Note

Hydration of Tetracalcium Aluminoferrite in an Acetic Acid Solution

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テトラカルシウムアルミノフェライトの酢酸水溶液中での水和反応

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Tetracalcium aluminoferrite was hydrated at 25°C with acetic acid solutions. The hydration rate of tetracalcium aluminoferrite was retarded remarkably when 1.00 mol/l acetic acid solution was used. When distilled water, 0.10 and 0.25 mol/l acetic acid solutions were used, tetracalcium aluminate tridecahydrate was formed. However, a hydrate characterized by two X-ray diffraction peaks with spacings of 10.9 and 5.4 Å appeared when 0.50 to 1.00 mol/l acetic acid solutions were used. This hydrate was stable up to 150°C in air, and was a complex of organic-tetracalcium aluminate hydrate. Acetic acid molecules were probably sorbed in the interlayer region of tetracalcium aluminate hydrate.

[Received June 7, 1989; Accepted September 18, 1989]

Key-words: Cement, Tetracalcium aluminoferrite, Hydration, Acetic acid

1. Introduction

There are many papers concerning the sorption of organic molecules on inorganic layer crystal. Clay minerals are well known as host inorganic materials.¹⁾ Tetracalcium aluminate hydrates (hereinafter abbreviated to $C_4AH_x^*$) formed in the hydration process of portland cement also have a layer structure, and they are able to sorb organic molecules in the crystal.²⁾ These C_4AH_x are hydration products of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). Giving a review of researches on the formation of organic-inorganic complexes up to 1967, Dosh³⁾ confirmed the formation of organic complexes of C_4AH_x , and then concluded that the fatty acids could form the complexes with C_4AH_{11} . On the other hand, extensive research has been performed to clarify the effect of organic substances on the hydration process of portland cement.⁴⁾⁻⁶⁾ Young⁷⁾ and Thomas et al.⁸⁾ proposed some retardation mechanisms by which organic substances influence the hydration process of portland cement. However, most research was carried out mainly with tricalcium silicate and tricalcium

aluminate.^{7),9)} C_4AF is one of the four major clinker minerals, but hydration products of C_4AF formed in the organic solutions have not been investigated in detail so far. Hydration products of C_4AF are considered to have the same structure as those of C_3A , but the substituted amount of iron to aluminium in the hydrates is not clear.¹⁰⁾⁻¹²⁾

In this paper, we investigated the hydration products of C_4AF formed in acetic acid solutions, i. e., the simplest fatty acid, and hope to report some new findings concerning their properties.

2. Experimental

C_4AF was synthesized in an electric furnace in an atmosphere of air for 4 hours at 1380°C from chemical grade $CaCO_3$, Al_2O_3 , and Fe_2O_3 . Grinding and burning were repeated until unreacted reagents were no longer detected by X-ray diffraction (XRD). Synthesized C_4AF was ground to a powder with 53 μm or less in diameter. 1.00, 0.75, 0.50, 0.25 and 0.10 mol/l acetic acid solutions were used for the hydration. The weight ratio of C_4AF to the solution was 1 to 1. Pastes were cured at 25°C for 1 to 10 days. The hydrates were dried for 2 days in a vacuum vessel in which the water vapour pressure was 5×10^{-4} mmHg (D-dry). Phase identification of the hydrates was

* abbreviated nomenclatures are used in the present paper;
C=CaO, A= Al_2O_3 , F= Fe_2O_3 and H= H_2O .

done by XRD and thermal analysis (DTA-TG). The amount of carbon in the hydrates was determined by total organic carbon analyzer (TOC). TG showed constant weight loss between 350° and 600°C, so TOC values refer to 1 g of the solids at 400°C. An infrared analysis (IR) was applied to examine the state of acetic acid. Moreover, dried hydrates were heated at intervals of 50°C up to 350°C in a furnace for 2 hours in air. Phase identification and TOC measurement were also done after heat treatment. Rehydration of the heated hydrates was carried out at 25°C for 1 day. Rehydrated hydrates were dried as above-mentioned. Distilled water was used for the rehydration, and the weight ratio of water to the heated hydrates was 1 to 1.

3. Results and discussion

Figure 1 shows the XRD patterns of the hydrates of C_4AF cured for 1 to 10 days with using various concentrations of acetic acid solution. According to these results, C_4AH_{13} is formed when 0.10 and 0.25 mol/l acetic acid solutions are added. However, the XRD intensity of this phase becomes weaker with the increase of the concentration of acetic acid. In contrast, new peaks, d values of 10.9 and 5.4 Å, appear. The intensities of these peaks increase with the increase of the concentration of acetic acid. The value of 10.9 Å is approximately double of the characteristic peak of tetracalcium aluminate hydrates of 5.4 Å.¹³⁾ A detailed account will be given later about this hydrate.

Fig. 1. XRD results of the hydrates in C_4AF -acetic acid soln. system. Hydration time was 1 day to 10 days.

