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FREE AND COMBINED CHLORIDE IN HYDRATING CEMENT AND CEMENT COMPONENTS

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Free and combined chloride in hydrating cement and cement components

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Normal portland cement, low C_3A cement, tricalcium silicate, and C_3A – gypsum mixtures are hydrated in the presence of 0, 0.8, 1.5 and 3.0% $CaCl_2$ for 1, 3, 7, 14 and 28 days and the amounts of extractable chloride determined by applying a pressure of 80 000 lb (449 MPa) or by treating the pastes with excess water. At early periods of hydration both methods yielded similar values for immobilized chloride. The amount of free chloride in the pore solution increased as the dosage of initially added chloride was increased. The C_3A – gypsum mixture immobilized much higher amounts of chloride than did the C_3S phase. Normal portland cement had lower amounts of free chloride than low C_3A cement.

INTRODUCTION

Properly placed, consolidated and cured reinforced concrete provides a highly alkaline environment that prevents corrosion of embedded steel. In the presence of chloride, either added as an admixture or introduced through extraneous sources, the corrosion potential of steel is enhanced. The threshold chloride content required for initiating corrosion has not, however, been established.

Chloride present in cement paste may be water soluble or insoluble, but only the soluble form is expected to accelerate corrosion. Owing to several problems associated with the determination of soluble and insoluble chloride in cement pastes there is no agreement on the relative amounts of either form present in cement paste. In early studies Monfore and Verbeck [1] concluded that only a small amount of free chloride remains in solution in concrete. Based on leaching techniques, other investigators came to a similar conclusion [2-9]. Using high pressure extraction techniques, however, recent investigations have revealed that a substantial amount of chloride remains in solution at all times [10, 11].

Such disagreement among workers may be due to variations in the types of material, experimental techniques, and calculations. In the present investigation two techniques, one based on extraction by water and the other on high pressure extrusion, were used to estimate the relative amounts of free and combined chloride in four types of cementitious material. A novel approach was adopted to determine the chloride content of pastes subjected to high pressure extrusion.

EXPERIMENTAL

Materials

Four sets of samples were used, viz, normal portland cement, low-C_3A cement, tricalcium silicate and C_3A + gypsum (*see* Table I).

Both C_3S and C_3A were supplied by Tetratech International, California. Tricalcium silicate had the following composition: $CaO = 73.5\%$, $SiO_2 = 26.0\%$, $MgO = 0.5\%$ and insolubles = 0.1%. Tricalcium aluminate had the following composition: $CaO = 61.6\%$, $Al_2O_3 = 37.8\%$, $MgO = 0.5\%$ and insolubles = 0.5%.

Gypsum was of analytical reagent quality. Calcium chloride hexahydrate of analytical reagent quality was used in the preparation of aqueous solutions. A known amount of this salt was added to distilled water and the exact concentration of the solution was determined by the argentometric method. A requisite volume was added to the cementitious materials to obtain known percentages of $CaCl_2$ with respect to solids.

Experimental procedure

Sample preparation

Each of the mixes was prepared at a solution/solid ratio of 1.0, except that in the C_3A-gypsum mixture the solution/C_3A ratio was 1.0. The volume of $CaCl_2$ solutions was adjusted so that the percentage of $CaCl_2$, with respect to solids, was 0, 0.8, 1.5 and 3.0%. In the C_3A-gypsum system the solid refers to C_3A.

