JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 224-229

Voltammetric behaviour of iron in cement
Part IV: Effect of acetate and urea additions

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Received 12 October 1990; revised 6 June 1991

The effects of acetate and urea on the cyclic voltammetric behaviour of iron in cured cement paste were investigated. The voltammetric results indicate that sodium acetate and urea do not cause depassivation of iron in cement. The addition of ~ 0.2 M of either sodium acetate or urea prevents depassivation of iron in cement exposed to 0.1 M sodium chloride upon potential cycling. However, the addition of even relatively high concentrations of sodium acetate or urea (e.g. 1.0 M), cannot prevent depassivation by 0.2 M sodium chloride upon potential cycling. The voltammetric results also indicate that sodium acetate, urea, and calcium magnesium acetate (CMA) are only marginally effective as corrosion inhibitors for reinforced concrete, compared with an inhibitor of known effectiveness, such as sodium nitrite. Thus, while acetates and urea may well be 'non-corrosive' deicers when used by themselves, large amounts of sodium chloride should not be mixed with acetates or urea as a cost-reducing measure.

1. Introduction

The chloride-induced corrosion of reinforcing steel in concrete is a pressing problem, because of corrosion-related damage to concrete structures such as bridges and parking garages [1, 2]. A stable, passivating film normally forms on the surface of reinforcing steel in the highly alkaline environment of Portland cement. Corrosion of the embedded steel occurs if this protective film is disrupted, e.g., through the action of chloride ions from sodium chloride deicing salt. Consequently, alternative, noncorrosive deicing chemicals are of interest.

Calcium magnesium acetate (CMA) is the most widely discussed alternative to sodium chloride for use as a deicing chemical [3, 4]. CMA, a mixture of calcium acetate [$Ca(CH_3COO)_2$] and magnesium acetate [$Mg(CH_3COO)_2$], has deicing properties close to those of sodium chloride [3]. However, the effective cost of using CMA as a deicing chemical is prohibitively high, being about 50 times that of sodium chloride [4]. New, less costly processes for manufacturing CMA are being developed, and other less costly alternatives, such as mixtures of CMA and sodium chloride, also have been suggested [4].

Urea [$CO(NH_2)_2$] also is frequently used as a deicer, e.g., on airport runways, and the use of urea in 'non-corrosive' deicing mixes also has been suggested [5–7].

In previous communications [8–10], we reported the development and use of a reliable method for cyclic voltammetric measurements on iron in cured Portland cement. This voltammetric method has proven useful for studying the effects of additions such as sodium chloride and various corrosion inhibitors on the passivation and corrosion of iron and steel in cement [8–10]. In this study, we have used the cyclic voltammetric method to investigate the effects of sodium acetate, CMA and urea on the passivation and corrosion of iron in cement.

2. Experimental details

The cyclic voltammetric experiments were conducted according to the procedure described in detail in Parts I and II [8, 9]. Briefly, the method involves embedding iron wire (Johnson-Matthey, 99.999% Fe, 0.25 mm diameter) in cement paste. The resulting iron-reinforced miniature cement cylinders are cured for three days at 100% relative humidity. *IR*-compensated cyclic voltammograms (CVs) then are run at $0.050\ \mathrm{V\,s^{-1}}$ from -1.4 V to $+0.4$ V (all potentials quoted herein were measured, and are reported, with respect to the saturated calomel electrode (SCE)). The electrodes were cycled in this manner at least 200 times. The electrochemical cell was of standard three-electrode design, except that four counter electrodes were used in order to maintain cylindrical geometry. Saturated $Ca(OH)_2$, or saturated $Ca(OH)_2$ containing various additions (e.g. sodium chloride, sodium acetate or urea) were used as the cell electrolyte. Solutions were prepared using BDH AnalaR chemicals and de-ionized water from a Millipore Milli-Q water system (resistivity $\sim 18\ \mathrm{M\Omega\,cm}$). All experiments were carried out at 25 ± 0.2° C.

