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Corrosion problems in reinforced concrete: why accelerators of cement hydration usually promote corrosion of steel

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The hydration of Portland cement and the corrosion of steel would seem at first sight to be two very different processes. However, it is observed that many additives which accelerate cement hydration also promote corrosion of steel, and those which retard hydration are usually corrosion inhibitors. There is found to be a mechanistic similarity between the two processes in that the retardation or inhibition of both processes depends on the existence of dense, impermeable films or coatings which protect the reactive surfaces beneath. Large, highly charged anions which have insoluble calcium and iron salts are good retarders of both processes. Mobile anions with highly soluble calcium and iron salts readily penetrate and cause breakdown of protective films, and are found to accelerate both processes. Such considerations are of importance in the search for cement hydration accelerators for use in reinforced concrete.

1. Corrosion problems in reinforced concrete

In recent years there has been growing concern about the corrosion of steel in reinforced concrete [1, 2]. Expansion associated with the formation of corrosion products gives rise to stresses which can crack the concrete. Once cracking and spalling begin to take place, the corrosion processes accelerate and may ultimately lead to structural failure.

The question arises as to why corrosion should take place at all, because a coating of good-quality concrete should provide excellent protection against corrosion. Interstitial fluids within Portland cement pastes usually have a pH in excess of 13 [3] and, according to the Pourbaix diagram for iron, at this pH the metal should remain passive over a wide range of potentials [4, 5].

There are two main factors responsible for the corrosion of steel in concrete. The first is carbonation of the alkaline components of cement by atmospheric carbon dioxide. Carbonation can cause a drop in pH to values below pH 9 and thereby removes the protection inherent in the concrete coating [1]. However, if the concrete is properly compacted and if the amount of cover exceeds the minimum recommended for the design life of the structure [6], then corrosion should not take place as a result of carbonation. The second factor is the presence of chloride ion. Calcium chloride is the most effective, cheapest and most widely used accelerator of Portland cement hydration, but unfortunately it appears that the presence of substantial amounts of chloride ion can cause depassivation of steel even in alkaline environments. Opinions differ as to the level of chloride which can be regarded as safe, but a survey carried out in the UK has shown that the risk of corrosion in reinforced concrete structures made from ordinary Portland cement (OPC) is low if the chloride content (by weight of cement) is below 0.4% and high for chloride contents above 1.0% [7]. However, because chloride is so obviously implicated in corrosion, there are strong recommendations that it is no longer used as an accelerator for reinforced concrete [8]. Of course, chloride can also find its way into reinforced concrete from other sources: e.g. from marine environments, from the use of chloride-contaminated aggregate (especially a problem in the Middle East) and chloride contamination from de-icing salts used on bridge-decks.

There is now a growing demand for chloride-free accelerators but it seems very difficult to find a satisfactory replacement for calcium chloride [9]. Calcium formate forms the basis of many of the commercially available chloride-free accelerators [10] but it is not as efficient as calcium chloride and although formate may not be classed as an aggressive anion, many of these products are formulated with corrosion inhibitors.

The ideal replacement for calcium chloride would be a good accelerator of cement hydration which also inhibits corrosion. However, these considerations lead one to the observation that, paradoxically, many additives which accelerate cement hydration also promote corrosion and those which inhibit corrosion often retard the hydration of cement. In this paper we explore and try to account for these observations.

2. The effect of inorganic admixtures on the hydration of Portland cement

Portland cement clinker consists mainly of a mixture of impure calcium silicates, namely tricalcium silicate and dicalcium silicate, which are written in abbreviated form as C_3S and C_2S. (The nomenclature used by

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cement chemists represents the oxides of calcium, silicon, aluminium and iron as C, S, A and F, respectively, and water is represented by H. Hence tricalcium silicate, which is $3Ca.SiO_2$, is abbreviated to C_3S). The other main ingredients are tricalcium aluminate, C_3A, and calcium aluminoferrite, C_4AF. A typical Portland cement would contain 55 wt % of C_3S, 22% of C_2S, 8% of C_3A, 8% of C_4AF, about 3% of other oxides and 4% gypsum to prevent flash-setting of the aluminate phases.

When Portland cement is mixed with water the constituents undergo hydration reactions to give a cement paste which eventually hardens. In terms of the development of the structure and mechanical properties of the hydrated cement matrix, it is the reaction of the two silicate phases, C_3S and C_2S, which are the most important. Although C_3S hydrates more rapidly than C_2S, both minerals react to form a colloidal calcium–silicate–hydrate (C–S–H) gel. This gel is amorphous and is of rather ill-defined composition [11]. It is extremely important in that it constitutes about 70 vol % of the hydrated material and is the principal binding agent responsible for the strength development of the cement paste. The other hydration products are crystalline and consist mainly of calcium hydroxide (Portlandite) with minor amounts of various complex calcium aluminate hydrates.