After thorough mixing the mixture was poured into a polymethylmethacrylate (PMMA) tube (1 1/4-in. diam)

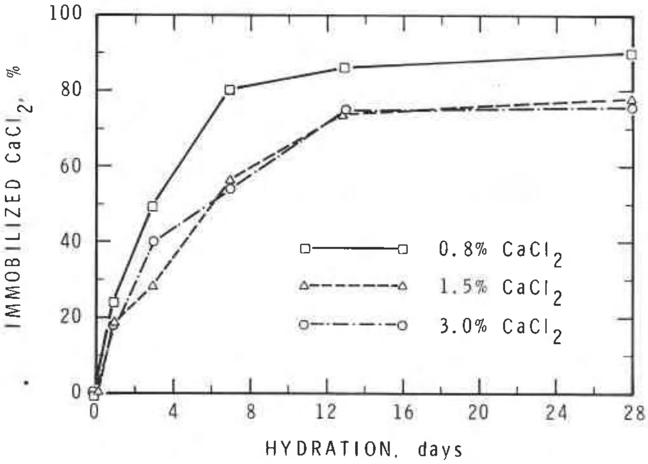

Fig. 1. — Pressure extraction of $CaCl_2$ from normal portland cement.

and placed on rollers for a day. The hardened paste was then removed and cut in the form of discs 1 in. thick and cured at 100% RH for 1, 3, 7, 14 and 24 days.

Extraction

Three discs were prepared at each of the curing periods and one was used for determination of free pore water; the other two (duplicates) were used for pressure treatment. The disc saturated with water was placed in a desiccator and subjected to vacuum for two days. Loss in weight was taken as the amount of pore water present in the discs. A small amount of non-evaporable water may have been lost, but this is not expected to affect the results.

Two other discs were subjected to pressure extrusion as follows. Each 1 1/4-in. disc was subjected to a load of 80 000 lb (449 MPa) using a specially fabricated mould similar to that used by Diamond and Federico [10]. Application of pressure forced a small amount of solution from the discs. A known amount was then taken, diluted, and analysed for chloride content using a selective ion electrode. From the concentration of chloride in the extruded solution and the amount of free water in the pore solution, the total amount of free chloride was computed as follows:

Amount of $CaCl_2$ added to cement (%) $= X_1$.

Mass of cured cement paste (disc) $= M_1$ g.

Mass of paste heated to 1 000°C $= M_2$ g.

Amount of free water in M_1 g of paste $= V_1$ cc.

Concentration of $CaCl_2$ in the extracted soluble (%) $= C_1$ (g/100 mL).

Total amount of free $CaCl_2$ in M_1 g of cement paste $= C_1 \times V_1/100$ g.

Percent free $CaCl_2$ with respect to M_2 g cement $= C_1V_1/M_2$.

Percent $CaCl_2$ immobilized in cement $= \left[X_1 - \frac{C_1V_1}{M_2} \right]$.

This method does not assume that all the pore solution is extruded from the sample by the application of pressure.

Aqueous extraction was carried out as follows. Samples were cured for different periods, as already described, and the discs were ground and wet sieved to pass a 300 µm sieve. The samples were kept in contact with distilled water (sample : water ratio = 1 : 20) for 3 h and the chloride content of the solution was determined as described.

RESULTS AND DISCUSSION

Figure 1 shows the amount of immobilized or combined $CaCl_2$ (that which is insoluble in water) at different stages of hydration in normal portland cement containing 0.8, 1.5 or 3% $CaCl_2$. This amount increases steeply in the first few days and becomes almost constant after 14 days. At 28 days about 75-85% of the added chloride is in a bound state because the cement phases (including C_3S) are capable of binding chloride to different extents [12].

Figure 2 compares results for the amounts of immobilized chloride determined by the pressure extrusion and aqueous extraction procedures. These pastes contained 1.5% $CaCl_2$ initially. The aqueous extraction procedure extracted more chloride than the pressure technique, indicating that when excess water is in contact with chloride complexes they become unstable. Ramachandran [12] has shown that $CaCl_2$ exists in different states in the C_3S-$CaCl_2$-H_2O system and that water is capable of decomposing some of these complexes.

