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An Assessment of the Corrosion Protection Offered to Various Steel and Aluminium Alloys by Al-Zn-In Metal Sprayed Coatings.

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Declaration

I Steven Michael Ford, do hereby declare that this thesis is my own, unaided work. This thesis has not been submitted in part or in full at this or any other university. This report is submitted in fulfilment of the degree of Master of Science in Engineering at the University of the Witwatersrand.

Signed : .....

Steven M. Ford

On this the 28th **day**

of April **1992**

Abstract

Aluminium, although often possessing adequate strength and toughness for a specific application, may be deemed unsuitable due to a less than satisfactory corrosion resistance. This unacceptable behaviour is especially prominent in the local mining industry where aluminium alloys corrode severely in the high chloride and sulphate containing waters. Of notable importance and the major motivating force for this research was the historically poor performance of aluminium alloy mine cages, which are suited to the task excepting for their unsatisfactory corrosion resistance. Of general importance however, is that the mining sector in South Africa represents a sizeable portion of the economy and could thus become a much greater consumer of aluminium if the metal's corrosion resistance could be improved. Apart from varying the composition of the alloy, the other basic technique of increasing a metal's resistance to an environment is by applying a coating of some sort. This research looks into the use of aluminium-based metal sprayed coatings as a form of protection for various aluminium and steel substrate alloys.

The purpose of a metal sprayed layer is not merely to isolate the substrate from the environment, but also to act as a sacrificial anode at regions where the substrate is exposed. Previous work suggested that alloys of aluminium/zinc/indium produced excellent sacrificial anodes and were thus selected for this research. The zinc and indium were always alloyed with pure aluminium, with the percentage zinc varying between 0 and 12%. All the coating alloys were sprayed onto AA6261 and AA5083 aluminium alloys, a metal matrix composite and a mild steel alloy. Various electrochemical and immersion trials were then carried out in several synthetic mine waters and other corrosive media.

The basic conclusion to be drawn from the results achieved is that the optimum coating for a particular substrate alloy is the one that provides the greatest potential difference between it and the substrate, while still lasting the required lifetime of the component. The reason for this is that the greater the potential difference, the better the sacrificial protection and hence the better the protection offered to any exposed areas on the surface. The fact that the coating corrodes away with time means that a balance must be found between sacrificial behaviour and required lifetime.

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Introduction

The mining sector of South Africa accounts for a large percentage of the country's economy. Although many diverse minerals are mined, by far the most important is the removal of gold from the earth's crust. Where the aluminium industry fits into this scenario is in the use of the metal and its alloys for the extensive structural requirements of the numerous gold mines across the land.

The major limiting factor with regard the use of aluminium and its alloys in this industry has been the extremely corrosive nature of the waters handled. Very high sulphate and chloride levels, relatively high temperatures and significant quantities of bacteria, to mention only three of the many mitigating factors, have combined to restrict the use of aluminium, which apart from its limited corrosion resistance is suitable in many of the applications. A specific example of the above stated problem, and the major motivational force behind this research, has been the poor performance of aluminium mine cages. The light weight and associated high strength of the metal makes it ideal for use in the construction of these cages, but the limitation is still corrosion resistance.

A viable solution to the problem would be to find a suitable coating material together with an application technique that would protect the existing structural aluminium alloys without impairing their performance. Previous work has established metal spraying as an excellent method of sacrificially protecting mild steel alloys. Thus, this research was initiated in an attempt to find a metal sprayed, aluminium-based coating that would effectively protect certain aluminium alloys from the extremely harsh gold mining environments.

The development of suitable coating alloys is the first stage of the research. Once the optimum coatings for specific substrates have been established in the laboratory, further tests in actual mining environments will be needed to confirm the lab results.

Literature Review

2.1 Introduction

The use of metallic coatings for the protection of other metals and alloys from corrosion is based on the fundamental principle that a metal will not corrode unless it is in contact with a corrosive environment. Thus, any form of barrier which is interposed between the metal surface and the corrodent will have anti-corrosive properties, even if the corrosion is only transferred from the constructional substrate metal to the thin protective metallic coating.[1]

In other words, the metal coating is used to add the qualities of the chosen coating material to selected areas of a component made from some other base material.[2] This allows a wide freedom in design by giving a choice in combining surface characteristics best suited to service conditions onto a component made from a base metal possessing other properties.

The choice of the substrate material is usually fairly straightforward, most commonly being based on cost, strength, weight, etc. The choice of the best protective coating which will permit the chosen constructional material to be used successfully may be more difficult. The coating must, in most cases, resist the environment to a greater degree than does the basis metal; it must in no way encourage local corrosion of the underlying material to such an extent as to be detrimental to the behaviour of the substrate alloy, and it must have physical properties of its own, for example, hardness, elasticity, wear-resistance, etc. Although metallic coatings are usually more corrosion resistant than the underlying metal, some coatings are anodic to the substrate and may not exclude the environment, but react with the base material to confer cathodic protection.

Metallic coatings can be applied to the substrate by several different techniques, including : hot-dipping, spraying, cementation, cladding, electroplating and chemical and physical vapour phase reaction.[3] The choice of process is dependant primarily upon the service application.

The main conclusion drawn from research into the effectiveness of these coatings has been that they provide excellent protection in a large variety of highly corrosive environments. Unsuccessful performances can usually be attributed to one or more of the following factors[4] :

(i) Poor application
(ii) Unnecessarily large damage occurring during transport and/or erection
(iii) Insufficient thickness of the metallic coating
(iv) Unsuitable type of paint overcoat
(v) Poor maintenance of the structural system.

In today's highly developed industrial countries where financial loss due to corrosion has traditionally been serious, economic considerations are now not the only factors that have to be considered. Public opinion and political aims now demand clean and non-toxic surroundings as well as preservation of resources. Metallic coatings not only satisfy these needs, but also offer viable economic solutions.

2.2 The Fundamentals of Metallic Coatings

2.2.1 Introduction

Metallic coatings are applied to substrates (metals, plastics, etc.) for a variety of reasons, but the major application is undoubtedly corrosion protection. This provides an economical means of combining the properties of the substrate and the metallic coating to give a composite material that has both satisfactory mechanical properties and good corrosion resistance. Mild steel for example, is easily fabricated and cheap, but has poor resistance to corrosion in most environments. On the one hand this disadvantage can be overcome by alloying the steel with more corrosion-resistant metals such as nickel or chromium, the drawback here being that alloys of this type are relatively expensive. Alternatively, a more economical approach is to apply a thin coating of nickel followed by an even thinner coating of chromium, thus creating a product with the properties of mild steel and the corrosion resistance of chromium and nickel.

Ideally, a metallic coating should form a continuous barrier that completely isolates the underlying material from the environment. This, however, is seldom the case and in practice, as a result of both the application and subsequent forming and handling operations, the coatings usually possess discontinuities such as pores, pits and cracks.

Thus, as a result of the discontinuous nature of metallic coatings, it is necessary not only to consider the corrosion of the substrate and the coating, but also their effects on one another when they are in contact.[5]

2.2.2 Galvanic Corrosion

A potential difference always exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in electrical contact this

potential difference produces electron flow between them.[6] As a result, attack of the less corrosion resistant metal is usually increased and that of the more resistant material is decreased, as compared with the behaviour of these metals when they are not in contact. The less resistant metal becomes the anode, which donates electrons to the more resistant, or cathodic metal. Thus, due to the galvanic coupling the cathode is protected by the anode and tends to corrode very slightly, if at all.

The behaviour of metals in a couple can be predicted by the galvanic series, with the more noble metal always behaving as the cathode. The figure below shows the galvanic series for elements in sea water.

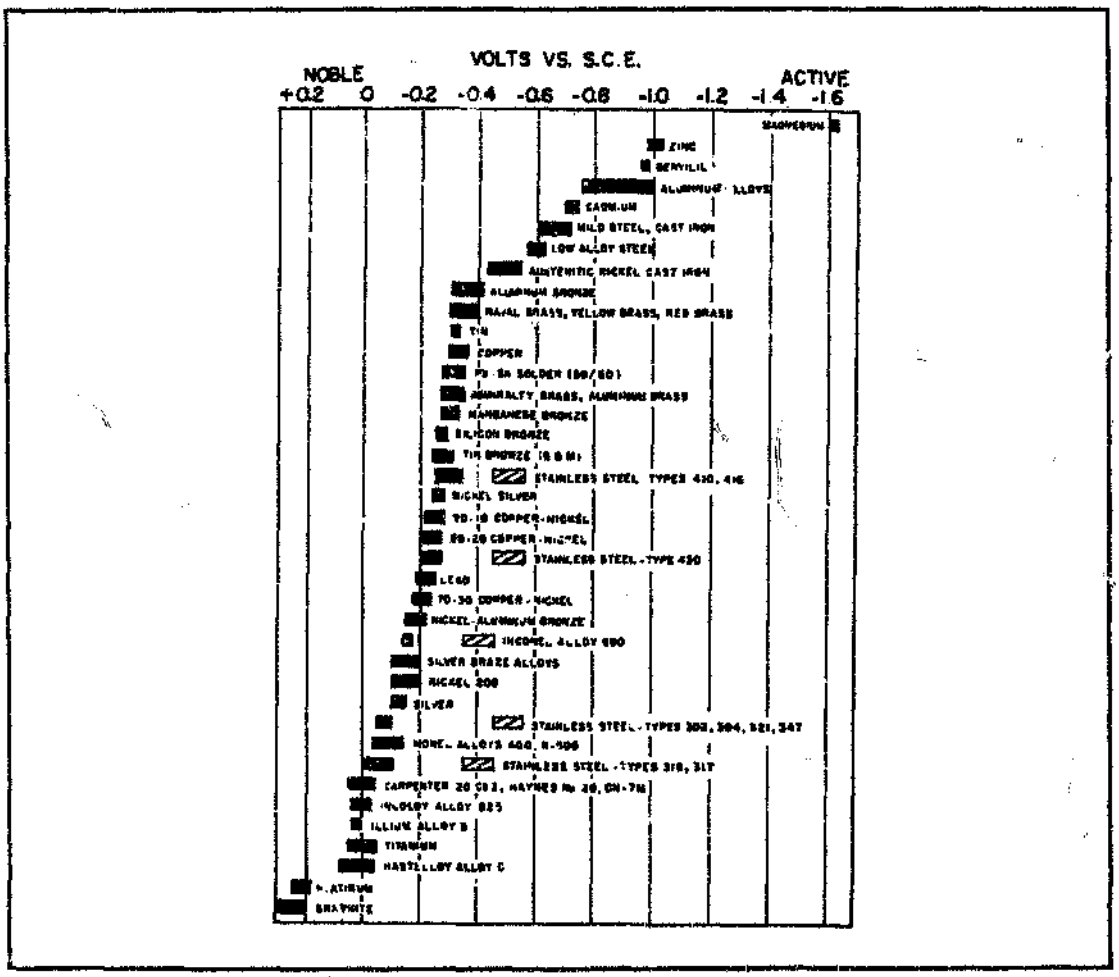


Figure 1 : Galvanic series for elements in contact in sea water.[17]

2.2.3 The Properties of Anodic Coatings

The coating of a substrate, in the past usually steel, with a metal that is anodic to it, typically zinc, tin, cadmium or aluminium, has the advantage that the coating will sacrificially protect the substrate under most environmental conditions.[5] However, this results in the removal of the coating over time so that its function as a barrier could be lost. It follows that the magnitude of the galvanic current flowing between the coating and substrate should be only just sufficient to protect the latter (as too large a current would cause the premature depletion of the coating).

Figure 2 illustrates the action of an anodic coating in sacrificially protecting the substrate at a discontinuity, with consequent consumption of the coating. If this progresses too far, the coating is no longer able to act as a barrier or to protect the substrate sacrificially at exposed areas some distance from the coating. The size of the bare substrate that can be completely protected depends upon the "throwing power" of the coating which is related to its corrosion potential and the conductivity of the solution within the discontinuity.

Figure 2(g) demonstrates the situation that often prevails in practice when the substrate is exposed at a discontinuity. Initially the coating corrodes resulting in the formation of corrosion products in and around the area of bare substrate. As the process continues so the corrosion products build up, thus creating a barrier between substrate and environment, resulting in a reduced amount of sacrificial protection being required. This additional form of protection is only really effective if the corrosion products of the coating are insoluble and thus don't get washed away from the pore.

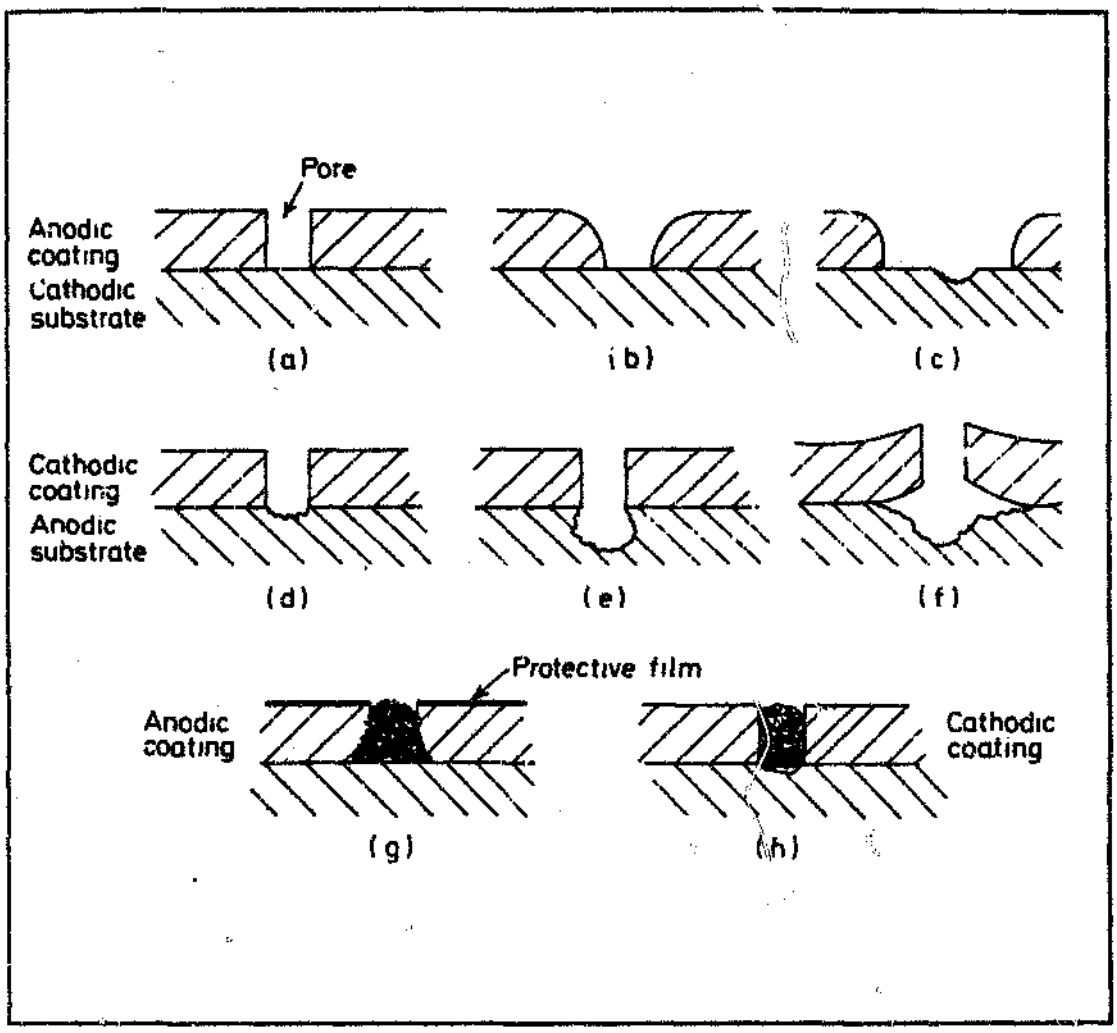


Figure 2: Diagrammatic representation of galvanic effects produced at a pore in a coating on a substrate.[5]

2.2.4 The Properties of Cathodic Coatings

Although it could be anticipated that cathodic coatings would stimulate attack of the substrate, leading to blistering and exfoliation of the coating (refer Figure 2), there are a number of mitigating factors, such as those that prevail in the case of anodic coatings.[5]

The nature of the environment is all important, and whereas there is considerable risk of intensified attack in immersed conditions this is rarely the case in atmospheric states.

With cathodic coatings, corrosion at a discontinuity is controlled, as with anodic coatings, by factors such as the conditions of exposure, corrosion potentials of the coating metal and substrate, nature and position and formation of corrosion products, resistance effects, etc.

A discontinuity in a cathodic coating would thus ideally be filled with corrosion product from the substrate (not from the coating as in the case above) and in so doing once again afford complete protection. There is no doubt, however, that if the coating is more noble than the substrate, continuity of the coat is far more important than if the opposite is the case.

2.2.5 Reasons for Applying Metal Coatings

Metal coatings are applied for two basic reasons:

(i) for decorative purposes
(ii) to protect the substrate metal.

These two categories are in no way mutually exclusive and in the majority of cases whichever of the two categories listed above provides the reason for applying a metal coating, the true purpose of its use is the control of corrosion. The most common reason for metal coating application is when the material found best suited to the specific function required does not provide adequate resistance to the corrosive effects of the environment.

2.2.6 Economic Considerations in the Use of Coatings

The economics of corrosion control are extremely difficult to assess accurately, since many factors must be taken into account and their relative importance may vary widely over the lifetime of the article in question.[5]

Uhlig[7] produced a general formula for assessing whether or not a corrosion control process (such as the use of a metallic coating) is economically sound:

$$If \quad 100\frac{\Delta T}{T}(1+\frac{L}{C})-100\frac{\Delta C}{C}<0 \quad money\ will\ be\ saved$$

where

T = life of structure or component (years)

L = labour costs of replacement of structure or component

C = cost of materials composing structure or component

ΔC = increased cost of using corrosion control process

ΔT = increased life achieved.

(Noting that this equation does not take inflation into account, a factor that further favours the use of coatings.)

Thus, even the use of a relatively expensive process of corrosion control (such as applying a thin coating of an expensive metal to a cheap metal substrate) can become economically viable if a greatly increased service life is achieved.

2.3 The Coating Process

Numerous metallic coatings are applied to a wide range of base metals. These coatings, as previously mentioned, can protect the substrate in two ways[8] :

(1) A coating metal of a cathodic character serves to keep out air and moisture from the surface of the metal it covers. Such a coating only remains effective as long as it is entirely undamaged, since corrosion of the base metal will result at locations where the coating is punctured.

(2) A coating metal anodic to the base metal, although corroding slowly itself due to the existence of polarisation effects, will sacrificially protect the substrate metal for its required lifetime.

2.3.1 Coating Processes

A variety of processes exist for applying metal coatings to the substrate. Although there are only limited variations in the corrosion behaviour of a given metal, the application techniques all produce coatings with differing characteristics.

A broad classification of the more commonly used procedures for applying metal coatings include[9] :

(a) Molten metal immersion
(b) Thermal spraying
(c) Chemical plating
(d) Electroplating
(e) Diffusion plating
(f) Mechanical Application.

Of the above coating processes thermal spraying is one of the most versatile and widely used procedure in industry. This research is concentrated upon the use of thermal spraying as a coating technique and this topic will thus be discussed in further detail.

2.4. Thermal Spray Coatings

Thermal spray coatings provide effective long-term corrosion protection over a wide range of corrosive environments.

The process originated from experiments conducted by M.V. Schoop in the late nineteenth century and today the utilisation of the process is limited only by the application of the specifier.[10]

2.4.1 Fundamentals of the Process

Thermal spraying comprises a group of processes in which finely divided molten metallic or non-metallic material is sprayed onto a prepared substrate to form a coating.[11] Figure 3 below illustrates the general thermal spraying process.

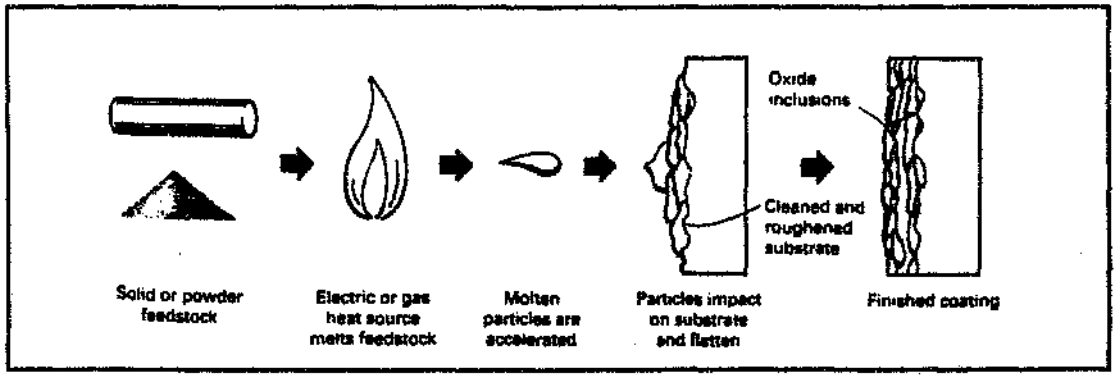


Figure 3 : Schematic of the general thermal spray process.[11]

The sprayed material is originally in the form of wire or powder. As this feedstock is fed through the spray unit, it is heated to a molten or plastic state and propelled by a stream of compressed gas onto the substrate. On striking the surface the particles flatten out and form thin platelets that adhere to the irregularities of the prepared surface and to each other. They then cool and accumulate into a lamellar, castlike structure.

The deposited structure of these coatings differ from those of the same material in the wrought form because of the nature of the coating build up and because the coating composition is often affected by reaction with the process gases. For example, where air or oxygen is used as the process gas, oxides of the material applied may be formed and become an integral part of the coating.

As previously mentioned, the bond between the sprayed coating and the substrate is purely mechanical. Thus, proper surface preparation of the substrate is often the most critical influence on the bond strength of the coating.

2.4.2 Methods of Deposition

The most common methods of depositing thermal spray coatings can be classified as[11] :

(a) Wire flame spray
(b) Powder flame spray
(c) Electric arc spray
(d) Plasma spray

(a) Wire Flame Spraying

Wire flame spraying is the oldest and still most commonly used spray process, utilising heat from a combustion reaction as the melting source. Common fuel gases are acetylene, propane, propylene and natural gas, each combined with oxygen. Any material available in the form of wire and capable of being melted at below 2600°C can be flame sprayed.

Figure 4 demonstrates the basics of the wire spraying process:

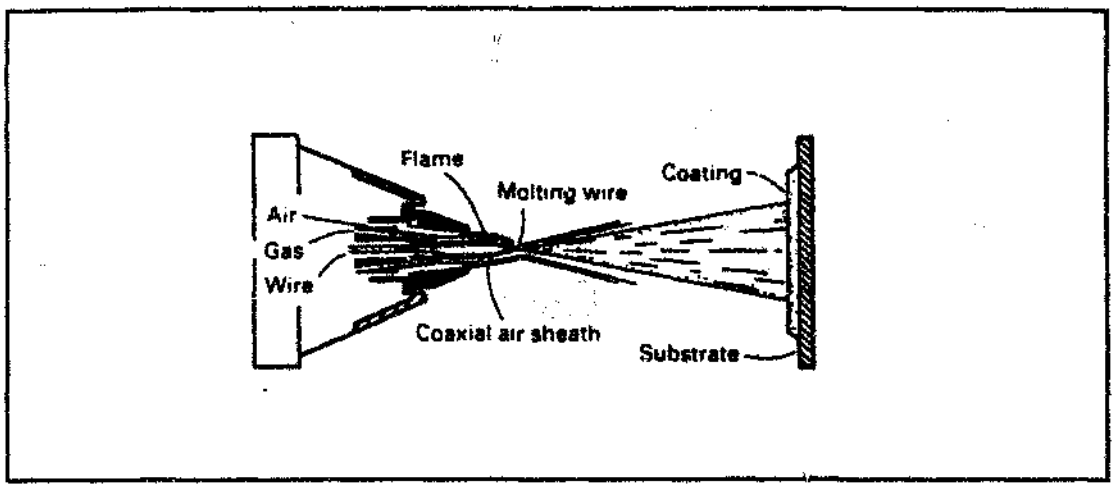


Figure 4 : Schematic of the wire flame spray process.[11]

The gas flame is used only to melt or soften the material. Spraying is then accomplished by surrounding this flame with a co-axial stream of compressed gas, which atomizes the molten material and propels it onto the workpiece.

The advantages of the wire process are the following :

(i) that the capital cost of equipment is low,

(ii) coatings are very easy to apply in a wide range of materials,

(iii) they are generally easy to finish either by machining or grinding

(iv) and they have a very long history of proven results.[12]

(b) **Powder Flame Spraying**

As the figure below demonstrates, this spray process also uses combustion gases as the heat source, but this time the feedstock is powder. This technique offers the advantage of being able to spray materials that are not available as wire (such as non-metallics).

The disadvantage of the process is that the particle velocities achieved are generally much lower, with the result that the coatings usually have lower bond strength, higher porosity and a lower overall particle strength than the coatings produced by other thermal spray processes.

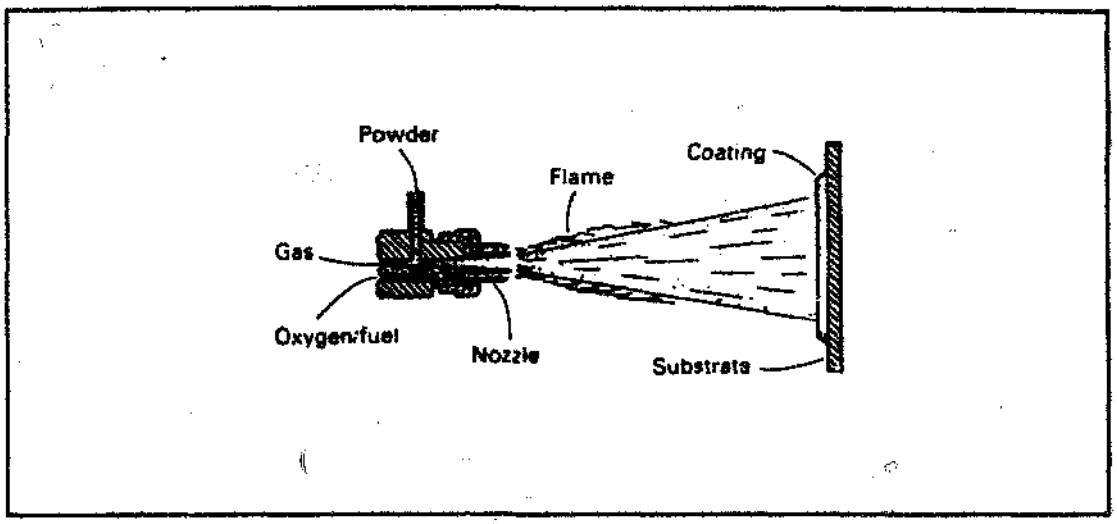


Figure 5 : Schematic of the powder flame spray process.[11]

(c) Electric Arc Spraying

This process uses metal in the form of wire without the need for combustion gases. In arc spraying, the melting of the coating metal is accomplished by means of a constant voltage d.c. electric arc instead of a gas flame.[13] Because of the high temperatures in the arc zone, the coatings generally have excellent adhesion and high cohesive strength.

(d) Plasma Spraying

The plasma spray process uses coating materials in the form of powders, which are melted in a plasma heat source. Plasma provides controllable temperatures that range well above the melting point of any known substance. Plasma systems produce excellent coatings, but the equipment is complex and expensive to operate.[14]

2.4.3 Surface Preparation of the Substrate

Haywood[15] states that coating failures, almost without exception, can be traced back to poor or inadequate surface preparation, the exception being the application of the wrong coating for the duty cycle.

2.4.3.1 Objectives in Preparing the Surface

Since corrosion and its prevention by anodic coatings are electrochemical processes, there must be good electrical contact between the metal to be protected and the protective coating. Furthermore, the protective metal must be well bonded mechanically to the substrate in order to maintain contact for the required period of time.[16] Thus, any contaminant will interfere with both the electrical contact and the mechanical adhesion. Every precaution must, as a result, be taken to remove this contaminant prior to the application of the coating.
Finally, to achieve the mechanical adhesion, the contact area between substrate and coating must also be optimised.

Therefore, the basic objectives in preparing the surface are:

(a) Cleanliness, i.e. removal of contaminants.
(b) Optimising the profile of the substrate.

(a) Surface Cleanliness

Surface contaminants are almost always present on materials as a result of production processes that have been carried out during early fabrication operations, or as a result of deliberate application in order to provide temporary protection or identification.

