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The hydration products of Portland cement in the presence of tin(II) chloride

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Abstract

The hydration products of Portland cement pastes cured using water containing tin(II) chloride have been compared with those using distilled water. In the latter case, the expected products—portlandite, ettringite and calcite—were observed. The X-ray diffraction patterns of the cement pastes cured in the presence of tin(II) chloride showed several additional peaks that have been attributed to the formation of calcium hydroxo-stannate, $CaSn(OH)_6$, and Friedel's salt (tetracalcium aluminate dichloride-10-hydrate), $Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O$. The amount of portlandite formed was reduced in the presence of tin(II) chloride. Calcium hydroxo-stannate contains tin in the + IV oxidation state and equations are presented to account for the oxidation of Sn(II) to Sn(IV) preceding the formation of $CaSn(OH)_6$ and Friedel's salt.

Keywords: Hydration products; Friedel's salt; Portland cement; Tin (II) chloride; X-ray diffraction

1. Introduction

As part of a program of research into the containment of elements present in radioactive waste streams within a cementitious matrix, the hydration products of neat Portland cement pastes have been studied using water containing the chlorides of amphoteric elements such as Al, Zn and Sn. Whereas it was not anticipated that small amounts of added aluminium would affect the nature of the hydration products formed, additions of zinc and tin salts were expected to lead to the formation of additional hydration products. The reaction of zinc salts to form a calcium hydroxo-zincate, $CaZn_2(OH)_6 \cdot 2H_2O$ [1–3], is well documented, but as far as we are aware, the comparable product in the presence of tin salts has not been reported. Indeed, in his thorough review of the role of minor elements in cement manufacture and use, Bhatty [4] states that not much is known about the effect of tin in clinker manufacture, although "the presence of trace amounts of tin in clinker should not affect cement properties."

2. Experimental

The chemical analysis for the Portland cement that was supplied by Castle Cement is shown in Table 1. A Bogue analysis indicates a potential phase composition of C_3S, 53.2%; C_2S, 20.1%; C_3A, 8.3%; C_4AF, 9.4%, suggesting a normal Portland cement.

For the control samples, the cement powder (500 ± 0.1 g) was added to distilled water (175 ± 0.1 g), giving a w/c ratio of 0.35. Once all the powder had been added, the cement was mixed manually for approximately 3 min. The paste was then poured into polytetrafluoroethylene (PTFE) moulds, creating 100 × 10 × 10 mm prisms. A second set of prisms was made following the same procedure, except that 5% (by weight of cement) tin(II) chloride was dissolved in the mix water.

The samples were cured at 23 ± 2 °C and 86 ± 2% relative humidity. This was achieved by placing the sample in an environmental cabinet in the laboratory and using a saturated solution of potassium sulfate, K_2SO_4, to control the humidity. The freshly cast samples were placed in the cabinet for 24 h and were then demoulded. The samples were returned to the cabinet and left until they were required for analysis.

For X-ray diffraction (XRD) analysis, a cement prism was crushed in a percussion mortar and then placed in an agate mortar. An excess of acetone was added (to stop further hydration of the cement and to aid grinding) and the

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Table 1
Chemical analysis of the Portland cement

	%
CaO	64.1
SiO_2	21.0
Al_2O_3	5.1
Fe_2O_3	3.1
MgO	2.5
SO_3	2.2
K_2O	0.7
Na_2O	0.3
Chloride	0.03
Insolubles	0.3
Loss on ignition	0.6
Free lime	0.8

cement was ground by hand to a fine powder of < 63 μm. The powder was packed into backfilled sample holders (to minimise preferred orientation) for use in the X-ray diffractometer.

A Philips 1710 X-ray diffractometer using monochromatic CuKα radiation operating at a voltage of 50 kV and current of 30 mA was used. A scanning speed of 2°2θ/min and a step size of 0.02° were used to examine the samples in the range 5–55°2θ.

3. Results

XRD patterns of the hydration products of (A) the neat OPC and (B) the same cement hydrated using water containing 5% $SnCl_2$ are shown after 28 days in Fig. 1 and after 180 days in Fig. 2. The XRD patterns of the neat OPC (cured with distilled water) (Figs. 1A and 2A) showed the expected hydration products, including calcium hydroxide (portlandite) (at $d = 4.90$, 3.11, 2.63, 1.93 and 1.80 Å), calcium carbonate (at $d = 3.96$, 3.04, 2.29 and 2.10 Å) and ettringite (at $d = 9.7$, 5.61, 4.69, 3.88 and 2.21 Å). It is sometimes dangerous to try to compare the relative amounts found because of preferred orientation that can particularly affect the intensity of the peaks of portlandite and ettringite, but all three reaction products are clearly evident in both patterns. Most of the other peaks can be attributed to unreacted alite, especially around 32–33°2θ, and these peaks decreased with increased curing time, indicating that hydration continued beyond 28 days.