The influence of chemical composition on the amount of immobilized $CaCl_2$ is illustrated in figure 3. Relatively large amounts of chloride are immobilized by normal as well as low C_3A cements. Although normal portland cement contains higher amounts of C_3A, it immobilizes lower amounts of $CaCl_2$. The differences other than C_3A content, viz, C_3S, C_2S, C_4AF and alkalis, may be responsible for this diffe-

TABLE I

COMPOSITION OF CEMENTS

Sample	Chemical Analysis, %							Compound Analysis, %			
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Ignition loss	C_3S	C_2S	C_3A	C_4AF
Normal portland cement.	20.28	4.67	2.47	63.95	2.85	4.03	1.80	59.81	12.98	8.20	7.52
Low C_3A-cement.	23.66	3.08	3.92	63.80	2.48	1.59	1.00	49.10	30.80	1.53	11.93

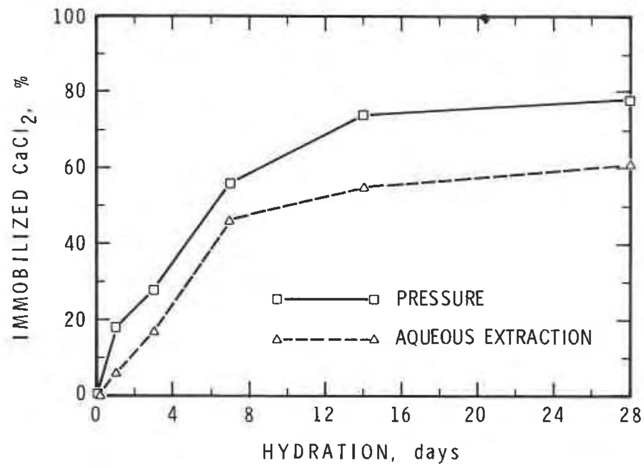

Fig. 2. — Relative amounts of immobilized chloride extracted by pressure or solution extraction procedures from portland cement.

rence. As already stated, even in low C_3A cements the aqueous extraction method dissolves more chloride than does the pressure method.

It has generally been assumed that the C_3S phase in portland cement does not bind any $CaCl_2$. Using both aqueous and pressure extraction methods, it is demonstrated that significant amounts of chloride are immobilized by the hydrating C_3S (*fig.* 4). As high as 40% of the added chloride may be bound by this phase. In figure 5 the immobilized $CaCl_2$ is expressed in terms of the weight of the solid phases.

It appears that the C_3A + gypsum mixture immobilizes much larger amounts of $CaCl_2$ than does the C_3S phase or cement (*figs* 6 and 7). Both procedures indicate that the C_3A + gypsum mixture immobilizes substantial amounts of chloride, and the amounts that react with the mixture increase as the dosage of $CaCl_2$ is increased (*fig.* 8).

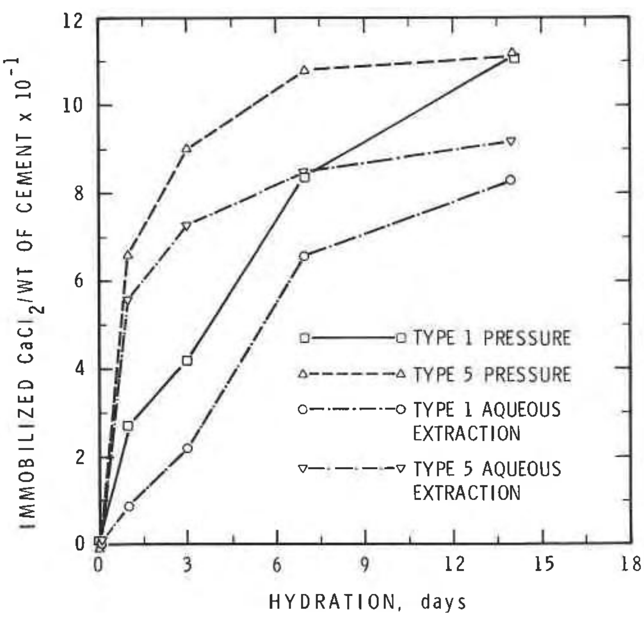

Fig. 3. — Comparison of amounts of immobilized $CaCl_2$ in normal and low tricalcium aluminate cements obtained by pressure or aqueous extraction technique.