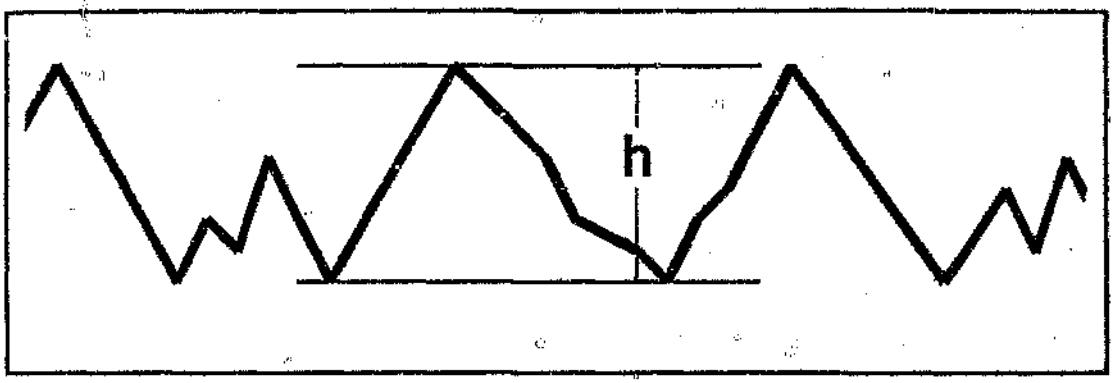
(b) Optimisation of the Surface Profile

The safest and most reliable method of surface preparation for anti-corrosion coating is the use of abrasive blasting techniques. Two types of abrasive are available[15] :

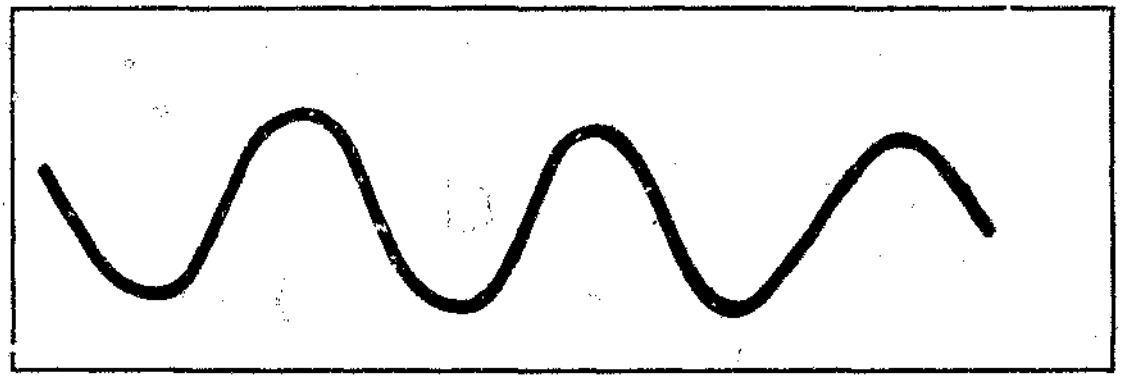
(i) Non-metallic - such as sand, aluminium oxide, etc.

(ii) Metallic - which are generally steel or cast iron grits.

The desired finish is shown in figure 6(a) and the undesirable in 6(b). The round profile is unsuitable for metal spray applications, since it does not provide sufficient mechanical keying and is probably not a virgin metal surface but a thin layer of adherent oxide.



(a) Sharp peaked profile produced by angular abrasives



(b) Rounded profile produced by shot

Figure 6 : Profiles produced after abrasive blasting.[16]

2.4.4 The Basic Principles of Wire Flame Spraying

Since all the metal spraying for this research will be carried out using commercial wire spraying equipment, the principles of the process will be examined in greater detail.
It is common practice in wire spray guns to have three feeds of gas[18], namely:

(i) compressed air, which serves to spray the metal,
(ii) the fuel gas, and
(iii) oxygen

The purpose of adding oxygen is two-fold; firstly to increase the temperature of the flame so that the wire can be melted as rapidly as possible, and secondly, to ensure that the flame commences at the nozzle and not at a distance from it.

2.4.5 Scope and Limitations of Flame Spraying

The following indicates the scope and limitations of both the coating and the substrate.[19]

(a) Those Pertaining to the Coating

(i) Materials.

Any material can be sprayed which can be produced in wire form, will melt in the environment of an oxy-fuel flame, and does not decompose on melting. Of materials commonly sprayed, molybdenum has the highest melting point, this being approximately 2600°C.

(ii) Structure.

The structure of flame sprayed coatings is typically lamellar, as the particles flatten on impact with the substrate. Typically the porosity is between 5% and 15% by volume, but this may rise in certain industrial situations.

(iii) Deposition rate.

Once again this varies depending on the material being deposited. For example, zinc coatings are usually deposited at between 7.6 and 8.8 g/s.

(iv) Thickness.

Although the thickness to which flame sprayed coatings can be applied varies according to the material being sprayed, there is a common tendency for all coatings to shrink due to the rapid quenching of the semi-molten particles.

Typically, in industry, sprayed coatings are used in thicknesses ranging from 125 to 2500μm.

(b) **Those Pertaining to the Substrate**

(i) Material.

Generally flame sprayed coatings are deposited onto metals. However, they can be applied to other materials such as glass, plastics, etc. The bonding to metallic surfaces is usually superior to that of non-metallics.

(ii) Temperature limitations.

These are defined by the substrate itself, but the temperature can to a very large extent be controlled by the particular spraying operation.

(iii) Pre-treatment.

In order to maximize bond strengths, substrate surfaces would normally be grit blasted.

2.4.6 Adhesion to the Substrate

The prime factor influencing the adhesion is the energy content of any given molten metal particle.[19] The higher the energy level (both thermal and kinetic), the higher the bond strength

will tend to be. The most common factors which influence the energy content of the particle are: particle mass, particle velocity, latent heat of fusion, specific heat and melting point.

2.5 The Coating of Aluminium and Steel Substrates

The corrosion protection afforded by a coating of metal depends on a number of factors. Each of these factors is individually important, but they must be considered in relation to each other.[20] Parameters to be considered include:

(i) The coating metal and the substrate to which the coating has been applied
(ii) The corrosive nature of the environment
(iii) The application technique
(iv) The presence of over or under coatings.

Some of the above aspects will now be discussed, with specific regard to the spraying of aluminium alloys onto aluminium and steel substrates.

2.5.1 The Protective Action of Aluminium Alloy Coatings

The object of spraying any material with aluminium is to control the corrosion of that material. However, aluminium, in itself, is not highly resistant to corrosion and like most metals the alloys of aluminium corrode to some extent under natural conditions of exposure.[21]

The protection by aluminium coatings depends upon two factors, namely[22] :

(i) the cathodic protection provided by the anodic nature of the aluminium coating, and

(ii) the formation of a physical barrier between the coated assembly and the environment.

The anodic nature of the coating with respect to the substrate implies that cathodic protection will be in the form of sacrificial corrosion of the sprayed aluminium. Thus, the substrate, be it steel or aluminium, is protected at the expense of the coating.

The corrosion of the aluminium will generally take place at pores or other imperfections in the coating, since these are the obvious places where protection of the substrate will be required the most. Thus, with time , corrosion products will build up in these pores and, because they are insoluble, will cause a reduction in the corrosion rates as they seal off the substrate from the environment.

Furthermore, aluminium coatings applied by metal spraying tend to have a relatively high oxide content, a factor which tends to reduce the number of active corrosion sites and thus increase the effective life of the coating , whilst still maintaining cathodic protection.[23]

2.5.2 The Extent of Sacrificial Protection

From a comparison of the standard electrode potentials of aluminium and iron it would be expected that aluminium should exert good sacrificial protection when coated onto iron based alloys. However, in practice the protection of steel by this mechanism is limited. This is as a result of the insulating oxide film formed on the coating which is more noble than aluminium itself, and hence restricts effective electrochemical protection of bare steel to cracks and pores in the coating.[24] Thus the extent of sacrificial protection depends upon the area of steel exposed and upon the environment.

When aluminium coatings are applied to aluminium alloy substrates a potential difference may still prevail due to variations in alloy additions, but in general the potential is greatly diminished. As a result, galvanic protection is usually vastly reduced and the creation of a physical barrier between substrate and environment becomes far more important. It is possible to increase the anodic nature of the coating through the addition of elements such as zinc or magnesium to the aluminium.

2.5.3 The Role of Zinc and other Alloy Additions

The obvious reason for alloying the aluminium with other elements is to create a more anodic coating while still retaining most of the favourable characteristics of the aluminium coat. Zinc coatings have the advantage of electrochemical activity, giving them the ability to provide effective cathodic protection to steel in a wide variety of environments.[25] However, the high electrochemical activity of zinc leads to rather excessive reaction rates, resulting in faster wasting of the coating, so tending to reduced coating lifetimes. The corrosion products formed as the zinc is attacked are also somewhat soluble and thus do not provide the additional protection that the insoluble corrosion products on aluminium coatings do.

Thus, when alloying aluminium with zinc, it is believed that the beneficial effects of both zinc and aluminium can be obtained. In so doing the alloy coating would provide the sacrificial protection of zinc and at the same time form an impervious oxide film that is characteristic of pure aluminium coatings. The major problem encountered in the development of these alloys is the tendency for the formation of zinc-rich and aluminium-rich layers in the coating. The corrosion of such coatings proceeds almost exclusively through the zinc rich areas to the substrate, resulting in flaking of the coating.[26]

The main criticism and resistance to sprayed aluminium coatings, as opposed to zinc, has in fact not been corrosion related, but rather related to the comparative ease with which the coatings sometimes become flaked or chipped away from edges and other exposed projections. Preparation by grit blasting of surfaces to receive aluminium demands much more stringent control than is required to promote quite good adhesion of zinc. In fact, when rust and scale is not completely removed, even temporary adhesion of aluminium is difficult to achieve using oxy-fuel gas spraying methods.[27]

Alloying magnesium with the aluminium coating has also been used in the same way as zinc to try and increase the anodic nature of the coating due to the increased electrochemical activity of the magnesium.[28]

Various other alloy additions have been proposed in the past and these will be considered

later in this report.

2.5.4 Electrochemical Relationship between Substrate and Coating

As previously mentioned, from the galvanic series it is clear that aluminium is more anodic than steel. However, under certain environmental conditions the steel has been found to be anodic to the aluminium coating. Tolley[29] has shown that a sprayed aluminium coating can be initially cathodic to steel but once the protective oxide film has been broken down the coating becomes anodic. This initial unfavourable polarity causes rust coloured stains that sometimes occur on thin aluminium coatings in the early stages of exposure. Rust staining is, however, usually quite innocuous as long as the aluminium assumes its anodic role fairly quickly.

The changes in e.m.f. resulting ultimately in the reversal of potential and consequent sacrificial protection usually prevail, even in those solutions in which the steel is appreciably anodic. Three factors are concerned in these changes of e.m.f.:

(i) Variation in the single-electrode potential of steel, mainly due to the formation of corrosion products. This usually leads to an increase in the cathodic area self-polarization, leading to more negative potentials.

(ii) The effect of the formation of corrosion products on aluminium. Probably the most important factor in the variation in electrode potential of aluminium is the penetration and possible break-up of the oxide film by ions in solution.

(iii) Changes in pH and ionic concentration in the solution, owing to the corrosion process.

Thus, the electrochemical behaviour of coating and substrate are closely related to the environment in which the system is placed.

2.5.4.1 Polarisation of the Coating

If the potential of the anode alloy changes in the direction of the substrate alloy potential with increasing current flow, the anodic alloy is said to polarise.[30] While some polarisation is expected, rapid polarisation (ie.low current flow = large potential change toward potential of substrate) indicates an unsuitable anode alloy. Polarisation is affected by a number of factors including alloy composition. With regard to aluminium alloy coatings, small additions of such metals as indium, mercury, gallium, or tin have been found not only to improve the anodic nature but also to minimize polarisation by promoting active surfaces on the alloys. (The exact role of indium and the other elements will be discussed later.)

2.5.5 The Corrosive Nature of the Environment

2.5.5.1 Immersed Conditions

An indication of the range of pH and potential in which a given metal will exhibit formation of protective corrosion products (passivation) is given by the theoretical potential-pH diagrams or Pourbaix diagrams. The potential-pH diagram for aluminium in water (shown below) demonstrates the formation of soluble corrosion products at low and high pH values with a region of passivation in between. The pH range for passivation of aluminium is from about pH 4 to 8.5.[31]

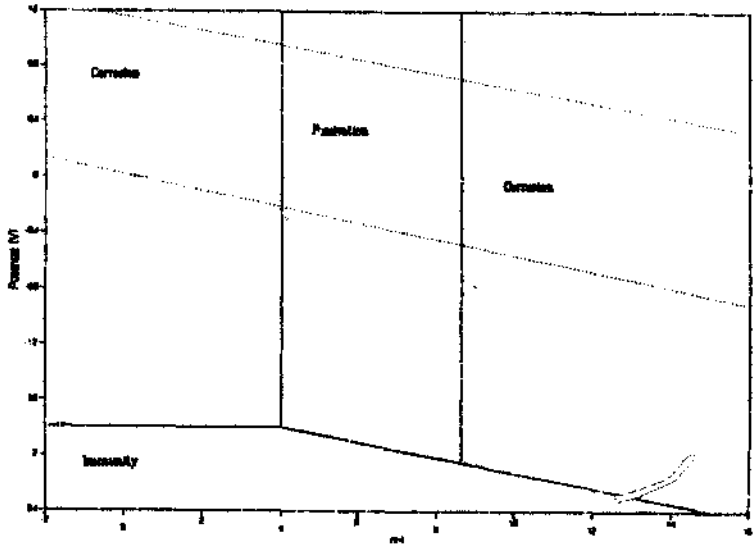


Figure 7 : Potential-pH diagram for aluminium at 25°C in water.[31]

The reason for the above behaviour is that aluminium has a very stable oxide surface film, with its domain of stability lying below that of water. In sufficiently acid solutions it decomposes with evolution of hydrogen but in solutions with pH values between 4 and 9 aluminium becomes covered with a complex protective film. Thus, the corrosion behaviour of the aluminium coating is determined essentially by the behaviour of the oxide film.[32] Aluminium is resistant to distilled water and fresh water, whether hard or soft, as long as sufficient oxygen is present to facilitate oxide formation. The presence of heavy metals, particularly copper, tin, lead and nickel are deleterious, and water high in chlorides, sulphates and carbonates are aggressive towards the coatings.

Fischer et al.[33] showed that at both ambient and high temperatures the aluminium coatings provided protection in sea water and that the aluminium was attacked by the halogen salts but not by the sulphates and nitrates.

It is quite normal for sprayed aluminium to become discoloured by brown, grey-brown or even black stains when immersed in fresh and salt water. The staining is associated with the cathodic areas and although its origin is still not clear, it may be that the stain is an optical effect produced by the formation of oxide films.[34] In alkali solutions a brown stain may discolour the whole of a sprayed aluminium surface. Sometimes the dark stains formed in neutral waters may disappear as exposure continues and this is thought to be the result of a thickening in the oxide films.

2.5.5.2 Atmospheric Exposure

When exposed to the atmosphere, fresh aluminium rapidly forms an impervious oxide film of alumina on its surface. The extent of sacrificial protection, however, depends upon the area of substrate exposed and upon the environment. In atmospheres containing a high chloride ion concentration, which destroys the oxide film, appreciable cathodic protection occurs. In urban and rural areas where the oxide film is not attacked, practically no galvanic protection occurs. As with immersed conditions the coatings show initial rust staining at and around the pores, but the corrosion products soon seal these pores and reduce the corrosion rate to a minimum.[32]

In polluted atmospheres, the corrosive severity of the atmosphere, water vapour in the air, and daily condensation combine to produce three possible effects:

(i) Precipitation of corrosion products from the substrate at the base of the coating.
(ii) Clogging of the pores of the coating.
(iii) Break-up of the oxide film around the aluminium particles.

It follows that a good deal of the protective value of sprayed aluminium coatings may be caused by the corrosion products precipitated in the pores of the coating.

2.5.6 Aluminium Sprayed Coatings : Their Use for the Protection of Aluminium Alloys

Localised corrosion problems have in the past restricted the commercial exploitation of various, otherwise suitable, aluminium alloys. Although other alternatives do exist, metal sprayed coatings have been considered as a suitable technique of generating the required protective conditions.[35]

Experimental work conducted in this field is limited and usually very specific in nature. The general approach taken in previous work been to identify the potential domain for immunity in the characterised environment and then to develop an aluminium based spray coating to ensure the required potential control.

2.5.6.1 Alloy Addition Proposals

Suggestions as to the alloy additions to be made for the most effective protection vary from author to author and are sometimes contradictory.

The work done by Scott[36] proposes the following:

(i) When coating Al-Zn-Mg-Cu alloys, an increasing zinc content diminishes the protection.

(ii) When coating 99.5% aluminium, 2% zinc in the coating, closely followed by 1% zinc, exhibits the greatest limiting effect upon substrate corrosion.

(iii) Even a sprayed coating of similar composition to the substrate offered protection, a factor that was attributed to the porosity of the coating giving more frequent, and consequently less deep, pitting of the core.

(iv) Lower purity, 99.5% aluminium , provides much greater resistance to blistering of the coating and consequently to corrosion than the intrinsically more corrosion resistant 99.99% aluminium. To support this finding Scott suggested that the common impurities of copper, silicon and iron afforded greater resistance to blistering than any of the common alloy additions.

(v) All the tests Scott conducted were performed in aggressive electrolytes. He proposed that in less conducting media, the aluminium-zinc coatings would provide the better protection.

Carter and Campbell[37] researched extensively the protection offered by aluminium and aluminium-zinc coatings to aluminium-copper-magnesium alloys. Their testing consisted mostly of an exposure program, whereby the sprayed samples were exposed to a number of atmospheric conditions, ranging from marine to industrial. The results achieved showed that complete coatings of sprayed 99.5% aluminium gave rather less effective protection to the substrate than either 99.99% aluminium or aluminium-1% zinc. This result was, however, not expected by Carter and Campbell[37] and was attributed to a slight variation in spraying technique rather than a difference in corrosion protection ability of the coatings.

Further research, conducted by Carter and Campbell[38], this time working with mainly aluminium-zinc-magnesium alloys found that once again the 99.5% aluminium, 99.99% aluminium or aluminium-1% zinc coatings all increased the life of the specimens (usually by a minimum of a factor of ten). Furthermore it was discovered that by limiting the copper impurity level in the coating to 0.01% an improvement of 100 times the life of the unprotected alloy could be achieved.

The app. ach adopted by Holroyd et al.[35] to develop the required aluminium spray coating to electrochemically protect aluminium-zinc-magnesium welds involved three stages, namely;

(i) Selection of wire compositions and their electrochemical assessment in neutral, acidic and saline solutions,

(ii) metal spraying of the most promising compositions onto welds,

(iii) electrochemical assessment and slow strain rate testing of sprayed welds.

The electrochemical results achieved by Holroyd et al.[35] showed that zinc additions of up to 5 wt % progressively decreased the free corrosion potential of the aluminium based alloy. However, the most negative potentials obtained were not in the required protection zone. As a result further alloying was conducted to try and reach the limits of the protection potentials. Success was obtained by additions of tin, indium, mercury and gallium (added individually and not together in one alloy).

Once again, the research demonstrated the benefit of a high aluminium purity level, with 99.5% aluminium being suggested as a minimum. Electrochemical evidence substantiated this finding, since a decrease in aluminium base purity level results in polarisation data moving to more positive values.

Finally, work done by Reboul et al.[39] further serves to support the fact that additions to aluminium of tin, mercury and indium decrease the free corrosion potentials of aluminium and aluminium-zinc alloys. This is clearly demonstrated in Figure 8 below.

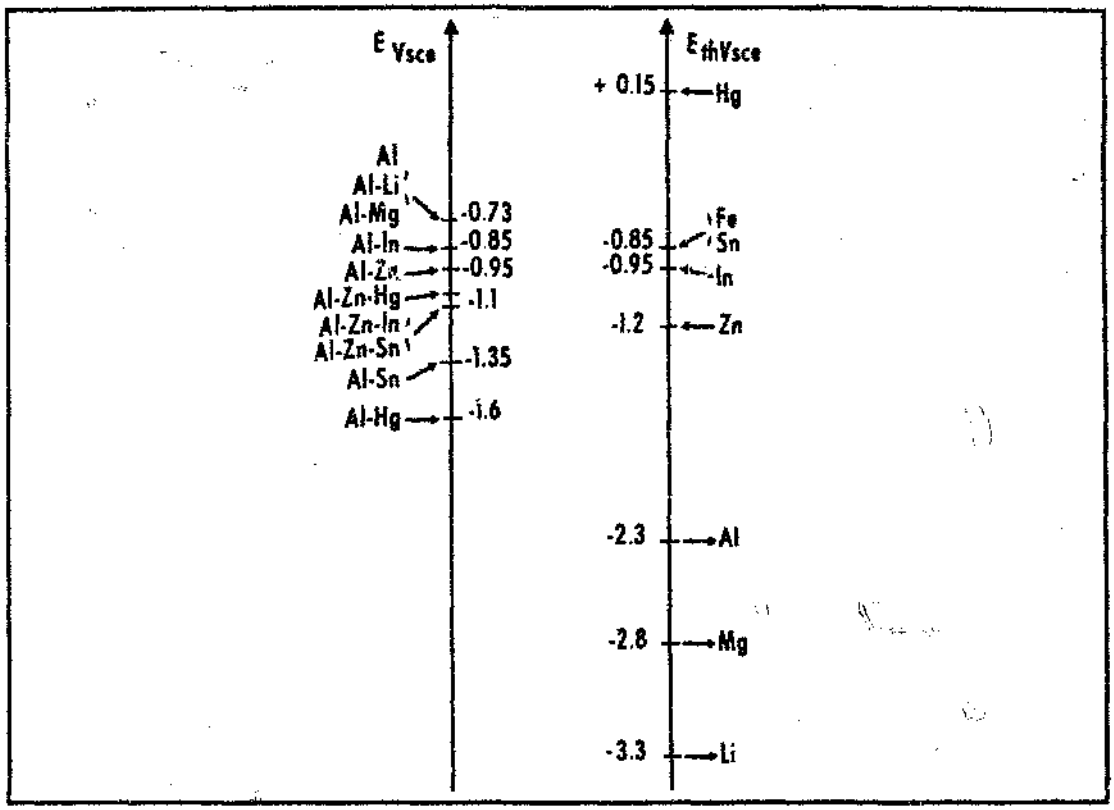


Figure 8 : Thermodynamic potentials of elements (right hand scale) and typical working potentials of aluminium alloys.[39]

2.5.7 Aluminium Sprayed Coatings : Their Use for the Protection of Steel

The anodic behaviour of aluminium alloys with respect to steel makes the metal an obvious choice when selecting a protective coating. Extensive use of the system was however not popular for a number of years, because of difficulty in achieving good adhesion to steel substrates. Nowadays, advanced surface preparation techniques ensure adequate adhesion and thus the coating of steel with aluminium alloys is used extensively.

Unlike the metal spraying of aluminium, the spraying of steel has been widely researched. Some confusion does, however, still exist as to the optimum alloys for specific environments.

2.5.7.1 Alloy Addition Proposals

Vesely and Horky[40] conducted extensive research into the electrochemical and corrosion properties of thermally sprayed coatings of aluminium alloys. The results achieved by their research can be summarised as follows:

(i) Zinc exhibited generally favourable effects on the protective properties at contents above 20%. On the other hand, corrosion of the base metal was more extensive at zinc concentrations of 1 to 2%.

(ii) Alloying aluminium with magnesium had a beneficial effect, with alloys containing more than 2.9% Mg exhibiting better anti-corrosive properties than 99.5% aluminium.

(iii) Alloying iron with the aluminium proved effective at iron contents in the range of tenths of a percent, since the degree of corrosion on the base steel was lower than that in the case of pure aluminium coatings. However, an iron content in excess of 2% brought about a marked deterioration of the corrosion properties.

(iv) Silicon as an alloying element improved the fluidity of the alloy, but the corrosion properties were adversely affected at silicon contents exceeding 0.1%

(v) Elements such as cerium, zirconium, calcium, chromium and nickel were all found to have a negative effect on the corrosion resistance in that they had worse corrosion properties than pure aluminium.

(vi) Additions of bismuth to the aluminium (to around 0.59% Bi) proved disastrous, with even atmospheric humidity causing marked corrosion.

(vii) Investigation of the corrosion properties of ternary alloys , (Al-Zn-X) , proved the negative effects of beryllium, zirconium, chromium and nickel, the presence of these elements being undesirable even in fractions of a percent.

(viii) Alloying Al-Zn with magnesium, on the other hand, had a favourable effect up to 3% magnesium, with the resulting properties being superior to those of pure aluminium.

The electrochemical tests conducted by Vesely and Horky[40] established relationships between electrochemical properties of the sprayed coating and its resistance to corrosion. The figures below demonstrate some of the results achieved:

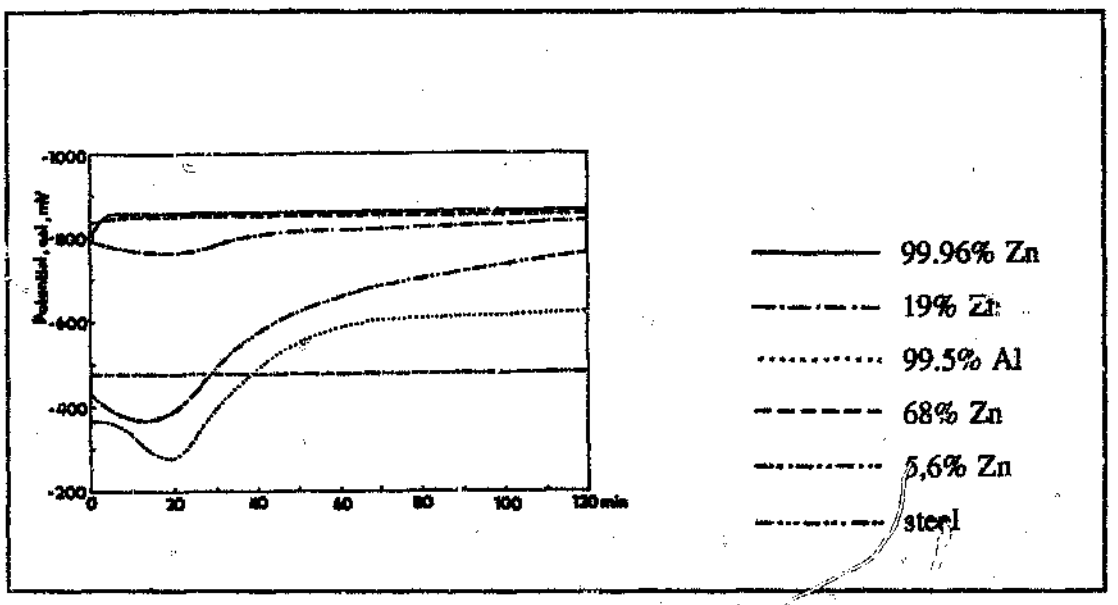


Figure 9 : Potential vs. time curves of flame-sprayed Al-Zn alloys; electrolyte - sulphuric acid.[40]

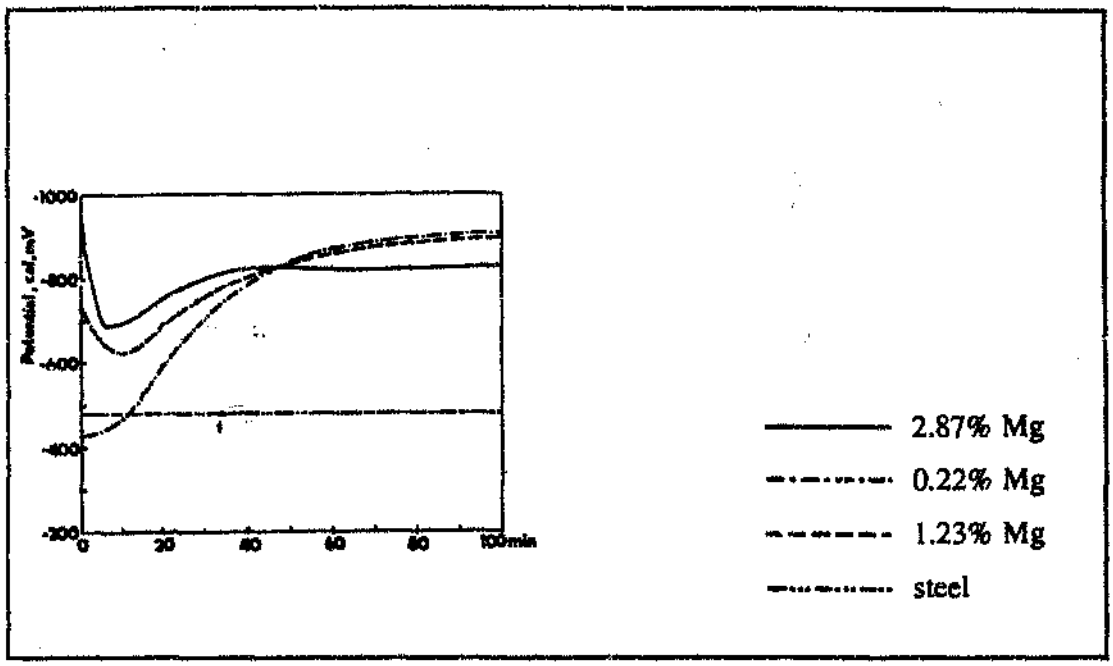


Figure 10 : Potential vs. time curves of flame-sprayed Al-Mg alloys ; electrolyte - sulphuric acid.[40]