The reaction of cement constituents with water is exothermic and so the early hydration process (i.e. over the first 24 h) can be monitored by measuring the rate of heat evolution as a function of time. Typical heat evolution profiles show two peaks, as shown schematically in Fig. 1. The first peak, which reaches a maximum after about five minutes of mixing, represents the heat of wetting of the cement clinker and is mainly due to the hydration of free lime and other alkalis and the reaction of C_3A with gypsum. There is a trough in the heat evolution curve when little or no reaction appears to be taking place and this is referred to as the "induction" or "dormant" period. After the induction period comes a second and lower heat evolution peak which reaches a maximum after around 5 to 7 h and is largely associated with the hydration of the principal clinker phase, C_3S.

The use of water-soluble admixtures to accelerate or retard the setting of cement is a well-established practice. The effect of admixtures on the hydration reaction is conveniently monitored by changes produced in the heat evolution curves. As shown in Fig. 1, accelerators of hydration generally bring about an increase in the height of the second heat evolution peak relative to that of the control and the peak maximum is shifted to an earlier time [12]. Conversely, retarders will depress the heat evolution peak and the maximum is shifted to a later time [13].

Extensive calorimetric studies have been carried out to investigate cement admixtures and some very interesting patterns emerge. The accelerating or retarding capability of various inorganic anions is ranked in Table I (the results are taken from the literature [12–19] as well as from the author's own work).

It must be stated that these rankings are only approximate because of various difficulties encountered in the comparison of results from the literature; for example, different parameters are used to measure rates of hydration in different studies. Also the concentration of admixture used affects its efficacy, as does the type of cation used in association with a given anion, e.g. calcium chloride is a better accelerator than sodium chloride [12] (at the same concentration of chloride ion). Wilding *et al.* [19] have also shown that the ranking of anions as accelerators is different when cobalt salts are investigated as opposed to sodium salts. Hence inorganic anions should be compared at the same molar concentration and in the presence of the same cation. Another factor is that in some cases pure C_3S has been used instead of OPC and although C_3S is undoubtedly the most important constituent of OPC, the effect of admixtures on the early hydration

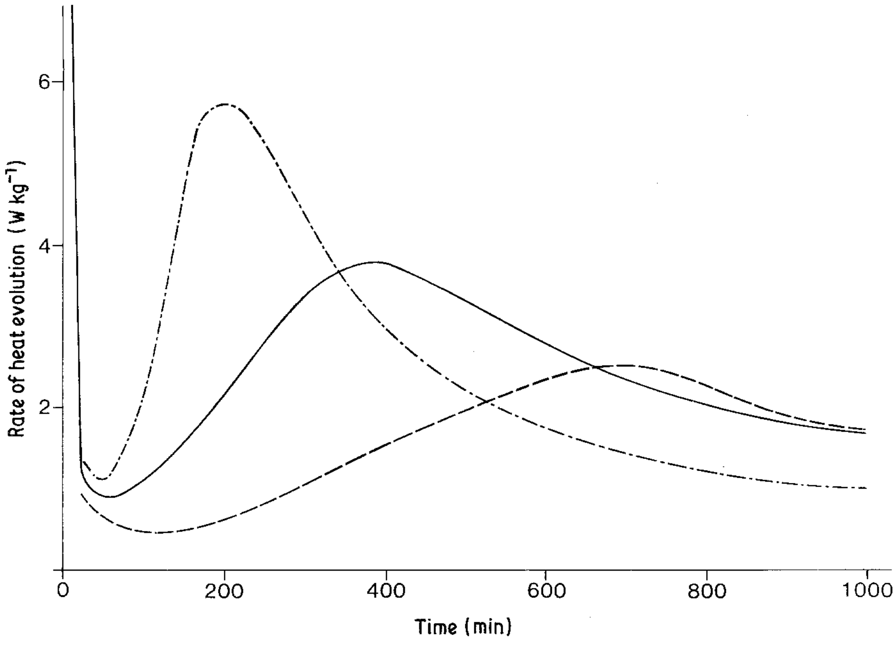

Figure 1 The effect of admixtures on heat evolution during the early hydration of OPC. (–·–) Accelerator, (– – –) retarder, (——) control.

