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The protective layer and decalcification of C-S-H in the mechanism of chloride corrosion of cement paste

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Abstract

Two processes of the chloride corrosion of cement paste are discussed: decalcification of C-S-H and the formation of the skin on the paste surface. Decalcification is relatively quick in the magnesium chloride solution, and brucite as well as basic magnesium chloride are formed. Taylor pointed out the possibility of magnesium silicate hydrate, which was proved in the works of other authors. A skin is formed on durable mortars immersed in the strong chloride solution. It is composed of brucite and basic magnesium chloride. The protective role of this skin, as foreseen by Taylor, was temporary, and sooner or later, the skin was destroyed. The alkali activated slag (AAS) mortar became then quickly destroyed. However, in high-alumina cement (HAC) paste, the dense layer was formed near the surface, which protected the paste, thus hindering the corrosion process.

Keywords: Basic magnesium chloride; Brucite; Protective layer, C-S-H; AAS; HAC

1. Introduction

The beginning of our investigations concerning the chloride corrosion of cement paste and the mortar was linked with the practical problem of dam durability in a salt mine. It is well known that the application of concrete in the salt mine presents a very difficult problem, and cement showing high stability in the strong salt solution is needed. The mine waters in salt mines are always strong chloride solutions, especially of sodium, magnesium and, in some cases, calcium and potassium.

The corrosion of cement paste in these chloride solutions appears very often in the form of high shrinkage, and microcracks are formed, which are the routes of quick migration of corrosive fluids into the concrete [1]. The chemical reactions of chlorides with cement paste start first with calcium hydroxide and calcium aluminate hydrates, depending on the cations in the solution, and new phases are formed. A simultaneous substantial lowering of the pH of the pore solution takes place, and many hydrates become unstable.

Smolczyk [2] has shown that in a highly concentrated chloride solution, the basic calcium and magnesium chlorides are formed, which are expansive and cause the destruction of concrete. Our experiments show that after different times, depending on the phase paste composition, the shrinkage is transformed into expansion, with numerous microcracks formed that enhances the corrosive liquid infiltration and formation of new destructive phases [3].

Calleja [4] mentioned that, in particular cases in solutions of moderate magnesium chloride concentration, an amorphous layer of brucite can be formed on the surface of concrete, which protects it from further corrosion.

This paper is devoted to chloride corrosion of different cement pastes and, particularly, to my discussions with Professor Taylor on this topic.

2. Decalcification of the C-S-H phase

It is well known that C-S-H is the most durable phase in the Portland cement paste and protects concrete in the corrosive environment. However, during a long action of several salts, this phase releases calcium ions to the liquid phase, with the decrease of C/S ratio. Gollop and Taylor [5] found that this process can even occur in the solution of sodium sulphate, which does not decrease the pH of the pore solution but is sluggish. In the case of magnesium sulphate, this process is much quicker [5,6]. The opinion that the magnesium solution

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is most aggressive to the C-S-H phase is generally accepted, and products brucite and basic magnesium chlorides, as well as the adequate calcium salt, are formed [7].

To verify the observations made with the cement paste and to obtain more information on the changes of the C-S-H gel in the strong chloride solution, the behaviour of X-ray pure C-S-H paste was investigated [7]. After 28 months of immersion of the small prism elements of C-S-H in the chloride solution of the composition (g/l) NaCl (195), $MgCl_2$ (77), KCl (98), $MgSO_4$ (3) and KBr (8), their composition was determined. The samples showed an altered layer about 3 mm thick, with unaltered cores. The two portions were obtained for investigation, and the classical chemical analysis was done. Their chemical composition is given in Table 1.

The results confirm a much quicker Cl^- diffusion in comparison with that of Mg^{2+}. The concentration of chloride ions is practically equal in the core and in the external layer. Contrary to this, the concentration of magnesium is much lower in the core, and the charge of chloride ions is balanced, at least partially, by sodium and potassium. In the core of the sample, the densification of C-S-H gel occurred (Fig. 1), which gave the decrease of porosity and surface area. The X-ray examination revealed the presence of diffuse lines of the basic magnesium chloride, but no peaks of brucite, then $Mg(OH)_2$, were totally amorphous.

From the chemical analysis, it is evident that the chemical composition of C-S-H in the external layer is strongly decalcified. The calculated C/S ratio is about 0.48, which means that C-S-H is partially decomposed with the formation of silicic acid because C-S-H is stable only at C/S ratio equal to 0.63 [8]. Calcium is present, at least partially, as basic calcium chloride, but this phase could be found only by SEM because it is amorphous.