In some of the experiments, sodium chloride, sodium acetate, urea, or combinations of sodium

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chloride and either sodium acetate or urea, were introduced into the cement by immersing the cement electrodes in solutions of saturated $Ca(OH)_2$ containing the desired additive(s) for 24 h, following the 3-day air cure, and before potential cycling. The cell electrolyte in these experiments was of the same composition as the solutions used for immersion. Also, sodium acetate, urea, CMA or various corrosion inhibitors (sodium benzoate, potassium chromate or sodium nitrite) were introduced into some of the samples as admixtures (i.e. dissolved in the cement mix water), as would be done in actual practice. The admixtures were added by weight, as a percentage of the dry cement in the cement mix.

3. Results and discussion

Anodically-formed films resulting from potential cycling do not duplicate naturally formed passive films found on reinforcement steel in concrete. However, although potential sweeping can affect the passive layer characteristics, the passivation produced during the voltammetric procedure is subject to reproducible and sensitive electrochemical measurement. Care has been taken to develop a reliable experimental procedure [8–10], in order that the differences in behaviour caused by additives such as urea and acetate can be noted with confidence. Thus, while caution is advised in the direct application of the results presented in this paper, these results can be used as a guide to the relative effects of urea and acetate, as compared with the effects of chlorides and known corrosion inhibitors.

3.1. *Effects of sodium acetate and urea additions*

The cyclic voltammetric behaviour of iron in cement after exposure to alkaline solutions containing deicing salts (e.g. NaCl) can provide useful information about the effects of these salts on the passivation and depassivation of iron in cement [9, 10]. To determine the effects of acetate and urea on the passivation of iron in cement, the voltammetric behaviour after exposure to solutions of saturated calcium hydroxide containing various concentrations of acetate or urea was investigated. The acetate was added as sodium acetate, in order to isolate the effect of acetate (calcium acetate or magnesium acetate additions would cause precipitation of calcium hydroxide or magnesium hydroxide, and consequently, reduction of the pH), and also to provide a more direct comparison with the effects of sodium chloride additions.

Voltammograms for iron in cement after exposure to solutions containing saturated calcium hydroxide alone, and with the addition of either 0.2 M sodium acetate or 0.2 M urea are shown in Fig. 1. The electrochemical reactions corresponding to the various peaks have been discussed previously (see [8] and references therein). In alkaline solutions, peaks 1 and 2 usually are attributed to the formation of ferrous hydroxide from the base metal. Peak 3 is the passivation peak, where poorly-protective ferrous species are converted into protective ferric species (possibly $CaFe_2O_4$ [8]). Peak 4 is the cathodic reduction peak associated with peak 3, while peak 5 is the reduction peak associated with peaks 1 and 2. Although there are minor effects on peaks 4 and 5, the main anodic voltammetric peaks remain unchanged upon addition of sodium acetate or urea, indicating that neither sodium acetate nor urea significantly affect the passivation process. Conversely, when 0.2 M sodium acetate or 0.2 M urea is replaced with 0.2 M NaCl, significant depassivation is observed, as shown by the extremely distorted voltammograms and the large currents flowing in the normally passive region at potentials anodic to peak 3 (see [9] and [10], also Fig. 3 below). Furthermore, no depassivation was observed even with, e.g. 1.0 M sodium acetate or 1.0 M urea in the external solution. Thus, according to the voltammetric results, acetate and urea, unlike chloride, do not directly cause depassivation of iron in cement. Therefore, even though it is well known that larger amounts of acetate deicing salts [4] or of urea must be used to achieve a deicing effect equivalent to that obtained using sodium chloride, the results shown in Fig. 1 suggest that less corrosion of reinforcing steel will occur if acetate deicing salts or urea are used instead of sodium chloride.