The XRD patterns of the OPC cured in the presence of tin(II) chloride (Figs. 1B and 2B) showed several new features, labelled X and Y. Although peaks due to the presence of calcium hydroxide, calcium carbonate and ettringite were still apparent, the intensities of those due to portlandite were so much reduced that it has to be concluded that much less had been formed than when cured with distilled water. The peaks labelled X and Y indicate the formation of additional hydration products associated with the addition of tin(II) chloride. Those labelled Y can all be attributed to the presence of Friedel's salt, tetracalcium aluminate dichloride-10-hydrate or $Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O$. The peaks observed in this study are compared with literature values in Table 2.

Whereas Friedel's salt is a well-known product of the hydration of Portland cement in the presence of chloride ions, the peaks marked X are not associated with any such product. A search of the X-ray powder diffraction index indicated that these peaks can be attributed to calcium hydroxo-stannate, $CaSn(OH)_6$. The observed data are com-

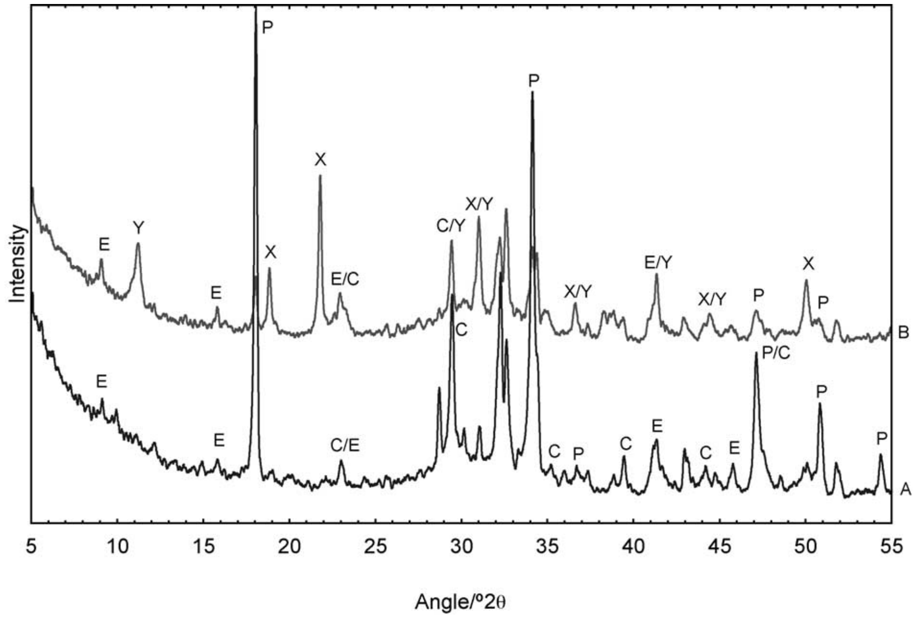

Fig. 1. XRD patterns of (A) ordinary Portland cement paste and (B) the same cement cured in the presence of 5% tin(II) chloride after 28 days.

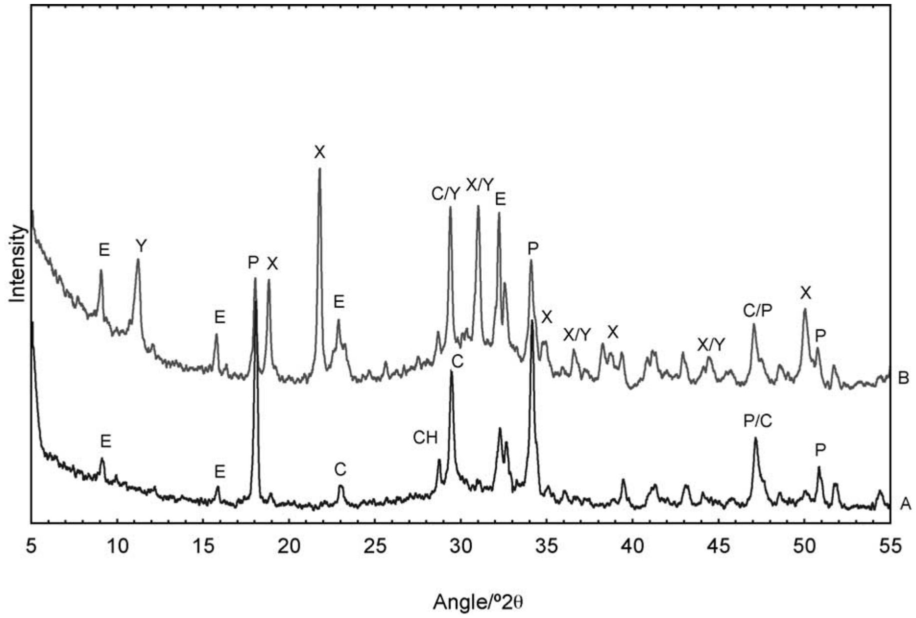

Fig. 2. XRD patterns of (A) ordinary Portland cement paste and (B) the same cement cured in the presence of 5% tin(II) chloride after 180 days.

pared with literature data in Table 3 and, in spite of some peaks overlapping with those of other hydration products, it can be seen that the agreement is excellent.

