

CORROSION OF THE ZINC ALLOY COATING IN GALVANIZED REINFORCED CONCRETE

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ABSTRACT

The corrosion of galvanized reinforcement in concrete is a multi-stage process. After a generally long period to the initiation of corrosion, dissolution of the galvanized coating commences with the loss of the outer pure zinc *eta* phase, followed by slow dissolution of the underlying *zeta* and *delta* phases. Corrosion of the parent steel does not commence till the zinc alloy layers are completely lost from extensive areas of the bar surface. This process results in the well documented delay in the appearance of corrosion of zinc coated steel reinforcement in concrete. This paper presents the results of a metallographic examination of the dissolution of the galvanized coating and the migration of the zinc corrosion product, identified as zinc oxide, away from the coating interface and into the adjacent concrete. The zinc corrosion products appear to cause little or no disruption to the cover concrete and have been observed to fill microcracks and small voids in the matrix, resulting in an apparent densification of the cement matrix, at distances up to 0.5 mm from the bar interface.

Keywords: galvanizing, reinforcement, concrete, corrosion, alloy layers, metallography, scanning microscopy, x-ray analysis, corrosion products, mobility, corrosion model

INTRODUCTION

The use of a hot dip zinc coating (ie. galvanizing) for corrosion protection of reinforcing steel in concrete has been shown both experimentally and in practice to extend the service life of reinforced concrete structures. However, despite a great deal of both laboratory based research and field assessment of galvanized reinforced structures over many years, precise determination of chloride thresholds for incipient corrosion of zinc in concrete and the prediction of actual time to corrosion of zinc coated steel reinforcement has not been a straight forward task.

The reasons for this are that the corrosion behaviour, and thus the service life, of galvanized steel depends on a variety of inter-related factors such as the severity of the environment to which the concrete is exposed, the nature of the concrete used in the structure, and the metallurgical characteristics of the zinc coating itself.

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What is clear is that the protection afforded by zinc to steel reinforcement in concrete is a multi-stage process. First, there is the delay to the initiation of corrosion due to the higher chloride tolerance of zinc compared to black steel; zinc can tolerate chloride levels several times higher than causes corrosion of black steel.^{1,2} Since zinc can remain passivated to somewhat lower pH than black steel, there is also substantial protection offered against the naturally occurring effects of carbonation of the cover concrete. Second, there is the additional time to corrosion of the steel substrate due to the continued protection afforded during the dissolution of the zinc alloy layers of the coating. Considering also that zinc cathodically protects regions where the underlying steel is exposed, there is a further limited measure of corrosion protection even when the coating is completely lost from local regions of the steel surface.

In order to visualise the various stages of the protection due to the zinc coating of steel reinforcement in concrete, a service life model has previously been presented.³ Based on the traditional Tuutti model which includes both an initiation stage and propagation stages for the corrosion of steel in concrete⁴, this model incorporates an additional *protection* stage between corrosion initiation and propagation (Figure 1).

For galvanized steel in concrete, the initiation of corrosion coincides with the onset of gradual dissolution of the outer-most layers of the galvanized coating. The protection stage is the following interval over which the zinc and zinc-iron alloys of the coating progressively dissolve. During this stage the coating continues to prevent corrosion of the underlying steel. At the end of the protection stage the exposed steel begins to corrode and the propagation stage coincides with continued rapid corrosion of the steel with consequential damage to the concrete due to the expansive forces generated by the iron corrosion products. Indications are that the life of the zinc coating on galvanized steel in concrete (to the end of the protection stage) is of the order of 4-5 times the period to the initiation of corrosion of black steel in equivalent concrete and exposure conditions.²

One important component of this complex process is that during the *protection* stage when the zinc coating is dissolving and zinc corrosion products are presumably migrating into the adjacent concrete matrix, very little disruption appears to occur to the cover concrete. This is in stark contrast to the situation when black steel in concrete corrodes whereby the iron corrosion products precipitating at the bar/concrete interface generate tensile stresses of sufficient magnitude (several MPa) to crack the cover concrete.