The new phases containing magnesium were basic magnesium chloride and, probably, brucite. No magnesium silicate hydrate was found, but its formation cannot be excluded. This point was the matter of a discussion with Professor Taylor. He was confident that this phase should be formed in a strong magnesium chloride solution. Later, during the examination of the products of tobermorite corrosion in the chloride solution, we found some evidence for the presence of magnesium silicate hydrate [9]. Finally, Larbi and Visser [10], examining cement paste immersed in the magnesium chloride solution, found magnesium silicate hydrate as the main phase containing this cation.

Table 1
Chemical composition and physical properties of C-S-H sample after 28 months of immersion in chloride solution very similar with salt mine water

Chemical composition (wt.%)	Core	External layer
SiO_2	29.9	27.3
CaO	27.8	12.1
MgO	0.7	18.1
Cl	7.4	7.9
Na_2O	4.8	3.3
K_2O	2.8	2.4
LOI	26.7	28.9
Density (g/cm^3)	2.12	1.90
BET surface area (m^2/cm)	37.4	14.11
Total pore volume (cm^3/g)	0.405	0.154
Average pore diameter (nm)	18.1	3.49

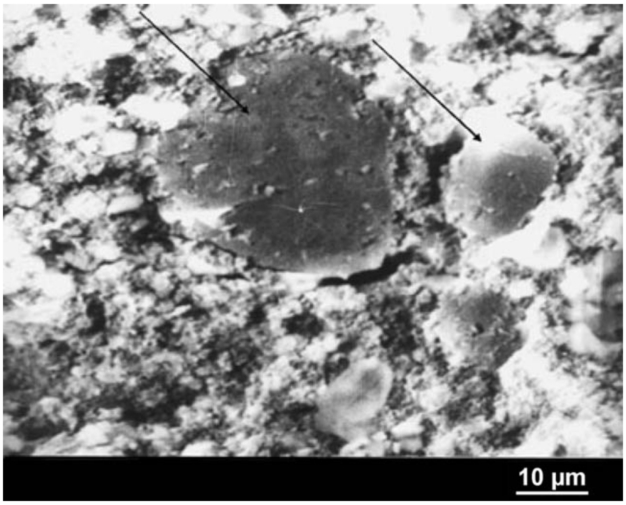

Fig. 1. Densification of C-S-H. The dense grains of this phase are shown with arrows.

One can thus summarize the following findings: C-S-H is relatively quickly decalcified in strong chloride solutions containing $MgCl_2$, and new phases are principally brucite and basic magnesium chloride, but magnesium silicate hydrate is also formed. It is amorphous as a rule and is thus difficult to identify; the best method seems to be SEM with EDAX.

3. Formation of skin on paste surface

During the examination of the corrosion of different types of cements in the strong chloride solution, we concluded that they could be divided into two groups. The first gives durable paste on the surface of which a layer of new products is formed, and the second gives paste of low durability, quickly destroyed in this environment, on the surface of which no stable skin was formed [11]. To the first group, the high-alumina cement (HAC) and alkali activated slag (AAS) must be included, to the second, Portland, and even slag, cement. On the surface of the latter cement, in some places, a layer of new products can be formed, but it is very unstable.

The skin formed on the surface of a mortar immersed in the solution of the composition mentioned in Point 2 is very stable in the case of AAS and HAC pastes (Fig. 2). It is composed of brucite and basic magnesium chloride (Fig. 3). This skin is very dense and impermeable, and under it, some new products are formed. They can be gibbsite, as well as Friedel salt, and even halite, all forming nests composed of relatively big crystals (Fig. 4).

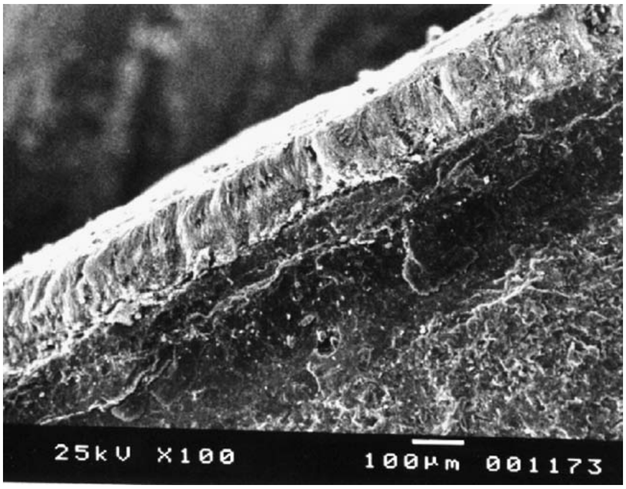

Fig. 2. Skin on AAS mortar after three years of immersion in chloride solution.