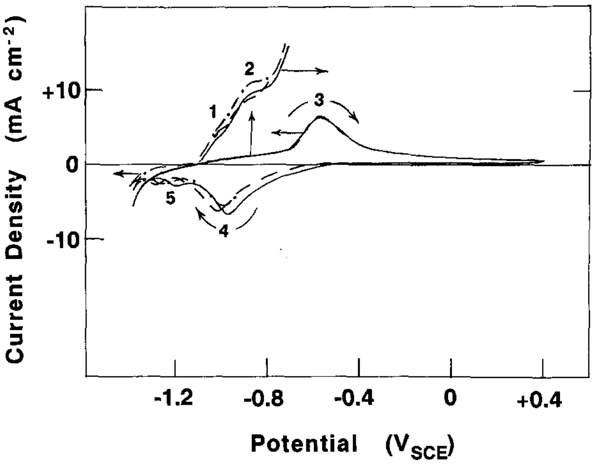

Fig. 1. CVs for iron in cement after 24 h exposure to saturated $Ca(OH)_2$ (———), saturated $Ca(OH)_2$ + 0.2 M sodium acetate (– – –), or saturated $Ca(OH)_2$ + 0.2 M urea (–·–·–). Water-to-cement ratio of cement mix = 0.45, sweep rate = 50 mV s^{-1}, 25 °C, cycle number 201.

3.2. *Effects of sodium acetate and urea in the presence of chloride*

In order to reduce the high cost of CMA, previous investigators recently have suggested that CMA be mixed with low-cost sodium chloride (at NaCl-to-CMA ratios as high as ~ 1 : 0.46 by weight) [4]. This suggestion is based on results which indicate that mixtures of CMA and sodium chloride may be less corrosive than sodium chloride alone [4]. To further investigate these results, the voltammetric method was used to examine the effects of mixtures of chloride and acetate on the passivation and depassivation of iron in cement. In these experiments, the cement electrodes

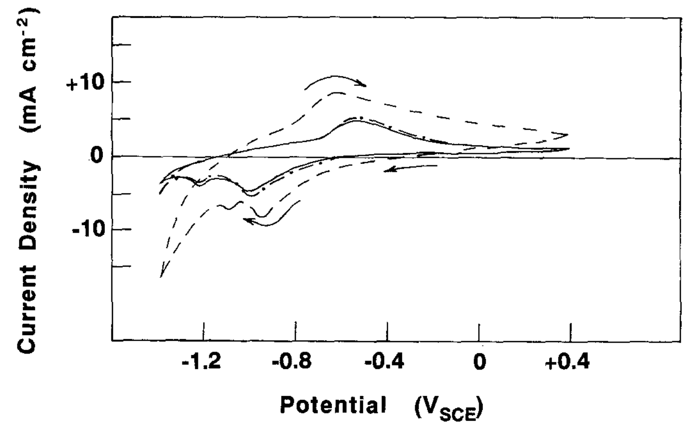

Fig. 2. CVs for iron in cement after 24 h exposure to saturated $Ca(OH)_2$ + 0.1 M NaCl (— — —), saturated $Ca(OH)_2$ + 0.1 M NaCl + 0.2 M sodium acetate (———), or saturated $Ca(OH)_2$ + 0.1 M NaCl + 0.2 M urea (–·–·–). Water-to-cement ratio of cement mix = 0.45, sweep rate = 50 mV s^{-1}, 25 °C, cycle number 201.

were immersed for 24 h in solutions of saturated calcium hydroxide, containing 0.1 or 0.2 M NaCl (significant chloride-induced depassivation occurs with 0.1 M NaCl, and extensive depassivation occurs with 0.2 M NaCl [9]), and various concentrations of sodium acetate (0 ~ 1.0 M). The voltammetric behaviour of the embedded iron then was determined according to our standard method. Similar experiments also were run to determine the effect of urea additions (0 ~ 1.0 M) in the presence of 0.1 or 0.2 M NaCl.

Typical voltammograms for iron in cement after exposure to sodium chloride + sodium acetate, or sodium chloride + urea, are shown in Figs 2 and 3. We also have found that the current density in the normally passive region at 0 V is a useful indicator of the effectiveness of the passive layers formed on each cycle [9, 10]. Accordingly, the variations of the current density at 0 V with sodium acetate and urea concentration are shown in Figs 4 and 5. The results for external solutions with no added NaCl are compared with those for 0.1 M NaCl (Fig. 4), and 0.2 M NaCl (Fig. 5).