For galvanized reinforcement, even though the zinc is corroding, the concrete mass usually remains intact until the underlying steel is exposed and it commences to corrode. This feature enhances the protective effect of the coating to the reinforcement and so considerably extends its useful life as a corrosion protection medium. The reasons for this can be traced to a number of factors originally proposed by Hoke, Pickering and Rosengarth.⁵ In summary it was postulated that zinc corrosion products, usually zinc oxide, are somewhat less voluminous with a swelling factor of about 150% compared to iron corrosion products (in excess of 250%) and thus develop lower expansive pressures in the concrete. They also tend to be friable in that they are loose and powdery minerals rather than bulky hard phases, and they migrate away from the reinforcement surface and fill cracks and voids in the cover concrete.

In order to further investigate the behaviour of galvanized reinforcement during the so-called *protection* stage, a two-part experimental program was undertaken involving: a detailed metallurgical examination of the behaviour of the galvanized reinforcing steel exposed to chloride-contaminated concrete; and a scanning electron microscopic investigation of the nature of the zinc corrosion products and their migration away from the bar/matrix interface, again as a result of chloride induced corrosion.

EXPERIMENTAL PROGRAM

A series of 50 mm diameter x 100 mm sand-cement mortar cylinders were cast with a centrally positioned 12.7 mm (No 4) reinforcing bar. Two mortars of differing w/c ratio were used (0.45 and 0.60), and duplicate cylinder sets with black steel and galvanized steel bars were prepared. The materials for the mortar mixes were ASTM C150 Type 1 Cement and ASTM C778 Graded Sand (Ottawa). The mix proportions followed the recommendations given in ASTM C109 with 1 part cement to 2.75 parts sand. The 45 day compressive strength of the two mortar mixes were 66 MPa (w/c 0.45) and 17 MPa (w/c 0.6). The higher w/c ratio mortars were clearly more permeable and were included to accelerate the chloride ingress from the exposure environments over that expected in the higher quality, lower w/c mortar.

The galvanized bars were zinc coated by hot dipping to ASTM A767 with an average alloy layer coating thickness of about 95 μ (micron). The hardened cylinders were lime water cured for 7 days then immediately exposed to a wetting and drying regime in either 3.5% or 5% salt solutions. The wetting and drying involved 4 days full immersion in salt water followed by 3 days drying in an oven at 70°C. After exposure periods of 65, 95 and 158 days, samples were withdrawn for detailed examination. Selected samples were transversely sectioned near the mid-height position using a high speed diamond masonry saw to extract several slices each about 6 mm thick.

Chloride concentration profiles were determined from mortar drillings taken at three successive depths from the cylinders, namely 3-8 mm, 8-13 mm and 13-18 mm. A chloride sensitive probe with a concentration range of 5×10^{-5} to 1M was used for the chemical analysis.

Sections of the reinforcement intended for metallographic examination were removed from the surrounding mortar then mounted, polished and etched using 1% nital. The average thickness of the remaining galvanized coating was determined using a graduated measuring eyepiece at 10 locations around the bar circumference. Because of the uneven nature of the loss of the zinc alloys from the coating, quantitative metallographic techniques were used to measure the area of the coating cross section to give a more reliable estimate of the coating loss.

Other disks taken from the cylinders were prepared for examination in the scanning electron microscope (SEM) and for elemental x-ray characterisation. The most important aspect of this was that the preparation of the sample for the SEM should not unduly disturb the nature and distribution of the mortar structure nor the zinc corrosion products. Immediately after sectioning, the thin disks were immersed in methanol for a minimum of two days and often much longer, during which time the bulk of the water in the specimen was displaced. They were then impregnated under low vacuum with a high fluidity epoxy resin which was able to flow into the capillary space and exposed pores. The resin impregnated specimens were then wet polished to carefully remove the surface resin layer and reveal the underlying matrix.

SEM images of the transverse section across the reinforcement interface and the surrounding mortar matrix were captured. Local x-ray spectral analysis was undertaken to characterise the various phases observed (primarily concentrating on the elements Ca, Fe, Zn, Cl and Si), in addition to line scans of selected elements showing their distribution across the microstructure. For several samples, x-ray powder diffraction was done on small quantities of hydration product and corrosion product exuded from the mortar microstructure.