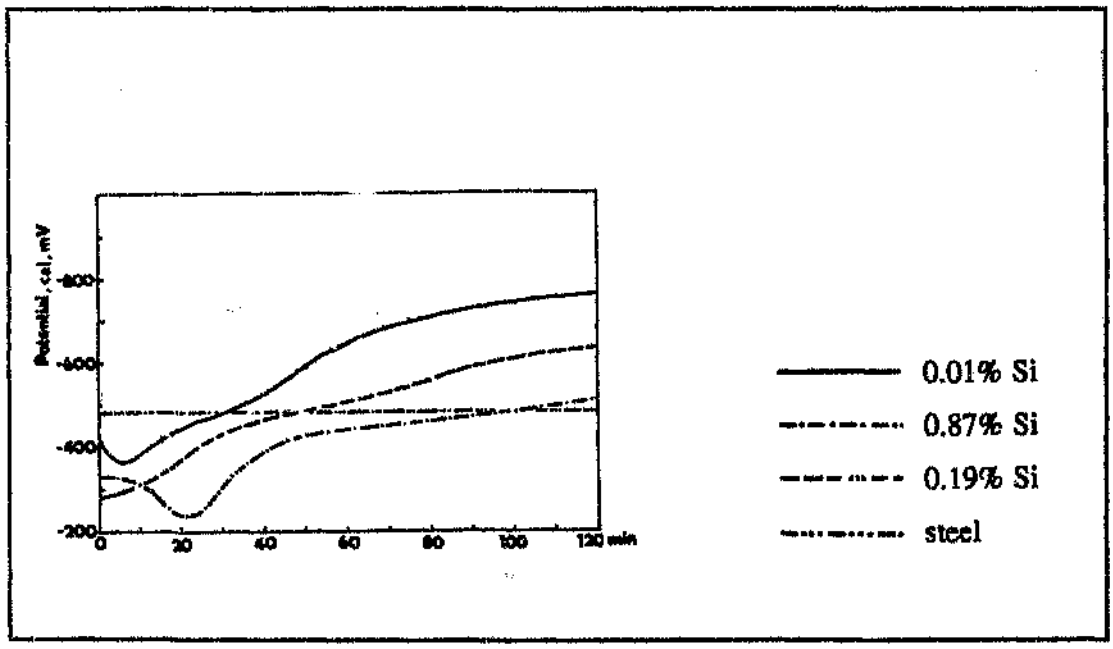


Figure 11 : Potential vs. time curves of flame-sprayed Al-Si alloys ; electrolyte - sulphuric acid.[40]

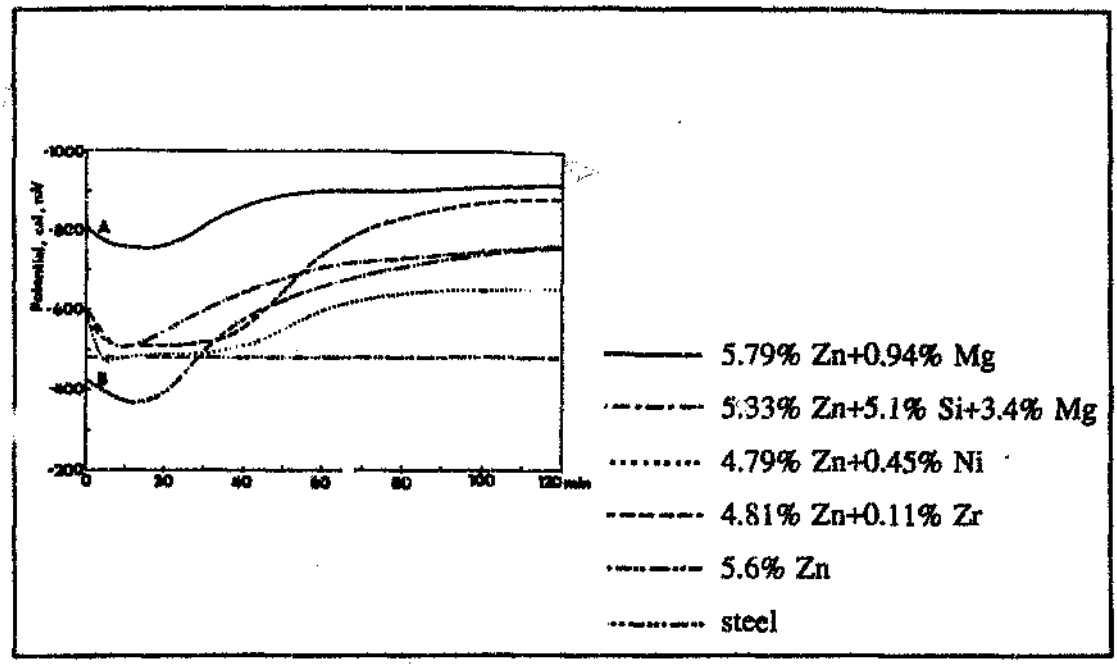


Figure 12 : Potential vs time curves of flame sprayed Al-Zn-X alloys ; electrolyte - sulphuric acid.[40]

The above potential-time relationships were compared with results obtained from accelerated corrosion tests. In most cases the potential peak was found, in a certain way, to be related to the corrosion of the metal-coated steel. Referring to the above plots, any potential of a coating more positive than that of the free corrosion po ntial of steel will result in the corrosion of the steel rather than the coating and is thus unsatisfactory. (This is because the steel becomes anodic to the coating and thus sacrificially protects it - i.e. the reverse of the desired effect).

Figure 9 shows how zinc contents of up to 5.6% have no marked effect upon the slope of the curve, with the 99.5% aluminium curve being very similar and the potential peak more positive than that of iron. The alloys containing more than 19% zinc, however, show a very slight potential peak and are also more negatively located than the curve for iron. As a result these alloys are expected to show the least amount of corrosion.

Figure 10 shows how, with increasing magnesium content, the courses shift to the region of negative potential with respect to iron. Thus, an increase in the Mg level improves the

protective potential (at the expense of the coating life).

When the silicon level in the aluminium is increased, the potential of the coating becomes more positive with respect to the iron and as a result offers less protection. This is shown in Figure 11.

The relationship between potential and time for some ternary alloys based on aluminium and zinc are plotted in Figure 12 . The curves show how the presence of magnesium brings about a significant change in the potential in the negative direction. The adverse effects of Be, Ti, Zr, Cr and Ni are also obvious.

Scott[36] conducted research using both a mild steel and an aluminium substrate. The criterion used to determine the effectiveness of a specific coating was to establish the time taken for the first rust staining to appear. This method, although an essential indicator, is often misleading as light rusting of aluminium sprayed steel frequently diminishes with time and further attack of the steel is stifled.[41]

The results achieved by Scott[36] showed that additions of 1% and 5% zinc or 5% magnesium, to various purities of aluminium base , when used as a coating , gave no consistent advantage compared with the 99.5% aluminium coating. Thus it was decided, for the environments tested , that the 99.5% Al was the optimum choice of sprayed coating for use on steel substrates, with the proviso however, that in some environments Al-Zn or Al-Mg coatings may possibly perform better.

Work done by Townsend and Zoccola[42] seems to have led to slightly different conclusions to those of Scott. Exposure tests of sheet steel coated with zinc, aluminium and 55% Al-Zn alloys were conducted for 13 years. They found that in all environments tested, which ranged from marine to industrial, the 55% Al-Zn coatings were several times more durable than the zinc coatings of equivalent thickness. Also, after long-exposure times in industrial and rural environments , the corrosion rates of the 55% Al-Zn became indistinguishable from that of the pure aluminium coatings. The success of this Al-Zn alloy was attributed to the unique two

phase microstructure, which comprises a fine network of aluminium-rich cored dendrites and zinc-rich interdendritic matrix. The zinc rich interdendritic portion of the coating is preferentially attacked, with the result that the coating behaves like a zinc coating. As the corrosion proceeds, however, corrosion products that wash away from ordinary galvanised coatings are mechanically trapped in the aluminium rich interdendritic network thus stifling further attack. It was concluded that although the pure aluminium coating provided effective protection, the addition of zinc increased the galvanic protection offered by the coating, thus making the 55% Al-Zn superior.

Other long term exposure programs have been conducted both locally and abroad. The American Welding Society[43] (AWS) published their 19 year report on the corrosion testing of flame-sprayed coated steel. The program was originally only scheduled for 12 years but due to the low corrosion rates, it was extended to 19 years. Although little alloying was performed, the report concluded that in sea water and also in severe marine and industrial atmospheres, aluminium-sprayed coatings gave superior protection to those of zinc coatings of up to double the thickness. Eskom's 10 year paint exposure[44] also included some aluminium and zinc coated mild steel samples. The results achieved here merely substantiate the conclusions drawn by the AWS after 19 years, with the aluminium far outperforming the zinc coatings.

Porter[45] in 1962 suggested the use of an aluminium alloy containing a half to three quarter percent cadmium for metal spray purposes. The theory behind the cadmium addition being that firstly during heat treatment the cadmium volatilises and thus acts as a deoxidising agent and secondly that it reduces the surface tension of the aluminium during the melting period which facilitates "wetting" of the steel and promotes alloying at the steel interface. It would appear, however, that no further research has been conducted into his suggestion and cadmium is today not a common addition to the aluminium.

Finally, Kain and Baker[28] exposed samples with varying percentage zinc for 34 years at the marine location of Kure Beach. The results achieved are represented in the figure below.

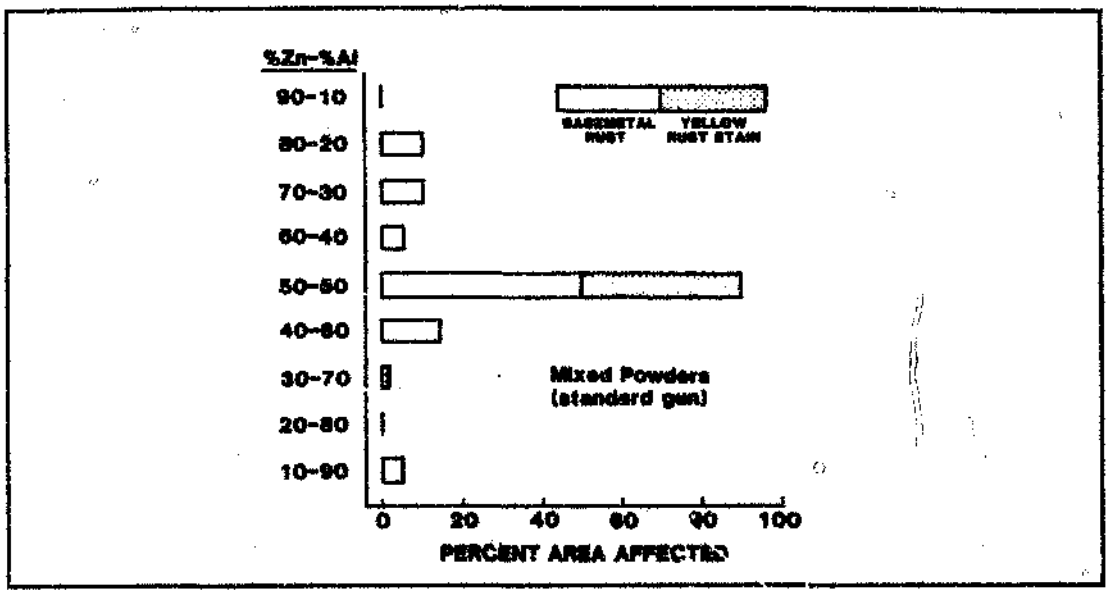


Figure 13 : Comparative performance of various Zn-Al coatings on steel exposed for 34 years.[28]

Further results achieved using other alloying additions are represented in the figure below.

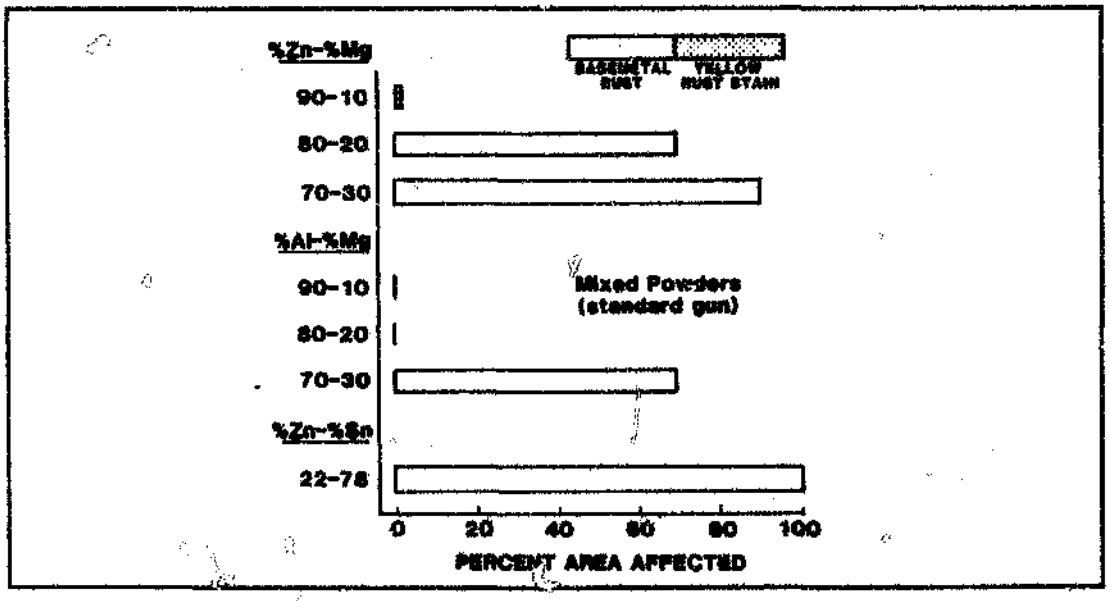


Figure 14 : Comparative performance of several magnesium containing and tin containing coatings after 34 years exposure.[28]

From these results Kain and Baker concluded that the highest aluminium-containing coatings exhibited the most consistently good results and that the most protective coatings were those containing 50% or greater aluminium.

2.5.8 The Role of Indium as an Alloy Addition

It is now well known that the addition of small amounts of indium to sacrificial aluminium anodes produces galvanic anodes with low polarised potentials and high galvanic efficiencies.[46] The mechanisms whereby this is achieved are not however well understood. Chavarin[47], suggests that without indium the dissolution of aluminium coupled to steel proceeds only at local sites while the rest of the surface maintains its passive state, i.e. dissolution is not uniform. The presence of indium improves the dissolution morphology, lowering the corrosion potential and reducing the local cell action. Further he postulates that this is only true in chloride containing environments. The reason for this being that indium is readily reduced and once in solution quickly combines with the chlorine ions in the pit. What results is the precipitation of the insoluble indium chloride salt which creates a thin film over the interior of the pit, so causing repassivation. The overall effect of this is the creation of many more smaller, shallower pit sites uniformally distributed over the coating surface.

2.5.9 Physical Properties of the Metallic Coatings

2.5.9.1 Thickness

In the metal spraying of components and structures for both corrosion protection and aesthetic appeal, film thickness is one of the most important physical parameters of the sprayed coating. Film thickness affects other characteristics either directly or indirectly such as porosity or permeability, adhesion, corrosion resistance and effective life.[48]

In the case of zinc and aluminium the control of film thickness of the metal sprayed coating is of utmost importance for both economic and technical reasons. A technical specification

usually calls for a minimum film thickness to provide a certain degree of protection for a particular component, where this thickness depends upon:

(i) the environment,
(ii) further coatings to be applied over the metal spraying, and
(iii) the required life.

The amount of metal actually deposited in order to obtain a certain minimum thickness always represents an average coating thickness considerably greater than the minimum called for. This is caused by two factors; firstly the profile of the blast cleaned substrate, and secondly the inherent irregularities in the spraying process.[49]

The philosophy that increasing the coating thickness increases the corrosion resistance is, in most cases, true only within limits. With special reference to aluminium coatings, too thick a coating reduces the adhesion to the substrate and usually causes blistering when the component is placed in the corrosive environment for any length of time.

2.5.9.2 **Porosity**

The porosity of a coating refers to the size and extent of the isolated cavities and interconnected pores found penetrating from the surface. It is difficult to accurately estimate the porosity and no values are available in the literature. The interconnected pores allow liquids or gases to penetrate to the base metal, a factor that may be a disadvantage in some applications.

Between 5 and 15% porosity commonly exists in flame sprayed coatings. This is usually not of any concern when spraying aluminium, as the coating is a sacrificial anode and thus dissolves, leaving behind an insoluble corrosion product, which blocks all the pores. This feature of the corrosion of aluminium coatings results in the corrosion rate under most conditions falling rapidly with time over the first few years of exposure.

Conversely, porosity in zinc based coatings can have an adverse effect, as the corrosion products are soluble and thus do not block the pores if water is present to wash them away.

2.5.9.3 Adhesion

The adhesion of sprayed metal depends primarily on the condition of the abrasive blasted surface immediately prior to spraying. The presence of excess fines, the use of rounded or well-worn grit and contamination such as dust, oil and moisture in the abrasive material impairs coating adhesion.[50] Adhesion may also be seriously impaired by the presence of moisture condensed on the surface thus making a dry substrate essential just prior to spraying. Corrosion problems related to a lack of adhesion, as stated previously, usually emerge as a severely blistered surface, with corrosion of the substrate taking place under the metallic coating.

2.5.9.4 Mechanical Properties

The table below gives the approximate mechanical properties of sprayed zinc and aluminium coatings.[51]

Table 1 : Properties of sprayed zinc and sprayed aluminium.[18]

Material	Density g/cm^3	Coating Weight oz/ft^2 .001in. Thickness	Brinell Hardness	Ratio of Contracti -on stresses in sprayed deposits	Compress -ive Strength (strength to collapse) ton/in^2
Sprayed Zinc	6.35	0.528	20-28	1	10.3
Sprayed Aluminium	2.35	0.195	25-35	4	12.0

The measurement of the above properties often pose problems due to the nature of the coating. There are, however, specialised tests, a large number of which are described in ASTM Standards.[51]

2.5.10 Coating Sealants

Sealants are applied to sprayed coatings to improve appearance and corrosion resistance by filling the pores in the coating and reducing the number of active surface areas where pits or blisters might form. A good sealant has a low viscosity, so as to enter all the pores of the coating and low water adsorption, to avoid a perpetually wet sealant/coating interface and increased risk of damaging corrosion.[52]

2.5.11 Corrosion Products on Aluminium, Zinc and Aluminium-Zinc Coatings

Identification of the corrosion products can yield information concerning the corrosion reactions; however, such identification is difficult for various reasons, such as[53]:

(i) solubility of the products in water,

(ii) interference from the substrate when attempting analysis of the coating surface,

(iii) difficulty in removing a sufficient volume of representative products for chemical analysis.

Friel's research[53], although conducted using hot dipped coatings, applies just as readily to the flame-sprayed coatings. The table below gives a list of probable solid corrosion products identified using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS).

Table 2 : Probable solid corrosion products.[33]

Industrial Atmosphere 9-y Exposure

Al-Coated	Zn-Coated	AlZn-Coated
Al Sulphate Hydrate	$Zn_5(CO_3)_2(OH)_6$	AlZn Sulphate Hydrate
$4Al_2O_3.H_2O$	ZnO	
	$ZnSO_4$	
	FeOOH	

Marine Atmosphere 9-y Exposure

Al-Coated	Zn-Coated	AlZn-Coated
Al Sulphate Hydrate	$Zn_5(CO_3)_2(OH)_6$	AlZn Sulphate Hydrate
$4Al_2O_3.H_2O$	FeOOH	$Al(OH)_3$
$Al(OH)_3$	ZnO	$Al_2(OH)_6.H_2O$
	$Zn_5(OH)_8Cl_2$	ZnO
	$ZnSO_4$	

Marine Atmosphere 3-y Exposure

Al-Coated	Zn-Coated	AlZn-Coated
Al Sulphate Hydrate	$Zn_5(CO_3)_2(OH)_6$	AlZn Sulphate Hydrate
$4Al_2O_3.H_2O$	$Zn_5(OH)_8Cl_2$	$Al_2OH_6.H_2O$
	$ZnSO_4$	ZnO
	ZnO	

The principal products found on Al and Al-Zn coated steel, in both industrial and marine atmospheres, were amorphous Al sulphate hydrates, along with Al hydroxides in the marine environment. In the Al-Zn coating, the Al sulphate hydrate also contained some zinc and was present in the formerly Zn-rich interdendritic regions as well as on the surface.

On the basis of the data achieved , Friel concluded the following:

(i) Sulphur is a significant factor in the atmospheric corrosion of aluminium and zinc coatings in both marine and industrial environments.

(ii) The Al-Zn sulphate hydrates that form in the first few years of exposure are adherent and stable corrosion products and may thus act as a barrier to further attack.

2.6 Corrosion of the Substrate Alloys

As well as assessing the corrosion behaviour of the coating alloys it is essential to consider that of the substrate materials. The substrates that are to be considered in this research are:

(a) 6261 and 5083 (aluminium alloys)
(b) Mild steel
(c) Metal Matrix Composite (6061 aluminium alloy matrix with a controlled dispersion of silicon carbide particles)

Due to the importance of aluminium in this research, and since its corrosion is of a complex nature, it will now be discussed in further detail.

2.6.1 The Corrosion of Aluminium and its Alloys

2.6.1.1 Introduction

Aluminium owes its favourable corrosion resistance to the barrier oxide film that bonds strongly to the metal surface and that, if damaged, reforms immediately in most oxygen containing environments. This protective film only arises when the metal is in the presence of oxygen and if formed in air is usually between 5 and 10 nm thick.

If the oxide film dissolves, which it does in certain chemicals, the metal will also dissolve, resulting in uniform corrosion. If, however, the film is damaged under conditions which do not allow the normal re-building of the layer, localized corrosion such as pitting or intergranular attack will tend to occur.[54]

2.6.1.2 The Physical Properties of the Film

It was shown by Hunter and Fowle[55] that the oxide film is in fact a duplex corrosion product. This duplex layer being made up of a thin, protective, non-porous, "barrier" film, immediately adjacent to the metal surface and a more permeable outer bulk film. The barrier film rapidly reaches its maximum thickness, which is generally controlled by the temperature alone. On the other hand, the bulk film thickness is dependant upon the surrounding environment, with this layer being much thicker in aqueous environments than in dry environments.

2.6.1.3 The Growth of the Oxide Film in Water

When immersed in water, the oxide film thickens rapidly even at low temperatures and the process is always faster than it is in air.[56] The rate of growth does, however, decrease with time, reaching a limiting thickness which depends upon the following:

(i) The oxygen content of the water
(ii) The ions present
(iii) The temperature

(iv) The pH.

2.6.1.4 Environmental Factors Affecting the General Corrosion Behaviour

Certain alloys of aluminium exhibit good corrosion resistance. It must however be noted that this behaviour is not a fundamental property of the metal[39] and will always vary according to the environment to which it is exposed.

The two most important environmental factors are :

(i) Water
(ii) Temperature.

(i) Water

In any aqueous environment the aluminium generally corrodes in three distinct ways : by pitting, uniform corrosion and intergranular attack. The predominant form of corrosion is dependent upon the temperature of the given environment.

Due to the amphoteric nature of aluminium, the pH of the environment is of considerable importance. The metal is generally regarded as being passive between the pH range of 4.5 to 8.5. Figure 15 clearly illustrates this passive region.

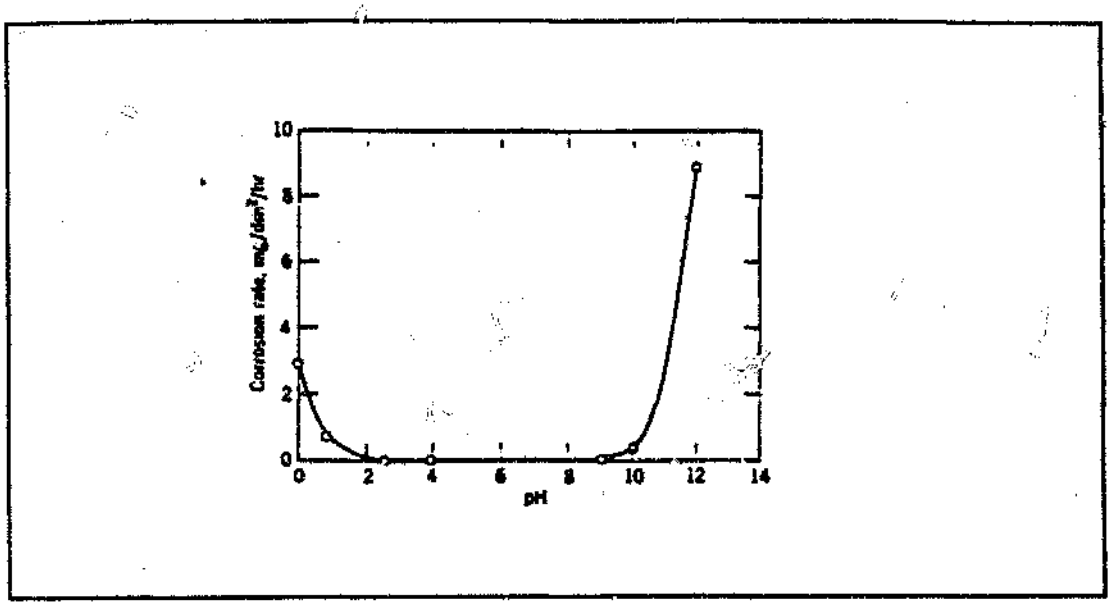


Figure 15 : The influence of pH on the solubility of the oxide film.

(ii) **Temperature**

An increase in temperature is usually associated with an increase in the corrosion rate. There are, however, situations where the converse is true. Godard[54] showed that temperatures above 40°C tend to reduce the rate of pitting of aluminium in water. In general, however, an increase in temperature can affect the corrosion in two ways, namely:

(a) by reducing the solubility of oxygen in the solution, and

(b) by stimulating the initiation of pitting.

2.6.2 The Pitting Behaviour of Aluminium

Pitting is the most important mode of corrosion of aluminium alloys. It occurs within the passive range (i.e. between pH values of 4.5 and 8.5). The major problem is that even though negligible thinning of metal due to uniform corrosion may have taken place, the ves may still have been perforated. It is thus necessary to know how and why pitting takes place, so that the nature of the problem can be properly understood and appropriate counter-measures

taken, if possible. The rate of pit penetration usually diminishes with time. Thus when the metal thickness is adequate perforation may not occur for a lengthy period. Only a small amount of metal is removed and as a result, the mechanical properties are not greatly affected.

2.6.2.1 The Mechanism of Pitting

It is generally agreed upon that the following four steps are involved in the pitting corrosion of aluminium, (The steps are listed below in time sequential order[57]) :

(i) The adsorption of the reactive anion on the oxide covered aluminium. (Assuming that the transport of the reactive species from the bulk solution to the metal surface is occurring at a sufficient rate).

(ii) The chemical reaction of the adsorbed anion with the aluminium ion in the aluminium oxide lattice.

(iii) The thinning of the oxide film by dissolution. (This also includes the penetration of the oxide film by the aggressive anion).

(iv) The direct attack of the exposed metal by the anion, which is sometimes called pit propagation.

The above four processes can be further classified into two distinct stages : pit initiation and pit growth.

