consist of mixtures of pure compounds but also somewhat more complex raw materials [25].

Our aim in this study was to determine the contribution of boron compounds with alkanolamines grinding aids to cement settings to find a setting mechanism that could be helpful for further studies. In cement experiments in the past, most studies on boron compounds with cement have focused on higher concentrations; thus it would be beneficial for future studies to see the result of lowering the boron compound concentration.

2. Materials and Methods

2.1. Materials and Equipment. In this study, the same batch of Portland cement clinker and gypsum was used as the main components of the cement samples reported in Table 1, and TEA and TIPA were used as grinding aids. Besides, boric acid (BA) and anhydrous borax (AHB) were used as boron compounds, and their effects on the performance of the grinding aids were researched. Lithium tetraborate (66%)

TABLE 1: Blaine, water demand, and the initial and final setting analysis results of the reference cement and ground cement with grinding aids and boron compound mixtures.

Grinding aid	Initial setting (min.)	Final setting (min.)	Blaine (cm ² /gr)	Water demand (%)
No grinding aid (reference)	140	215	3704	23
% 100 TEA	170	255	4030	26.3
% 100 TIPA	150	215	4106	26.1
% 75 TEA + % 25 BA	170	260	4052	25.5
% 75 TIPA + % 25 BA	150	220	4004	25.5
% 75 TEA + % 25 AHB	150	225	4075	25.8
% 75 TIPA + % 25 AHB	140	215	3995	25.4
% 67 TEA + % 33 BA	155	225	4085	25.8
% 67 TIPA + % 33 BA	140	205	4001	25.3
% 67 TEA + % 33 AHB	155	230	4088	25.8
% 67 TIPA + % 33 AHB	150	210	3997	25.5

was the fluxing agent for the fuse beads. Deionised water was used for mortar preparation and water demand tests.

Precision scales, a laboratory-scale crusher, a laboratory mill, a mortar mixer, Blaine fineness test equipment, Vicat test equipment (manual and automatic), molds, an X-ray fluorimeter for the X-ray fluorescence (XRF) analysis, a fusion machine, and a platinum crucible were used equipment in the experiments.

2.2. Preparation and Experimental Method. The size of the clinker was reduced to 3 mm or less by passing it through a laboratory-scale crusher before the experiments to ensure homogeneity and then mixed. Portland CEM I-type cement was produced in the tests, and grinding aids were used in all the cement produced except for the reference cement. The grinding aid amount was chosen as constant as 0.1 % by mass which was mostly the determined portion of the literature [3, 16, 25] and to receive both standard limitations of TS EN 197-1 and ASTM C465 [26]. For each experiment, 3000 g of clinker was weighed, and then the grinding aid + boron compound was added to a weight of 0.1%, after which the ingredients were thoroughly mixed. This mixture was loaded to the laboratory-type ball mill and ground for 40 min. Following this, the samples were taken from the stopped mill, and the SO₃ content was checked in XRF. The calculated amount gypsum was added to the mill according to the final SO₃ content target of cement which was 3.05 ± 0.05 %. Then, the mill was rerun for 40 min with gypsum. For each experimental set, after a total of 80-minute grinding process, the cement samples were taken separately for XRF elemental analysis.

For the Vicat tests of the cement samples, each was subjected to consistency testing according to the TS EN 196-3:2017 standard [27]; the cement samples with consistency water were prepared for the Vicat test, and the beginning and the final setting times were determined with the automatic Vicat device.

The Blaine fineness tests of cement samples were tested according to TS EN 196-6:2010 standard [28]; the Blaine fineness test equipment was used for these tests.

3. Results and Discussion

The average Blaine fineness value of cement ground at a fixed time was about $4043 \text{ cm}^2/\text{gr}$ (Table 1). In general, the values were obtained in 4043 ± 63 Blaine range. The Blaine fineness of the reference cement was $3704 \text{ cm}^2/\text{gr}$ at the same fixed time grinding. All cement ground using the grinding aid had the advantage of fineness of about 300 Blaine and more.