Fig. 4. Nest of gibbsite crystals under the skin, HAC paste as in Fig. 3. The outer surface lays above the skin.

The mechanism of this skin formation consists in the oversaturation of the pore solution with magnesium compounds, due to the rapid diffusion of chloride ions into the interior of the paste, which must be counterbalanced by the diffusion of OH^- ions in the opposite direction. Thus, two fronts of high concentration of ions of Cl^- and OH^- meet, and the quick precipitation of magnesium compounds occurs. This precipitation can catch all the ions of magnesium, chloride and OH^-, thus hindering the transport of magnesium and chloride ions into the cement paste. Without doubt, this skin plays the role of a protective layer in this period of corrosion. However, the question is how long this role of skin can be maintained. The properties of the skin and the unaltered paste are very different, and the diffusion of ions, although very slow, must proceed.

On the surface of the pastes of HAC and AAS, which are very durable in the chloride solution, the skin remained very stable for seven years, and under it, a relatively low altered layer of paste remained. In the case of AAS paste, the X-ray examination of external layer, laying under the skin, showed principally the lines of C-S-H and some very weak peaks of basic magnesium chloride. Without doubt, a corrosion process proceeds, but is very slow. The external layer of HAC paste showed only the lines of Friedel salt, and no peaks of magnesium compounds could be found. Hence, in both cases, after seven years, the protective action of the skin was well marked. However, the HAC paste was more durable than the AAS paste.

We discussed with Professor Taylor the problems related to the role of the skin during the Materials Research Society Symposium in Boston on the 28th of November 1995. He was of an opinion that the positive role of skin hindering the corrosion process would be transitory and, sooner or later, this skin would become less impermeable, and, furthermore, quick destructive processes of concrete would start.

We found the proof that the precipitating front is not always so impermeable in Portland cement paste. In Fig. 5,

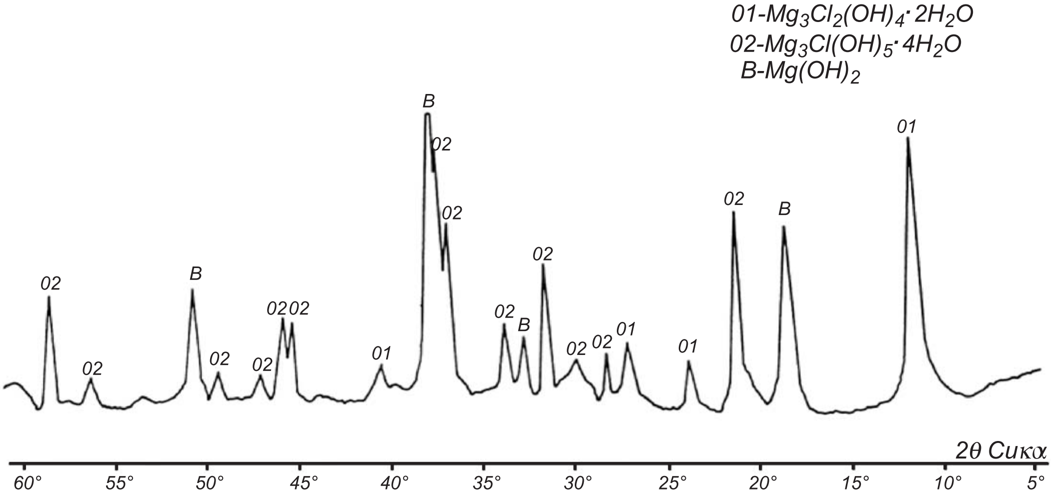

Fig. 3. X-ray of the skin on HAC paste after two years of immersion in chloride solution.

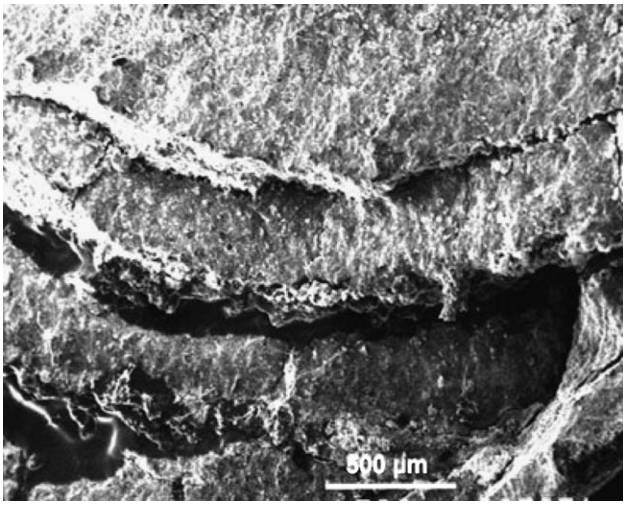

Fig. 5. Three layers of basic magnesium chloride in Portland cement mortar. The outer surface is in the bottom of the figure.