(i) Pit Initiation

Pit formation is due to the creation of localised anode regions resulting due to potential differences between one place and another at the metal-liquid interface. At these local cells, corrosion proceeds at a higher rate than on the remainder of the passive surface. The corresponding high corrosion current at these sites leads to a local increase in the surface salt concentration as a result of transport processes (migration and diffusion) and anion

absorbtion.[56] The increased concentration of anions displaces the water molecules from the passive layer and suppresses the passivation reaction which is responsible for the "repair" of the oxide film. As a result of this , film dissolution takes place. As the film thickness decreases, so the current density increases, which in the presence of aggressive anions will result in the penetration of the oxide film. Finally, the oxide layer loses its passivating properties and is transformed to a non-passivating oxide capable of sustaining high corrosion current densities.[56]

(ii) **Pit Growth**

Once a pit in the aluminium has survived the initiation stage and developed a cavity, it propagates by local cell action. This basically involves metal dissolution and because of the high activity of aluminium and the small area involved, attack is usually very rapid. As the pit cavity grows, it begins to accumulate insoluble corrosion products which form a cap around the pit and slowly begin to fill the cavity. This cap becomes a physical barrier to the diffusion of oxygen to the anode and thus creates a differential aeration cell between anode and cathode which results in continued local cell action. Some of the numerous reactions that take place in an aluminium pit are shown in the figure below[57] :

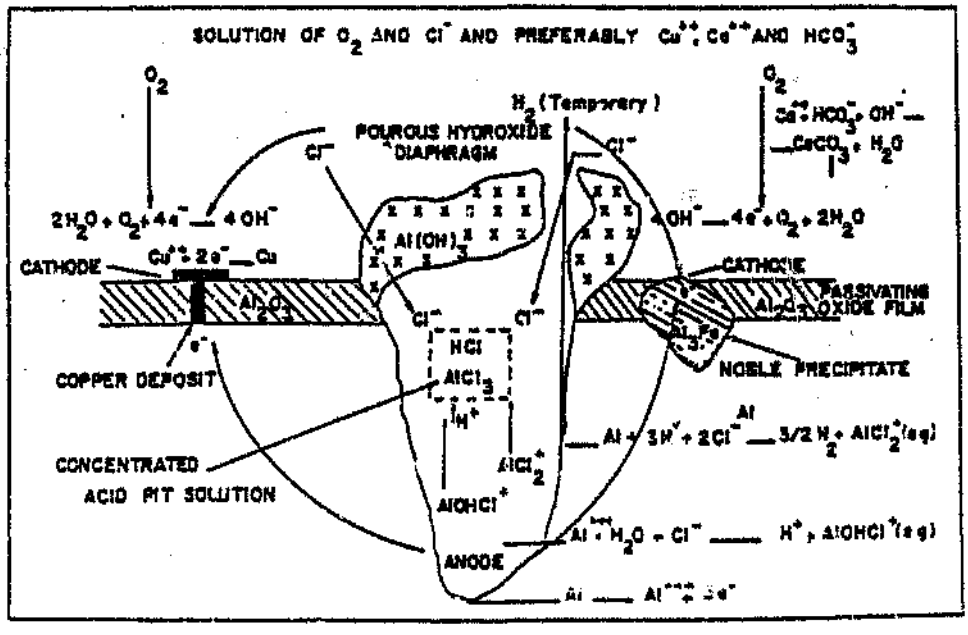


Figure 16 : Multiple reactions occurring in an aluminium pit, with the hydrolysis reaction resulting in acid formation.[57]

2.6.2.2 The Effects of Alloying on Corrosion Behaviour

Generally speaking, pure aluminium has the highest corrosion resistance and this decreases with alloying as can be seen in Figure 17 below[62]:

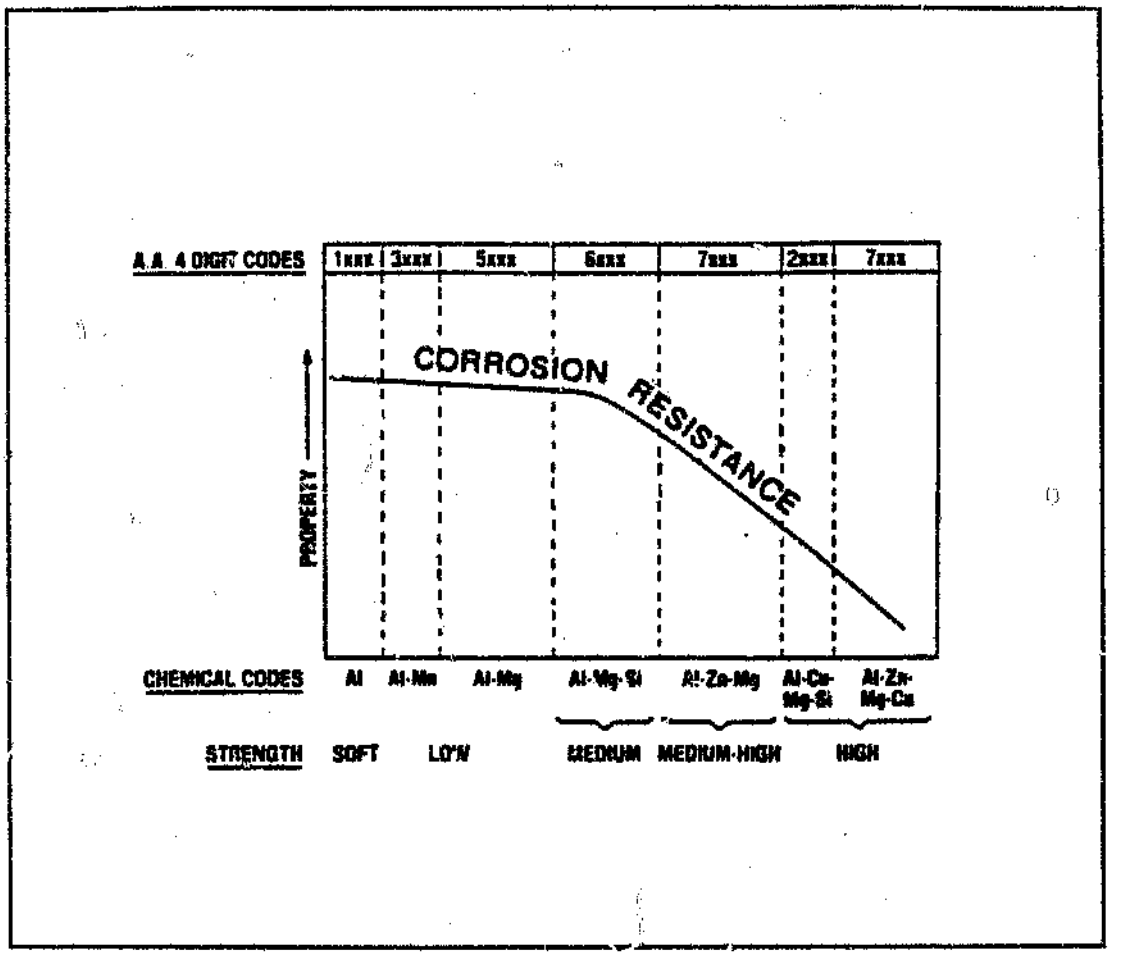


Figure 17 : The effect of alloying on corrosion resistance[62].

Due to the electrochemical nature of corrosion processes the solution-potential relationships among the microstructural constituents of a particular alloy significantly affect its corrosion behaviour. Compositions of solid solutions and additional phases, as well as amounts and spacial distributions of the additional phases, may affect both the type and extent of corrosion.[11] The effects of principal alloying elements on solution potential of high purity

aluminium are shown in the figure below. For each element, the significant changes that occur do so within the range in which the element is completely in solid solution. Further addition of the same element, which forms a second phase, causes little additional change in solution potential.

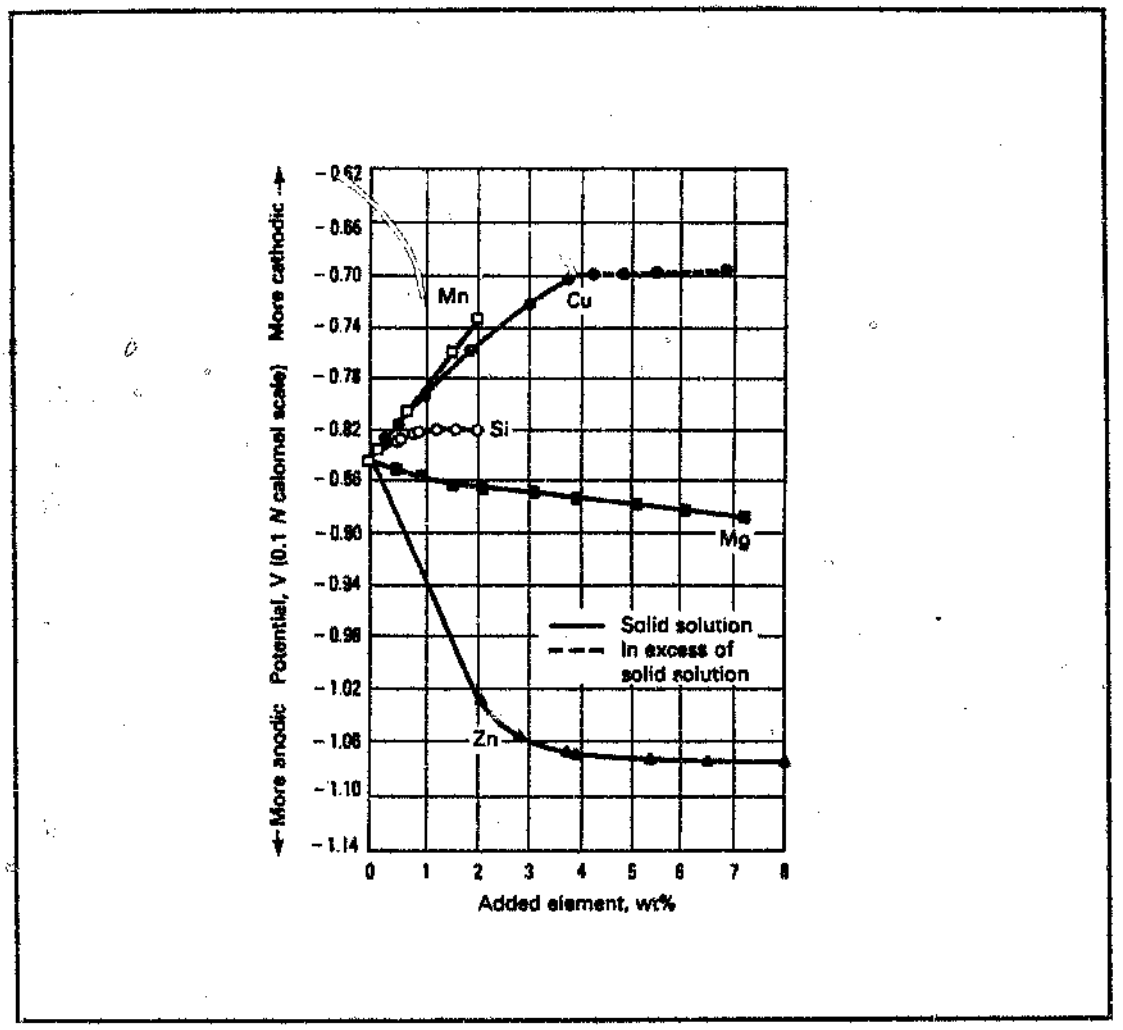


Figure 18 : Effects of principal alloying elements on the electrolytic-solution potential of aluminium. (Potentials are taken in a solution of 53g/L NaCl plus 3g/L H_2O_2 at 25°C.)[11]

The corrosion behaviour of the specific alloy series being considered in this research will now be looked at in greater detail.

(i) **5XXX Series Alloys**

The major alloying element in the 5XXX series is magnesium (although manganese and chromium are often present in smaller amounts).

Alloys in which the magnesium is present in amounts that remain in solid solution, or as partially precipitated Al_8Mg_5 particles, are generally as resistant to corrosion as the commercially pure metals.
Where 3% or more magnesium is present however, the Al_8Mg_5 may form an almost continuous intergranular precipitate. This reduces the corrosion resistance considerably and has thus led to the development of various tempers which result in the precipitation of the secondary phase particles within the grain rather than at the grain boundary.

(ii) **6XXX Series Alloys**

The 6XXX series (aluminium-magnesium-silicon) generally exhibit moderately high strength and very good corrosion resistance. These alloys are heat-treatable and the Mg_2Si phase, which is the basis for the precipitation hardening has a negligible effect on the corrosion behaviour. Copper additions are often made to the metal to improve the strength and ductility of the alloy. The level of corrosion resistance does however tend to decrease with increasing copper levels.

2.6.3 The Corrosion of Metal Matrix Composites

Fibre or particle reinforced aluminium alloys have recently become popular due to the added strength, modulus, and stiffness properties they exhibit over conventional alloys. In particular the 5000 and 6000 series aluminium alloys, reinforced with either graphite or silicon carbide (SiC), have found successful applications, particularly in seawater and related environments.[58] These reinforcements of graphite and SiC, which are either in whisker or particle form, promote additional corrosion concerns besides the pitting attack which is typical of the substrate alloys.

Of specific importance to this research is the behaviour of SiC/Al composites. Aylor and Kain[58] found that the mode of attack in these alloys was also pitting. The pits do however concentrate around the SiC particles, suggesting that crevices, formed at the SiC/Al interfaces, contributed to the corrosion.

A variety of surface treatments have been applied to SiC/Al composites to identify adequate corrosion protection systems. Of the protection methods evaluated, coatings of aluminium and Al_2O_3 demonstrated the best corrosion resistance.

2.7 Selecting a Coating

The selection of the best coating or combination of coatings for any particular corrosion control application necessitates consideration of all the factors involved. This ensures that the most economic choice may be made , consistent with the performance required. Some of the more important factors that are likely to be considered are the following[59] :

(i) The service environment(s)
(ii) The service life required
(iii) Aesthetic appeal and the degree of deterioration that can be tolerated
(iv) The substrate material
(v) The size and shape of the article
(vi) Any subsequent fabrication requirements
(vii) Mechanical factors.

2.8 Testing Coatings

One of the most important aspects of coating technology involves thorough and adequate testing of the coating quality, thus ensuring compliance with specification requirements. Also,

corrosion testing in both naturally occurring and specially controlled corrosive environments are required. This makes sure that the true optimum service performance can be accurately predicted and achieved in practice. Thus the testing of coatings may be seen to fall within two broad categories[59] :

(i) quality control testing
(ii) corrosion resistance testing.

There is an interrelationship between these divisions, since the results of some quality control tests may indicate changes in expected corrosion resistance performance and vice versa.

2.8.1 Quality Control Testing

Test for quality control may be divided into the following groups[59] :

(i) visual inspection
(ii) chemical composition
(iii) thickness
(iv) porosity
(v) adhesion
(vi) stress
(vii) ductility
(viii) strength
(ix) hardness
(x) wear resistance.

In any given coating system or application the series of tests that must be made varies. The testing method to be used also depends upon the materials concerned and the methods of coating application used.

2.8.2 Corrosion Resistance Testing

The purpose of corrosion testing is twofold[59] :

(i) testing is required to predict the performance of a given coating system in a particular corrosive environment, and

(ii) suitable corrosion tests may be used to reveal defects in a coating that could lead to inferior performance in service.

The ideal corrosion test is exposure to the service condition. However, if the coating fulfils its function, the period of breakdown should be inordinately long, and a more rapid means of testing must be sought. Accelerated corrosion tests may thus be devised to hasten breakdown by maintaining maximum severity continuously. This usually achieved by altering temperature or humidity or by using a specially aggressive artificial corrosive environment.

2.9 Techniques of Quantifying Corrosion Rate Measurements

Standard practice in evaluating the performance of metal sprayed coatings is to report the percentage of rusted base metal area. This is most commonly done by comparing the panels with the European Scale of Degree of Rusting for Anti-Corrosion Paints - Swedish Standard SIS 185111 - 1964. This is a pictorial standard with 10 plates ranging from Re0 (rust free surface) to Re9 (100% surface rust).[60]

Usually, the appearance and condition of the coating itself is also fully described to accurately assess the status of coating deterioration. This assessment is visual and thus the results depend upon the interpretation of the individual inspector. To avoid this, a standardised inspection form is usually devised. This is typically based on the terminology mentioned below.[61]

Table 3 : Terminology used to describe condition of test panels.[61]

Appearance and Condition terms.

R - *Red rust*,originating from the base metal.Usually well-defined and entirely different from red rust stain.

W - *White rust*,the corrosion product of zinc or aluminium.Not necessarily white in colour;may be stained by contamination.

D - *Foreign deposit*,such as dirt,etc.

S - *Stain*,any discolouration other than white rust or red rust stain.

RS - *Red rust stain*,originating from the base metal with no evidence of blisters,coating failure,or loss of adhesion.

DS - *Deposit stain*,originating from some source other than the panel.

B - *Blisters* in seal coats or sprayed metal.

P - *Pits* in sprayed metal,resulting from corrosion.

N - *Nodes*,well-defined growths or lumps of corrosion product.

F - *Flakes*,loose segments of seal coat or sprayed metal.

Degree and Descriptive Terms

h - **Large defect* over 9.5mm diameter.

m - **Medium defect* over 3.2 to 9.5mm diameter.

s - **Small defect* less than 3.2mm diameter.

p - **Pinpoint defect.*

f - *Few* - less than 6 per square inch (6.45 sq cm) of surface.

i - *Intermediate* - 6 to 20 per square inch (6.45 sq cm) of surface.

m - *Many* - over 20 per square inch (6.45 sq cm) of surface.

g - *General* - covering all or most of the panel.

bl - *Blotchy* - any irregular pattern.

gr - *Gray* in colour.

d - *Dark* in colour.

*These terms generally used to describe size of nodes,pits,blisters,or spots.

2.10 The Properties of Local Mine Waters

For this investigation, a major portion of the work will be carried out in solutions of similar composition to local mine waters . These waters are frequently extremely corrosive due to their composition and/or environment in which they are found.

The waters may have very high levels of dissolved and suspended solids, and temperatures varying from 4°C up to 55°C. Many mines have high sulphate and chloride levels in their water, and most are contaminated with microbial organisms.

These mine waters are used for general service, use such as dust suppression, water spraying after blasting, as a coolant in rock drills, for washing down the working face etc. It has been estimated that between 0.5 and 5 tons of water are required per ton of rock removed.[62]

For a proper understanding to be achieved of the various corrosion mechanisms the properties of this water must be carefully assessed.

2.10.1 Water Composition

In South African mines there are three general groupings of water type.[62]

(i) The Orange Free State mines, which have waters that contain high levels of dissolved salts, mostly chlorides and to a lesser extent sulphates.

(ii) Very hard, Far West Rand waters, with medium chlorides and high sulphate ion concentrations.

(iii) Those on the Witwatersrand, having low chlorides , high sulphates and low pH's.

Higginson and White[63] analysed the composition of 46 South African mine waters and their results are tabulated on the following page. The figure below is the key to the table.

Key :

Cond.	= Conductance, µS
TDS.	= Total dissolved solids, mg/l
Cl^-	= Chloride, mg/l
SO_4^{2-}	= Sulphate, mg/l
NH_3	= Ammonia, mg/l
NO_2	= Nitrite, mg/l
NO_3	= Nitrate, mg/l
TH.	= Total hardness (as $CaCO_3$, mg/l)
Cal.Hard.	= Calcium hardness (as $CaCO_3$, mg/l)
Alk.	= Alkalinity (to methyl orange, mg/l)
TSS.	= Total suspended solids, mg/l
pH	= pH value at time of analysis
pHO.	= pH value at time of sampling
WaterT.	= Water temp. at time of sampling, °C
Diss.O.	= Dissolved oxygen at time of sampling, mg/l
Na.	= Sodium, mg/l
Cu.	= Copper, mg/l
Fe.	= Total iron, mg/l.

Figure 19 : Key to Table 4.[63]

Table 4 : Analysis of 46 of South Africa's gold mine waters.[63]

Property	Maximum	Minimum	Average
Cond.	9450	420	3354
TDS.	7789	583	2644
Cl^-	2535	26	656
SO_4^{2-}	2504	76	754
NH_3	43.0	<1.0	≤12.9
NO_2	21.0	<1.0	≤2.65
NO_3	129.0	<1.0	≤29.9
TH.	3249	115	847
Cal.Hard.	1826	87	558
Alk.	374	6	107
TSS.	2706	0	≤94
pH	9.0	2.8	7.2
pHO	9.1	3.1	7.2
Water T.	43	10	28
Diss.O.	10.4	2.0	≤6.8
Na.	1651	29	471
Cu.	<1.00	<0.01	≤0.1
Fe.	<5.00	<0.02	≤0.1

The frequently acidic nature of the waters, evident from the table, is mainly due to the presence of iron pyrites in the gold bearing reef. These oxidise and in the moisture form ferric sulphate and sul[illegible]ic acid. As a control for this acidity, lime is usually added in order to keep the pH between [illegible] and 9.

Work by Higginson[64] clearly showed the importance of these lime additions, since, as can be seen in the graph below, a drop in pH to less than 4 causes a severe increase in the corrosion rate. (The graph also shows how the level of oxygen in the water effects the corrosion rate.)

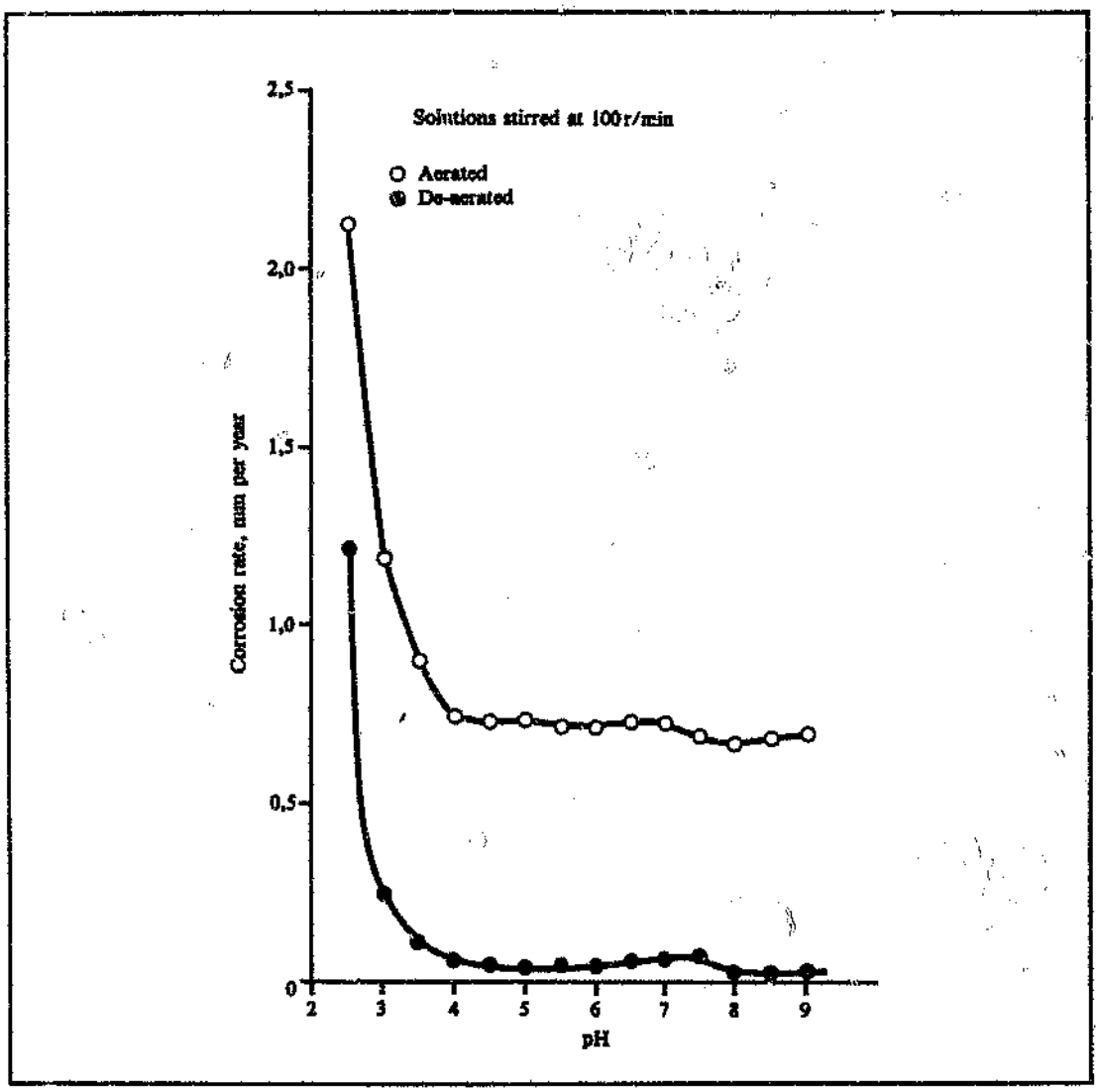


Figure 20 : Effect of pH on corrosion rate of mild steel in synthetic mine water.[64]

2.10.2 Water Temperature

As previously mentioned, the water temperatures vary between 4°C and 50°C in South African mines. Figure 21 illustrates the temperature dependence of the corrosion rate by considering the corrosion of mild steel in a synthetic mine water at pH values of 2.5 and 6.5.

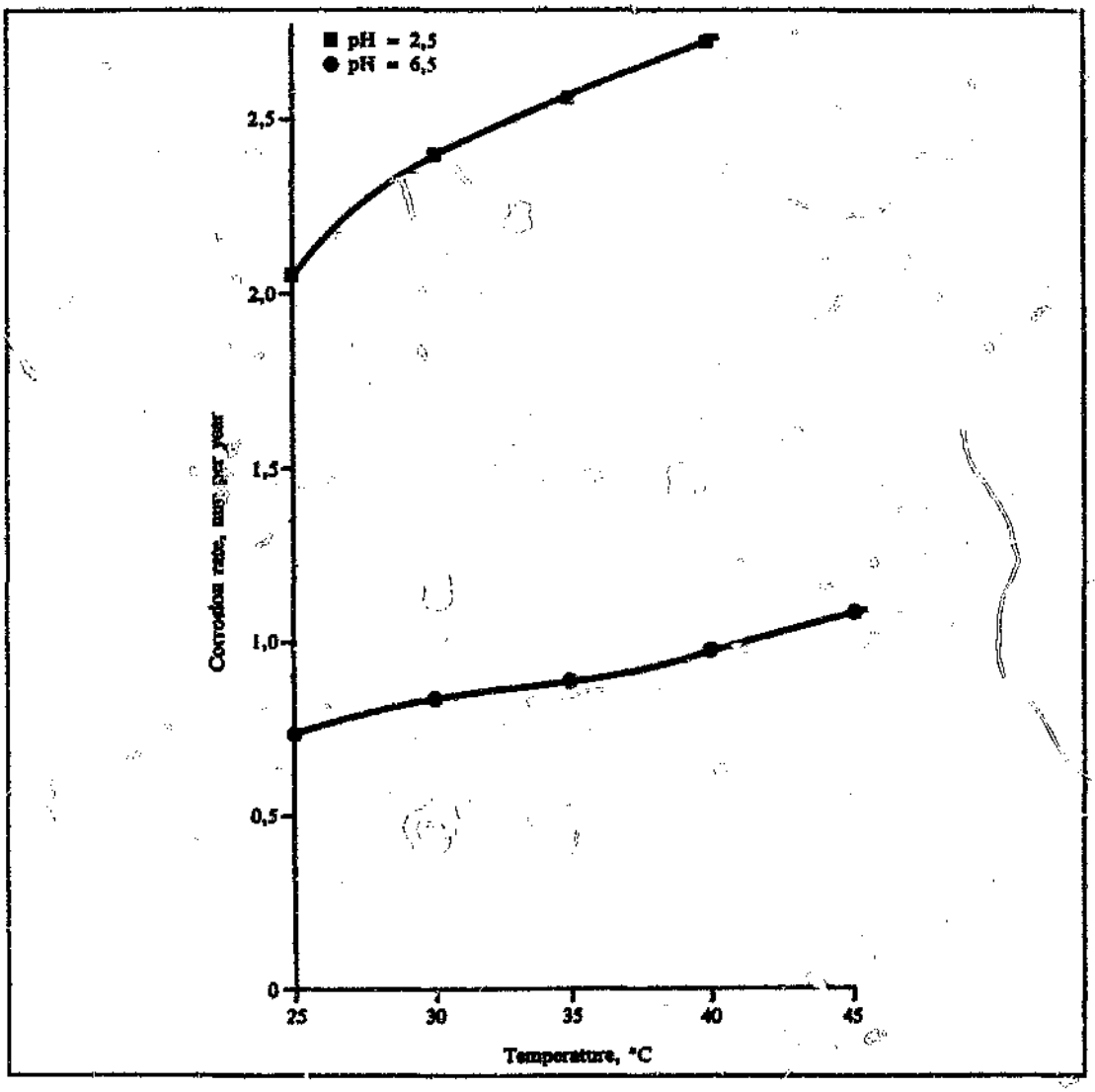


Figure 21 : Variation in corrosion rate with temperature in solutions of synthetic mine water.[64]

Experimental Procedure

3.1 Creation of the Metal Spray Alloys

From conclusions drawn from the results of previous research on aluminium-based sprayed coatings, (see Literature Review), and discussions with experts both locally and abroad, it was decided to produce the following alloys for spray purposes:

(i) Pure Aluminium
(ii) Aluminium / 4.5% Zinc
(iii) Aluminium / 4.5% Zinc / 160 ppm Indium
(iv) Aluminium / 8% Zinc
(v) Aluminium / 12% Zinc.

NOTE : All aluminium and zinc raw materials were reported to have greater than 99.90% purity.

3.1.1 Melting and Casting of the Alloys

The alloys were melted in a small (20 kg) induction furnace and cast using a laboratory-scale semi-continuous casting facility[65]. The equipment required had previously been designed and constructed at the University of the Witwatersrand for the explicit task of casting aluminium alloys. The cast billets had the following dimensions:

diameter : 155 mm (6 inches)
length : ±400 mm.

Once cast, all the billets were analysed to ensure that the target points had been met.

3.1.2 The Production of Wire

The standard requirement for most wire-fed metal spray-guns is wire with a diameter of 3.125 mm (⅛th of an inch). In order to produce wire of this dimension the 155 mm diameter billets were first extruded down to 9 mm rod. This rod was then passed through a series of drawing stages and finally pulled through a 3.125 mm die. All this work was carried out at Hulett Aluminium's plant in Olifantsfontein using full-scale plant machinery.

