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Analysis of triethanolamine in white cement pastes by voltammetric methods

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Abstract

Triethanolamine (TEA) in cement paste has been analysed by square wave voltammetric technique. The technique is sensitive for the quantitative determination of small amounts of TEA. The percentage of the adsorbed TEA is very dependent upon the original TEA content of the cement sample. The adsorption reached a saturation level after 12 hours of hydration and remained almost invariant at longer times.

Keywords: Triethanolamine; Adsorption; Cement paste; Voltammetry

Water-soluble admixtures are widely used to accelerate or retard the setting time of cement. The most commonly used organic admixture is triethanolamine (TEA) alone or together with other organic and inorganic products [1]. The effect of TEA on the cement hydration is not completely resolved. Depending on the cement type and the addition rate, TEA can either accelerate or retard the setting. At an addition rate of 0.02% to the type I Portland cement, TEA acts as a set accelerator, at 0.25%, it acts as a mild set retarder, at 0.5%, TEA acts as a severe retarder, and at 1%, it is a very strong accelerator [2,3].

It was Heren and Ölmez [4] who carried out the study to understand the addition effect of TEA in white Portland cement. They reported that in the case of the addition amounts of 0.1, 0.5, and 1%, the setting time is retarded. In order to understand the rate of TEA in cement hydration, some analytical methods of TEA in the aqueous phase of cements were established. It was McCall and Mannone [5] who used gas chromatography and infrared spectroscopy to analyse cement pastes for triethanolamine. Pauri and colleagues [6] used UV spectroscopic method to determine the TEA content in the aqueous phase. Yilmaz and Menek developed a new analytical method based on the measurement of concentration of TEA-Fe^3+ complex in high-alkaline medium ($pH > 12$), and then applied this method to the TEA-3 $CaO \cdot Al_2O_3$-$CaSO_4 \cdot H_2O$-H_2O system [7].

In this study, the amount of TEA adsorbed on the white cement and the alteration in the adsorption level with time were determined.

1. Experimental

Cement pastes with the following TEA contents were prepared:

1. 50 g white cement + 25 mL 2% TEA solution
2. 50 g white cement + 25 mL 1% TEA solution
3. 50 g white cement + 25 mL 0.2% TEA solution

1.1. Stock solutions

Solutions were prepared as follows:

1. A stock solution of TEA was prepared by dissolving 1 g of TEA (Merck extra pure) in a liter of distilled water.
2. 86.35 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ (BDH Chemicals Ltd. > 98%) was dissolved in a liter water. This solution contains 10 g of Fe^{3+} per liter.
3. 1 M NaOH solution (40 g NaOH/L).

The samples having different amounts of TEA percentage in white cement (1, 0.5, and 0.1%) were prepared. These cement-TEA solution mixtures were stirred for 3 minutes and stored at room temperature (20°C) for 10 minutes, 1, 3, and 12 hours before analysing for TEA in the cement. The specimens were shaken in 50 mL of hot water (40°C) for 10 minutes and then filtered off and the filtrates were diluted to 100 mL. From these solutions 50–500 μL were transferred to a 10-mL voltammetric cell that con-

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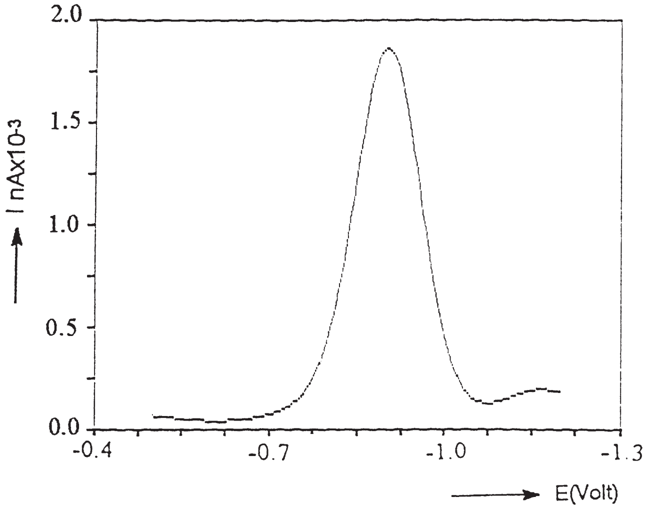

Fig. 1. The voltammogram of the TEA-Fe^3+ complex.

tained 0.15 M NaOH solution. The solutions were placed in the voltammetric cell and deaerated with nitrogen gas for 4 minutes. The voltammograms of these solutions were obtained by an EG&G Princeton Applied Research (PAR), model 384B, polarographic analyser using square wave voltammetry (SWV) made of the instrument. An inert atmosphere (N_2) was maintained over the solutions during measurements. The setting parameters were as follows: pulse height 50 mV, scan increment 4 mV, scan rate 400 mV/s, potential -0.6–-1.2 V vs. AgCl/Ag (saturated KCl).

1.2. Application of analysis method

0.15 M NaOH solution was used as supporting electrolyte. 10 mL of 0.15 M NaOH and 50–500 μL of the diluted TEA-cement filtrates were placed in the voltammetric cell. and $NH_4Fe(SO_4)_2 \cdot 12H_2O$ was added into the voltammetric cell until the point was reached where the current was constant. The amount of unadsorbed TEA was determined from these peak currents. Since the added TEA was known, the amount of adsorbed TEA was calculated from the difference. The voltammograms of these solutions were obtained by EG&G PAR model 384B polarographic analyser using SWV instruments.

2. Results and discussion

TEA is not an electroactive matter, so alone does not give any voltammogram. But TEA-Fe^3+ complexes are stable and the voltammogram produced by the TEA-Fe^3+ complex can be used for the indirect analysis of TEA. In a previous paper [7], a new analytical method was put forward to analyse the TEA content in cement by analysing TEA-Fe^3+ complex in alkaline solution with voltammetric techniques.

The voltammogram of the TEA-Fe^3+ complex using 0.15 M NaOH as supporting electrolyte is shown in Fig. 1. The peak current linearly increases with increasing amounts of the TEA-Fe^3+ complex in the aqueous phase.

It is accepted that all of the TEA in the solution is converted to the TEA-Fe^3+ complex at their constant peak current region. Their current-concentration curves were formed. At the end, the amount of TEA adsorbed by the hydrated cement matrix were calculated for each TEA-cement solution from these curves. Table 1 shows the amounts of TEA adsorbed by the hydrated cement matrix at various hydration times.

3. Conclusion

TEA in cement matrix is converted into the TEA-Fe^3+ complex by adding NaOH and Fe^3+ solutions and analysed by using SWV techniques. Quantitative determination of TEA was realised by the voltammogram produced by the complex. Our results show that the amount of adsorbed TEA in the cement paste increases with an increase in the amount of time and that the adsorption is approximately completed at 12 hours. After 12 hours the percentage of TEA adsorbed is approximately constant at different times of hydration for

Table 1
Amount of the adsorbed TEA (%)

Set number	Percent TEA in cement paste by weight of cement	Hydration time (minutes)	Amount of TEA originally in the paste (mg)	Amount of the unadsorbed TEA (mg)	Adsorbed TEA (%)
1	0.1%	5	50	45	10
		60	50	43	14
		180	50	22	37
		720	50	2	96
2	0.5%	5	250	231	8
		60	250	115	54
		180	250	76	70
		720	250	14	95
3	1.0%	5	500	466	7
		60	500	233	54
		180	500	48	91
		720	500	36	93

all specimens. For different amounts of TEA added to the cement paste, the amount of TEA adsorbed increases with an increase in the initial TEA concentration.

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