TABLE I The ranking of inorganic anions as cement accelerators or retarders of OPC and C_3S hydration [12–19]

Accelerators		Strong	*Alkaline*
	↑	Cl^-	OH^-
		$S_2O_3^{2-}$	
		Br^-	CO_3^{2-}
		NO_2^-	HCO_3^-
		CrO_4^{2-}	SiO_3^{2-}
		NO_3^-, SCN^-	
		I^-	$Al(OH)_6^{3-}$
		ClO_4^-	
		SO_4^{2-}	
		Weak	
Retarders		Weak	
		F^-	
		SiF_6^{2-}	
		AsO_4^{3-}	
		$B_4O_7^{2-}$, PO_4^{3-}, BO_2^-	
	↓	BO_3^{3-}, $P_2O_7^{4-}$, VO_4^{3-}	
		Strong	

process is likely to influence the reactions of the aluminate phases present. However, despite all these difficulties, there is surprisingly good agreement between the various studies reported in the literature.

3. The mechanism of hydration of OPC and an explanation of inorganic admixture behaviour

The major hydration product of Portland cement is C–S–H gel, which provides the cohesive matrix responsible for strength development of the paste. This gel is amorphous and of variable composition and can adopt a variety of morphologies, which have been variously described as colloidal spheres, crumpled foils, fibres, needles, plates and rosettes [11, 20–23]. There is a consensus of opinion that gelatinous coatings of C–S–H are formed on the surface of clinker particles soon after contact with water [24, 25]. Such observations provide the basis of protective coating theories of cement hydration [26]. The protective envelope of C–S–H gel formed around the cement grains inhibits further hydration and gives rise to the "dormant" period shown in the heat evolution curves (Fig. 1).

One explanation for the end of the dormant period, and subsequent renewed hydration, is provided by the osmotic membrane model of Double *et al.* [24] and Birchall and co-workers [27, 28]. This model is based on the observation that membranes of C–S–H gel exhibit semi-permeable properties – as for example in the phenomenon of "silicate gardens" [29, 30] or even the reaction of rice husk ash with saturated lime [31]. It is proposed that during the dormant period, water is preferentially imbibed through the C–S–H membrane coating and the end of the dormant period occurs when the gel coatings rupture under osmotic pressure, by analogy with silicate gardens. Renewed hydration and growth of secondary hydration products can then take place. The model is consistent with the observed morphologies of secondary growth products – hollow or solid fibres, sheets or foil-like structures [30, 32]. It is also consistent with the very low levels of silica (generally less than 0.05 mM) found in the bulk aqueous phase during the early hydration of Portland cement and C_3S [33]. The very low solubility of C–S–H gel and the low levels of silica found in solution right from the time of mixing indicate that the hydration reaction cannot occur by a "through solution" mechanism, but must take place on the surface of the cement grains.

According to the osmotic model, hydration of cement is controlled by the diffusion of water and solute species through a C–S–H membrane around the cement grains, and so the rate of hydration will depend on the thickness and permeability of these membranes [34], as well as on the ability of ions to diffuse through them. To explain the role of accelerating and retarding admixtures, the factors which need consideration are the effect of the admixtures on the chemistry of precipitation of the C–S–H gel coating and the mobility of anions through that coating.

Admixtures which give rise to denser, more compact C–S–H gel coatings will be retarders of the hydration process. Retarders, such as phosphate, which have insoluble calcium salts are considered to operate by precipitation of dense coatings of the calcium salt which is incorporated in the C–S–H gel membrane around the cement grains. The permeability of the C–S–H coating is thus reduced and hence the processes of osmotic pressure build-up, and subsequent rupture of the coating, will be delayed. The solubilities of the calcium salts of all the anions ranked as cement accelerators or retarders in Table I are shown in Table II (data from [35–37]). All the inorganic retarders of cement hydration have calcium salts with low solubilities. Note however that some organic retarders, e.g. sucrose, operate by a different mechanism and are considered to prevent the precipitation of calcium hydroxide and/or C–S–H gel [38–40].

As regards calcium salt solubilities, the accelerating admixtures fall into two main groups: those with highly soluble calcium salts, and those which have insoluble calcium salts but accelerate hydration because they are alkaline and aid the dissolution of silica and alumina.