we can see three consecutive fronts of basic magnesium chloride with the microcracks formed. The greater permeability of this layer is probably due to the higher porosity of the cement paste as compared with the porosity of HAC or AAS pastes. It is probably the reason why the stable skin was not formed on the surface of the Portland cement and slag cement mortars.

After 15 years of immersion in the chloride solution, we examined once more the pastes of HAC and AAS [12]. In both cases, the skin became destroyed in several places, much less in case of HAC paste (Fig. 6). Simultaneously, the paste of AAS became totally destroyed, and several new phases have been formed; aragonite, calcite, halite and gypsum were found, among others.

On the contrary, HAC paste shows no destruction. Its strength remained high, almost 70 MPa. In the bars, three layers can be distinguished. Under the skin, there is a dark external layer about 2–3 mm thick. Then, there is a bright transitional layer about 1 mm thick. This bright layer surrounds the “unchanged” core of the sample (Fig. 7).

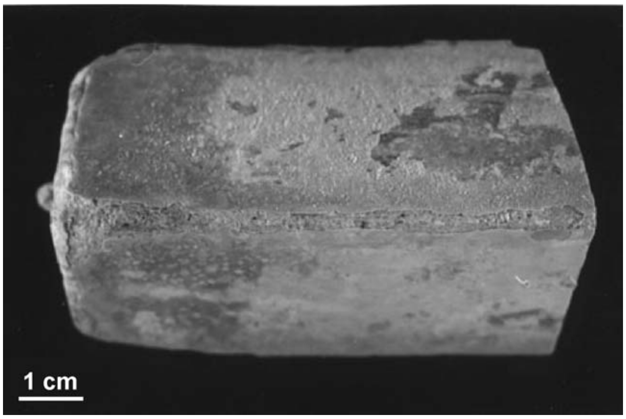

Fig. 6. General view of the cut bar of HAC paste after 15 years of immersion in chloride solution. Half of the bar, 4 × 4 × 16 cm, is shown.

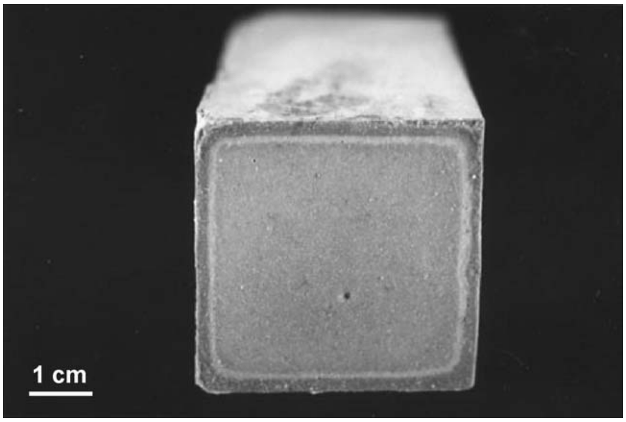

Fig. 7. The section of the HAC paste bar. The dark, the bright and the core are visible.

These consecutive layers were relatively easily separable for further examination. The MIP of these layers shows that the porosity of bright transitional zone is very low, much lower than the core (Table 2).

The chemical composition of the three zones of the bar, determined by EDAX, is very similar. The content of three elements in question, i.e., Ca, Al and Cl, is practically the same in the transitional zone and in the core.

The X-ray examination of the skin shows that it is composed principally of brucite and aragonite. However, SEM revealed also the presence of basic magnesium and calcium chlorides, but in minor quantities. A trace of halite was also found.

The phase composition of three layers differs significantly from each other (Fig. 8). The external layer contains a small quantity of Friedel’s salt but a high content of calcite. The content of gibbsite is relatively high. Aragonite and CA_2 are the remaining phases.

The transitional layer is much richer in Friedel’s salt. In addition, the X-ray lines of hydrogarnet have a high intensity. Gibbsite concentration is considerable. The content of CA_2 seems to be on the same level in all three layers of the sample. A small quantity of calcite is to be noted. The core is composed mainly of three phases, namely, Friedel’s salt, gibbsite and hydrogarnet.