RESULTS AND DISCUSSION

Metallography

The original microstructure of the galvanized layer is shown in Figure 2. This reveals the typical alloy layer structure of the coating with the pure zinc *eta* layer at the outside, and the *zeta* (5-6% Fe) and *delta* (7-12% Fe) phases progressively below. The thin iron-rich *gamma* phase (21-28% Fe) at the interface with the underlying steel is not visible at this magnification. The average coating thickness of this sample is of the order of 90-95 μ .

For this particular coating, the pure zinc *eta* layer is about 10-15 μ thick and produces the finished smooth surface of the galvanized layer. The bulk of the coating is comprised of the "flowery" *zeta* phase, infilled at depth with *eta*, and the "blocky" *delta* phase to a combined thickness of approximately 70 μ - about two-thirds of the total coating thickness. While this alloy layer structure is fairly typical of many galvanized coatings, different types of steels (some called reactive steels) and different galvanizing practices (such as heat treatment) may produce different morphologies in the coating layers. This fact alone - the natural variability of the coating - is part reason for the difficulty in uniquely characterising the corrosion behaviour, and thus the service life, of galvanized coatings in general.

The examination revealed that once the galvanized steel comes in contact with cement mortar, there is an immediate loss of an amount of zinc, primarily the pure zinc *eta* layer, from the coating surface. This feature of the corrosion of zinc in concrete, namely the consumption of a small quantity (perhaps as much as 10 μ thickness) of pure zinc at the coating surface for the passivation process, is well documented.^{6,7} At this stage, the coating is, on the whole, only slightly reduced in thickness though there is preliminary evidence of tunnelling through the coating beneath the outer layers of the coating where intrusions of pure zinc (*eta*) between the larger *zeta* flowers have dissolved (see Figure 3). On this basis, the effective metal loss from the coating (in terms of the remaining cross section) is of the order of 5-10% by mass.

As further corrosion occurs, the *eta* layer continues to dissolve until it is totally lost from the coating surface. This effect is shown in Figure 4 for sample G16 (w/c 0.6), exposed for 65 days to a 5% salt solution. For this sample, the average thickness of the remaining coating is approximately 70 μ but it is clear that the regions loss of the zinc are intruding deeply into the body of the coating around the *zeta* phase. There is also here evidence of extensive tunnelling through the remaining alloy layers of the coating. As a result, the average coating thickness again does not properly represent the coating thickness loss. When the area of the coating remaining is estimated, it is clear that the amount of metal lost from the surface by this time is of the order of 30%. Note however, that the underlying *delta* alloy layer and much of the *zeta* structure is still largely intact.

At a later stage in this process, the *eta* phase has been totally lost and the flowers of *zeta* which remain appear as virtually isolated pockets with many large holes and tunnels through them. This is shown in Figure 5 for sample G15 (w/c 0.6), exposed for 158 days to a 5% salt solution. In Figure 5 it would appear that the coating is seriously deteriorated, though there is in fact a complete alloy layer of protection to the underlying steel from the remnants of the *zeta* "flowers" and the "blocky" *delta* phase and so no attack on the substrate has yet occurred. While difficult to measure precisely, the average thickness of the remaining coating is still about 60-70 μ (of the original 90 μ), though the mass of coating loss is of the order of 50%.

Thus, after this period of severe salt water exposure, somewhat more than half of the zinc coating remains on the surface of the bar to protect the steel. This clearly demonstrates the ability of the *zeta* and *delta* alloy phases to survive on galvanized reinforcement in concrete for extended periods of time even in high chloride environments, certainly well above that for the corrosion of black steel. In sample G15 for example, the acid soluble chloride concentration in the mortar adjacent to the embedded bar was 0.3% by weight of cement, many times higher than recommended chloride levels for black steel in concrete.

These experimental observations mirror results often obtained from field surveys of galvanized reinforced structures (eg. bridge decks) which reveal that as little as 10-30% only of the original coating thickness (not mass) is lost from the bar surface even after quite long exposure to elevated chloride levels. Over longer periods (20 years and more), only minor further loss of the zinc coating thickness occurs such that more zinc generally remains on the bar surface in situ than the specified minimum original coating thickness.⁸ ASTM A767 specifies an original minimum coating thickness of 150 μ (a coating mass of 1070 g/m²) for Class I coatings on steel rebar over 10 mm thick, and 86 μ (610 g/m²) for Class II coatings.

