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Influence of Gluconate, Lignosulfonate, and Glucose Admixtures on the Hydration of Tetracalcium Aluminoferrite in the Presence of Gypsum with or without Calcium Hydroxide

M. COLLEPARDI,* S. MONOSI, G. MORICONI, AND M. PAURI

Department of Materials and Earth Sciences, University of Ancona, Ancona, Italy

The influence of 0.3 wt% gluconate, lignosulfonate, or glucose on the hydration of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ in the presence of gypsum with or without $\text{Ca}(\text{OH})_2$ was examined. In the absence of $\text{Ca}(\text{OH})_2$ all the admixtures retard both ettringite production and subsequent conversion of ettringite into the monosulfate in the decreasing order glucose > lignosulfonate > gluconate. In the presence of $\text{Ca}(\text{OH})_2$ all the admixtures accelerate early ettringite production but do not affect subsequent conversion of ettringite into the monosulfate, at least up to 28 d.

GLUCONATE, lignosulfonate, and glucose are widely used as raw materials in the production of water-reducing admixtures for concrete. They also retard the early hydration of portland cement as well as the setting time.

Both C_3A^* and C_4AF affect the setting time of portland cement. In previous papers^{1,2} the influence of these admixtures on C_3A hydration with or without CH and gypsum CSH_2 has been examined. The purpose of the present paper is to study the

effect of gluconate, lignosulfonate, and glucose on the C_4AF hydration in the presence of CSH_2 and CH. Since these admixtures strongly retard C_3S hydration³ and therefore the CH production, it is useful to study also their effect on the hydration of the system $\text{C}_4\text{AF}\text{-CSH}_2\text{-H}$ without CH.

The hydration of C_4AF in the presence of CSH_2 ^{4,5} occurs through the same stages as those for the C_3A hydration with CSH_2 ; they are ettringite production and the subsequent transformation of ettringite into the monosulfate. However, both these reactions for C_4AF appear to be much slower than the corresponding processes for C_3A .⁷ Moreover, a certain amount of F replacing A is present^{8,9} in ettringite, $\text{C}_3(\text{A},\text{F})_3\text{CSH}_2\text{H}_{12}$, or monosulfate $\text{C}_3(\text{A},\text{F})\text{CSH}_2\text{H}_{11}$; whereas some noncrystalline ferric hydrate is produced.¹⁰

EXPERIMENTAL PROCEDURE

Tetracalcium aluminoferrite was synthesized from reagent-grade CaCO_3 , Al_2O_3 , and Fe_2O_3 by heating the mixture in the proper molar ratio at 1350°C and grinding the obtained C_4AF with a free-lime content <0.2% to a blaine fineness of $\sim 3000\text{ cm}^2/\text{g}$.

Quartz, sodium gluconate, desugared sodium lignosulfonate, and glucose are the same as those used in previous works.^{1,2} Pure, finely ground quartz ($\approx 40\ \mu\text{m}$) has been used as inert material to keep constant the C_4AF percentage in all the mixes both in presence and absence of CH, CSH_2 , and admixtures obtained from carbonation of hexagonal ferric monosulfate hydrate. Calcium hydroxide and gypsum were dry-mixed with the materials in the proportions shown in Table I. Hydration of pastes with and without admixtures (0.3 wt% C_4AF) was conducted at 20°C with a water/solid ratio of 0.50.

No rigorous attempt was made to exclude CO_2 . Therefore the results cannot be extended to similar systems in the absence of CO_2 . At hydration times from 30 min to 28 days, DTG analysis was conducted as described previously.² In some cases XRD analysis was conducted to confirm the DTG identification of hydrated phases.

RESULTS AND DISCUSSION

Table II summarizes the accelerating or retarding effect of the admixtures on ettringite production and the subsequent transformation of ettringite into monosulfate. Figure 1 shows the DTG curves of the hydration products for the $\text{C}_4\text{AF}\text{-CSH}_2$ system in the absence of admixtures, with and without CH. The specimens exhibit various peaks that can be described^{11,12} as

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*Member, the American Ceramic Society.