3.2 Preparation of the Substrate Alloys

Four materials were selected as substrate alloys, these being:

(i) AA6261 aluminium alloy
(ii) AA5083 aluminium alloy
(iii) A metal matrix composite (MMC)
(iv) Mild Steel.

Once again, prior to use all the alloys were analysed to ensure that they fell within the designated specifications.

3.2.1 The Reasons for the Alloy Selections

The two aluminium alloys were selected as they are the most likely to be used in the structural applications requiring high corrosion protection. Mild steel was included as most of the research and actual on-site spraying of aluminium-based alloys has been on low carbon steels. The metal matrix composite, although having high strength, has extremely poor corrosion resistance. Thus, the idea was to give the MMC improved corrosion resistance, whilst maintaining its excellent mechanical properties.

3.2.2 Coupon Size and Dimensions

All the alloys were supplied in 3mm thick sheet form. Coupons were then guillotined from the sheet in order to create a smooth uniform edge to each specimen. Coupon sizes were varied for each trial, partly for identification purposes, but mainly to ensure that the relevant ASTM standards for the minimal representative area for each trial were adhered to.

(i) Salt Spray coupons : 60 x 50 mm (ASTM B117).
(ii) Alternate immersion coupons : 70 x 30 mm (ASTM G44).
(iii) Total immersion coupons : 60 x 25 mm (ASTM G31).

(NOTE: See section 3.5 for actual trial details).

3.2.3 Grit Blasting of Coupons

Grit blasting of all surfaces that are to be metal sprayed is essential. This ensures firstly that the bare metal is exposed and secondly that the surface will permit good mechanical keying of the sprayed metal to it.

SABS 064 specifies that the surface should be prepared by abrasive blasting. The compressed air should be free from oil, grease and moisture and the abrasive must be a clean angular grit of appropriate size, so as to ensure an adequate and sharp surface profile. After blasting, all the dust and debris must be removed by dry brushing with a clean brush, followed by vacuum cleaning (SABS method 769). Subsequent contamination of the surface must then be avoided.

Aluminium grit was used to blast both the aluminium and steel coupons. The photograph below illustrates the effect of the blasting.

Figure 22 : Aluminium and steel samples grit blasted with Al_2O_3.

3.2.4 Metal Spraying of Alloys

The test coupons were sprayed on all sides (including edges) using a METCO hand-held wire spray gun. All the substrate alloys were sprayed with each wire alloy in sufficient quantities for all the corrosion trials and electrochemical test work. Although coating thickness was difficult to control, large batches were sprayed at one time, in order to achieve as much uniformity as possible. The appearance of the sprayed samples is illustrated below:

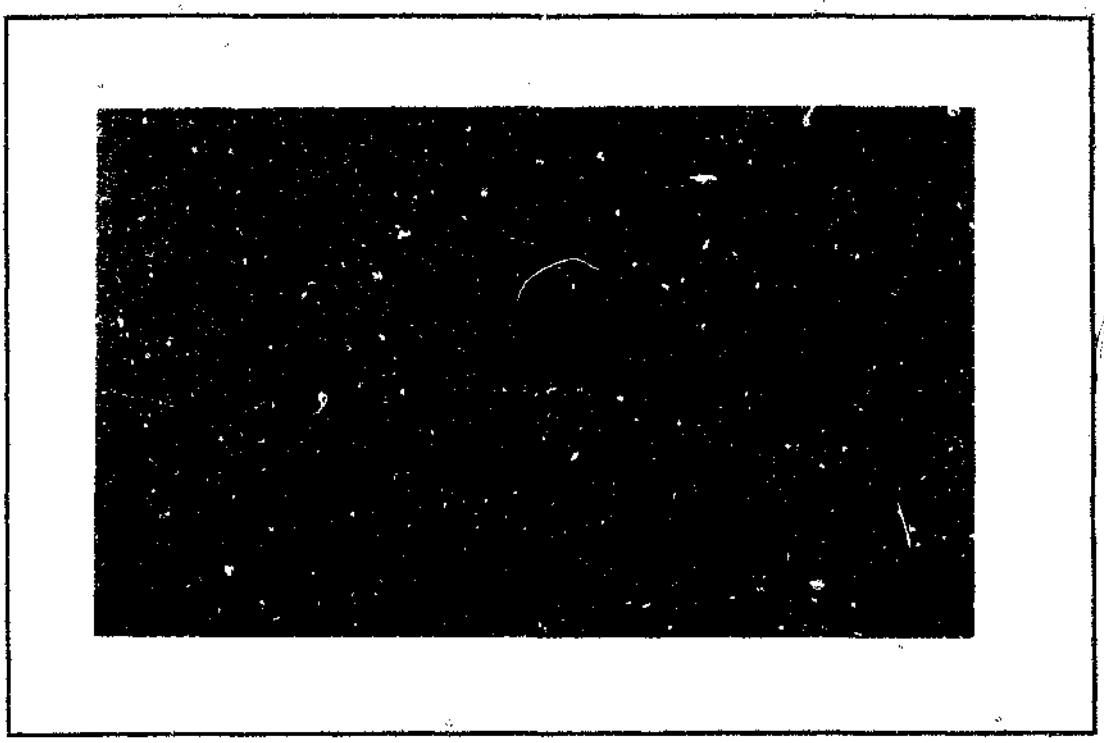


Figure 23 : Metal sprayed coupons.

3.2.5 Final Preparation of Coupons

In order to judge the degree of sacrificial protection offered by each coating, some of the coupons had controlled defects created in their surfaces. The photograph below shows the arrangement of these defects.

Figure 24 : Controlled defects in test coupons.

This technique is used by the Galvanisers Association of Australia[66] and it was thought that it would work just as well for metal sprayed test specimens.

Furthermore, the edges of these test pieces were masked off by an epoxy-type glue. The reason for this being that in most accelerated corrosion tests it is always the edges that get attacked first. It must be noted that the edges of the rest of the specimens were left unmasked as they had been metal-sprayed and for accurate weight loss measurements masking off would introduce inaccuracies.

3.3 Synthetic Mine Water Make-up

The original synthetic mine water decided upon is based on samples of machine water taken from a mine in the Orange Free State[67]. The reason for this selection is that corrosion problems in these mines are generally considered to be more serious than elsewhere. The

composition is listed in the table below.

Table 5 : Composition of synthetic mine water.

Constituent.	Concentration mg/l.
$NaHCO_3$	42
$CaSO_4.2H_2O$	1290
$MgSO_4.7H_2O$	608
NaCl	2040
Na_2SO_4	142
NH_4NO_3	317
KNO_3	216
KNO_2	60
$FeSO_4.7H_2O$	15

The relatively high levels of ammonium salt results from the explosives used underground. Suspended solids were not added to the water, as it was feared that the machinery used for the testing would get clogged up if any were added. No biological constituents were added to the water.

The make-up of the water was then changed to vary only the sulphate and chloride levels. The relative amounts of each chemical were thus altered to achieve two more waters with the following SO_4^{2-} and Cl^- compositions:

(i) SO_4^{2-} : 2000 ppm
Cl^- : 500 ppm

(ii) SO_4^{2-} : 500 ppm
Cl^- : 2000 ppm

Each water was analysed, with the analysis being given in the results section of the report.

3.4 Electrochemical Corrosion Testing

3.4.1 Sample Preparation

Samples of approximately 1 cm^2 of sprayed metal surface were cut from larger specimens. An insulated wire was then attached to the back of the sample by a screw, turned into a small hole drilled in the back. The wire was then soldered to the screw to ensure good electrical contact, using resin cored solder. This sample was then degreased in an ultrasonic bath in 100% pure alcohol for five minutes. The sample was then coated with a clear lacquer, leaving only a small region of the surface exposed. This area was then accurately measured and the desired corrosion scan was carried out. The photograph below shows a test specimen ready for testing.

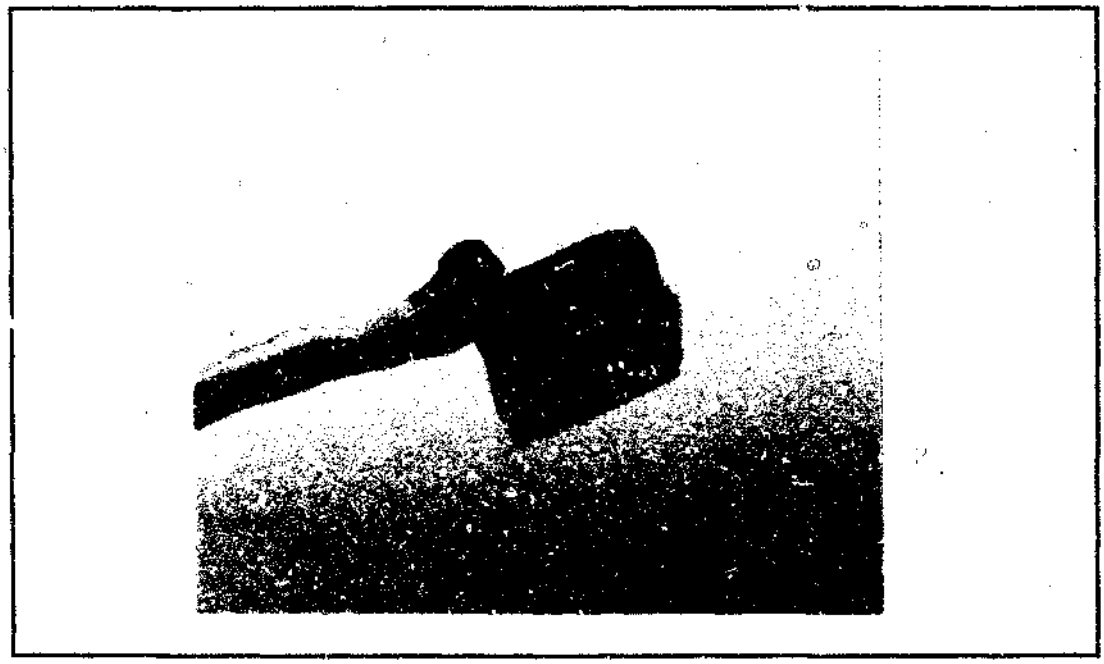


Figure 25 : An electrochemical test specimen.

3.4.2 Corrosion Testing

Accelerated electrochemical corrosion tests were conducted with a PRINCETON MODEL 273

corrosion measurement system and MODEL 342 software. All of the corrosion tests were carried out in a standard one litre, round-bottomed flask, modified by the addition of various necks to permit the introduction of two graphite counter electrodes, a gas bubbler, a sample and a saturated calomel reference electrode (SCE), all of which conform to the ASTM G5 standard. This arrangement, shown in the figure below, was then connected to the potentiostat and placed in a water bath, which was kept at a constant temperature of 25°C. The test solution inside the corrosion flask was de-aerated with ultra high purity argon for at least one hour before testing commenced.

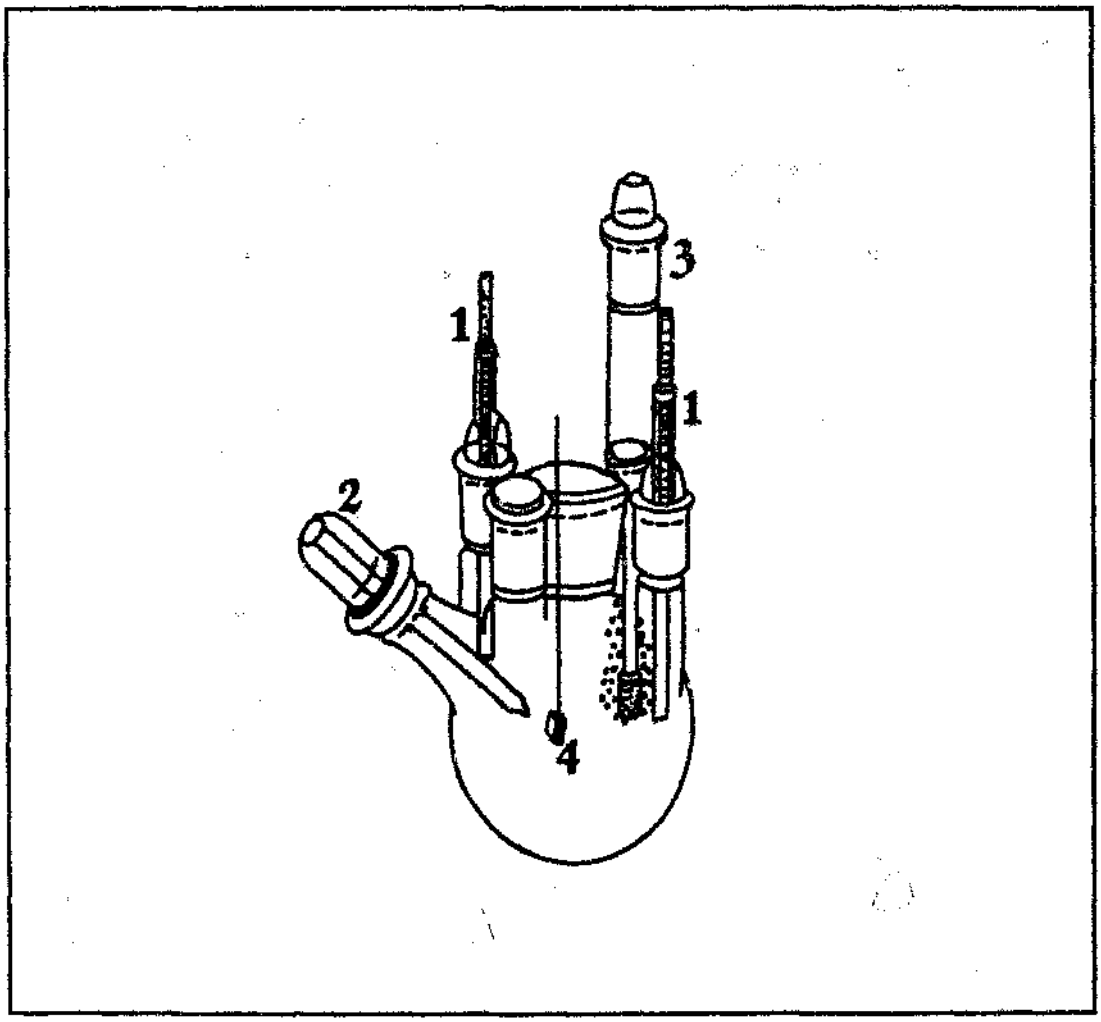


Figure 26 : Typical electrochemical polarisation cell : (1) counter electrodes, (2) reference electrode (SCE), (3) gas bubbler, (4) the sample.

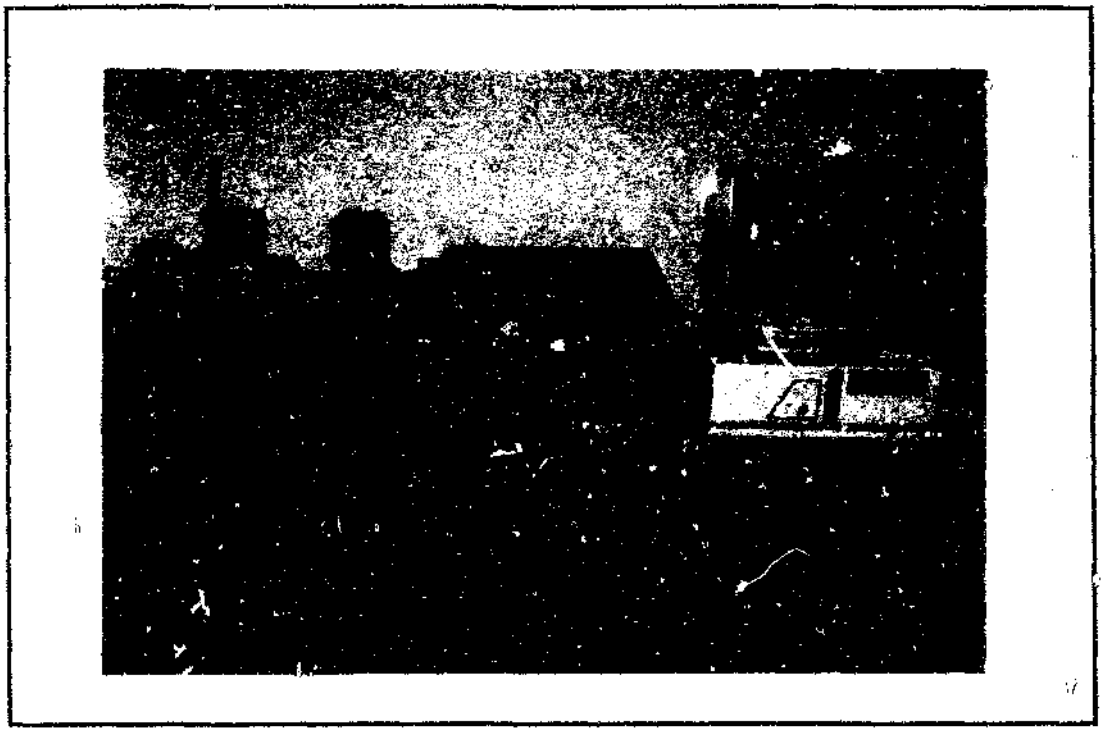


Figure 27 : Photograph of the EG & G Princeton Model 273 potentiostat, with its peripheral devices.

3.4.2.1 Potentiodynamic Tests

These tests produced polarisation curves of the potential versus the current density. The scans were performed in all the synthetic solutions mentioned in section 3.3, at 25°C. These potentiodynamic curves were used to obtain a general corrosion rate of the samples and also to give an indication of the overall corrosion behaviour of the samples at various potentials. (i.e. Active or passive potential ranges can be identified as well as the regions of pitting and general corrosion).

3.4.2.2 E_{corr} versus Time Tests

These scans were carried out to establish the variation of the free corrosion potential as a function of time. The purpose of this was to determine the stable potential of the coatings relative to the substrates, so that the degree of anodic behaviour could be established.

It was initially thought that these tests would be conducted in all the waters. However, due to the length of time taken for each trial (in excess of 12 hours) and the scatter of the results initially achieved, it was decided to limit them to only one solution, the high sulphate and high chloride synthetic mine water. This was thought to be adequate, as the trends established under these conditions would be similar to those found in the other waters.

3.5 Accelerated Corrosion Testing

3.5.1 Salt Spray Testing

A top loading HERAEUS VÖTSH salt spray cabinet complying with the pre-requisites specified in ASTM B117 and DIN 50021 was used for all the salt spray trials.

In an attempt to simulate actual mining conditions, it was decided initially to use the high chloride and high sulphate synthetic mine water in the salt spray cabinet. After continual monitoring for 1000 hours, it was ruled that a more aggressive solution would be required, as the coated samples were not showing marked signs of corrosion. These samples were then removed from the cabinet and analysed according to specifications dealt with in section 3.5.4.

New samples were then exposed to the standard salt spray solution specified in ASTM B117. This solution is prepared by dissolving 5 ± 1 parts by weight of sodium chloride in 95 parts of distilled water. After 1000 hours of testing it was decided to once again increase the corrosivity of the solution, as it was still not possible to rank the performance of the various coatings.

For the final test, the salt water used in the previous trial was modified to adhere to ASTM B287 - the standard method for acetic acid - salt spray testing. This brought the pH of the brine down to between 3.1 and 3.3.

In order to adhere to all the standards care was taken to ensure that the following conditions were met:

(i) The specimens were supported between 15 and 30 degrees from the vertical.

(ii) The specimens were not touching each other, or any other metallic material. (Perspex racks were used to hold the coupons).

(iii) Each specimen was placed so as to permit free settling of fog on their surface.

(iv) No salt solution was allowed to drip from one specimen to another.

(v) All the tests were carried out at 35°C.

3.5.2 Alternate Immersion Testing

An alternate immersion corrosion testing apparatus was designed and constructed at the University specifically for this research. The completed item of equipment is shown in the following photographs - Figures 28 and 29.

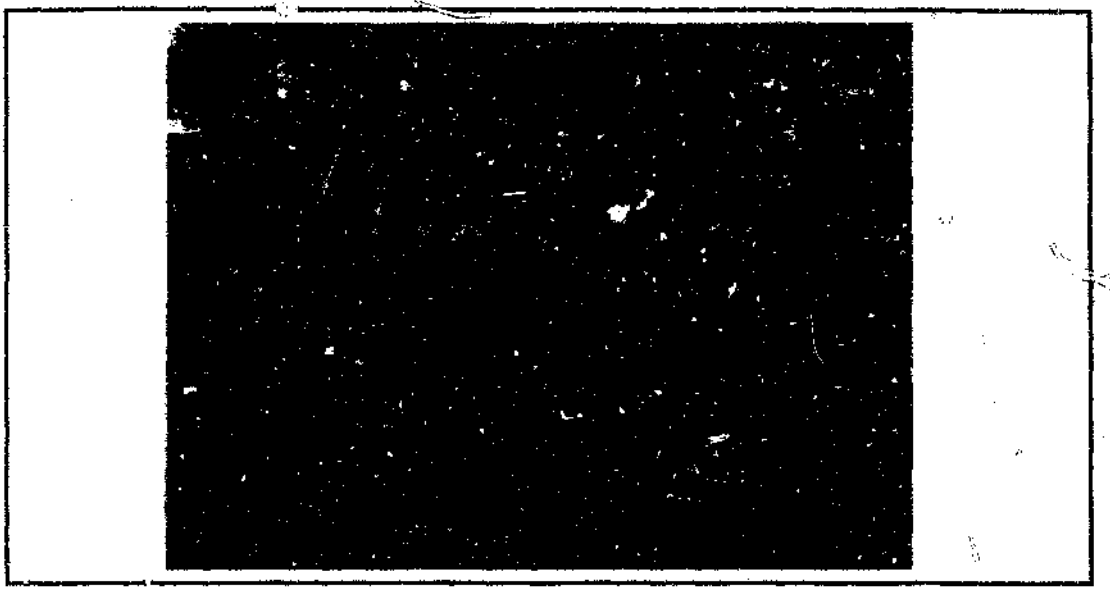


Figure 28 : The alternate immersion corrosion testing apparatus.

Figure 29 : Controls for the alternate immersion corrosion testing apparatus.

The pneumatic cylinders allow the simultaneous raising or lowering of all the test pieces at a rate well within the time limit specified in ASTM G44. The four separate tanks and the large number of sample holders enabled a major portion of the trials to be run concurrently.

Initially, three of the tanks were filled with the synthetic mine waters selected previously and the fourth with tap water, to act as a control. After 1000 hours the tap water tank was changed to synthetic sea water in an attempt to speed up the corrosion rate of the samples. Following this, after 2000 hours, the mine water proving to be the least aggressive of the three (the high chloride and low sulphate water) was changed to 0.1 normal sulphuric acid, in a bid to try and rank the various coating/substrate combinations.

These trials were run at room temperature and for a minimum of 1000 hours and maximum of 3000 hours, with the water in each tank being changed every 300 hours to try and prevent any microbial action.

3.5.3 Complete Immersion Trials

The three synthetic mine waters and Rand Water Board tap water were once again used for the total immersion trials. The water make-up was not changed during the exposure period and the trials were run for in excess of 3000 hours. To comply with ASTM G31, the test coupons were suspended vertically and completely immersed in the test solution.

Similarly to the case of the alternate immersion trials, the waters were changed every two weeks in order to minimize microbial attack.

3.5.4 Preparing, Cleaning and Evaluating the Corrosion Test Specimens

All preparation, cleaning and evaluation was performed in accordance with ASTM G1, the standard practice for these procedures.

3.5.4.1 Sample Preparation

With regard to the preparation of both coated and mill finish test coupons, the following steps were followed prior to all trials:

(i) The specimens were cleaned by rinsing, first in acetone, then alcohol and then distilled water.

(ii) They were then dried and left in a desiccator for a minimum of one hour.

(iii) For identification purposes each sample holder was numbered and labelled, thus avoiding the necessity of marking of the specimens themselves - something that would have affected to results achieved.

(iv) The clean, dry specimens were then weighed to the fifth significant figure, for those tests in which mass-loss measurements were required.

3.5.4.2 Sample Cleaning

Upon completion of every trial the following cleaning procedure was observed: (Ref:ASTM D2688)

(i) Coupons were scraped with a plastic knife and scrubbed with a nylon brush to remove any bulk corrosion product.

(ii) Chemical cleaning was then carried out. The table below shows the details of the cleaning operation for the various alloys and coatings.

Table 6 : Chemical cleaning procedure for the removal of corrosion products.

Material.	Solution.	Time.	Temp.
All aluminium alloys All coated samples and the MMC.	50ml phosphoric acid & 20g chromium trioxide in reagent water to make 1000 ml.	10 min	90°C to boiling
Mild steel	0.2g - hexamine in 1000 ml hydrochloric acid.	10 min	25°C

(iii) Rinse in tap water.

(iv) Rinse in distilled water.

(v) Rinse in acetone.

(vi) Following the rinsing operation, which was intended to remove any remaining corrosion product and the cleaning chemicals, the samples were dried in paper towels and stored in a desiccator for a minimum of one hour.

(vii) Finally, the samples were re-weighed to establish the mass loss.

3.5.4.3 Sample Evaluation

Throughout the duration of the corrosion testing all the tanks were monitored and notes made of any developments. Photographs of these observations were taken when necessary. On the completion of each trial, photographs were immediately taken of a representative sample of each coating/substrate combination. If the cleaning operation revealed interesting features it was also photographed.

Sufficient samples were available to allow extensive mass loss measurements. From the mass-loss data the corrosion rate could be calculated using the following equation:

$$Corrosion\ Rate\ (in\ mm\ per\ year) = \frac{K \times W}{A \times T \times D}$$

where : K = 8,76 x 10^4,

W = mass loss in grams,

A = area in cm^2,

T = time of exposure in hours, and

D = density in g/cm^3.

Where necessary optical, stereo or scanning electron microscopy was conducted to confirm the results achieved.

3.6 Surface Roughness Evaluation

Prior to spraying, surface roughness measurements of random grit-blasted specimens were taken, the purpose of these measurements being to ensure that the surfaces were sufficiently rough (as specified by SABS 1391) to ensure satisfactory keying of the sprayed metal to these surfaces.

Both longitudinal and transverse measurements were taken using a **HOMMEL T1000** Surface Finish Tester.

3.7 Coating Adhesion Measurements

This testing procedure, as covered in ASTM C633, deals with the determination of adhesion of a coating to a substrate. It is particularly adapted for testing coatings applied by flame spraying. The test consists of coating one side of a substrate fixture, bonding this

coating to the face of a loading fixture, and subjecting this assembly of coating and fixtures to a tensile load normal to the plane of the coating. The basic principles of the operation are shown in the figure below.

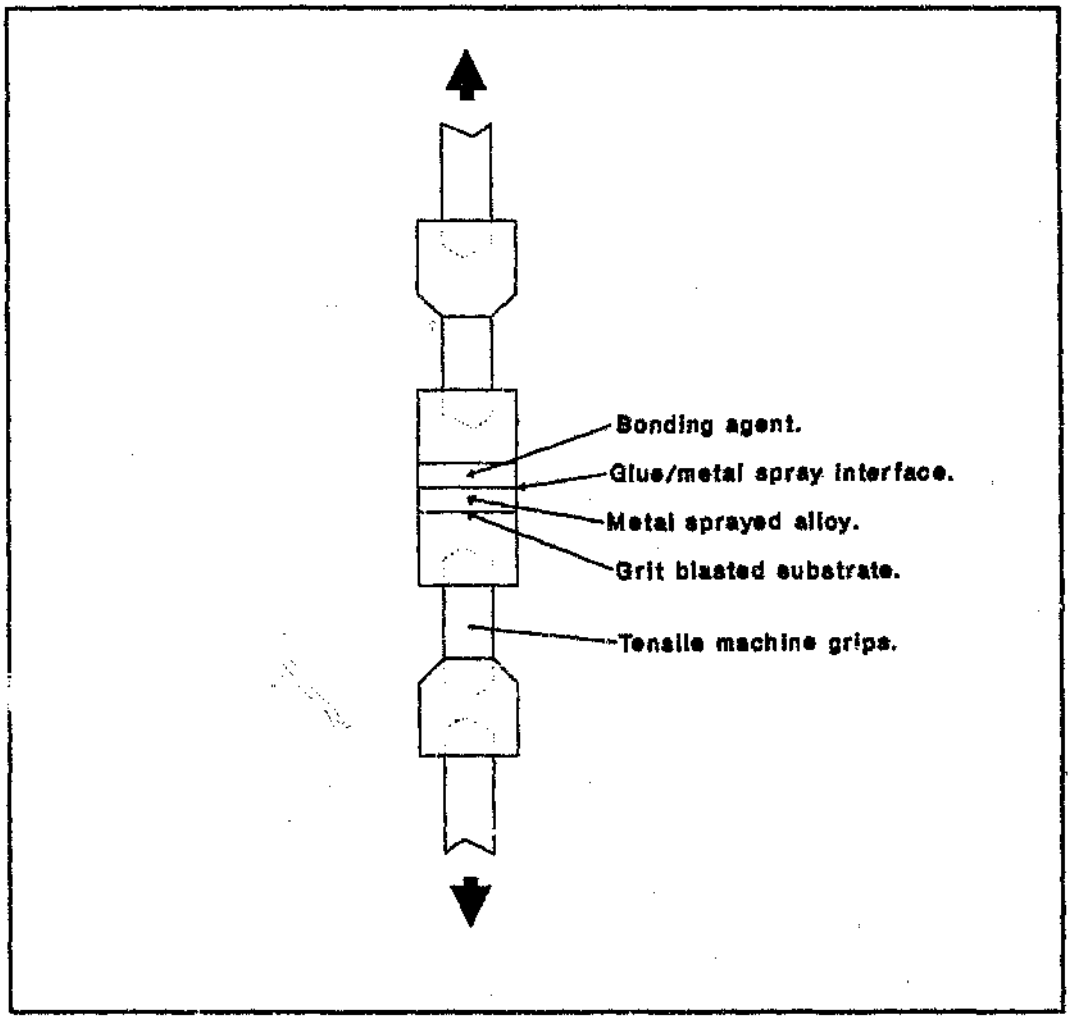


Figure 30 : The tensile test rig for testing coating adhesion.