Figure 2 shows that the addition of 0.2 M of either sodium acetate or urea to 0.1 M NaCl greatly reduces the depassivation observed with 0.1 M NaCl. As can be seen from Fig. 4, the current densities at 0 V decrease by about 70% between 0.05 ~ 0.2 M sodium acetate or urea to almost the same value observed with acetate or urea alone. Thus, the voltammetric results indicate that acetate and urea inhibit the depassivation of iron in cement exposed to 0.1 M NaCl. On the other hand, the results for 0.2 M NaCl shown in Figs 3 and 5 indicate that at this higher chloride ion concentration the addition of even high concentrations of sodium acetate or urea, (e.g. 1.0 M), cannot prevent the depassivation of iron in cement (although the large currents flowing at 0 V are reduced by ~30%).

Results of immersion-type corrosion tests reported in [4] suggest that the corrosion behaviour of steel exposed to solutions containing sodium chloride and CMA at weight ratios less than about 1 NaCl : 0.46

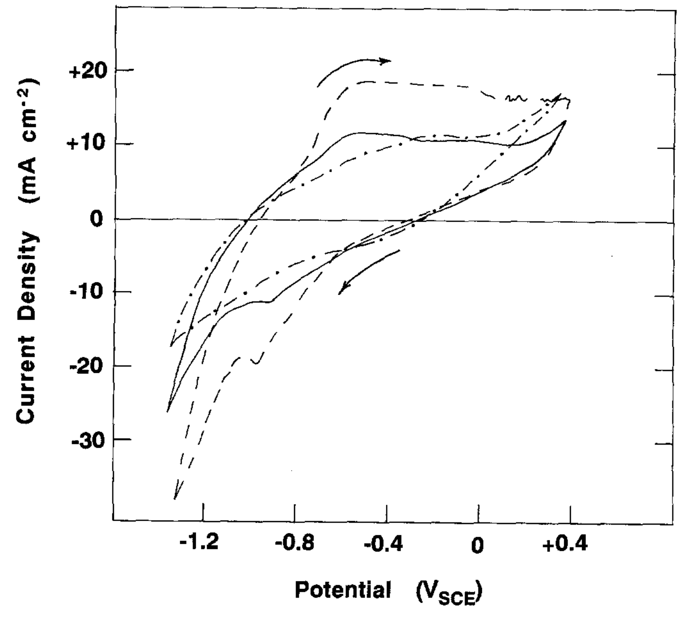

Fig. 3. CVs for iron in cement after 24 h exposure to saturated $Ca(OH)_2$ + 0.2 M NaCl (— — —), saturated $Ca(OH)_2$ + 0.2 M NaCl + 1.0 M sodium acetate (–·–·–), or saturated $Ca(OH)_2$ + 0.2 M NaCl + 1.0 M urea (———). Water-cement ratio of cement mix = 0.45, sweep rate = 50 mV s^{-1}, 25 °C, cycle number 201.

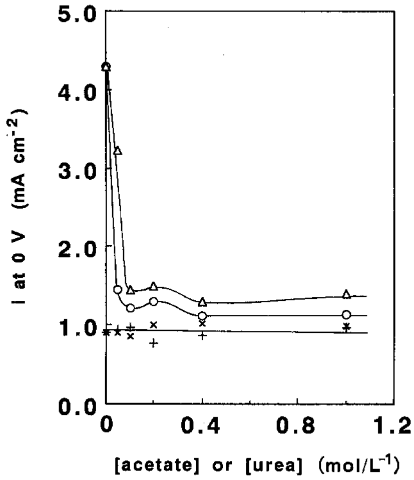

Fig. 4. Variation of current density in normally passive region at 0 V with sodium acetate or urea concentration, for external saturated $Ca(OH)_2$ solutions containing 0 M or 0.1 M sodium chloride. (+) = urea alone; (○) = urea + 0.1 M NaCl; (×) = acetate alone; (△) = acetate + 0.1 M NaCl. Other conditions: water-to-cement ratio of cement mix = 0.45, sweep rate = 50 mV s^{-1}, 25 °C, cycle number 201.