It was also found that acetic acid could retard the rate of the hydration of C_4AF from the results of XRD examination in which XRD patterns do not show any particular changes from 1 to 10 days when 1.00 mol/l acetic acid solution is added. The hydrate which has XRD peaks of 10.9 and 5.4 Å is seemingly very similar to C_4AH_{13} , with 0001 reflection at 10.6 Å and 0002 reflection at 5.32 Å of C_4AH_{13} .¹⁴⁾ C_4AH_{13} releases water molecules with an increase of temperature as $C_4AH_{13} \rightarrow C_4AH_{11} \rightarrow C_4AH_7$, without losing its layer structure. Basal spacings of these hydrates are 10.6, 8.2, 7.9 and 7.4 Å, respectively.³⁾ The

Fig. 2. Effect of the heating temperature on the hydrates in C_4AF -1.00 mol/l acetic acid soln. system.

Fig. 3. IR and TOC results of heated hydrates in C_4AF -1.00 mol/l acetic acid soln. system.

effects of the heating temperature on the hydrates are shown in Fig. 2. XRD results show that the two peaks of acetic acid hydrate of 10.9 and 5.4 Å remained until 150°C. without changing their values. Whereas stable phases of C_4AH_x at 100°C and 150°C in air are C_4AH_{13} and C_4AH_7 , and the stable phase at 200°C is not clear.¹³⁾ XRD intensities of the two peaks of acetic acid hydrate decrease with the increase of temperature and they disappeared at 200°C. From these results, the hydrate which has two peaks of 10.9 and 5.4 Å is not C_4AH_{13} but an organic- C_4AH_x complex. Figure 3 shows the IR and TOC results of heated hydrates. According to the result, two absorption bands of 1560⁻¹cm and 1410⁻¹cm are seen up to 300°C. These are assigned to the symmetric vibration and asymmetric one of carbon-oxygen bond of carboxylate, respectively.¹⁵⁾ Organic component was burnt between 300° and 350°C proved by DTA-TG. The amount of carbon in each of the heated hydrates is approximately the same up to 300°C, and then considering the boiling point of acetic acid, 117.8°C, the organic substance in the hydrates is not in the form of acid but of salt or chelate.¹⁶⁾

Figure 4 shows the XRD results of rehydrated products of pre-heated hydrates. It is found that two peaks, 10.9 and 5.4 Å, appear after rehydration of the hydrate heated at 200°C. Considering the fact that there were no changes in the amount

of carbon in the hydrates up to 300°C, it is supposed that the organic molecules remain in the interlayer region of tetracalcium aluminate hydrate crystal at least up to 150°C. Water lost tetracalcium aluminate hydrate heated at 200°C and organic molecules remained formed organic-tetracalcium aluminate hydrate again after rehydration. The character of the hydrates of C_4AF formed in an acetic acid solution could be affected by heat treatment above 150°C since C_3AH_6 not found in acetic acid hydrates was formed when the heated hydrates were hydrated again.

It is concluded from these results that the hydration of tetracalcium aluminoferrite was remarkably retarded by 1.00 mol/l of acetic acid solution, and acetic acid could form an organic complex of tetracalcium aluminate hydrate stable up to 150°C in air. Acetic acid molecules were probably sorbed in the interlayer region of the tetracalcium aluminate hydrate.

References

- 1) M. S. Whittingham and A. J. Jacobson, Ed., "Intercalation Chemistry", Academic Press, London and N. Y. (1982) pp. 55-99.
- 2) W. Dosch, *Clays and Clay Minerals*, 15, 273-92 (1967).
- 3) W. Dosch, *Neues Jahrb. Mineral.*, 106, 200-39 (1967).
- 4) P. E. G. Banfill and D. C. Saunders, *Cement and Concrete Res.*, 16, 399-410 (1986).
- 5) N. B. Singh, S. P. Singh and A. K. Singh, *ibid.*, 16, 545-53 (1986).
- 6) S. Monosi, G. Moriconi, M. Pauri and M. Collepari, 8th Int'l Symposium on Chem. Cement, Brazil, Vol. 3 (1986) pp. 130-35.
- 7) J. F. Young, *Cement and Concrete Res.*, 2, 415-33 (1972).
- 8) N. L. Thomas and D. D. Double, *ibid.*, 11, 675-87 (1981).
- 9) H. F. W. Taylor and A. B. Burner, *ibid.*, 17, 613-23 (1987).
- 10) M. Fukuhara, S. Goto, K. Asaga, M. Daimon, R. Kondo and Y. Ono, *Yogyo-Kyokai-Shi*, 88, 436-40 (1980).
- 11) F. Hannawayya, 8th Int'l Symposium on Chem. Cement, Brazil, Vol. 3 (1986) pp. 217-24.
- 12) P. W. Brown, *J. Am. Ceram. Soc.*, 70, 493-96 (1987).
- 13) F. G. Buttler, H. S. D. Glasser and H. F. W. Taylor, *ibid.*, 42, 121-26 (1959).
- 14) H. F. W. Taylor, "The Chemistry of Cements", Vol. 2, Academic Press, London and N. Y. (1964) p. 392.
- 15) K. Nakanishi, "IR Absorption Spectroscopy—Practice", Nanko-do, Tokyo (1960) p. 49.
- 16) Y. Yamamoto, *Semento-Gijutsu-Nempo*, 27, 148-52 (1973).

Fig. 4. XRD results of rehydrated products. Hydrates for the rehydration were heated at various temperatures.