As a final stage to this process, it is interesting to note that where the coating has locally been completely lost and the underlying steel exposed, the steel in close proximity to the remaining zinc is cathodically protected by the sacrificial nature of zinc. An example of this is shown in Figure 6. This can be expected to provide some additional protection to the underlying steel depending on the conductivity of the electrolyte. In accelerated laboratory tests on galvanized rebar in concrete specimens, protection of exposed steel to a distance of about 8 mm has been reported.²

Scanning Electron Microscopy

The SEM analysis revealed evidence of the migration of zinc corrosion products away from the concrete/bar interface, and the filling of micro-cracks and small voids in the matrix with zinc corrosion products at some distance from the reinforcement. Typical examples of this are shown in Figures 7 and 8. In Figure 7, the surface of the galvanized coating (at left) reveals the loss of the *eta* phase generally and the intrusion of the *eta* around and through the *zeta* "flowers". The matrix to the right is comprised of cement particles, hydration product and fine sand particles. The plume of corrosion product (the so-called bright phase) is clearly contrasted against the matrix. In Figure 8, the bright corrosion product phase has migrated into the matrix and between sand particles and shows as discrete pockets at distance from the bar interface.

X-ray spectra of the mortar matrix and bright phase product are shown in Figures 9 and 10 respectively. The matrix remote from the bar shows strong Ca, Si and Al peaks, and Cl because of the salt water exposure. X-ray powder diffraction of equivalent matrix material revealed the majority presence of Ca(OH)₂ as the mineral Portlandite. The spectra for the bright phase shows similar Ca, Si and Cl peaks but also has strong Zn and Fe peaks. XRD of exuded corrosion product identified the bright phase as the oxide mineral Zincite (ZnO) with no evidence of the presence of complex zinc oxy chloride type minerals. The presence of zinc in the bright phase was also confirmed by a Zn line spectra which clearly

showed a high concentration of zinc both in the galvanized layer and coinciding with the bright phase in the adjacent matrix.

Examination of many such SEM images revealed a number of features of the corrosion behaviour of galvanized steel in concrete. Some important observations were:

- ◆ The migration of the zinc corrosion product into the mortar matrix did not necessarily follow a two dimensional planar interface. In many cases, the zinc product migrated between sand particles or along their interface. In others, small pockets of the corrosion product appeared at remote pore sites in the matrix at greater distance from the bar. There is clear evidence of three dimensional mobility of the zinc oxide corrosion product.
- ◆ The corrosion product appeared to fill small pores and microcracks or it lined the surface of larger voids. As a result, there was a noticeable densification of the matrix adjacent to the bar interface where smaller voids and capillary spaces had been completely filled.
- ◆ At high magnifications an interfacial zone between the bar and the matrix was observed which was also rich in zinc. This zone, filled with a mix of hydration product and corrosion product, and which was only about 10 μ wide, may have coincided with the position (in the matrix) of the edge of the original coating.
- ◆ Loss of zinc from the coating reveals the same features as shown metallographically. As the zinc is consumed, intrusions, holes and tunnels develop in the underlying alloy layers, some of which become backfilled with a mix of hydration and corrosion product.
- ◆ There was no evidence to suggest that the zinc corrosion products caused any physical disruption to the interfacial region between the bar and the mortar, nor the bulk matrix itself.

In combination, these characteristics of the corrosion of zinc in concrete lend support to the view that, during the *protection* stage, relatively low stresses develop around the reinforcement and thus little or no damage to the cover concrete occurs. This enhances the corrosion protection of the reinforcement by maintaining the integrity of the cover concrete until the zinc is completely lost from the surface.

It could be inferred from this that the corrosion process itself, resulting in the formation of zinc oxide corrosion product which fills the pore structure in the matrix adjacent to the bar, may in fact create a barrier region of decreased permeability to the continued ingress of aggressive species such as chlorides. An effect similar to this has been reported in connection with the adhesion and ultimate bond strength of galvanized reinforcement in concrete.⁹ In this work, the so-called *densification* of the transition zone between the zinc coating and the cement paste due to the penetration of non-expansive zinc corrosion products into adjacent concrete pores, has been used to justify the significant increase in the ultimate bond strength of galvanized bars in concrete exposed to sodium chloride aqueous solution. This process, facilitated by the presence of chloride which promotes the corrosion and dissolution of the zinc, results in the formation of bridges between the metal and the concrete which increases adhesion and reduces load induced slip.