At longer hydration times, the amounts of Friedel’s salt and $CaSn(OH)_6$ increased. The amount of $Ca(OH)_2$ formed also increased, but not to the levels observed in the neat cement paste.

4. Discussion

There is no doubt that the addition of tin(II) chloride to the water changed the hydration products of the Portland cement. In the absence of the additive, the progress of cement hydration was predictable, giving rise to calcium hydroxide, calcium carbonate and ettringite. C–S–H gel was undoubtedly formed, but could not be observed by XRD.

Table 2
XRD data for Phase Y and Friedel’s salt

Present work (Phase Y)		Literature data (Friedel’s salt)
28 days	180 days	JCPDS 28-207
7.88	7.87	7.92
3.87	3.88	3.86
3.03	3.04	3.04
2.88	2.88	2.88
2.45	2.45	2.45
2.35	2.35	2.34
2.28	2.28	2.28
2.18	2.18	2.17
2.04	2.04	2.03
1.628	1.627	

In contrast, when tin(II) chloride was added to the mix water, two additional products, labelled X and Y in Figs. 1B and 2B, were readily observed. These were unambiguously identified as Friedel’s salt, $Ca_3Al_2O_6{\cdot}CaCl_2{\cdot}10H_2O$, and calcium hydroxo-stannate, $CaSn(OH)_6$. This latter phase is clearly a mixed hydroxide of calcium and tin, so it is not surprising that the amount of calcium hydroxide formed was much less than in the system without the admixture, although this phase did increase in intensity with increasing hydration time. It seems that the addition of tin(II) chloride had caused some retardation of the cement hydration and this has been the subject of further study [5].

More surprisingly, phase X contains tin in the +IV oxidation state, so oxidation of the Sn(II) had occurred. It has been confirmed that the same phase was formed when additions of tin(IV) chloride were made to the mix water.

Tin(II) readily oxidises in the presence of atmospheric oxygen. When $SnCl_2{\cdot}2H_2O$ is dissolved in water, an acidic

Table 3
XRD data for Phase X and $CaSn(OH)_6$

Present work (Phase X)		Literature data ($CaSn(OH)_6$)
28 days	180 days	JCPDS 9-30
4.71	4.71	4.69
4.07	4.07	4.06
2.88	2.88	2.87
2.57	2.58	2.57
2.45	2.45	2.45
2.35	2.35	2.34
2.18	2.18	2.17
2.04	2.04	2.03
1.821	1.821	1.814
1.663	1.664	1.658

solution is formed, and unless metallic tin is added, tin(IV) chloride (stannic chloride) and stannous oxychloride are formed [6], according to the equation:

$$6SnCl_2 + 2H_2O + O_2 = 2SnCl_4 + 4Sn(OH)Cl.$$

The formation of phases X and Y can then be understood according to the equation:

$$\begin{gathered} SnCl_4 + 2Ca_3Al_2O_6 + 3Ca(OH)_2 + 20H_2O \\ \downarrow \\ \underset{\text{Phase Y}}{2Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O} + \underset{\text{Phase X}}{CaSn(OH)_6}. \end{gathered}$$

The new products are formed from the tricalcium aluminate and calcium hydroxide present in the cement once some alite has been hydrated. The chemical equations shown above are an idealized representation of the process because the $SnCl_4$ that is formed will be rapidly hydrolysed. Furthermore, the continuing formation of phases X and Y between 28 and 180 days is probably via reaction with the initial products of hydration of the C_3A present in the cement. The progress of the reaction may be controlled by the availability of calcium hydroxide. The reduction in the amount of this phase present in the hydrated cement containing the tin salt, as well as the formation of Friedel's salt, is clearly explained by the chemical equation.

5. Conclusions

The hydration of Portland cement using mix water containing tin(II) chloride is somewhat retarded and leads to the formation of two additional hydration products, Friedel's salt, $Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O$, and calcium hydroxo-stannate, $CaSn(OH)_6$. The formation of the latter mixed hydroxide phase involves oxidation of Sn(II) to Sn(IV). Chemical equations that account for this oxidation process and hence the formation of new products are given above.

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