The water demand of the reference cement sample was 23%. In experiments carried out with 100% TEA and TIPA, the water demand of ground cement was increased to $26.2 \pm$ 0.1%. This increase in water demand is likely due to the rise in Blaine fineness. The water demand for samples using 25% or 33% boron compounds in the grinding aid mixture increased to $25.6 \pm 0.3\%$ compared with reference cement. The reason is again the increase in Blaine fineness of samples ground with grinding aids containing boron compounds. But the water demand of samples ground with boron compound containing grinding aid mixture was slightly lower than the water demand of samples ground with 100% TEA and TIPA. Since the Blaine values for all experiment except the reference sample were similar $(4043 \pm 63 \text{ cm}^2/\text{gr})$, the reason of the water demand differences probably could be because of narrower particle size distribution of cement and the higher proportion of fine particles [3]. The slight retardations of the hydration reaction of cement samples might be because of this narrower particle size distribution of cement and the higher proportion of fine particles.

Setting time testing with different grinding aid contents was performed under constant laboratory conditions ($20^{\circ}C$ and relative humidity >50%). The average of three test readings was taken as the final reading. The setting time of the cement paste without a grinding aid was used as a reference for comparing the change in setting time caused by the addition of the grinding aids. The setting times were recorded in minutes.

All of the cement samples with TEA mixtures had initial setting values of more than 75 minutes, which makes them suitable according to the TS EN 197-1:2012 standard [29]. A total of 3g of material (0.1 wt.% cement) was used as a grinding aid in each experiment. For the cement samples in Table 1 and Figure 1, the beginning and final setting times were higher for the cement sample ground with 100% TEA according to the reference cement, which demonstrates the mild retarding effect of the TEA in the hydration reactions that is compatible with the studies of Dodson' [1] and Allahverdi' and Babasafari [15].

When the TEA content in the total cement was reduced by the addition of BA instead of 25% TEA, the beginning and final settings were very similar to the 100% TEA study (Table 1; Figure 1). By increasing the BA ratio to 33% when 67% TEA was used as a grinding aid, the initial setting time was faster than experiments with 100% TEA and 75% TEA + 25% BA. The final setting of this sample was also earlier than that of the 100% TEA and 75% TEA + BA samples (Table 1; Figure 1). The addition of BA showed midacceleration in setting points compared to the 100% TEA results, which is contradictory to the results mentioned in the previous studies [2, 3, 9, 10, 13, 15]. The mechanism of



FIGURE 1: The initial and final setting points of the reference cement and cement mixtures milled with TEA and different ratios of BA and AHB mixtures as grinding aids.

this contradiction could have been because of the reaction between TEA and BA, as was discussed in the study of Sonoda' et al. [24]. Up to a pH level of 10.9 and at low temperatures, these two compounds consume each other and make a new complex: TEA borate (TEA-B). Thus, the TEA-B complexes formed during the preinduction and dormant period of cement hydration reactions by adding the BA to the system, which reduced the concentration of the TEA and boron compounds in the liquid phase. Hence, the retardation effect of TEA was reduced, as was seen in the 75% TEA + 25% BA and 67% TEA + 33% BA samples.

The average B_2O_3 contents of BA and AHB are 56.5 and 68.5%, respectively, which means 14.13% B₂O₃ in the 25% BA mixture and 18.65% B₂O₃ in the 33% BA mixture. Similarly, the B₂O₃ contents of 25% and 33% AHB are 17.25% and 22.61%, respectively. It is understood from the setting points of the 75% TEA and 25% AHB sample that a reaction between the TEA and AHB molecules occurred in the aqueous cement paste as well. Like the mechanism for BA, the AHB and TEA molecules balanced each other out and only the remaining grinding aid mixture (mostly TEA) slightly retarded the cement setting points (Figure 1). The initial and final setting points of 66% TEA + 33% BA and 75% TEA + 25% AHB were very similar because the total B₂O₃ content in the mixtures was similar at 18.65% and 17.25%, respectively. The mix of 67% TEA + 33% AHB had nearly the same setting points as the 25% AHB containing mixture. The 5-minute retardation might have been because of a higher SO₃ content (0.06% or more), which was able to react with C₃A (Table 2).