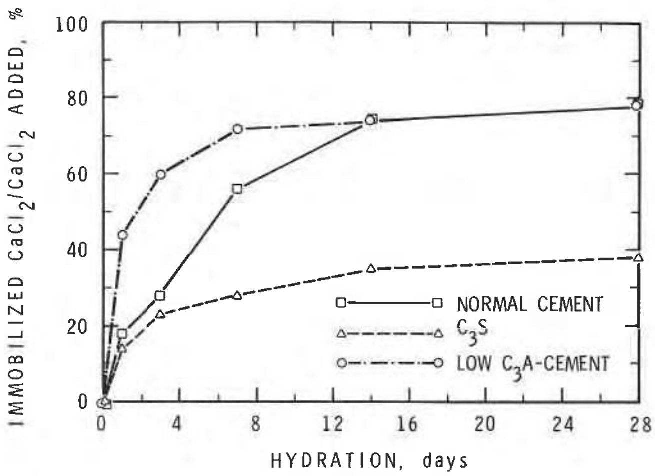

Fig. 4. — Amount of immobilized $CaCl_2$ in C_3S and cement paste subjected to pressure extraction.

Corrosion of reinforced steel in concrete worsens as the concentration of chloride in the aqueous phase is increased. Figures 9 and 10 show the amounts of free $CaCl_2$ or Cl^- present in the pore solution of portland cement pastes containing different amounts of initially-added chloride. At about 28 days the cement paste containing 1.5% has less than 0.5% $CaCl_2$, while that containing 3% $CaCl_2$ has about 1.0% free $CaCl_2$. At the dosage of 0.8% $CaCl_2$, free chloride amounts to about 0.1%. The amount of free chloride in the pore solution increases as the initial dosage of $CaCl_2$ is increased, but the relation is non-linear.

CONCLUSIONS

The amount of free chloride present in pore solutions of cement paste can be determined by applying the

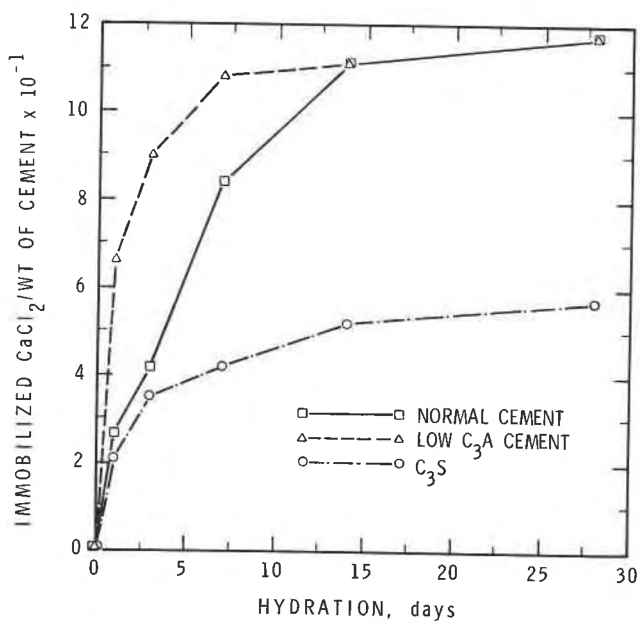

Fig. 5. — Immobilized $CaCl_2$ in C_3S and cement pastes subjected to pressure extraction.