The essential requirements of the bonding agent is that it has greater adherence to the loading fixture and the sprayed metal than the sprayed metal has to the substrate. ARALDITE epoxy was used for this purpose.

All the tensile testing was carried out using a CLOCKHOUSE INSTRUMENT COMPANY MODEL A12 tensile testing machine.

3.8 Coating Thickness Measurements

An ELCOMETER 300 coating thickness gauge was used to determine the average thicknesses of the metal sprayed coatings. The purpose of these measurements was not only to measure the film thickness, but also to ensure that there was no great variation across a specimen surface or from specimen to specimen.

3.9 Scanning Electron Microscopy

Samples from electrochemical tests, as well as from other corrosion testing, were examined under the SEM (a JEOL GSM-840). Before the corroded samples were evaluated, they were first cleaned to remove the corrosion products. The samples were then washed off with alcohol, dried and mounted into brass holders using a graphite/alcohol suspension.

Results and Discussion

4.1 Analysis of the Metal Spray Wires

As was previously discussed (section 2.5.7.1 of Literature Review), the purity of aluminium used for metal spray purposes is considered of critical importance. The feedstock prior to melting and alloying was thus analysed, and the composition given in the table below.

Table 7 : Analysis of the "pig" aluminium used as the basis raw material.

Sample	Si	Fe	Cu	Mn	Mg	Cr	Zn	In	Pb	Sn	Ti
"Pure" Al	.04	.046	.001	.004	.001	.001	.003	.000	.001	.000	.002

Further analyses were then carried out after the desired alloys had been cast. The column on the left of the table below shows the primary alloy compositions aimed for and the other columns the actual values achieved.

Table 8 : Analysis of the spray wire alloys.

Sample	Si	Fe	Cu	Mn	Mg	Cr	Zn	In	Pb	Sn	Ti
Pure Al	.03	.03	.000	.001	.002	.000	.002	.000	.002	.001	.008
Al 4.5%Zn	.03	.04	.002	.003	.005	.000	4.40	.000	.001	.054	.008
Al 4.5%Zn 160ppm In	.03	.05	.002	.003	.002	.001	4.45	.016	.001	.053	.008
Al 8%Zn	.04	.06	.002	.003	.003	.002	7.87	.000	.001	.054	.006
Al 12%Zn	.05	.04	.000	.000	.002	.001	12.6	.000	.000	.000	.008

The low impurity levels and roughly correct alloy additions confirmed the suitability of the above compounds.

4.2 Analysis of the Substrate Alloys

Prior to the application of the metal sprayed coatings the two aluminium and the mild steel alloys were analysed to ensure their conformity to the specified compositions.

Table 9 : Analysis of the aluminium substrate alloys.

Sample	Si	Fe	Cu	Mn	Mg	Cr	Zn	In	Pb	Ti
5083	.17	.33	.028	.76	4.39	.080	.024	.017	.002	.030
6261	.66	.25	.40	.28	.71	.019	.023	.024	.020	.021

Table 10 : Analysis of the mild steel substrate alloy.

Sample	C	Mn	S	P	Si	Cr	Mb	Ni	Cu	Al	V
Mild steel	.08	.27	.021	.007	<.01	.07	.07	.05	<.01	<.01	<.01

The imported metal matrix composite composed an AA6061 aluminium matrix impregnated with 10% alumina particles of between 15 and 20 micron in diameter.

4.3 Water Analysis

The principal waters to be used were analysed prior to usage to ensure, once again, that they had the correct make-up. The four waters labelled A to D in the table were made according to the specifications listed in section 3.3 of the experimental procedure. The important chemical constituents of each water are the following :

Water A : Aimed for 1000 ppm Cl^- and 1000ppm SO_4^{2-}.
Water B : Aimed for 2000 ppm Cl^- and 500ppm SO_4^{2-}.
Water C : Aimed for 500ppm Cl^- and 2000 ppm SO_4^{2-}.
Water D : Johannesburg potable water used in making up the other three waters.

Table 11 : Test water analysis.

Sample Marks	Water A	Water B	Water C	Water D
pH value	7.84	7.87	7.6	7.86
Conductivity, mS/m	641	896	462	33.2
Tot. dissolved solids	4728	5064	4488	304
Tot. alkalinity as $CaCO_3$	112	112	108	96
Ca. hardness as $CaCO_3$	804	390	1134	62
Mg. hardness as $CaCO_3$	280	144	506	40
Sodium, Na	865	1320	454	22
Potassium, K	227	123	205	8.2
Bicarbonate, HCO_3	137	137	132	117
Carbonate, CO_3	nil	nil	nil	nil
Chloride, Cl	1321	2093	610	26
Sulphate, SO_4	1128	558	1771	31
Nitrate, NO_3	311	281	337	0.8
Nitrite, as N	7.1	7.7	7.2	<0.1
Free and saline ammonia	50	54	52	3.1
Total iron, Fe	2.1	2.1	2.0	0.04

Values expressed in mg/l where applicable.

Some variations from the aim points are recorded.

4.4 Electrochemical Test Work

4.4.1 Potentiodynamic Trials

Each coating/substrate combination was systematically tested in every water. A minimum of three tests were conducted per combination to ensure the accuracy of the results. In the event of a lack of reproducibility, a further two tests were carried out. Due to the nature of the coatings, (ie. porosity, uncontrolled oxide levels, etc.), discrepancies were often encountered. This meant that once five trials had been done, if consistent curves were still not achieved, the average had to be taken as representative of the alloy.

4.4.1.1 Performance of the Coatings

The relative performance of each coating is best related back directly to the actual potentiodynamic plot. Figures 31, 32 and 33 on the following pages illustrate the results achieved from all the tests carried out in water A, the synthetic mine water with roughly 1000ppm sulphates and chlorides. Although the other waters gave rise to different scans, the trends established were the same.

The superimposed scans clearly show the effect of the zinc additions on both the corrosion potentials and current densities of the coating alloys. Zinc, being more anodic than aluminium, has the effect of lowering the corrosion potential of the alloy as increasing percentages are added. The addition of 4.5% zinc to the pure aluminium consistently lowers the potential by between 100 and 300 millivolts, the largest difference encountered.

A small passive region, of typically between 300 and 600 mV, appears in all the plots. This shows that the corrosion does not take place primarily as a result of the dissolution of zinc-rich areas. The reason for this is that zinc does not exhibit much of a passive region, as can be seen in figure below, since its corrosion product is largely soluble in water. This is a favourable occurrence as extensive loss of zinc from the coating would reduce its effectiveness as an anodic barrier considerably.

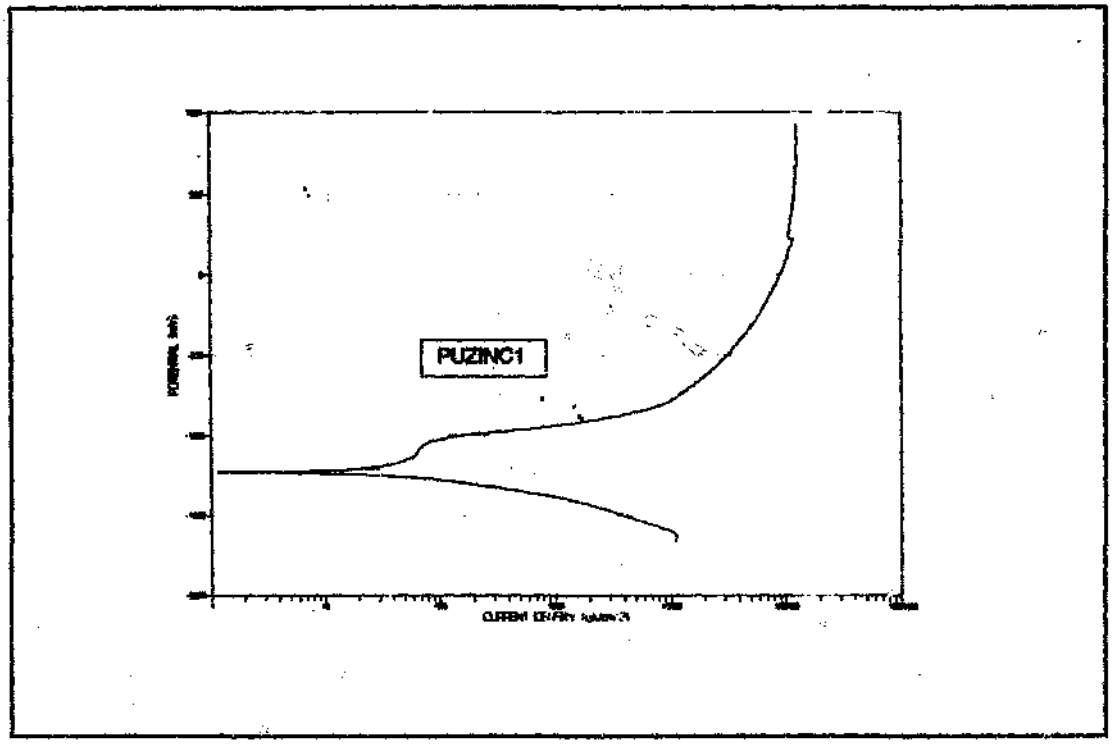
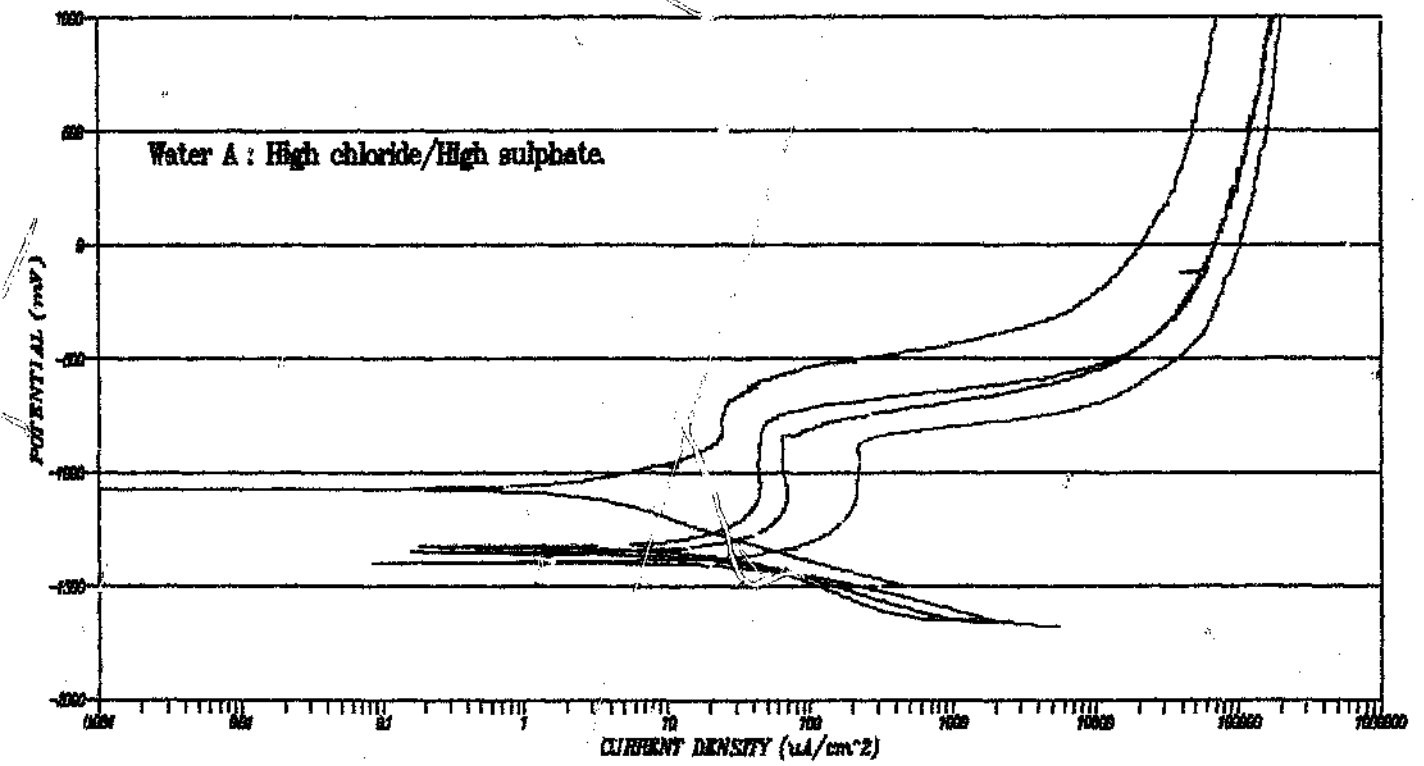


Figure 34 : Potentiodynamic plot of pure zinc in water A.

The effect of the small indium addition (160ppm) is also clearly illustrated by the potentiodynamic plots. For the same level of zinc, the indium decreases the corrosion potential and increases the current density. This results due to its dissolution in the chloride-containing environment which, although promoting corrosion, is in more generalised rather than localised attack.

Figure 31.

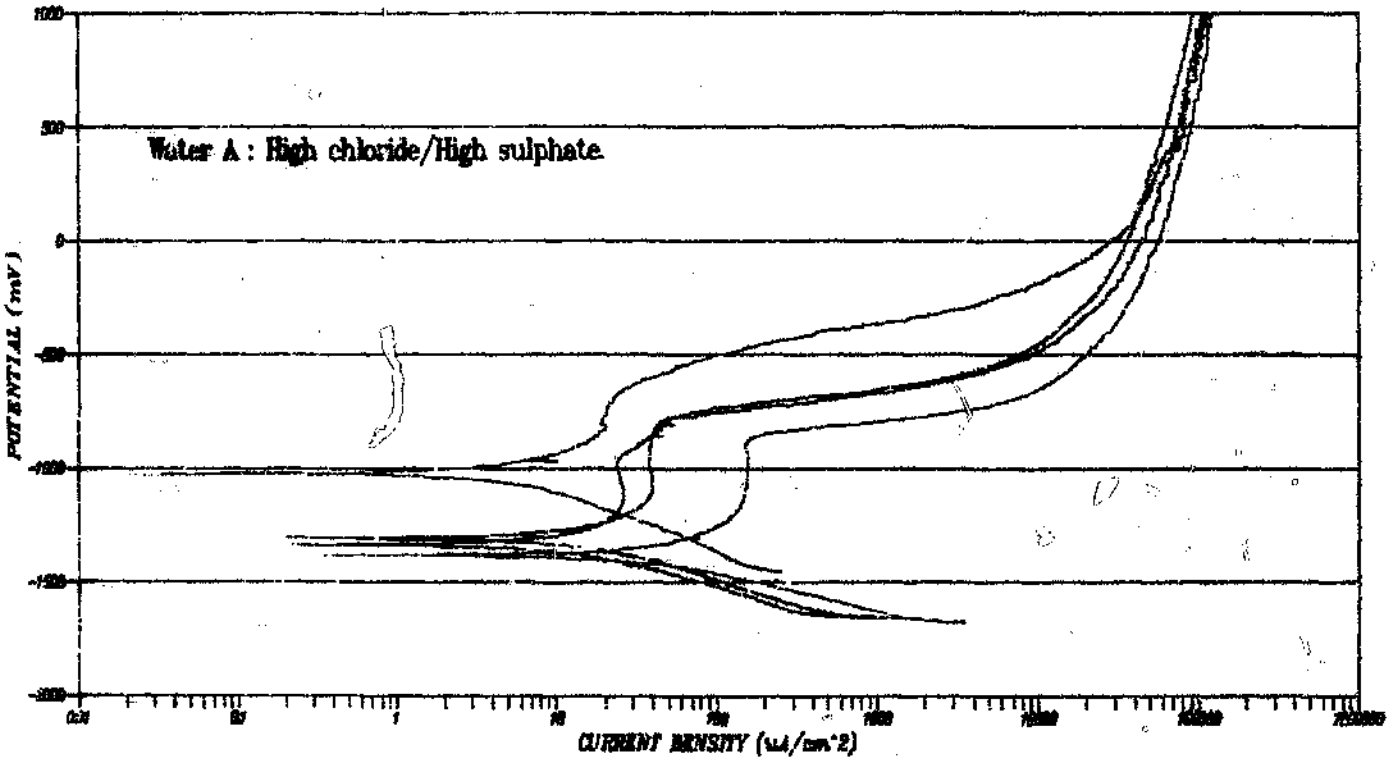
SUPERIMPOSED POTENTIODYNAMIC SCANS.
Coated AA5083 aluminium alloy.



Pure aluminium. — Al/4.5% Zinc. — Al/4.5% Zinc / In.
Al/8% Zinc. — Al/12% Zinc.

Figure 32.

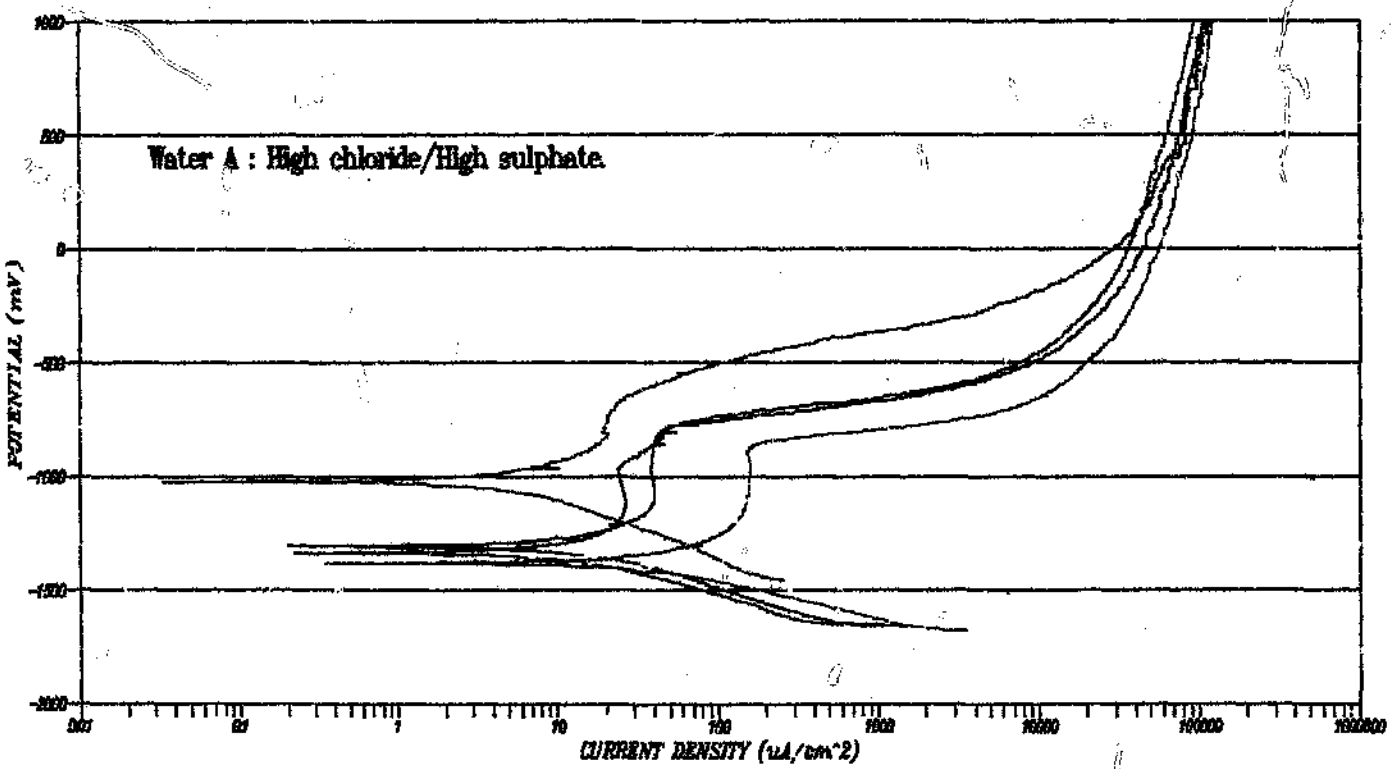
SUPERIMPOSED POTENTIODYNAMIC SCANS.
Coated AA6261 aluminium alloy.



—— Pure aluminium.	—— Al/4.5% Zinc.	—— Al/4.5% Zinc / In.
Al/8% Zinc.	—— Al/12% Zinc.	

Figure 32.

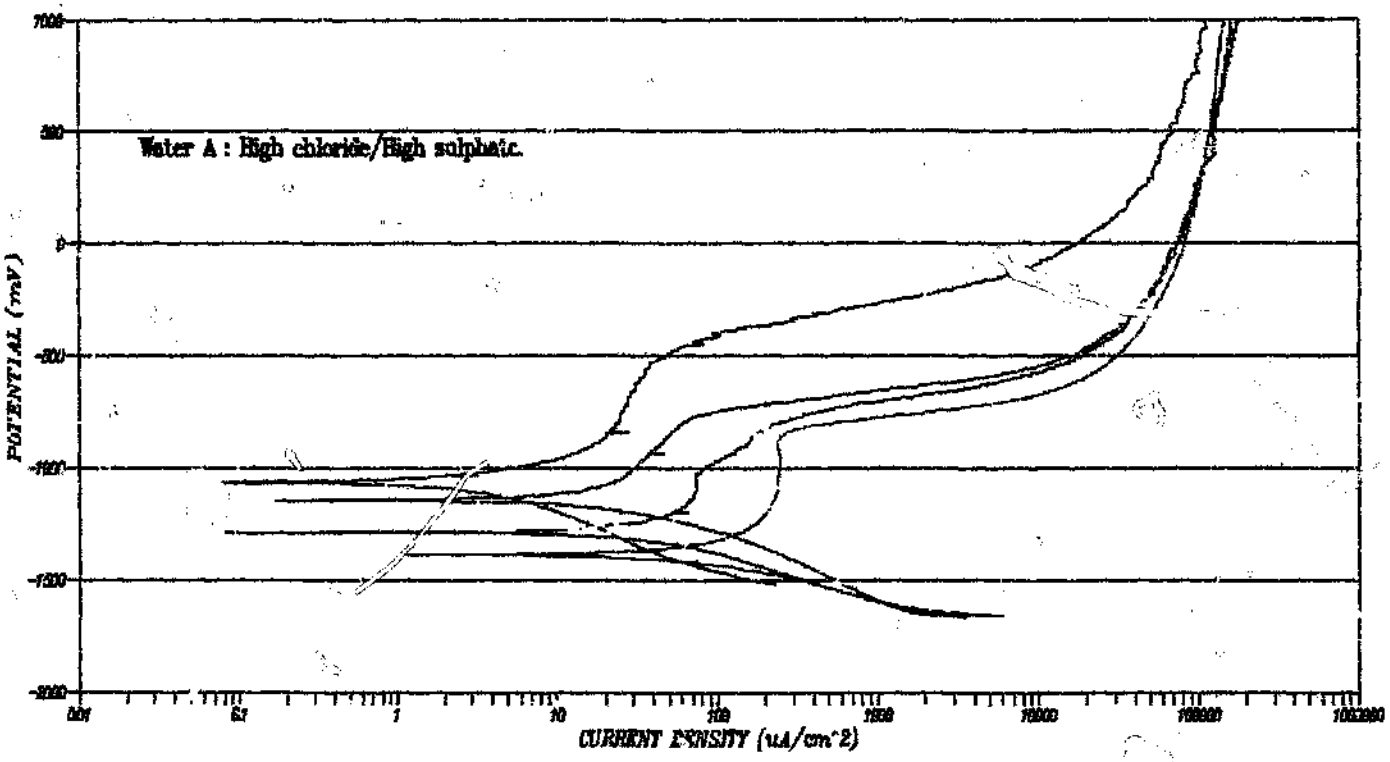
SUPERIMPOSED POTENTIODYNAMIC SCANS.
Coated AA6261 aluminium alloy.



Pure aluminium.	Al/4.5% Zinc.	Al/4.5% Zinc / In.
Al/8% Zinc.	Al/12% Zinc.	

Figure : 33.

SUPERIMPOSED POTENTIODYNAMIC SCANS.
Coated mild steel.



Pure aluminium.	Al/4.5% Zinc.	Al/4.5% Zinc / In.
Al/8% Zinc.	Al/12% Zinc.	

4.4.1.2 Performance of the Substrate Alloys

Table 12 : Corrosion potentials and corrosion rates of alloys in water A.

Alloy.	Corrosion potential mV.	Corrosion rate mm/year.
Pure aluminium	-1092	0.87
Pure zinc	-1219	5.76
AA5083	-1166	1.66
AA6261	-1128	0.93
Mild steel	-736	7.9

Once again the above table illustrates results achieved from tests done in water A. The trends established are the same for all the waters.

When considering the above table, it should be borne in mind that the AA6261, AA5083 and the mild steel will be galvanically coupled to the previously mentioned coating alloys. The highest potential difference will thus exist between the mild steel and the 12% zinc alloy and the smallest between the AA5083 and the pure aluminium coating. The two aluminium alloys although having similar results do show a small difference, with the AA5083 alloy being slightly more susceptible to corrosion.

4.4.1.3 Corrosivity of the Waters

(i) The Synthetic Mine Waters

The charts on the following pages clearly illustrate the relative corrosivities of each of the synthetic mine waters. Water A (1000ppm Cl^- and 1000ppm SO_4^{2-}) is consistently the most corrosive, with the corrosion potentials of the coating alloys generally being the lowest in this water. The high chloride addition in water B also clearly makes it more corrosive than water C which has 2000ppm sulphate, a factor which is notably clear in the aluminium/indium coating.

The bar charts further substantiate the results attained from the potentiodynamic plots, as the increased zinc additions steadily decrease the corrosion potentials.

(ii) Tap and Sea Water

As was expected the synthetic sea water proved to be far more corrosive than the tap water. In fact the salt additions made the water the most corrosive of all, with some of the corrosion potentials even dropping below -1400 mV.

4.4.1.4 Coating/Substrate Combined Performances

Table 14 lists the exact corrosion potentials obtained for each coating/substrate combination in every synthetic mine water. No consistent changes in potential were obtained by altering the substrate. Thus it is not possible, using potentiodynamic tests, to establish the effects of the various substrates on the performance of the coating.

Table 13 : A comparison of the corrosion potentials of the various coating/substrate combinations in the synthetic mine waters.

Substrate Alloys	Water Types	Corrosion potentials of the coating alloys. (mV.)				
		Pu.Al.	*Al/4.5Zn.*	*Al/In.*	*Al/8Zn.*	*Al/12Zn.*
AA5083	Water A	-1072	-1329	-1354	-1347	-1395
	Water B	-1106	-1140	-1265	-1312	-1291
	Water C	-909	-1099	-1190	-1290	-1367
AA6261	Water A	-1023	-1307	-1337	-1367	-1383
	Water B	-953	-1281	-1361	-1375	-1388
	Water C	-1030	-1151	-1106	-1317	-1329
Mild Steel.	Water A	-1062	-1143	-1280	-1277	-1388
	Water B	-1057	-1132	-1207	-1222	-1350
	Water C	-986	-1034	-1107	-1221	-1304

The similarity of the above figures was not unexpected as the metal spraying process, although creating a coating with some porosity, does distribute the alloy evenly over the substrate.