All of the cement samples produced using TIPA were compatible with the initial settings values specified in TS EN 197-1:2012. A total of 3 g of material (0.1 wt.% of cement) was used as a grinding aid in each experiment. It can be seen in Table 1 and Figure 2 that the cement sample ground with

% 67 TIPA + % 33 AHB

Grinding aid	LOI	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	SO ₃ (%)	K ₂ O (%)	Na ₂ O (%)
No grinding aid (reference)	1.13	20.73	4.73	3.89	63.55	1.12	3.14	0.83	0.20
% 100 TEA	1.50	20.44	4.72	3.90	63.32	1.12	3.00	0.87	0.22
% 100 TIPA	1.43	20.41	4.76	3.92	63.37	1.13	3.02	0.86	0.21
% 75 TEA + % 25 BA	1.32	20.61	4.71	3.91	63.35	1.12	3.07	0.87	0.20
% 75 TIPA + % 25 BA	1.36	20.45	4.74	3.89	63.32	1.10	3.02	0.87	0.21
% 75 TEA + % 25 AHB	1.36	20.46	4.72	3.89	63.23	1.11	3.05	0.88	0.24
% 75 TIPA + % 25 AHB	1.34	20.54	4.72	3.91	63.3	1.12	3.03	0.87	0.22
% 67 TEA + % 33 BA	1.48	20.43	4.76	3.88	63.07	1.15	3.09	0.88	0.20
% 67 TIPA + % 33 BA	1.30	20.44	4.69	3.9	63.09	1.12	3.11	0.88	0.25
% 67 TEA + % 33 AHB	1.32	20.37	4.74	3.88	63.08	1.12	3.11	0.88	0.21

3.89

TABLE 2: XRF elemental analysis of the reference cement and ground cement mixtures with grinding aids and boron compounds.



1.46

20.60

4.73

FIGURE 2: The initial and final setting points of the reference cement and cement mixtures milled with TIPA and different ratios of BA and AHB mixtures as grinding aids.

100% TIPA retarded the initial setting and similarly the final setting by 10 minutes compared to the reference cement. Although it has been suggested in the literature that TIPA behaves as a setting accelerator, there were no significant changes in setting times when 100% TIPA was used in the cement samples. Similarly, no substantial differences in setting points were found in the 25% BA and 33% AHB mixture experiments because of the cancelation of their setting effects.

4. Conclusions

When BA is used as a grinding aid in a boron compound and TEA mixture, this would typically be expected to retard the setting points of the cement, but according to the results of this study, it decreased the retardation effect of TEA. The reason for this was due to the chemical reaction between TEA and BA so that only a small amount of TEA acted as a retarder in the hydration reactions in the cement samples. The B_2O_3 content of the boron compounds was important; AHB had the same effect on setting time as BA when mixed with TEA as a grinding aid. AHB decreased the total

retarding effect of TEA + AHB mixture, and the setting points of the cement were much closer to reference cement. The decrease of water demand by adding boron compound to grinding aid mixture despite no change in Blaine fineness could be because of narrower particle size distribution of cement samples. This can also be a reason for decreased retardation effect of TEA for the experiments. The experiments using TIPA as a grinding aid showed that the cement set more quickly than when using TEA concerning initial and final setting results. Compared to the reference cement, there was no significant change in settings of the cement when either BA or AHB was mixed with TIPA and used as a grinding aid.

3.08

0.87

0.25

Abbreviations

62.69

1.11

- TEA: Triethanolamine
- TIPA: Triisopropanolamine
- BA: Boric acid
- AHB: Anhydrous borax
- C₃A: Tricalcium aluminate or aluminate, 3CaO·Al₂O₃
- C_3S : Tricalcium silicate or alite, $3CaO \cdot SiO_2$
- C_2S : Dicalcium silicate or belite, $2CaO \cdot SiO_2$
- C₄AF: Tetracalcium alumino ferrite or ferrite, 4CaO·Al₂O₃·Fe₂O₃
- CSH: Calcium silicate hydrate
- MEA: Monoethanolamine
- DEA: Diethanolamine
- CBH6: Calcium diborate
- TEA-B: Complex between triethanolamine and boron.

Data Availability

The data set supporting the conclusions of this article included within the report that stored in https://figshare. com/articles/Experimental_Data_M1-M31_pdf/5840712.

Conflicts of Interest

The authors declare that they have no conflicts of interests.

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