CMA is similar to that of steel exposed to solutions of CMA alone. Our voltammetric results indicate that while similar behaviour may be expected for iron in cement exposed to relatively low sodium chloride concentrations (e.g. 0.1 M NaCl – see Fig. 4), at relatively high sodium chloride concentrations (e.g. 0.2 M NaCl), depassivation cannot be prevented by the presence of acetate (see Fig. 5). For 0.1 M NaCl, the acetate concentration corresponding to 1 NaCl : 0.46 CMA by weight is ~0.05 M. Thus, the results reported in [4] imply that for 0.1 M NaCl, depassivation should be inhibited by the addition of more than ~0.05 M acetate, in agreement with the voltammetric results shown in Figs 2 and 4. Similarly, according to the 1 : 0.46 ratio given in [4], for 0.2 M NaCl, depassivation should be inhibited by the addition of more than ~0.1 M acetate. However, as shown in Figs 3 and 5, our voltammetric results indicate that the addition of even 1.0 M acetate cannot prevent the depassivation of iron in cement by 0.2 M NaCl. Very similar voltammetric results were obtained for urea additions (Figs 2–5). Accordingly, we caution that while acetate and urea may provide significant protection from depassivation at relatively low concentrations of sodium chloride (e.g. less than ~0.1 M), acetate and urea cannot prevent depassivation at higher concentrations of NaCl (e.g. 0.2 M), and thus the risk of rebar corrosion may be increased significantly by mixing large (economical) amounts of sodium chloride with either acetate deicing salts or urea.

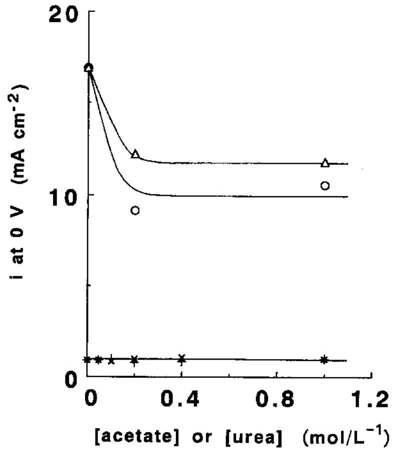

Fig. 5. Variation of current density in normally passive region at 0 V with sodium acetate or urea concentration, for external saturation $Ca(OH)_2$ solutions containing 0 M or 0.2 M sodium chloride. (+) = urea alone; (○) = urea + 0.2 M NaCl; (×) = acetate alone; (△) = acetate + 0.2 M NaCl. Other conditions: water-to-cement ratio of cement mix = 0.45, sweep rate = 50 mV s^{-1}, 25 °C, cycle number 201.

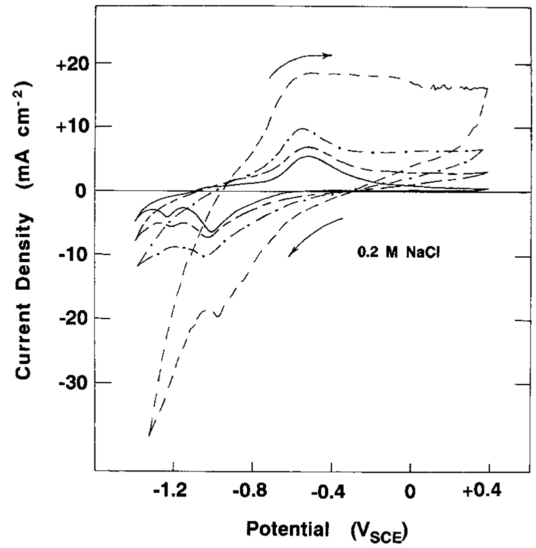

Fig. 6. CVs for iron in cement containing: no admixtures (— — —), 0.95% (–·–·–) and 1.9% (– – –) admixed sodium acetate, and 0.6% admixed sodium nitrite (———), after 24 h exposure to saturated $Ca(OH)_2$ + 0.2 M NaCl. Water-to-cement ratio of cement mix = 0.45, sweep rate = 50 mV s^{-1}, 25 °C, cycle number 201.