One of the implications of the osmotic model is that acceleration will occur if the C–S–H gel coating is modified to give a more open, permeable structure and if the accelerating species is mobile enough to penetrate this coating. These ideas lend themselves to an explanation of the accelerating effect of chloride ion on the hydration of OPC. In some theories it has been proposed that the initial acceleration is due to the precipitation of crystalline chloroaluminate hydrates [41–43] but this would not account for the remarkable accelerating effect of $CaCl_2$ on C_3S hydration [44, 45]. Solution analyses indicate that there is a small but significant reduction in the chloride concentration in solution [33], probably caused by preferential adsorption of chloride on to the colloidal hydration products

TABLE II Calcium salt solubilities of accelerating and retarding anions (grams per 100 cm^3 water at ambient temperature [35–37])

Accelerators	Strong				
	↑	$CaCl_2$	74.5	$Ca(OH)_2$	0.185
		$CaS_2O_3 \cdot 6H_2O$	100		
		$CaBr_2$	142	$CaCO_3$	0.0065
		$Ca(NO_2)_2 \cdot H_2O$	45.9		
		$CaCrO_4 \cdot 2H_2O$	16.3		
		$Ca(NO_3)_2$	121.2	C_2S	0.0095
		$Ca(SCN)_2$	150		
		CaI_2	209	C_3A	0.025
		$Ca(ClO_4)_2$	188.6		
		$CaSO_4$	0.3		
	Weak				
Retarders	Weak				
		CaF_2	0.0016		
		$CaSiF_6$	0.33		
		$Ca_3(AsO_4)_2$	0.013		
		CaB_4O_7	0.31		
		$Ca_3(PO_4)_2$	0.002		
		$Ca(BO_2)_2 \cdot 6H_2O$	0.25		
		$Ca_2P_2O_7$	Insoluble*		
		$Ca_3(BO_3)_2$	Insoluble*		
	↓	$Ca_3(VO_4)_2$	Insoluble*		
	Strong				

*Precise data unavailable, but solubility expected to be low.

[46]. Studies of C_3S hydration in the presence of calcium chloride have revealed changes in the microstructure of the outer hydration products [17, 44, 45, 47]. The C–S–H gel was generally found to be less compact and consisted of a more open, spongy structure. Coatings of such material will be more permeable and more readily ruptured, giving rise to a shortened induction period and hence accelerated hydration. It has also been proposed that the mobility of chloride ions is such that they can readily diffuse through the C–S–H gel membranes, increasing the internal osmotic pressure and thus facilitating membrane rupture and the consequent hydration processes [45].

If the effect of the anion on the structure of C–S–H gel membranes is an important consideration, then, as pointed out by Double [34], there may be similarities between the ranking of anions as accelerating or retarding admixtures and the Hofmeister series [48–50], which relates to the efficacy of flocculation of hydrophilic colloids by dissolved electrolytes. The Hofmeister series (Table III) ranks anions in order of their decreasing flocculating power, i.e. their increasing ability to adsorb on to and peptize colloids. The series depends on the structure of the ions, notably on their charge to radius ratio.

Comparison of Tables I and III reveals that there are broad similarities between the ranking of inorganic anions as cement hydration accelerators and retarders and the Hofmeister series. In general terms the highly polarizable anions which readily adsorb on and deflocculate colloids are all accelerators of cement hydration. Presumably their ability to cause deflocculation would give rise to a more porous C–S–H gel structure, as described above for the effect of chloride. The anions with the highest charge to radius ratio, i.e. those with the greatest flocculating power, are on the whole cement retarders.

Detailed agreement between the ranking of accelerating anions and the Hofmeister series is, however, not particularly good. If peptization was the only important criterion, then the large monovalent and highly polarizable anions such as SCN^-, ClO_4^-, I^- and NO_3^- would be the best accelerators, but this is not borne out by experimental results. Mobility is another important factor and this tends to favour smaller monovalent or more highly charged anions, and it is found that $S_2O_3^{2-}$ and Cl^- are the best accelerators.

Kondo *et al.* [51] examined the accelerating effect of a number of inorganic electrolytes on the hydration of

TABLE III The ranking of inorganic anions according to the Hofmeister series [48, 49, 50]

↑	↑	SCN^-
		ClO_4^-
		I^-
		ClO_3^-
		NO_3^-
		Br^-
		CN^-
		Cl^-
		HCO_3^-
		OH^-
Increasing adsorption and peptization	Decreasing flocculating power	F^-
		MoO_4^{2-}
		$S_2O_3^{2-}$
		WO_4^{2-}
		CrO_4^{2-}
		CO_3^{2-}
		HPO_4^{2-}
		SO_4^{2-}, SiF_6^{2-}
		PO_4^{3-}
		BO_3^{3-}
		VO_4^{3-}
		AsO_4^{3-}
		$[Fe(CN)_6]^{4-}$, $P_2O_7^{4-}$

TABLE IV Ionic conductivities (at 25° C and infinite dilution) [51, 52]

Anion	Conductivity ($cm^2 \Omega^{-1} mol^{-1}$)
OH^-	197
$\frac{1}{2}S_2O_3^{2-}$	84.9
$\frac{1}{2}CrO_4^{2-}$	83
$\frac{1}{2}SO_4^{2-}$	80
Br^-	78
I^-	77.1
Cl^-	76.4
$\frac{1}{2}CO_3^{2-}$	74
NO_2^-	72
NO_3^-	71.1
ClO_4^-	67
SCN^-	66
F^-	55
HCO_3^-	54.4

C_3S and found that the higher the anion mobility the greater the accelerating effect on the hydration. Their ranking of anions (which is a slightly different order from that in Table I) was with increasing accelerating ability as follows: F^-(retarder) $< ClO_3^- < I^- < NO_3^- < SCN^- < Br^- < Cl^- < S_2O_3^{2-} < CrO_4^{2-} < SO_4^{2-}$. There is reasonably good agreement between this list and the ionic conductivities of the anions, as shown in Table IV [51, 52].