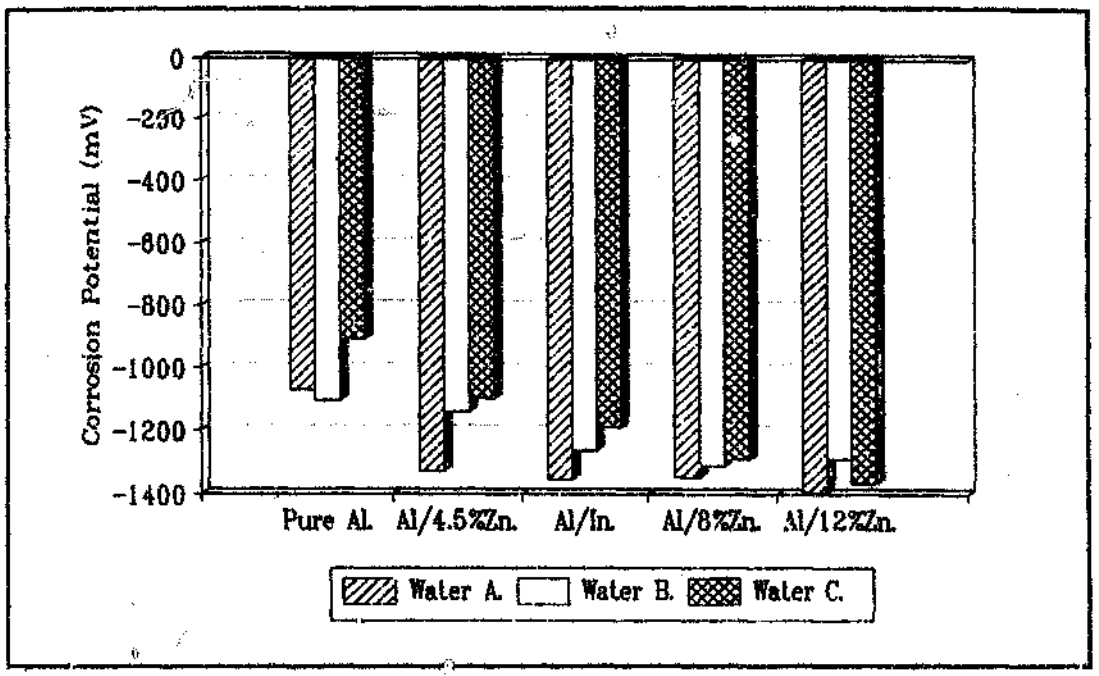


Figure 35 : AA5083 metal sprayed samples. Results from the synthetic mine water trials.

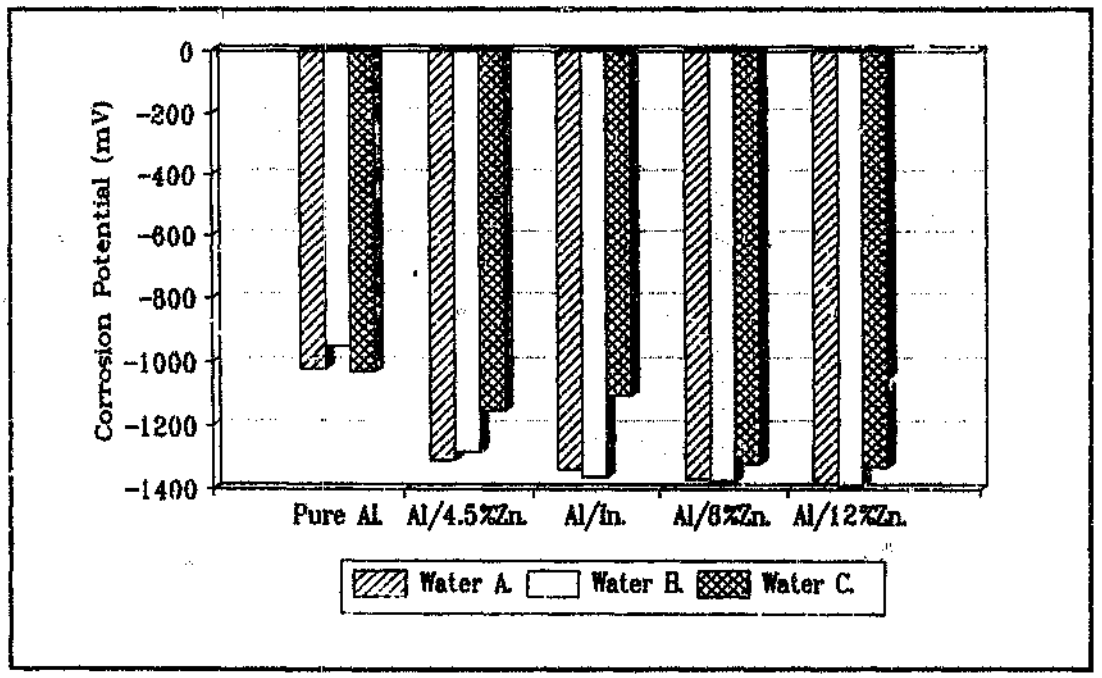


Figure 36 : AA6261 metal sprayed samples. Results from the synthetic mine water trials.

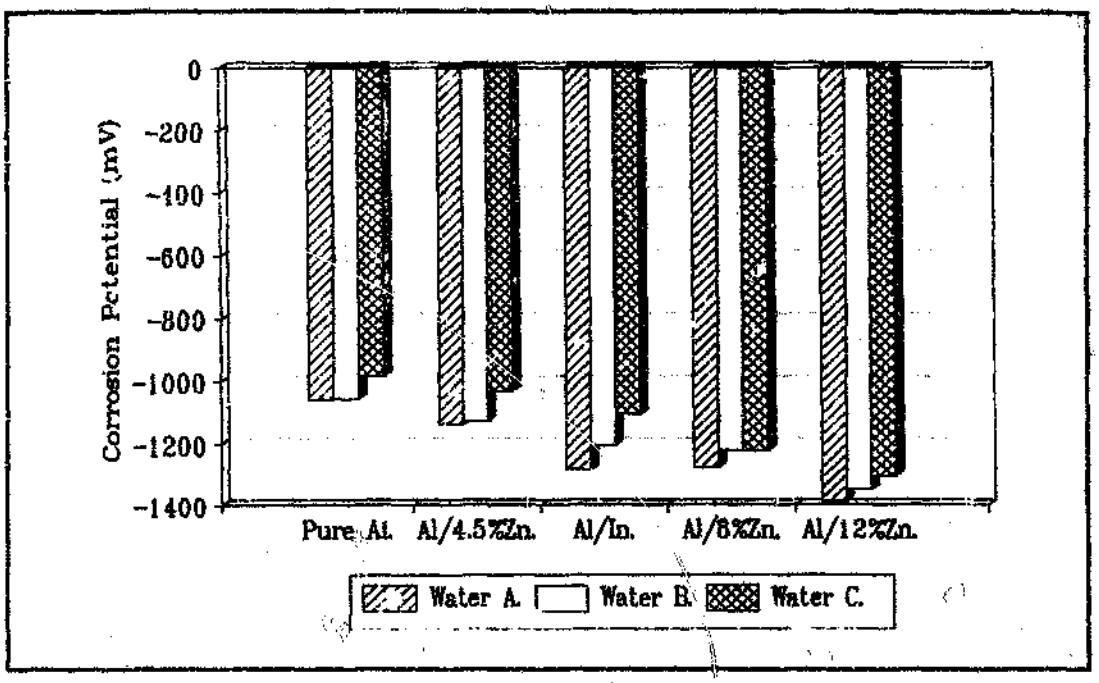


Figure 37 : Mild steel metal sprayed samples. Results from the synthetic mine water trials.

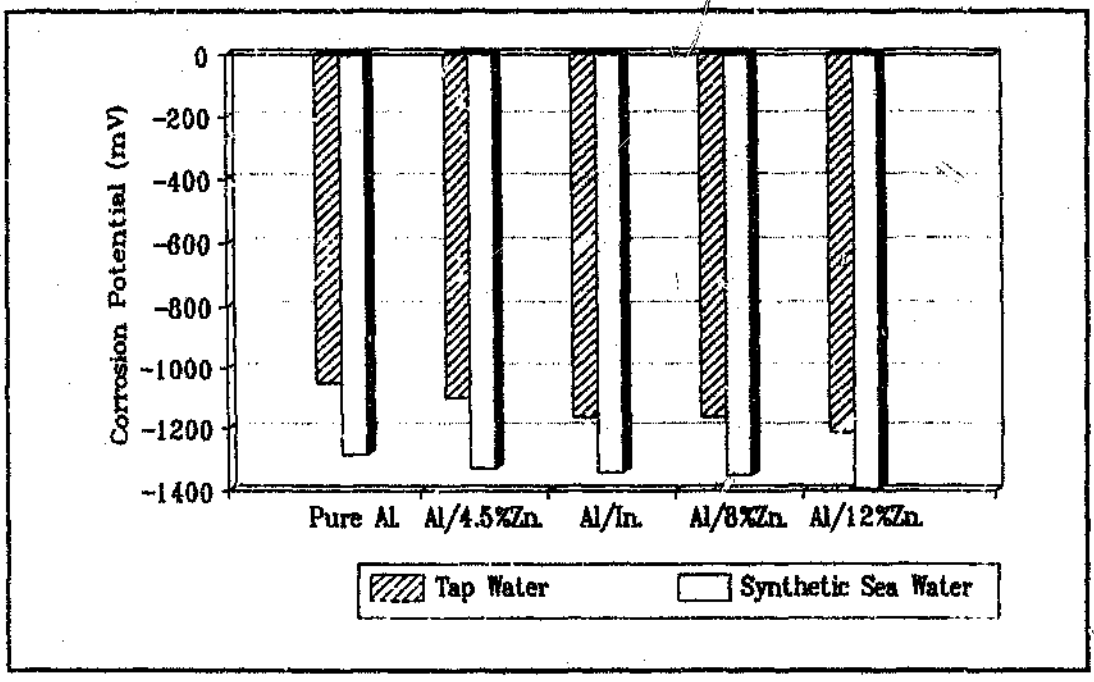


Figure 38 : AA5083 metal sprayed samples. Results from the synthetic sea water and tap water trials.

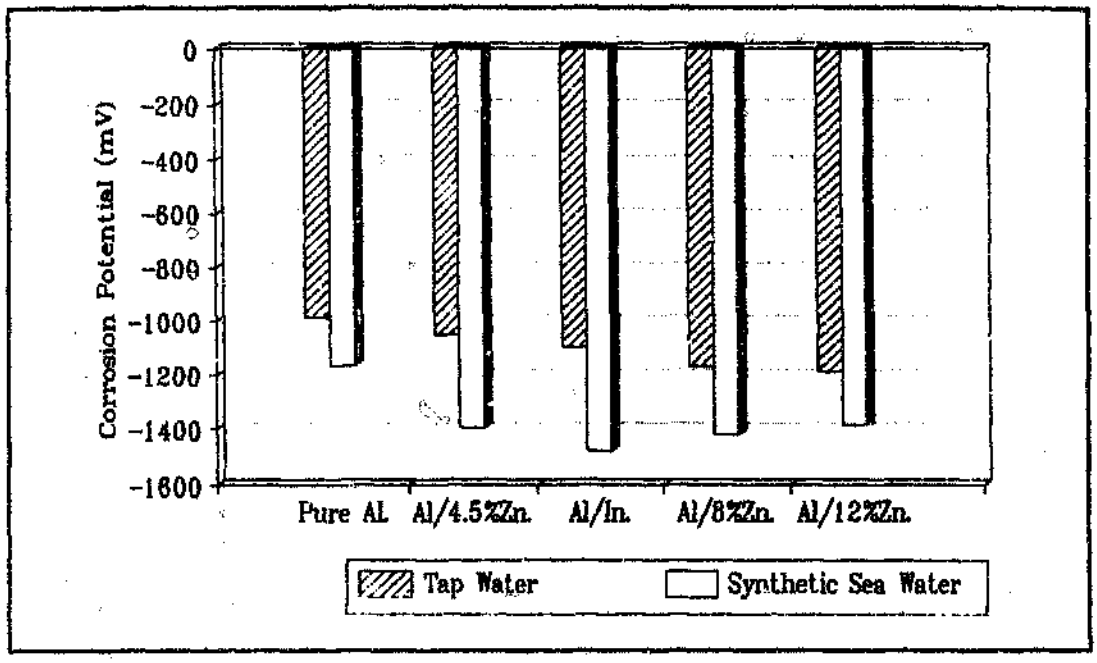


Figure 39 : AA6261 samples. Results from the synthetic sea water and tap water trials.

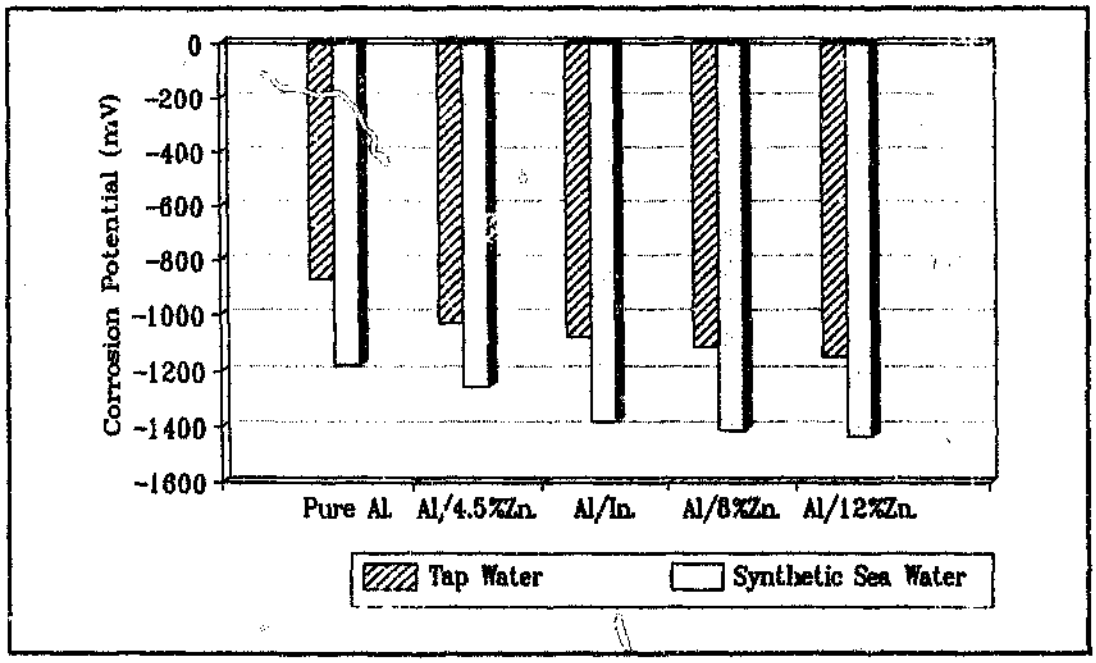


Figure 40 : AA5083 metal sprayed samples. Results from the synthetic sea water and tap water trials.

4.4.1.5 Summary of the Results Achieved

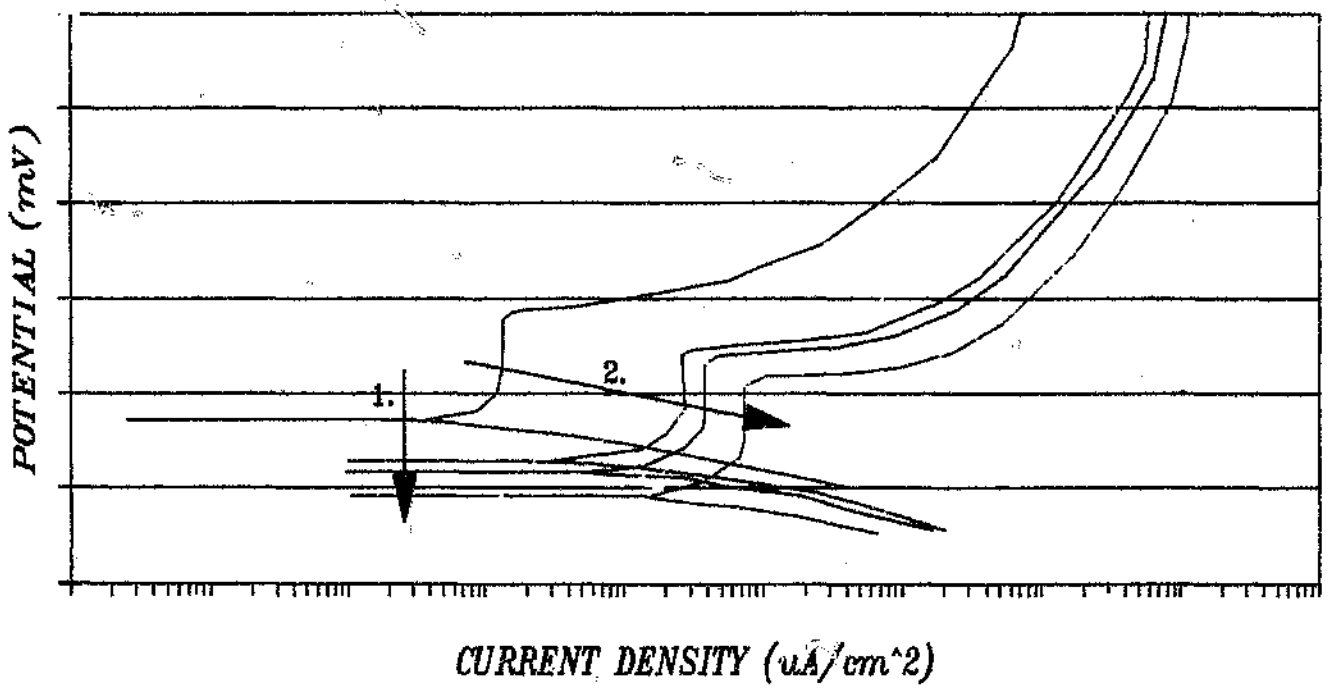
Figure 41 illustrates the trends established in all the potentiodynamic work. Arrow 1 shows the decreasing corrosion potentials as the percentage zinc is increased and arrow 2 the increasing corrosion current.

These curves clearly rank the coatings in terms of their relative anodic behaviour but they do not indicate which will behave best in practice.

Figure 41.

POTENTIODYNAMIC SCANS.

Trends established from the trials.



Pure aluminium. Al/4.5% Zinc. Al/4.5% Zinc / In.
Al/8% Zinc. Al/12% Zinc.

4.4.2 E_{corr} versus Time Trials

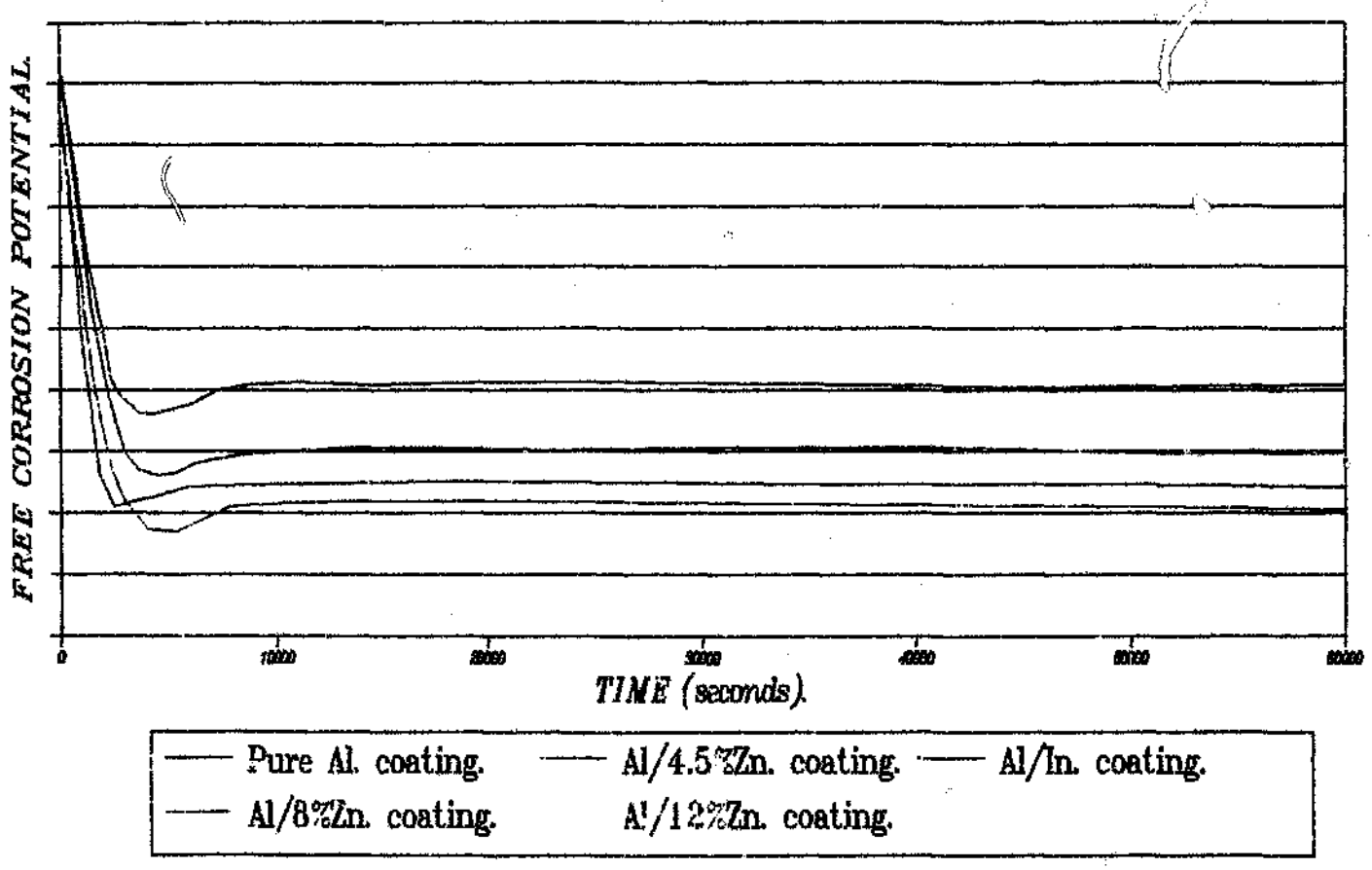
The purpose of these trials was not merely to establish the free corrosion potentials of the coatings but also to determine the time taken for the alloy to stabilize at this potential. The trends established from this work are shown in figure 42.

As the potentiodynamic trials demonstrated the corrosion potential decreases as the percentage zinc is increased. The plots also show how the coating starts out at a potential far more cathodic than its stable free corrosion potential, a factor that can be attributed to the lack of stability of the oxide film. The most important aspect of these plots, however, is that the indium containing alloy took roughly half the time to stabilize than the rest of the coating/substrate combinations. This can probably be attributed to the rapid dissolution and subsequent precipitation of the active indium ions. Most of the coatings took around 10000 seconds to reach a stable value, while the indium containing coatings took around 5000 seconds. This has the advantage that even if the coating is initially anodic to the substrate, which is the opposite to the desired scenario, it will soon drop down in potential to its more anodic potential.This is of obvious importance in extremely corrosive environments.

Figure 42.

Ecorr VERSUS TIME SCANS.

Trends applicable to all water types.



4.5 Accelerated Corrosion Testing

4.5.1 Salt Spray Testing

4.5.1.1 Synthetic Mine Water Trial

Although not an ASTM test, the best way of assessing the behaviour of all the coating/substrate combinations in actual underground mining applications was thought to be in a synthetic mine water. Thus, the high chloride, high sulphate water was selected to be used in the salt spray cabinet.

Within 100 hours the uncoated mild steel had corroded severely, with the entire surface being covered in a thick layer of brown rust. The other samples, although hardly corroded, had become discoloured. This brown discolouration was probably hydrated iron oxide settling out from the water vapour, resulting from the corrosion of the mild steel. Unlike the steel panels, the uncoated aluminium alloys, although slightly tarnished, did not show any visible signs of corrosion after 100 hours of exposure.

The coupons were monitored as the trial continued, not only to determine the extent of the corrosion but also to try and rank the various coating/substrate combinations in this specific environment. After 1000 hours it was decided to stop the trial as differences in behaviour were not emerging, especially with regard the coated aluminium samples. Photographs of representative samples after the completion of the trial period can be seen on the following pages.

A white corrosion product started to appear on the coupon surfaces as the trial continued. As can be seen in the photographs this corrosion product is especially abundant around the defects purposely introduced into the coated mild steel samples. This heavy build-up is caused by the coating sacrificially protecting the substrate, as it was designed to do. Close-ups of this phenomenon are shown in the photographs below.

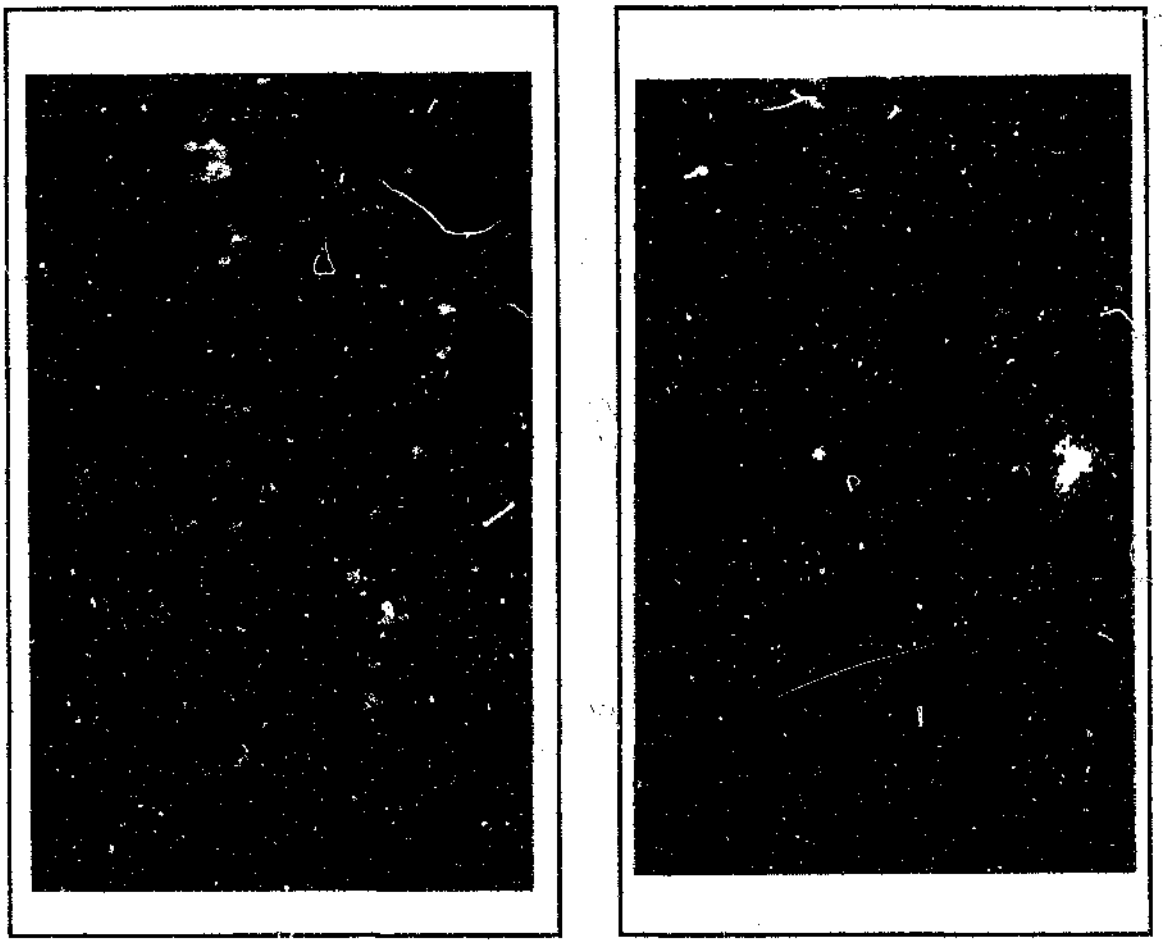


Figure 43 : Close-ups of two corroded salt spray samples.

These photographs clearly illustrate the following :

(i) Firstly, the exposed areas, although showing signs of rust, are well protected especially relative to the uncoated samples.

(ii) Secondly, as the size of the defect is increased so does the effectiveness of the protection decreases. The photographs show how the smallest holes are by far the least corroded.

Thus, the sprayed aluminium coatings clearly protect the mild steel substrates by sacrificially corroding at regions where the substrate is exposed to the corrosive environment.

The results achieved for the coated aluminium coupons are not nearly as clear. The reason for this can be attributed to the higher corrosion resistance of the substrate aluminium alloys in comparison with steel. Hence the amount of sacrificial protection required, relative to the steel substrates, is a lot less, resulting in the formation of smaller amounts of corrosion product. In fact from these trials it is not completely clear whether or not the coatings are anodic to the aluminium substrates, although discolouration in the centre of some of the larger controlled defects does suggest it.

The main criteria by which all the panels were evaluated were firstly the condition of the substrate material within the controlled defects, and secondly the amount of corrosion product found on the surface. The most important coupons were thus the mild steel ones which, as previously discussed, exhibited the most corrosion. The photographs show how the higher zinc-containing coatings all have more corrosion product on them than those with small or no zinc additions. This fact does not however make these coatings any worse than those without zinc. This is both because the corrosion product merely indicates that sacrificial protection is required by the substrate and is so supplied by the coating, and the finding that the corrosion product will block the pores, thus actually preventing further corrosion as it separates the substrate from the environment. Thus one could deduce that an increase in the zinc content would reduce the life of the coating if intensive sacrificial protection was required, as it would corrode away sooner. Conversely, if less zinc was present the coating may not be able to supply sufficient anodic current under more severe corrosion conditions and hence not protect exposed areas satisfactorily. The above conclusions all revolve around the fact that the addition of zinc makes the coating more anodic to a given substrate, a fact that was proven in the electrochemical test work.