The results of the examination of the HAC paste show that it is very durable when immersed in the strong chloride solution. The skin became practically destroyed, but on the superficial zone of the bar, the transitional layer is formed, which is very tight and hinders the diffusion of chloride ions in the deeper part of the bar. The concentration of chloride

Table 2
Porosity of three zones of the bar

Layer	Total pore volume (mm^3/g)	Porosity (%)	Average pore radius (µm)
Core	3.00	0.66	0.016
Transitional	0.73	0.16	0.44
External	2.14	0.45	0.23

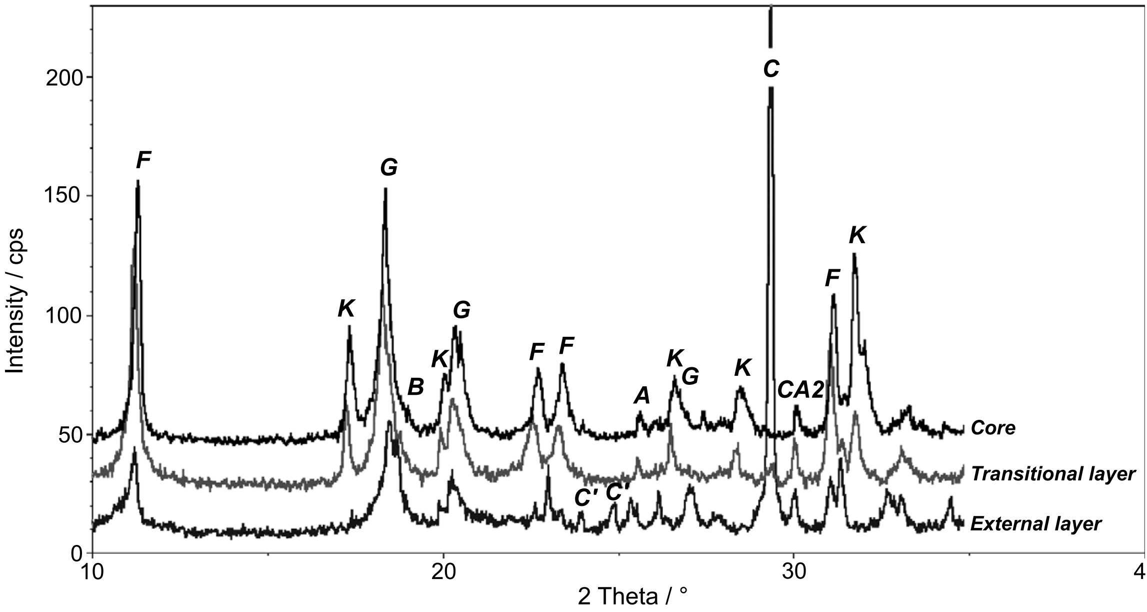

Fig. 8. Phase composition of two layers and a core in HAC paste bar. F—Friedel salt, K—hydrogarnet, G—gibbsite, C—calcite, A—corundum, C′—aragonite and B—brucite.

ions in this transitional layer is significantly lower than in the external layer and is the same as in the core. In addition, the mineralogical composition of the transition zone is almost identical with that of the core and differs drastically from that of the external layer.

Contrary to this, the skin is not stable and plays a minor role as a corrosion barrier. In addition, its mineralogical composition changed significantly during the long period of aggressive action of chloride solution. Previously, the main constituents were basic chlorides and amorphous $Mg(OH)_2$ [13]. Now, under the influence of the atmosphere that enriched the solution in CO_2, aragonite prevails, but also, a crystalline brucite is in high concentration. The trace of halite can be caused by different nest formations under the skin, which was found in our first study [13]. Calcite and Friedel's salt are the main products of corrosion in the external layer.

In the core of the sample, Friedel's salt is formed preferentially on the surface of cement grains and frequently forms a solid solution with C_4AH_{13} and thus has a lower chloride concentration [12].

HAC paste is very durable in the chloride solution, and the main corrosion product is Friedel's salt. Simultaneously, the paste phase composition is changed from CAH_{10} towards hydrogarnet, which has become the main hydration phase. In addition, alumina hydroxide gel is transformed into gibbsite. It is evident from the obtained results that the formation of Friedel's salt is not accompanied by the crystallisation pressure and porosity increase (Table 2). The formation of Friedel's salt is thus not dangerous for the durability of the paste.

In summary, I must say that Professor Taylor's previsions on the role of the skin were right. Its protective action is transitory, and if the paste itself cannot form further tight zones, its destruction must happen.

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