In summary, it is proposed that the effect of inorganic admixtures on cement hydration is controlled by their effect on the chemistry of precipitation of the C–S–H gel coating and the mobility of anions through that coating. Retarders such as phosphate and borate have insoluble calcium salts and precipitate as dense coatings incorporated in the C–S–H gel membrane, leading to thickening and loss of permeability of the coating and hence a slowing down of the hydration process. The effect of anions with soluble calcium salts is twofold. Firstly, it is proposed that they will affect the structure of C–S–H gel coatings through adsorption on to and deflocculation of colloidal C–S–H particles. The more open and permeable the coating, the greater the acceleration of hydration. Secondly, anion mobility is an important factor. Accelerating anions would be expected to diffuse readily through C–S–H coatings to increase internal osmotic pressure and thus facilitate membrane rupture and renewed hydration at the end of the dormant period.

4. The effect of inorganic anions on corrosion processes

The corrosion of steel in the presence of air and water is an electrochemical process which consists of two distinct electrode reactions. At neutral pH in aerated solutions the overall anodic and cathodic half cell reactions are as follows:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{oxidation/anodic}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{reduction/cathodic}$$

These reactions take place at discrete anodic and cathodic sites on the sample. The ferrous and hydroxyl ions produced migrate towards one another and precipitate ferrous hydroxide:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

This is oxidized to a hydrated ferric oxide, the familiar red-brown rust, $Fe_2O_3 \cdot H_2O$ or FeO(OH). Of course, there are several other anodic and cathodic reactions which may take place depending on the availability of oxygen and the pH at the steel surface [5, 53]. There are also many other possible reaction products [54].

Any means of decreasing the rate of either or both of these electrode reactions, or any of the steps involved in them, will result in some degree of corrosion inhibition. The inhibition of corrosion is of great practical importance and there has been much work done in the area (for reviews see [53, 55–58]).

In Table V inorganic anions are ranked as corrosion accelerators and inhibitors for ferrous metals at neutral and alkaline pH. The results are taken from published data [58–62]. This list is only approximate because the aggressive or inhibitive character of anions can change as a function of their concentration and of the pH of the environment. For example, it is well known that anodic inhibitors (such as nitrite, chromate, silicate, orthophosphate and carbonate) can have an undesirable effect; at low concentrations of inhibitor there may be insufficient present to cover the whole of the anodic metal surface. Under conditions of cathodic control this dangerous combination of small anode and large cathode can lead to pitting. Hence, for reactions which are cathodically controlled, anodic inhibitors are dangerous unless used in excess of a critical concentration.

Marshall and Greaves [59] investigated the corrosion rates of mild steel samples in distilled water in the presence of various sodium salts over a range of concentrations. Their investigations showed that anions appear to fall into three main types: aggressive anions incapable of producing passivation, anions capable of

TABLE V Approximate ranking of inorganic anions as corrosion accelerators and inhibitors for ferrous metals at neutral and alkaline pH [58–62]

Aggressive	Strong
	$S_2O_3^{2-}$
	S^{2-}
	SO_4^{2-}
	SCN^-
	Cl^-, Br^-
	ClO_4^-
	I^-
	HS^-
	NO_3^-
	Weak
	F^-
Inhibiting	Weak
	SiO_3^{2-}
	HCO_3^-
	CO_3^{2-}
	WO_4^{2-}, VO_4^{3-}, AsO_4^{3-}
	MoO_4^{2-}
	BO_3^{3-}, $B_4O_2^{2-}$
	PO_4^{3-}, $P_2O_7^{2-}$
	$\left.\begin{array}{l} CrO_4^{2-} \\ NO_2^- \end{array}\right\}$ oxidizing
	Strong

passivating only in the presence of oxygen, and anions capable of producing passivation in the presence and absence of oxygen. The inhibitive action of non-oxidizing anions (e.g. silicate, bicarbonate, carbonate, borate and phosphate) is largely due to repair of the oxide film by plugging with an insoluble iron compound. Hence a very important factor distinguishing inhibiting anions from aggressive anions is the solubility of the iron compound. Aggressive anions, incapable of passivating, have soluble ferrous and ferric salts (with the exception of sulphide) whereas the non-oxidizing passivating anions have insoluble ferrous and ferric salts.

