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Analysis of triethanolamine in trass cement pastes by voltammetric methods

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Abstract

Triethanolamine (TEA) in trass cement pastes has been analyzed by the Square Wave Voltammetric (SWV) technique. It has been observed that the adsorption effect of TEA on the trass cement increases with time and the adsorption is approximately complete at 12 h. The technique is sensitive for the quantitative determination of small amounts of TEA. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Water soluble admixtures used in concrete as water-reducing or accelerating agents may contain small amount of triethanolamine (TEA). The amine reduces the excessive retardation effect of the water-reducing admixture. TEA is generally preferred to $CaCl_2$ because in large amounts $CaCl_2$ may promote corrosion of the embedded metals in concrete. TEA is also used as a grinding aid [1].

The action of the TEA in the hydration of cement is not completely understood. It is not yet even resolved whether it is an accelerator or a retarder [2]. In order to assess the actual role of TEA in cement hydration, it would be very useful to analyze the aqueous phase of cements for TEA. It was McCall and Mannone [3] who used gas chromatography and infrared spectroscopy to analyze cement pastes for TEA. Pauri et al. [4] used the UV method to determine the TEA content in the aqueous phase.

It is known that TEA has the ability to chelate certain metallic ions in highly alkaline medium (pH>12), one of which is the ferric ion [5].

Yilmaz et al. [6] developed a new analytical method based on the measurement of the concentration of a TEA–Fe^{3+} complex by using polarographic techniques.

In the previous paper, we have determined the amount of TEA adsorbed on white cement pastes by the square wave voltammetric (SWV) technique [7].

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

2. Experimental

The trass cement used in this work contained 25% trass and 75% Portland cement. It had a Blaine surface area of 3100 cm^2/g. Stock solutions were prepared as follows.

Stock solutions:

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 >98%) was dissolved in a liter of 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 by weight of trass cement 1.0%, 0.5% and 0.1%) were prepared. These trass cement–TEA solution mixtures were stirred for 3 min and stored at room temperature (20°C) for 10 min, 1, 3 and 12 h before analyzing for TEA in the trass cement. The specimens were shaken in 50 ml of hot water

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(40°C) for 10 min and then filtered off and the filtrates were diluted to 100 ml. From these solutions 50–500 μl were transferred to 10 ml voltammetric cell that contained 0.15 M NaOH solution. The solutions were placed in the voltammetric cell and de-aerated with nitrogen gas for 4 min. The voltammograms of these solutions were obtained by an EG&G PAR model 384B polarographic analyzer using the SWV mode 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 to −1.2 V versus AgCl/Ag (saturated KCl).

2.1. Application of analysis method

NaOH (0.15 M) solution was used as a supporting electrolyte; 10 ml 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 where the current was constant. The amount of unadsorbed TEA was determined from these peak currents. Since the added TEA is known, the amount of adsorbed TEA was calculated from the difference.

3. Results and discussion

TEA does not give any voltammogram because it is not an electroactive compound in the basic medium. But TEA–Fe^{3+} complexes are stable and they can be used for the indirect analysis of TEA [6,7].

The voltammogram of the TEA–Fe^{3+} complex using 0.15 M NaOH as a 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 [6].

It is accepted that all of the TEA in the solution is converted to the TEA–Fe^{3+} complex at the constant peak current region (Fig. 2). The current–concentration curves were formed and quantitative determination of the TEA adsorbed by the hydrated trass cement matrix was accomplished.

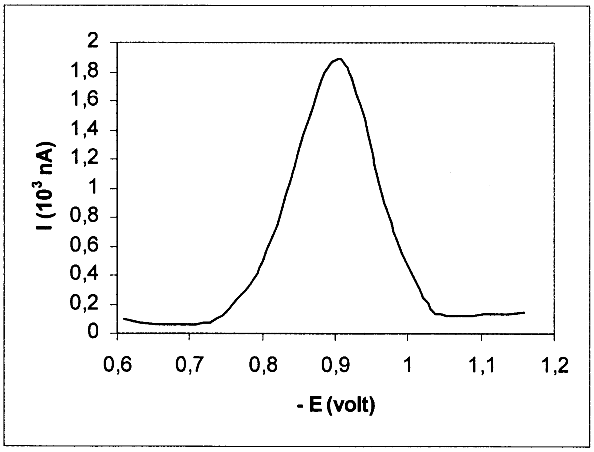

Fig. 1. The voltammogram of the TEA–Fe^{3+} complex.

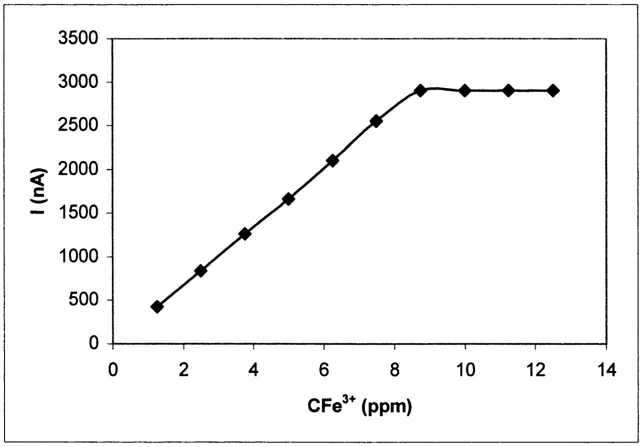

Fig. 2. The change of the peak current of the TEA–Fe^{3+} complex with Fe^{3+} concentration at 5 min for 1% TEA.

The current variations of the TEA–Fe^{3+} complexes for 1.0% TEA–trass cement matrix are given in Fig. 2. Table 1 shows the amounts of TEA adsorbed by the hydrated cement matrix at various hydration times.

4. Conclusion

For the different amounts of TEA added to the trass cement paste, the amount of TEA adsorbed increases with time and the adsorption is approximately complete at 12 h for the samples containing 0.1% and 1% TEA. The adsorption results of these two samples are very close to the values for samples prepared with Portland cement and 0.1% and 1% TEA by weight [7].

The sample with 0.5% TEA gives the minimum adsorption values. Also these adsorption results are lower than Portland cement with 0.5% TEA.

Table 1
Amount of the adsorbed TEA (%)

Set no.	Percent TEA in trass cement paste by weight of cement	Hydration time (min)	Adsorbed TEA (%)
1	0.1%	5	30
		60	44
		180	50
		720	94
2	0.5%	5	5
		60	31
		180	43
		720	75
3	1.0%	5	7
		60	91
		180	92
		720	92

Since the critical content of the admixture varies depending on the cement used, it may be that very different effects obtained by using equal contents of TEA with trass cement.

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