CONCLUSIONS

This experimental program has provided an opportunity to better understand the corrosion of galvanized reinforcing steel in concrete. Of particular interest has been the processes occurring during the so-called *protection* period when the gradual dissolution of the zinc coating extends the time to corrosion of the steel substrate with little or no apparent distress to the cover concrete.

The corrosion product resulting from the dissolution of the galvanized coating in high chloride levels has been identified as the mineral Zincite (ZnO) with no evidence of other complex zinc oxy chloride type products being present. The ZnO clearly has a high degree of mobility and migrates radially from the bar surface into the adjacent matrix filling pore space and microcracks with an apparent densification of the matrix. There is no visible distress to the surrounding cement matrix due to the formation and migration of the ZnO corrosion product.

As the pure zinc *eta* phase is lost from the surface of the galvanized coating, the underlying zinc-iron alloys *zeta* and *delta* are exposed. The loss of zinc from the coating does not occur uniformly but rather is initially a process of selective dissolution of isolated pockets and tunnels of the pure zinc *eta* phase from within and around the underlying *zeta* phase. This results in the appearance of many voids and cavities in the coating. The remaining zinc alloy layers survive for a further substantial period of time before the underlying steel is exposed. Even when this occurs in local regions of the bar surface, the adjacent zinc remaining on the bar surface cathodically protects the exposed steel.

This process can be used to account for the long period of protection, beyond the onset or initiation of corrosion, afforded to the underlying steel reinforcement. It is to be noted however, that many factors are known to influence the longevity of the galvanized coating and so prediction of the actual service life of the galvanized steel in concrete remains a difficult and uncertain task.

Since the loss of zinc from the coating surface is not uniform, measurement of the remaining coating thickness via the use of electromagnetic type surface gauges does not properly indicate the state of the remaining coating. A preferable method is to examine the coating metallographically and determine a remnant coating mass (volume) or an average coating thickness taking into account the intrusive and multi-directional nature of the zinc metal loss.

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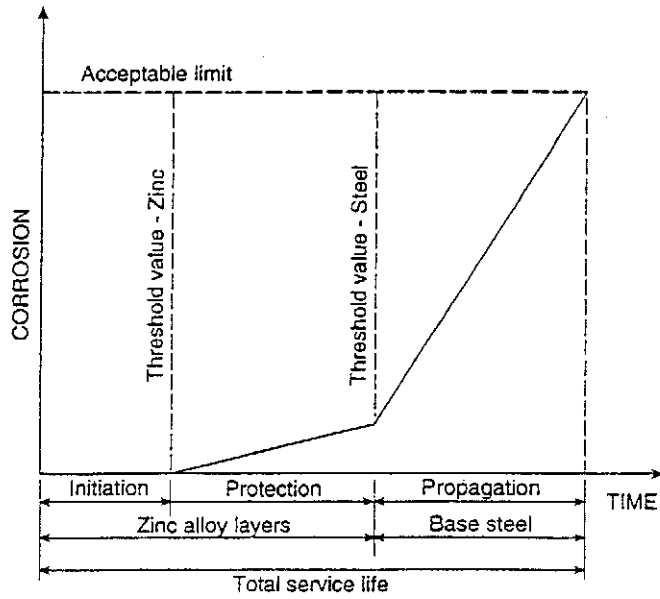


Figure 1. Service life model for galvanized steel in concrete

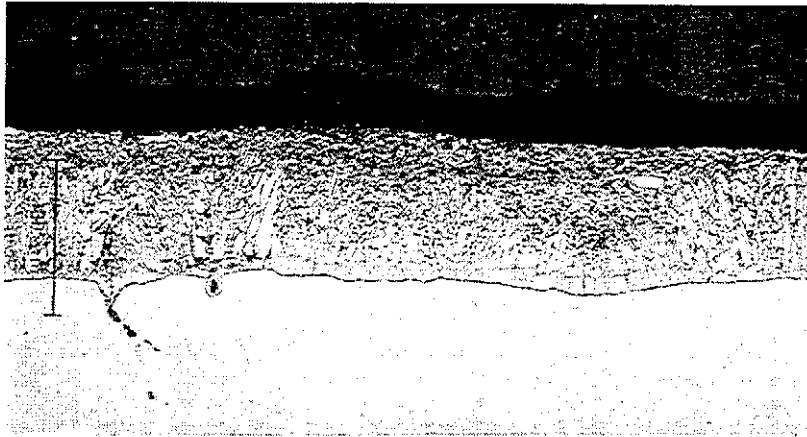


Figure 2. Microstructure of hot dip galvanized layer (200x)