3.3. *Inhibition of chloride-induced depassivation by acetate and urea*

The voltammetric results described above indicate that sodium acetate and urea may have some limited effectiveness as corrosion inhibitors. To obtain a better indication of the extent of the effectiveness of acetate and urea as corrosion inhibitors for reinforced concrete, the voltammetric behaviour of iron in cement containing sodium acetate or urea was compared with that of iron in cement containing corrosion inhibitors of known effectiveness, such as benzoates, chromates and nitrites [9, 11, 12], which have already been tested according to the standard voltammetric method [9, 10]. The sodium acetate and urea were admixed (i.e. added to the cement mix, as is done in actual practice with corrosion inhibitors), and the resulting cement electrodes were exposed to solutions containing various concentrations of NaCl (0 ~ 0.4 M) for 24 h before running the voltammetric experiments according to our standard method [9, 10].

Voltammograms for iron in cement after exposure to 0.2 M NaCl, with admixed sodium acetate, or admixed urea, are compared in Figs 6 and 7, respectively, with the corresponding voltammograms for no admixture, and for admixed sodium nitrite. (In Figs 6 and 7, additions of 0.95% sodium acetate and 0.7%

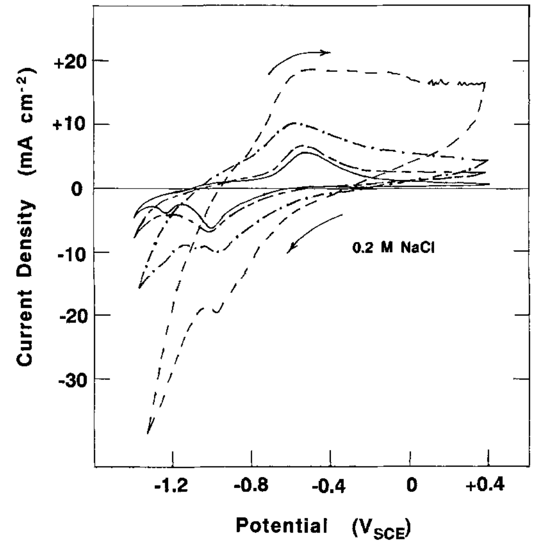

Fig. 7. CVs for iron in cement containing: no admixtures (— — —), 0.7% (–·–·–) and 1.4% (– – –) admixed urea, and 0.6% admixed sodium nitrite (———), after 24 h exposure to saturated $Ca(OH)_2$ + 0.2 M NaCl. Water-to-cement ratio of cement mix = 0.45, sweep rate = 50 mV s^{-1}, 25 °C, cycle number 201.

urea are comparable to 0.6% sodium nitrite on a molar basis.) Although the extent of depassivation after exposure to 0.2 M NaCl is reduced by admixing sodium acetate or urea, significant depassivation still is observed. On the other hand, with 0.6% admixed sodium nitrite, no depassivation is observed, even after exposure to concentrations of up to ~0.4 M NaCl (see [9], and Table 1 below). Thus, inspection of the voltammograms is sufficient to see that sodium acetate and urea are only marginally effective as corrosion inhibitors, compared with sodium nitrite. The effectiveness of nitrites as corrosion inhibitors for reinforced concrete is well documented [9, 11–13], and the addition of nitrites to the concrete mix may delay the onset of corrosion of reinforcing steel in chloride-contaminated concrete by several years [13–17]. Accordingly, our voltammetric results suggest that the presence of sodium acetate or urea would not be likely to appreciably delay the onset of depassivation of reinforcing steel in chloride-contaminated concrete.

*Table 1. Effect of admixed sodium acetate, urea, CMA, and various inhibitors on current density at 0 V after 200 cycles for various external NaCl concentrations**

Concentration	*Current density at 0 V* (mA cm^{-2})§					
[NaCl] (mol L^{-1})	*0*	*0.05*	*0.10*	*0.20*	*0.40*	*0.60*
No admixture	0.9	1.1	4.3	17‡	28‡	
0.95% NaAc†	0.9	1.1	1.4	5.3	12‡	
1.9% NaAc†	0.9	0.9	1.4	3.1	12‡	
0.7% Urea	0.9	1.1	2.1	4.8	12‡	
1.4% Urea	0.9	1.0	1.8	3.0	12‡	
0.9% CMA†	0.9	1.3	1.6	13‡	25‡	
1.7% K_2CrO_4	0.7	0.7	0.7	1.8	2.9	8.0‡
1.6% NaB†	0.8	0.9	0.9	1.1	7.9‡	
0.6% $NaNO_2$	0.9	0.9	0.9	0.95	1.1	12‡

* The line in Table 1 separates regions of passivity from regions of film breakdown. All admixture concentrations are expressed as weight percents with respect to the weight of dry cement in the mix. The results shown in Table 1 should be used only as a guide to the relative performances of sodium acetate, CMA, potassium chromate, sodium benzoate and sodium nitrite as corrosion inhibitors.