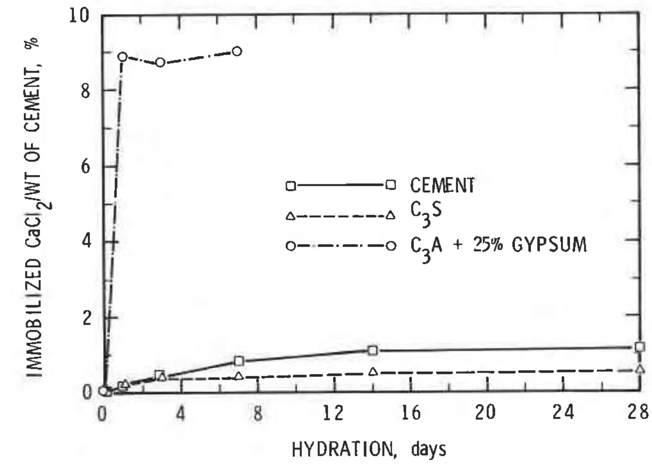

Fig. 6. — Relative amounts of immobilized $CaCl_2$ in various pastes, using pressure extraction.

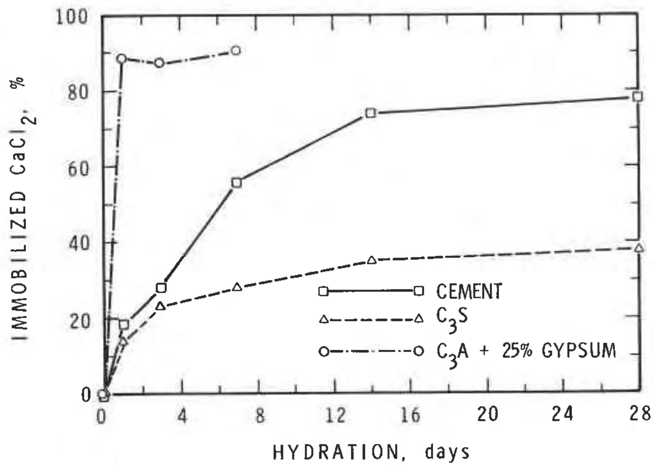

Fig. 7. — Amount of immobilized $CaCl_2$ in various pastes subjected to pressure extraction.

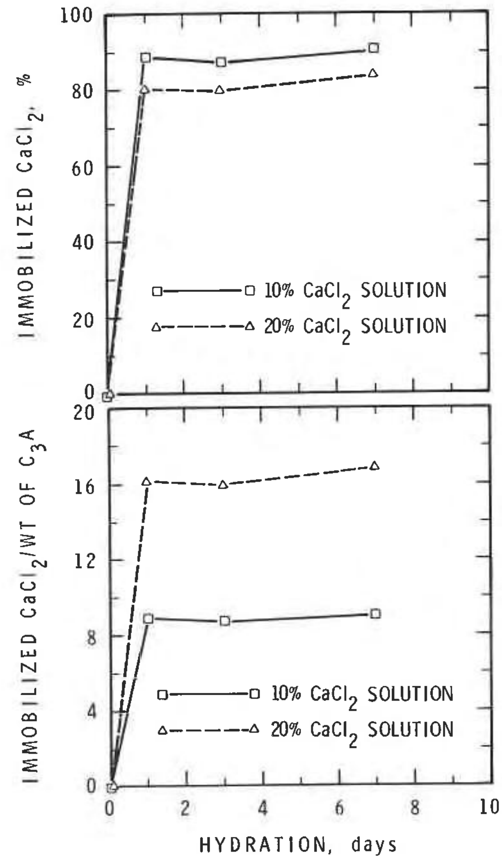

Fig. 8. — Immobilized chloride relative to amount of added $CaCl_2$ or C_3A obtained by aqueous extraction procedure in the C_3A-gypsum-water system.

pressure technique. This is accomplished by determining the evaporable water in the cement paste and measuring the chloride concentration of a portion of the solution forced from the pores by high pressure. The trend in results is similar for both methods. Normal portland cement binds more chloride than does low C_3A cement. Contrary to general opinion the C_3S phase immobilizes measurable amounts of chloride, and the C_3A-gypsum phase immobilizes larger amounts of chloride than the C_3S phase. The amount of free chloride in the paste increases as the initially-added chloride is increased.