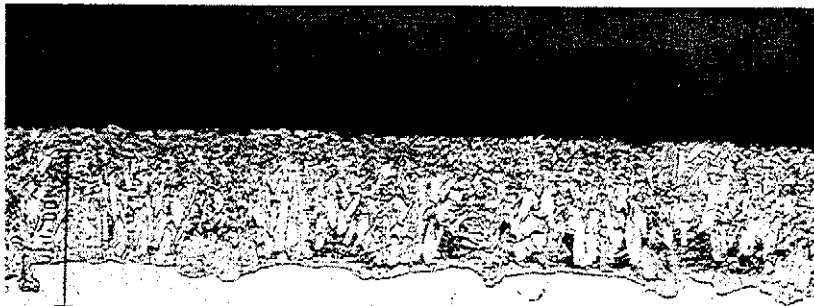


Figure 3. Microstructure of hot dip galvanized layer after short term exposure to cement (200x)

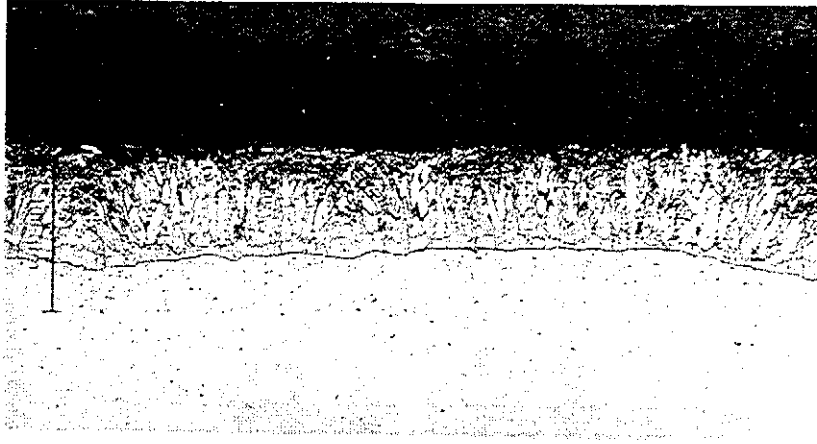


Figure 4. Sample G16 (w/c 0.60, 5% salt solution) after 65 days exposure. (200x)



Figure 5. Sample G15 (w/c 0.60, 5% salt solution) after 158 days exposure. (200x)



Figure 6. Showing zinc protection of exposed steel sections (200x)



Figure 7. SEM image across interface for sample G15 (1000x)

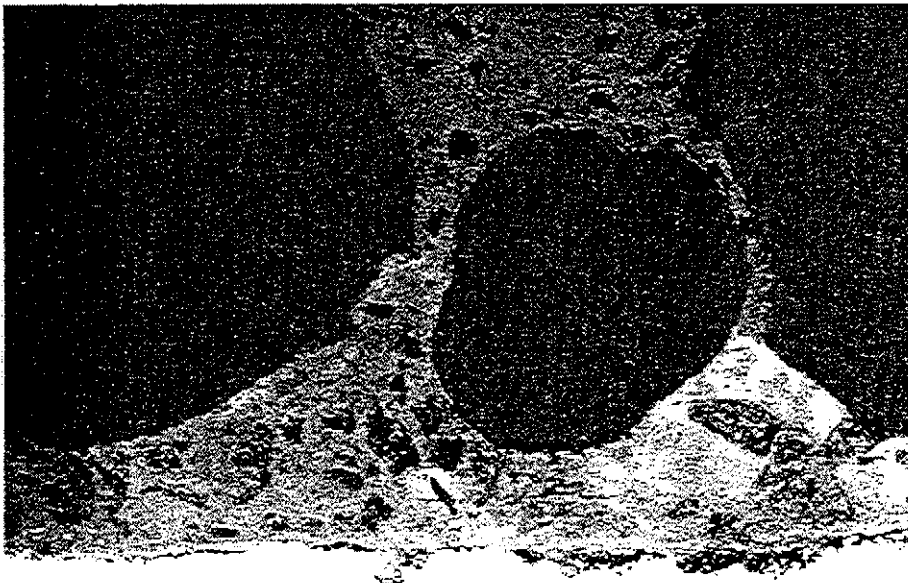


Figure 8. SEM image across interface for sample G11 (100x)