Another factor in the action of aggressive anions is the possibility that the oxide film is weakened by the incorporation of these anions, giving rise to points where film breakdown could occur. Much work has been done on the local breakdown of normal passivation caused by chloride (e.g. [63]) and it is generally agreed that breakdown is due to adsorption and penetration of Cl^- in to the oxide film, resulting in a large increase in conductivity of the film.

Wranglen [60] has pointed out that aggressive anions (such as chloride and sulphide) are those with a high molar polarization. Such anions will readily adsorb on to oxide surfaces on metals and catalyse corrosion reactions, and it is very difficult to maintain or develop protective oxide films in the presence of these ions. He has drawn a parallel between the Hofmeister series and the ranking of inorganic anions as corrosion accelerators or inhibitors. Anions which are highly polarizable, i.e. the deflocculating anions in Table III, have a great ability to adsorb on to and peptize colloids and are found to be corrosion accelerators. They readily penetrate and give rise to the breakdown of oxide films. Conversely anions with a low molar polarization and which are weakly peptizing are found to be passivating. As mentioned above, their effectiveness as inhibitors is due to the formation of insoluble salts which can repair points of damage in the protective oxide films.

As in the case of cement hydration, correlation between the Hofmeister series and the ranking of aggressive and inhibiting anions is not exact. Ionic mobilities also need to be taken into consideration – the higher the mobility the more aggressive the anion. Hence the divalent anions such as $S_2O_3^{2-}$ and SO_4^{2-} are ranked as more aggressive than the halide ions (Cl^- and Br^-), which are found to be more aggressive than some of the monovalent highly polarizable ions such as I^-, NO_3^- and ClO_4^-.

5. Comparison of the effect of anions on cement hydration and corrosion

Comparison of Table I with Table V reveals some striking similarities between the ranking of cement hydration accelerators and ions classed as aggressive to mild steel, and also between cement hydration retarders and anions found to be corrosion inhibitors. All the anions found to be aggressive to steel are cement hydration accelerators (with the possible exception of S^{2-}) and all the anions classed as retarders of cement hydration are corrosion inhibitors. The two groups which are exceptions to this general pattern are the oxidizing anions, chromate and nitrite, which passivate iron but accelerate cement setting, and the alkaline cement accelerators which inhibit the corrosion of steel.

Despite the fact that OPC hydration and corrosion of mild steel are two such different processes, there is a mechanistic similarity between them. The retardation or inhibition of both processes depends on the existence of dense, impermeable films or coatings which protect the reactive surfaces beneath. Hence the large highly charged oxyanions which have highly insoluble calcium and iron salts are good retarders of both processes. Anions which readily adsorb on to and peptize colloids, and which are classified as deflocculating in the Hofmeister series, accelerate both processes. Such anions have highly soluble calcium and iron salts and readily penetrate protective coatings.

These considerations are of importance in the search for new cement hydration accelerators for use in reinforced concrete. For example, the oxidizing inhibitors nitrite and chromate have both been used successfully as admixtures to protect steel in reinforced concrete [2, 64–68] while having a desirable accelerating effect on cement hydration. Their use is not without problems, however. If the concentration of inhibitor falls below the amount required for complete inhibition, then attack may be localized and intensified – as for example is observed in the case of sodium nitrite, especially where chloride is present [66, 67, 69]. Another problem observed with both nitrite and chromate was that, although these additives accelerate the setting and early hardening process (up to 7 days), the compressive strength at later times is reduced [66, 67, 70]. Toxicity may also make them undesirable, especially chromate [71].

The other group of materials which may be used as corrosion inhibiting accelerators of cement hydration are those designated as "alkaline" accelerators in Table I. In choosing accelerators from this group it is important to consider those that will buffer the system at high pH so that it remains passive to steel. However, too high a pH is undesirable because cements with very high alkalinity can, in the presence of reactive aggregates, promote the alkali silica reaction (the phenomenon known as "concrete cancer" [72]).

Indeed it is proving very difficult to find a corrosion-inhibiting accelerator of cement hydration. Perhaps when one considers that the mechanisms of cement hydration acceleration and corrosion inhibition are, as it were, working "in opposition" to one another, it is not difficult to see why.

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References

1. C. L. PAGE and K. W. J. TREADAWAY, *Nature* **297** (1982) 109.
2. D. A. LEWIS, in Proceedings of 1st International Congress on Metallic Corrosion, London, 1961 (Butterworths, London) p. 547.