¹ $\text{C}=\text{CaO}$, ² $\text{S}=\text{SiO}_2$, ³ $\text{A}=\text{Al}_2\text{O}_3$, ⁴ $\text{F}=\text{Fe}_2\text{O}_3$, ⁵ $\text{H}=\text{SO}_3$, ⁶ $\text{C}=\text{CO}_2$, and ⁷ $\text{N}=\text{H}_2\text{O}$.

follows. The DTG peak at $\approx 150^\circ\text{C}$ with a shoulder on the right side is assigned to a stepwise thermal decomposition of CSH_2 into CSH_2 and CS . The peak at $\approx 120^\circ\text{C}$ is attributed to the dehydration of ferric ettringite, whereas the peaks at $\approx 200^\circ$ and 280°C are attributed to the thermal dehydration of ferric monosulfate. The peak at $\approx 500^\circ\text{C}$ is proper of CH, while two different peak temperatures appear for the decomposition of carbonated products, according to presence or absence of lime.^{1,2} In the presence of lime (Fig. 1(B)) the peak at $\approx 780^\circ\text{C}$ is due to the thermal decomposition of CC obtained from CH carbonation. In the absence of lime (Fig. 1(A)) the peak at $\approx 820^\circ\text{C}$ is attributed to the thermal loss of CO_2 in the ferric monocarboaluminate. Similar results have been obtained by carbonation of other hexagonal hydrates, such as $\text{C}_2\text{A}\cdot\text{H}_2$ or $\text{C}_2\text{A}\cdot\text{CaSO}_4\cdot\text{H}_2$.^{1,2}

The DTG curves shown in Fig. 1 confirm^{1,2} that the addition of CH to the system $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CSH}_2$ retards the disappearance of gypsum and the formation of ettringite, stabilizing ettringite so long as its conversion into monosulfate does not occur, even after 28 days. Similar results have been found for C_2A hydration.^{1,2}

Figure 2 shows the DTG curves of the hydration products for the system $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CSH}_2$ with and without CH and admixtures. In the absence of CH (Fig. 2(A)), the ettringite production is strongly retarded by the addition of 0.3 wt% gluconate so that the relative amounts of ettringite and gypsum present after 6 h of hydration without admixture (Fig. 1(A)) can be observed only after 3 days of hydration in the presence of the admixture (Fig. 2(A)). Consequently, the ettringite conversion into monosulfate, appearing after 1 day of hydration without admixture, is shifted to 7 days of hydration by the addition of 0.3 wt% gluconate. So ettringite seems to be stabilized by the addition of organic products like sodium gluconate. According to Young,³ this effect is due to the penetration of organic molecules into intercolumnar region of ettringite crystal structure.

In the presence of CH, the early production of ettringite is accelerated by the addition of gluconate, so that the stage reached after 6-h hydration with the admixture (Fig. 2(B)) is attained only after 14 days of hydration without admixture (Fig. 1(B)). However, no ettringite conversion into monosulfate can be observed in the presence of gluconate as well as in the system $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CH}\cdot\text{CSH}_2\cdot\text{H}$ without admixture.

In the absence of CH, 0.3 wt% sodium lignosulfonate (Fig. 2(C)) delays the ettringite production rate approximately to the same extent as does 0.3 wt% sodium gluconate (Fig. 2(A)). On the other hand, lignosulfonate retards ettringite conversion into monosulfate more effectively than does gluconate.

In the presence of both CH and CSH_2 , 0.3 wt% lignosulfonate (Fig. 2(D)) affects

Table I. Proportions (wt%) of Anhydrous Mixes

$\text{C}_2\text{A}\cdot\text{AF}$	CH	CSH_2	S	Sodium gluconate	Sodium lignosulfonate	Gluconate
50		10	40			
50	10	10	30			
50		10	39.85	0.15		
50		10	29.85	0.15		
50	10	10	39.85		0.15	
50	10	10	29.85		0.15	
50		10	39.85			0.15
50	10	10	29.85			0.15

Table II. Effect of Admixtures on Etringite Production Rate and Conversion into Monosulfate with Respect to the Control Mix

Reaction	Rate with respect to control mix					
	With CH			Without CH		
	Sodium gluconate	Sodium lignosulfonate	Gluconate	Sodium gluconate	Sodium lignosulfonate	Gluconate
Etringite production	Accelerated	Accelerated	Accelerated	Strongly retarded	Strongly retarded	Strongly retarded
Etringite conversion into monosulfate	No effect	No effect	No effect	Retarded	Strongly retarded	Very strongly retarded

the $\text{C}_2\text{A}\cdot\text{AF}$ hydration to the same extent as does sodium gluconate (Fig. 2(B)). In the absence of CH (Fig. 2(E)), 0.3 wt% glucose addition retards the monosulfate appearance more significantly than do gluconate and lignosulfonate; the monosulfate peaks at $\approx 200^\circ$ and 280°C appear at 7 days in the presence of gluconate

(Fig. 2(A)) and at 14 days in the presence of lignosulfonate (Fig. 2(C)), whereas they cannot be observed even at 28 days in the presence of glucose (Fig. 2(E)).