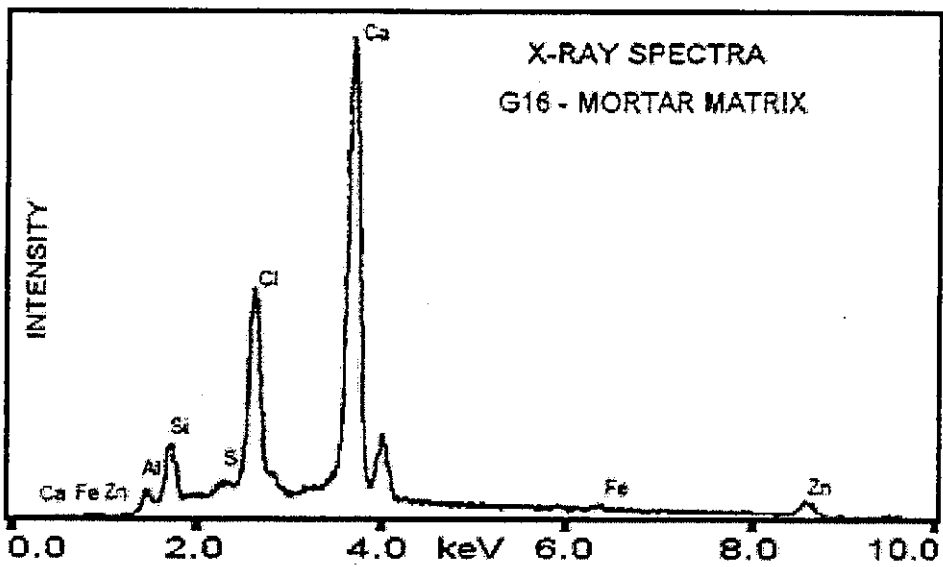


Figure 9. X-ray spectra of mortar matrix for sample G16

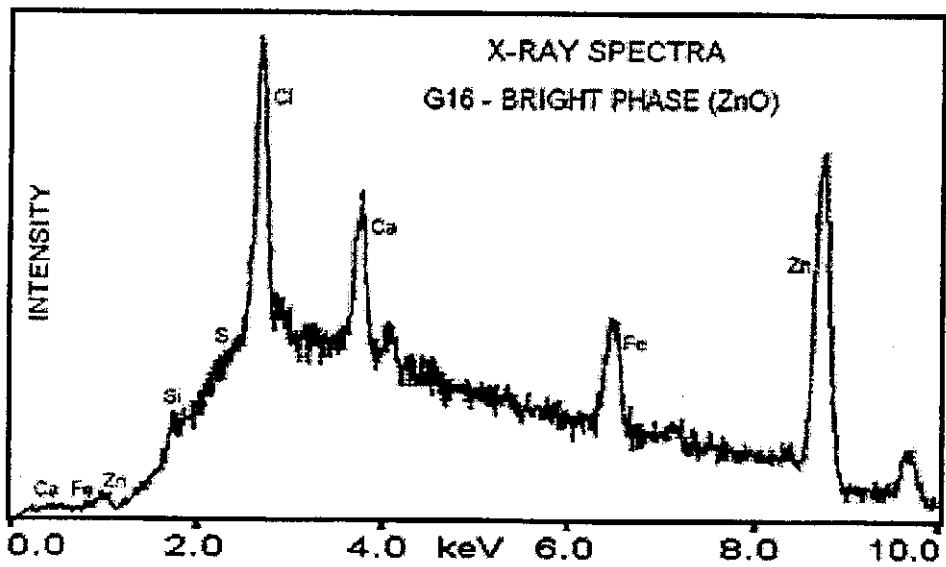


Figure 10. X-ray spectra of bright phase (ZnO) for sample G16