3. R. S. BARNEYBACK Jr and S. DIAMOND, *Cem. Concr. Res.* **11** (1981) 279.
4. M. POURBAIX, "Atlas of Electrochemical Equilibria in Aqueous Solutions" (Pergamon, Oxford, 1966).
5. C. M. HANSSON, *Cem. Concr. Res.* **14** (1984) 574.
6. K. W. J. TREADAWAY, in Proceedings of Symposium on Corrosion of Steel Reinforcements in Concrete Construction, London, Vol. I (Society of Chemical Industry, London, 1979).
7. L. H. EVERETT and K. W. J. TREADAWAY, Building Research Establishment Information paper IP 12/80 (1980).
8. British Standards Institution Code of Practice CP110: 1972 Part 1, "The Structural Use of Concrete" (as amended May, 1977).
9. "The Role of Calcium Chloride in Concrete", *Concr. Constr.* **21** (1976) 57.
10. W. R. Grace & Co., US Patent No. 3 210 207.
11. S. DIAMOND, in Proceedings of Conference on Hydraulic Cement Pastes: Their Structure and Properties, Sheffield, April 1976 (Cement and Concrete Association, Slough, England, 1976) pp. 2–30.
12. D. L. KANTRO, *ASTM J. Test. Eval.* (1975) 312.
13. W. LIEBER, *Zement-Kalk-Gips* **26**(2) (1973) 75.
14. *Idem, ibid.* **34**(9) (1981) 473.
15. G. C. EDWARDS and R. L. ANGSTADT, *J. Appl. Chem.* **16** (1966) 166.
16. P. A. ROSSKOPF, F. J. LINTON and R. B. PEPPLER, *ASTM J. Test. Eval.* **3** (1975) 322.
17. J. F. YOUNG, R. L. BERGER and F. V. LAWRENCE, *Cem. Concr. Res.* **3** (1973) 689.
18. J. F. YOUNG, H. S. TONG and R. L. BERGER, *J. Amer. Ceram. Soc.* **60** (1977) 193.
19. C. R. WILDING, A. WALTER and D. D. DOUBLE, *Cem. Concr. Res.* **14** (1984) 185.
20. H. M. JENNINGS, B. J. DALGLEISH and P. L. PRATT, *J. Amer. Ceram. Soc.* **64** (1981) 567.
21. D. MENETRIER, I. JAWED, T. S. SUN and J. SKALNY, *Cem. Concr. Res.* **9** (1979) 473.
22. H. M. JENNINGS and P. L. PRATT, in Proceedings of 7th International Congress on the Chemistry of Cement, Paris, July 1980, Vol. II (1980) p. II-141.
23. D. D. DOUBLE, in Proceedings of International Congress on Admixtures, C.I. 80, London (Construction Press, 1980) p. 32.
24. D. D. DOUBLE, A. HELLAWELL and S. J. PERRY, *Proc. R. Soc.* **A359** (1978) 435.
25. H. M. JENNINGS and P. L. PRATT, *Cem. Concr. Res.* **9** (1979) 501.
26. J. SKALNY and J. F. YOUNG, in Proceedings of 7th International Congress on the Chemistry of Cement, Paris, July 1980, Vol. I (1980) p. II-1.3.
27. J. D. BIRCHALL, A. J. HOWARD and J. E. BAILEY, *Proc. R. Soc.* **A360** (1978) 445.
28. J. D. BIRCHALL, A. J. HOWARD and D. D. DOUBLE, *Cem. Concr. Res.* **10** (1980) 145.
29. R. D. COATMAN, N. L. THOMAS and D. D. DOUBLE, *J. Mater. Sci.* **15** (1980) 2017.
30. D. D. DOUBLE, *Silicates Industrials* **11** (1978) 233.
31. J. JAMES and M. SUBBA RAO, *Cem. Concr. Res.* **16** (1986) 296.
32. D. D. DOUBLE, N. L. THOMAS and D. A. JAMESON, in Proceedings of 7th International Congress on the Chemistry of Cement, Paris, Vol. II (1980) p. II–256.
33. N. L. THOMAS and D. D. DOUBLE, *Cem. Concr. Res.* **11** (1981) 675.
34. D. D. DOUBLE, *Phil. Trans. R. Soc.* **A310** (1983) 53.
35. R. C. WEAST (ed.), "CRC Handbook of Chemistry and Physics", 63rd Edn (1982/83) (CRC Press).
36. W. F. LINKE, "Solubilities of Inorganic and Metal Organic Compounds", Vol. I (Van Nostrand, New York, 1958).