† 'NaB' = sodium benzoate, 'NaAc' = sodium acetate, 'CMA' = calcium magnesium acetate.

‡ These points are less well defined.

§ All current densities reported in Table 1 were calculated on the basis of the nominal iron surface area of about 0.08 cm^2, the accurately measured areas being in the range 0.080 ± 0.005 cm^2. No baseline corrections were applied to the voltammograms.

The effectiveness of sodium acetate and urea as corrosion inhibitors is compared in a more quantitative manner with the effectiveness of other corrosion inhibitors (sodium nitrite, potassium chromate and sodium benzoate [9] in Table 1. However, we must emphasize that the results shown in Table 1 are to be used only as a guide to relative performance of sodium acetate, urea and the various corrosion inhibitors. The currents in the normally-passive region at 0 V for the various admixtures are compared for various NaCl concentrations. The inhibitor addition levels are all comparable (0.06 ~ 0.08 moles per kg cement mix), except for 1.9% sodium acetate and 1.4% urea, which represent approximately twice the other molar addition levels. The zig–zag line separates regions of stable passivation (indicated by low current densities, less than ~ 1 mA cm^{-2}) from regions of depassivation (indicated by high current densities). Results are also shown in Table 1 for 0.9% admixed CMA, which is comparable on a molar basis to 0.95% admixed sodium acetate (0.08 moles acetate per kg of cement mix). The CMA was a 3 : 7 molar mix of calcium acetate and magnesium acetate (both BDH AnalaR).

The results in Table 1 show that while the current densities in the normally passive region at 0 V are lowered by the admixing of sodium acetate and urea, neither sodium acetate nor urea, even when admixed at relatively high concentrations (e.g. 0.16 moles per kg of cement mix), can prevent extensive depassivation of iron in cement after exposure to 0.2 M NaCl. Passivation is not extended to significantly higher sodium chloride concentrations by admixing 0.95% ~ 1.9% sodium acetate or 0.7% ~ 1.4% urea. Passivation is maintained only up to 0.05 ~ 0.1 M NaCl, whereas passivation is extended to 0.1 ~ 0.2 M NaCl by 1.7% potassium chromate, to ~0.2M by 1.6% sodium benzoate, and to ~0.4M by 0.6% sodium nitrite. Furthermore, although the current densities at 0 V for 0.9% CMA are slightly lower than those observed with no admixture, the current densities are higher than those for admixed sodium acetate or urea, perhaps because of a lowering of the pH in the cement pore solution resulting from the presence of admixed magnesium. Thus, the voltammetric results indicate that acetate and urea are only marginally effective as corrosion inhibitors for reinforcing steel in concrete. Accordingly, it is recommended that large quantities of sodium chloride should not be mixed with acetate deicing salts or urea.

4. Summary

The effects of acetate and urea additions on the cyclic voltammetric behaviour of iron in cured cement were investigated. Sodium acetate and urea do not cause depassivation of iron in cement upon repeated potential cycling. While the addition of ~0.2 M of either sodium acetate or urea prevents depassivation of iron in cement exposed to 0.1 M sodium chloride, the addition of even relatively high concentrations, such as 1.0 M sodium acetate or 1.0 M urea, cannot prevent depassivation by 0.2 M sodium chloride. The voltammetric results also indicate that admixed sodium acetate, urea and CMA are only marginally effective as corrosion inhibitors for reinforced concrete, compared with an inhibitor such as sodium nitrite. Thus, while acetates and urea may well be 'non-corrosive' deicers when used by themselves, large amounts of sodium chloride should not be mixed with acetates or urea as a cost-reducing measure.

Acknowledgement

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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