In the presence of CH, the 0.3 wt% glucose addition (Fig. 2(F)) accelerates ettringite production approximately to the same extent as do gluconate and ligno-

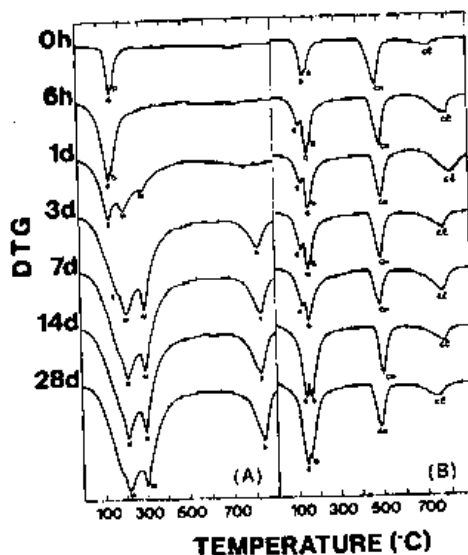
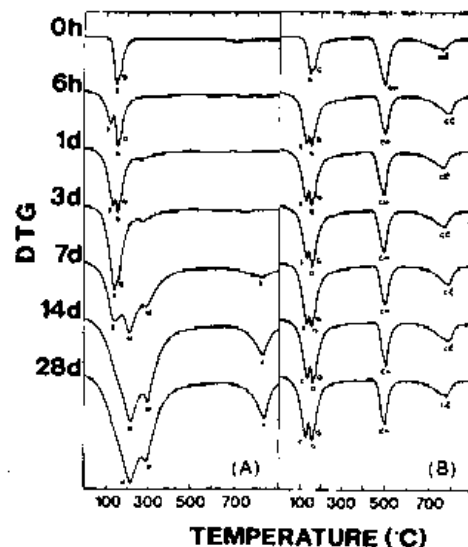
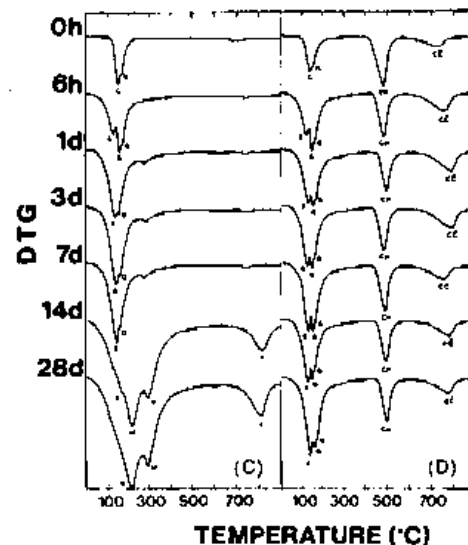


Fig. 1. DTG curves for $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CSH}_2\cdot\text{H}$ system (A) without admixture and (B) with CH. G = gypsum, E = ettringite, M = monosulfate, CH = calcium hydroxide, CC = calcium carbonate, X = monocarboaluminate.



TEMPERATURE ($^\circ\text{C}$)



TEMPERATURE ($^\circ\text{C}$)

Fig. 2. DTG curves for $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CSH}_2\cdot\text{H}$ system in the presence of (A) 0.3% sodium gluconate, (B) 0.3% sodium gluconate + CH, (C) 0.3% sodium lignosulfonate, (D) 0.3% sodium lignosulfonate + CH, (E) 0.3% glucose, and (F) 0.3% glucose + CH.

production, whereas the transformation of ettringite into monosulfate does not occur during the first 28 days of hydration even in the reference mix without admixtures. Conversely, in the system $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CH}\cdot\text{CSH}_2\cdot\text{H}$ the admixtures do not affect the rates of these processes, except glucose which retards both the ettringite production and its conversion into monosulfate.¹

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sulfonate additions (Fig. 2(B) and 2(D)). In the presence of 0.3 wt% glucose, monosulfate does not appear even after 28 days hydration. On the other hand the effect of 0.3 wt% glucose addition on the ettringite conversion to monosulfate seems to be similar to those caused by gluconate and lignosulfonate additions.

CONCLUSIONS

In the system $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CSH}_2\cdot\text{H}$ the admixtures examined retard the ettringite

production and its conversion into monosulfate. At 0.3 wt% addition the retarding effect is in the decreasing order: glucose, lignosulfonate, and gluconate. Conversely, the effect of these admixtures on C_2A hydration in the system $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CSH}_2\cdot\text{H}$ appears to be negligible. This behavior seems to agree with the more retarding effect of these admixtures on ferric cements than on ordinary portland cements.

In the system $\text{C}_2\text{A}\cdot\text{AF}\cdot\text{CH}\cdot\text{CSH}_2\cdot\text{H}$ the admixtures accelerate the early ettringite