37. H. STEPHEN and T. STEPHEN, "Solubilities of Inorganic and Organic Compounds", Vol. I (Pergamon, London, 1963).
38. N. L. THOMAS and J. D. BIRCHALL, *Cem. Concr. Res.* **13** (1983) 830.
39. J. D. BIRCHALL and N. L. THOMAS, *Proc. Br. Ceram. Soc.* **35** (1984) 305.
40. P. F. G. BANFILL, *J. Mater. Sci. Lett.* **5** (1986) 33.
41. W. C. HANSEN, in Proceedings of 3rd International Symposium on the Chemistry of Cement, London (1952) p. 318.
42. G. L. KALOUSEK, C. H. JUMPER and J. J. TREGONING, *J. Res. Nat. Bur. Stand.* **30** (1943) 215.
43. J. BENSTED, *World Cement Technol.* **8**(5) (1977).
44. P. J. LE SUEUR, D. D. DOUBLE and G. W. GROVES, *Proc. Br. Ceram. Soc.* **35** (1984) 177.
45. N. B. SINGH and P. N. OJHA, *J. Mater. Sci.* **16** (1981) 2675.
46. G. W. GROVES, *ibid.* **16** (1981) 1063.
47. A. TRAETTEBERG, V. S. RAMACHANDRAN and P. E. GRATTAN-BELLEW, *Cem. Concr. Res.* **4** (1974) 203.
48. F. FRANKS, "Water", (Royal Society of Chemistry, London, 1983) Ch. 10.
49. W. A. P. LUCK, *Topics Curr. Chem.* **64** (1976) 113.
50. K. J. MYSELS, "Introduction to Colloid Chemistry" (Interscience, New York, 1959) Ch. 17.
51. R. KONDO, M. DAIMON, E. SAKAI and H. USHIYAMA, *J. Appl. Biotechnol.* **27** (1977) 191.
52. A. L. HORVATH, "Handbook of Aqueous Electrolyte Solutions" (Ellis Horwood, Chichester, 1985).
53. Z. A. FOROULIS, in Proceedings of Symposium Coupling of Basic and Applied Corrosion Research, 1969 (National Association of Corrosion Engineers) p. 24.
54. J. KASSIM, T. BAIRD and J. R. FRYER, *Corr. Sci.* **22** (1982) 147.
55. S. W. DEAN, R. DERBY and G. T. VON DEM BUSSCHE, *Mater. Perform.* **20** (1981) 47.
56. O. L. RIGGS, in "Corrosion Inhibitors", edited by C. C. Nathan (National Association of Corrosion Engineers, Houston, Texas, 1973) p. 7.
57. J. G. N. THOMAS, in Proceedings of Symposium on Practical Aspects of Corrosion Inhibition, Teddington, England, 1979, p. 35.
58. R. N. PARKINS, in "Comprehensive Treatise of Electrochemistry", edited by J. O'M. Bockris, B. E. Conway and E. Yeager (Plenum, New York, 1981) p. 307.
59. A. MARSHALL and B. GREAVES, in Proceedings of 6th European Symposium on Corrosion Inhibitors, Ferrara, Vol. 2 (1985) p. 1051.
60. G. WRANGLEN, "An Introduction to Corrosion and Protection of Metals" (Institut für Metallskydd, Stockholm, 1972).
61. V. K. GOUDA and S. M. SAYED, *Br. Corr. J.* **8** (1973) 71.
62. D. M. BRASHER, *Nature* **193** (1962) 868.
63. T. P. HOAR, D. C. MEARS and G. P. ROTHWELL, *Corr. Sci.* **5** (1965) 279.
64. V. M. MOSKIN and S. N. ALEXSEEV, *Beton i. Zhelezobeton* **1** (1957) 28.
65. J. T. LUNDQUIST Jr, A. M. ROSENBERG and J. M. GAIDIS, Paper 126 presented at Corrosion 77, San Francisco, California (National Association of Corrosion Engineers).
66. K. W. J. TREADAWAY and A. D. RUSSELL, *Highways and Public Works* **36** (1968) 19–21.
67. *Idem, ibid.* **36** (1968) 40.
68. A. CELANI and G. SCHIPPA, *Ric. Sci.* **38** (1968) 155.
69. T. P. HOAR, *J. Soc. Chem. Ind.* **69** (1950) 356.
70. E. I. VED, E. F. ZHAROV, V. S. NITCHENKO, T. A. SIDOROVA, V. UVAROVA and A. MALIMON, *Budivel'ni Mater. Konstr.* **5** (1969) 32.
71. H. PISTERS, *Zem-Kalk-Gips* **19** (1966) 467.
72. "Contract Journal", December 22/29 (1983) pp. 16–17.

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