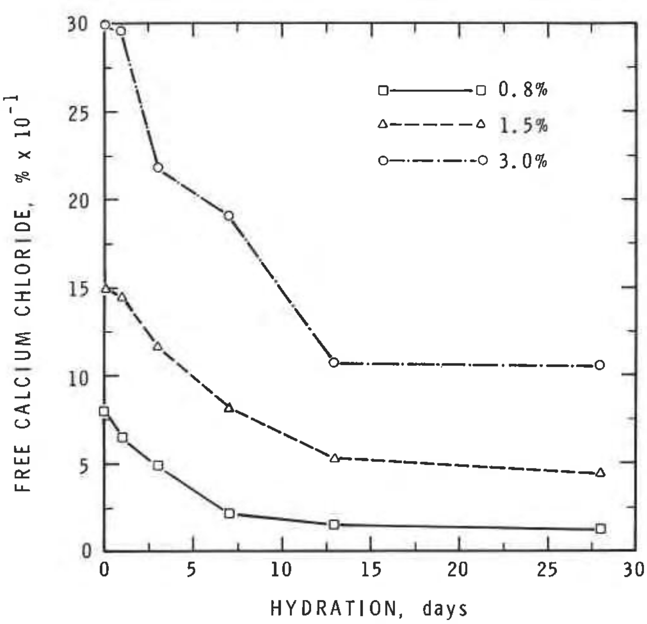

Fig. 9. — Amount of $CaCl_2$ extracted by pressure technique from normal portland cement paste.

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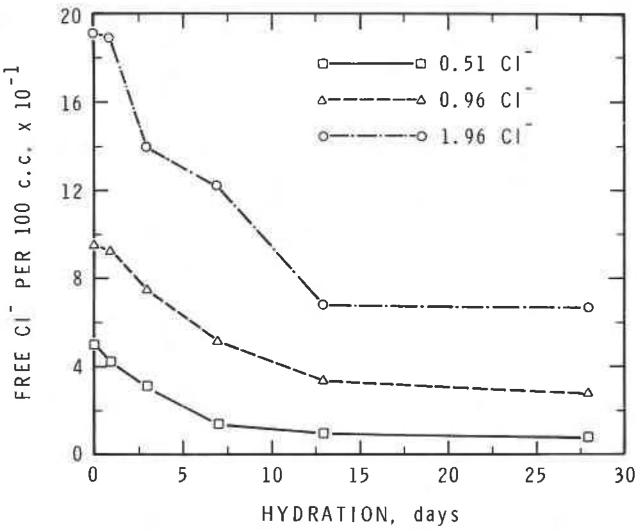

Fig. 10. — **Amount of free Cl^- extracted by pressure technique from normal portland cement paste.**

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RÉSUMÉ

Chlorures libres et combinés dans le ciment en cours d'hydratation et ses composants. — *Du ciment Portland normal, du ciment CAP, du silicate tri-calcique et des mélanges de C_3A-plâtre sont hydratés en présence de 0, 0,8, 1,5 et 3% de $CaCl_2$ en 1, 3, 7, 14 et 28 jours; les quantités de chlorure que l'on peut extraire sont déterminées par application d'une pression de 449 MPa ou par traitement des pâtes avec un excès d'eau. Dans les premiers temps de l'hydratation les deux méthodes donnent des quantités voisines de chlorure retenu. La quantité de chlorure libre dans la solution interstitielle augmente avec le dosage de chlorure initialement ajouté. Le mélange de C_3A- plâtre retient des quantités beaucoup plus grandes de chlorure que ne le fait la phase C_3S. Le ciment Portland normal montre des quantités plus faibles de chlorure libre que le ciment CAP.*