There thus exists a balance between zinc additions and substrate alloy composition that will provide the optimum protection in a specific environment. This balance would obviously be upset if any of the above three constants, ie. the coating, substrate or environment, were altered. Furthermore the suitability of a specific coating would naturally depend upon the size of defect in any coating. This is important as the larger the holiday, the greater the "throwing power" needed to protect exposed areas furthest from the coating, and hence the more anodic

the coating would have to be.

When considering this first salt spray trial it is believed that a pure aluminium or a low zinc coating would be the optimum for the metal spraying of both the aluminium alloys. The reason for this selection is that although the environment is highly corrosive, it is not corrosive enough to warrant any greater anodic current, due to the intrinsic corrosion resistance of the aluminium alloys. With regard the steel substrates however, a higher zinc addition, preferably in excess of 12% is recommended. The low corrosion resistance of the steel and thus the accompanying high degree of sacrificial protection required justifies this selection.

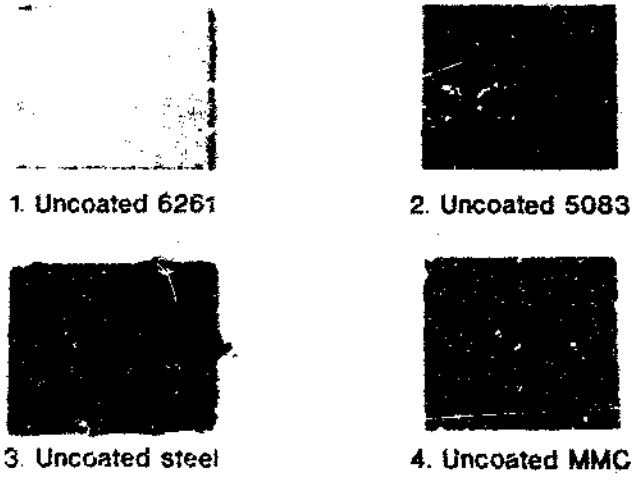


Figure 44 : High $SO_4^{=}$/high Cl^- salt spray coupons.

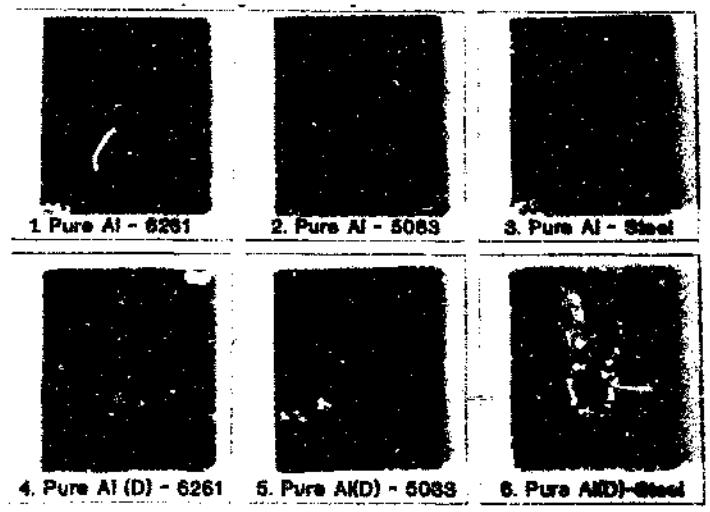


Figure 45 : High $SO_4^{=}$/high Cl^- salt spray coupons.

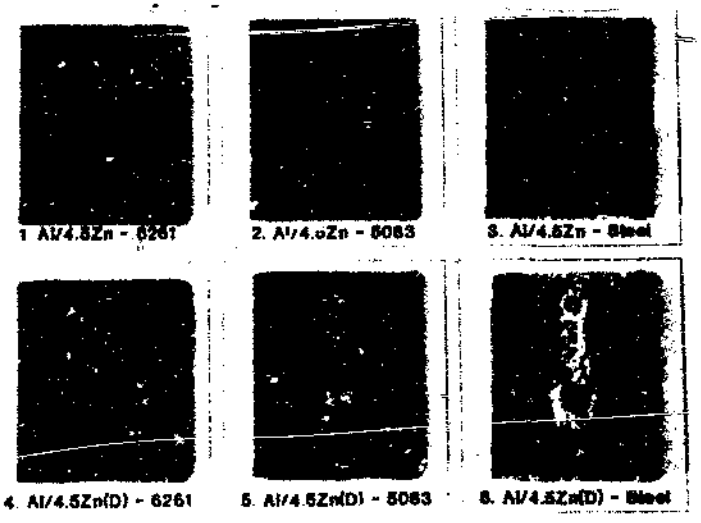


Figure 46 : High $SO_4^{=}$/high Cl^- salt spray coupons.

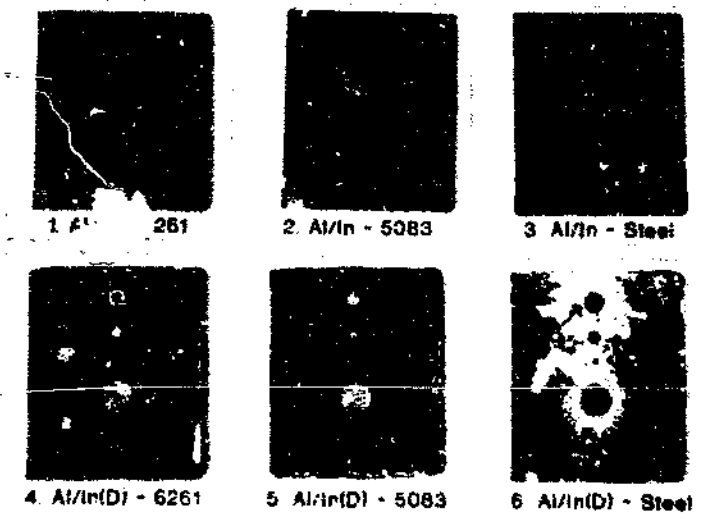


Figure 47 : High $SO_4^{=}$/high Cl^- salt spray coupons.

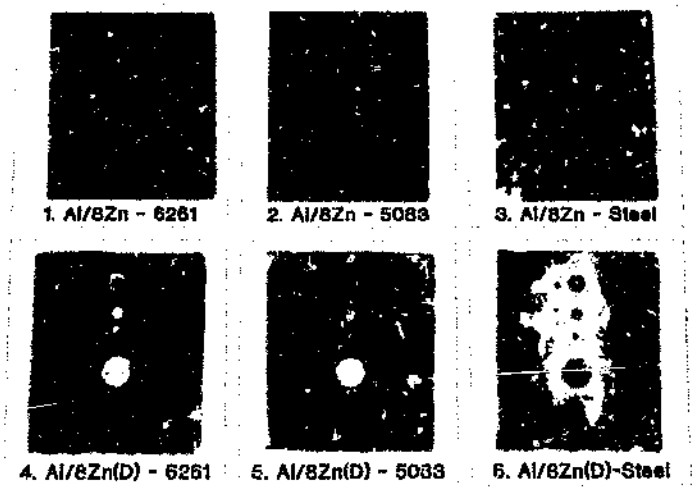


Figure 48 : High $SO_4^{=}$/high Cl^- salt spray coupons.

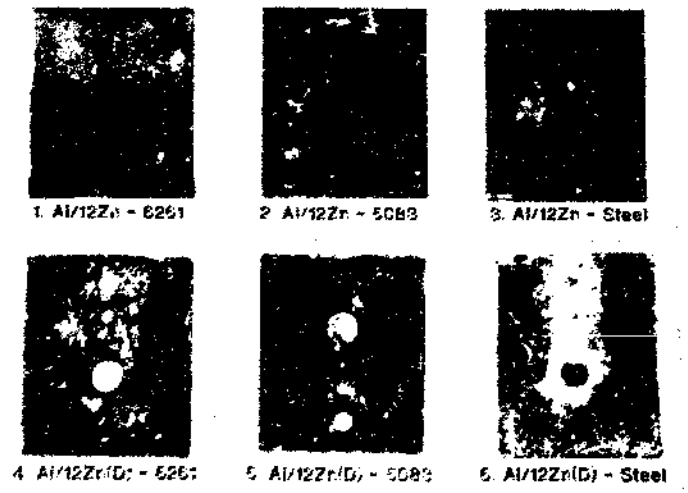


Figure 49 : High $SO_4^{=}$/high Cl^- salt spray coupons.

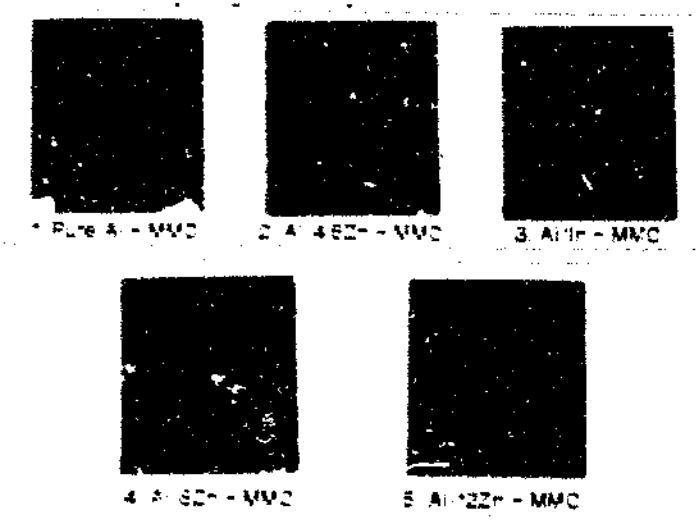


Figure 50 : High $SO_4^{=}$/high Cl^- salt spray coupons.

4.5.1.2 Synthetic Sea Water Trial

The photographs on the following pages illustrate the appearances of representative samples achieved from the synthetic salt water trial after the completion of the 1000 hour test.

Because of the difficulty in obtaining differentiation from the previous salt spray trial, it was decided to increase the corrosivity of the environment. A new series of specimens were thus exposed to the standard ASTM salt spray solution.

As in the previous trial, the uncoated mild steel coupons were rapidly corroded. They were thus removed after 100 hours so as to limit their interference on the other samples. The uncoated aluminium alloys started to show signs of pitting, with a noticeable difference between the AA5083 and AA6261 being observed. The ranking of the various uncoated alloys was thus as follows :

1. AA5083 (best)
2. AA6261
3. MMC
4. Mild steel (worst).

The photographs demonstrate clearly that the coated mild steel samples once again showed the far clearer results. As before, the discolouration of all the specimens was thought to be due to the presence of the uncoated steel coupons which, although removed early in the trial, had still corroded severely prior to that. Looking at the damaged specimens it is evident that the coatings are sacrificially protecting the substrates very effectively, even the mild steel still has somewhat of a shine to it. The white corrosion product on the coated steel coupons, as the photographs show, is surrounded by a black band. The photograph below looks more closely at this region.

Figure 51 : Corrosion product on a coated mild steel sample.

The above photograph illustrates clearly how the black beads of liquid surround the white corrosion product band. Since this corrosion product will "grow" outwards as more sacrificial protection is required by the exposed substrate it would appear that the white powder starts off as this hygroscopic black compound. The excellent throwing power of the coating is also evident from the figure above, as even the largest contrived holiday is well protected.

Ranking the performance of the various coating/substrate combinations again revealed that the aluminium substrates performed best with different coatings to the steel substrates. Pure aluminium onto 5083 or 6261 was, unlike the previous trial, not anodic enough as corrosion was observed to be taking place within the larger defects. Thus the addition of 4.5% zinc is considered to be the most favourable option. With regard the steel coated coupons, the large amount of protection required once again explains why the highest zinc coupons yielded the best results.

Figure 52 : Synthetic sea water salt spray coupons.

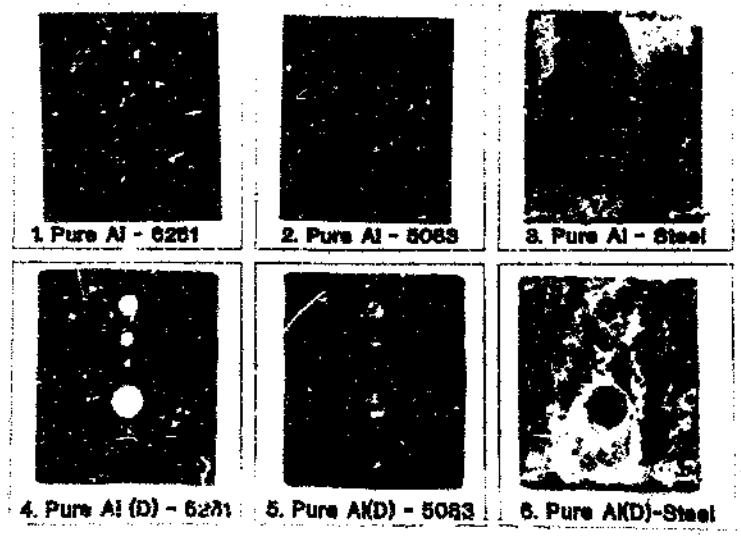


Figure 53 : Synthetic sea water salt spray coupons.

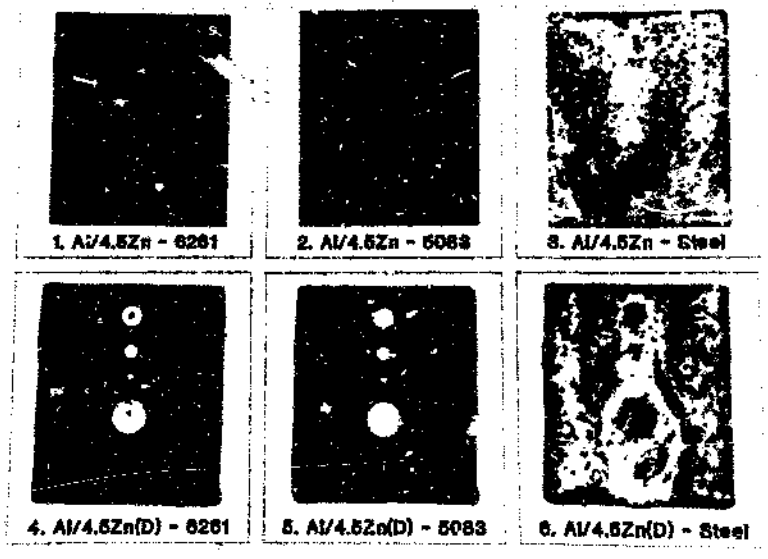


Figure 54 : Synthetic sea water salt spray coupons.

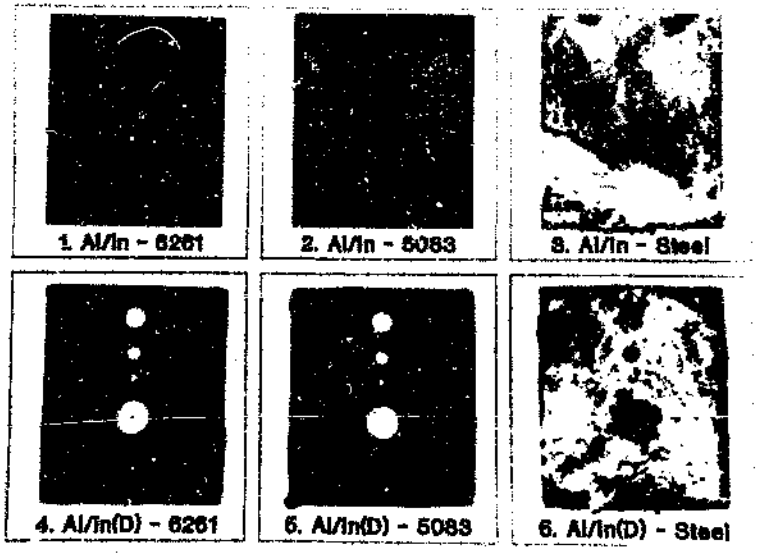


Figure 55 : Synthetic sea water salt spray coupons.

Figure 52 : Synthetic sea water salt spray coupons.

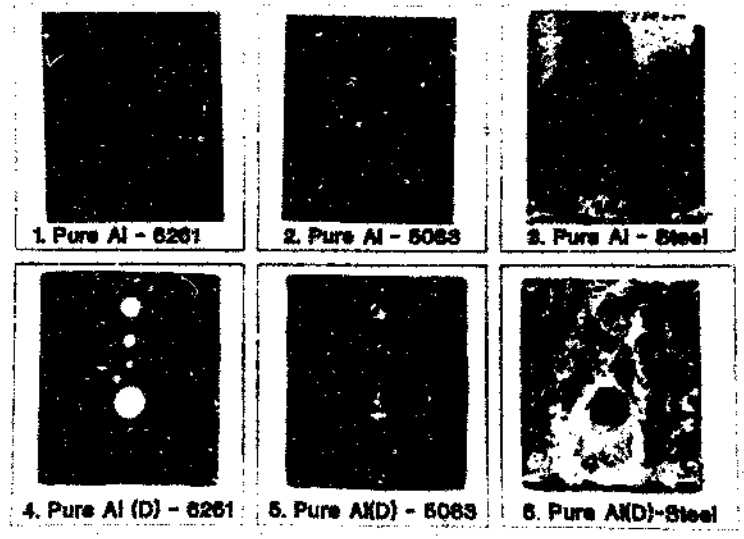


Figure 53 : Synthetic sea water salt spray coupons.

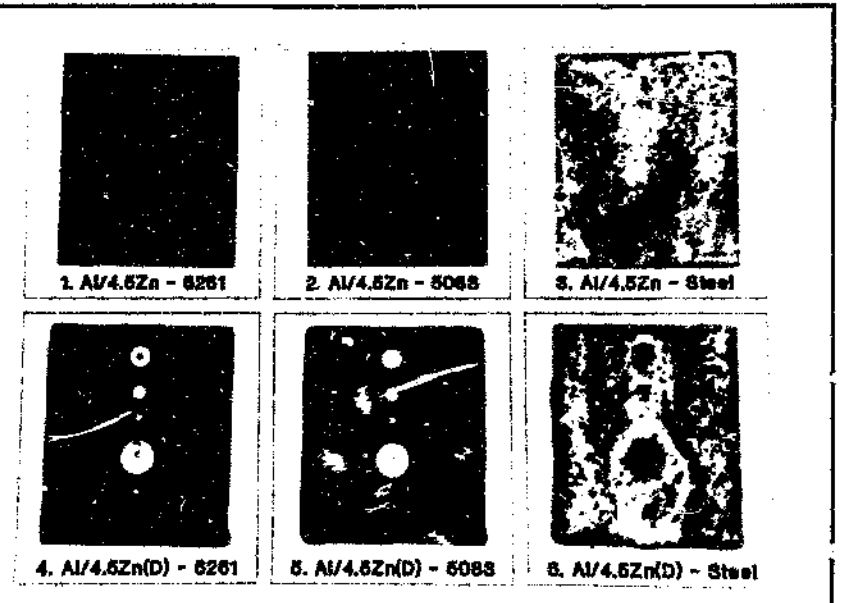


Figure 54 : Synthetic sea water salt spray coupons.

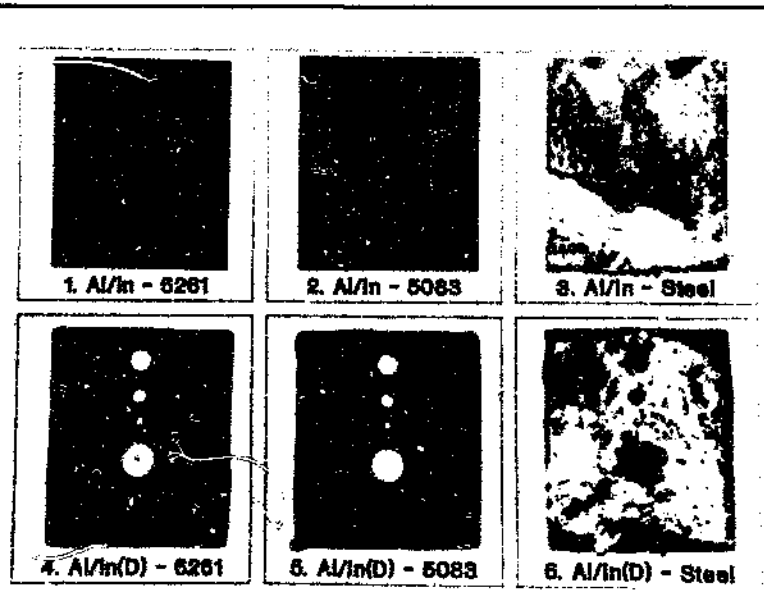


Figure 55 : Synthetic sea water salt spray coupons.

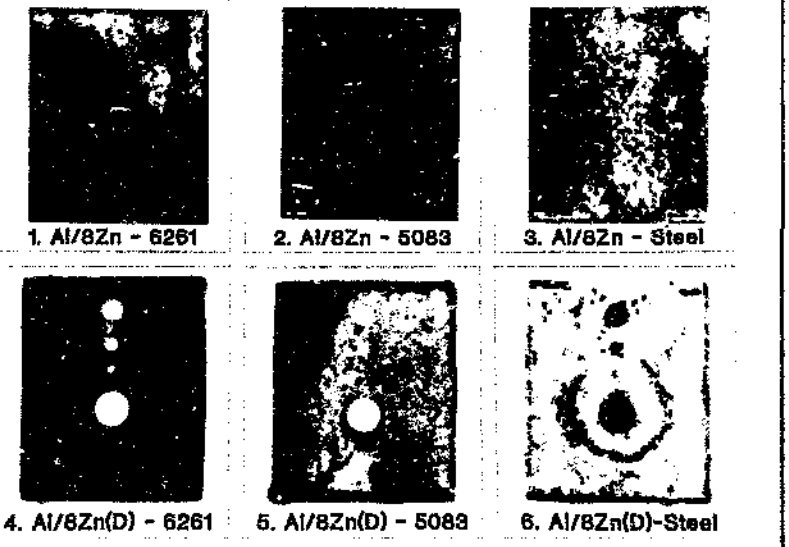


Figure 56 : Synthetic sea water salt spray coupons.

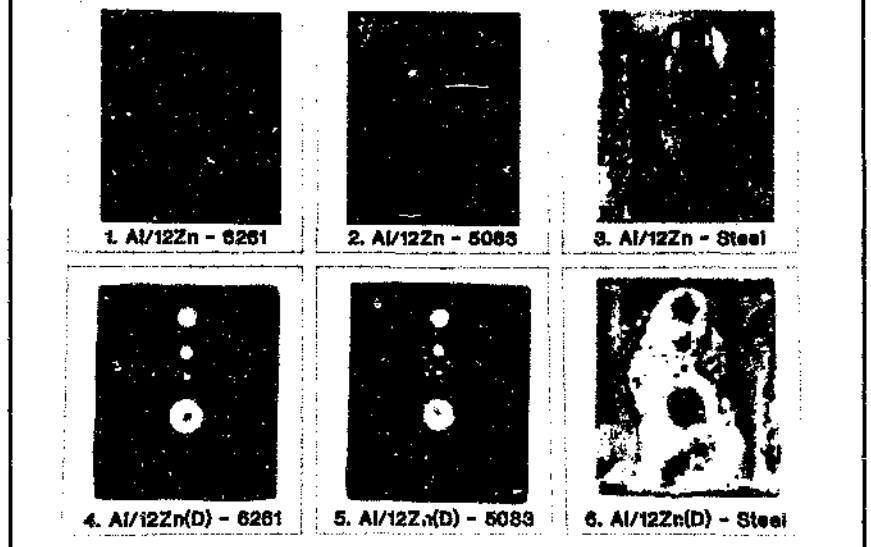


Figure 57 : Synthetic sea water salt spray coupons.

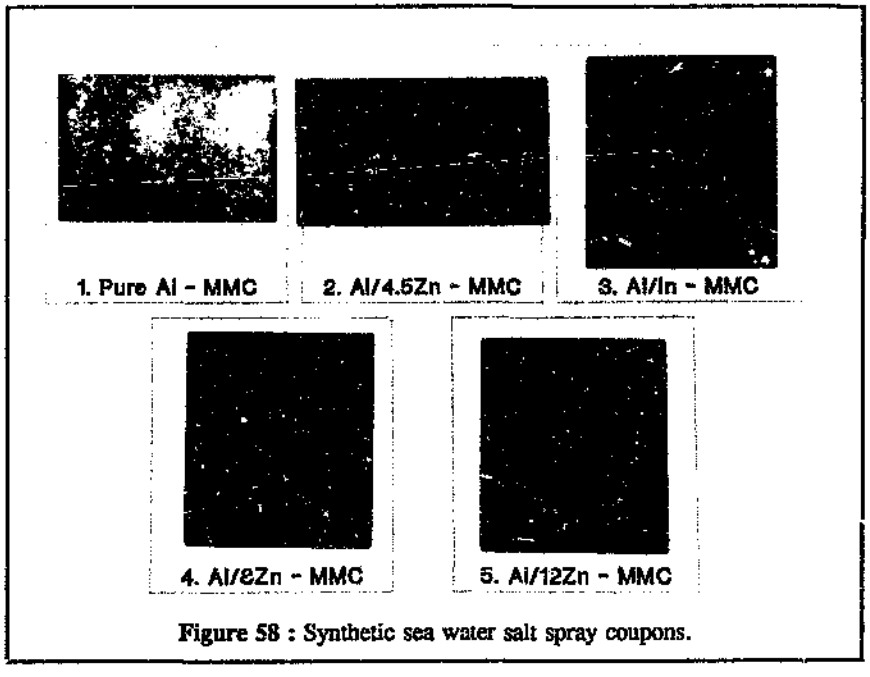


Figure 58 : Synthetic sea water salt spray coupons.

4.5.1.3 Acetic Acid Trial

The ASTM acetic acid test solution is made up by additions of acetic acid to the standard synthetic sea water, in order to bring the pH down to between 3.0 and 3.2. The high chloride concentration, combined with the low pH, makes this the most corrosive of the salt spray solutions used.

The uncoated coupons shown in figure 59 demonstrate the marked difference in behaviour between the AA5083 and AA6261 alloys, with 5083 showing far less corrosion. Of the three samples shown in the photograph the MMC, as expected, has suffered the worst corrosion.

The highly aggressive salt spray environment attacked the coated mild steel specimens vigorously, with the result that the test coupons had to be removed after only 1000 hours. The coated aluminium samples were left in the tank for a further 1000 hours in an attempt to find the optimum combination. Figures 60 and 61 representing the undamaged and damaged coated mild steel coupons respectively show somewhat conflicting results. As the photographs show, an increase in the percentage zinc improves the protective action of the coating. This is expected as the greater the amount of zinc the greater the potential difference between coating and substrate and hence the better the sacrificial protection. The pure aluminium coating however, goes against the trend and out-performs all but the 12% zinc coating. This phenomenon is explained by the fact that the solution is highly corrosive and since the pure aluminium is the least anodic of the coatings it will tend to last the longest. (Although not providing the best protection when compared to the other coatings if they are in good condition.) Thus, the coating performance is affected by two factors, firstly the corrosive nature of the environment and secondly the potential difference between coating and substrate. Clearly, a zinc addition of 4.5%, even in combination with the indium, is not enough to protect the substrate and is also not cathodic enough to last as the pure aluminium coating does.

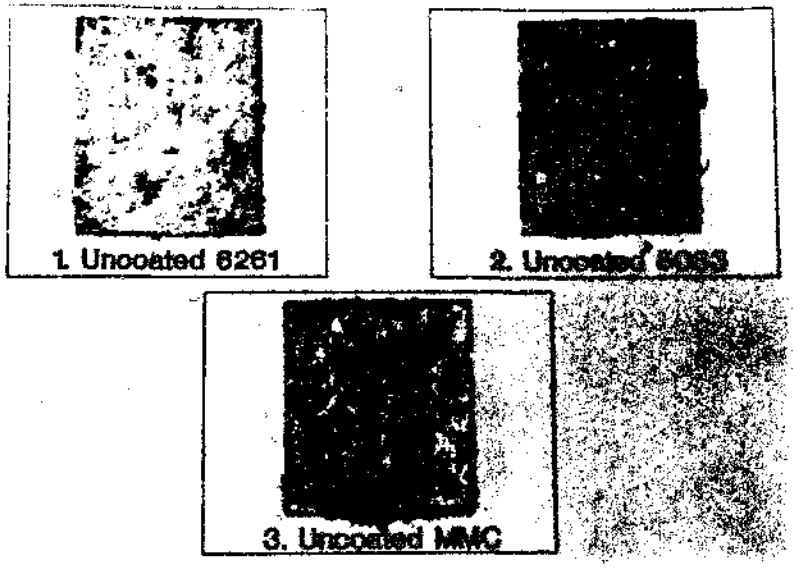


Figure 59 : Acetic acid salt spray coupons.

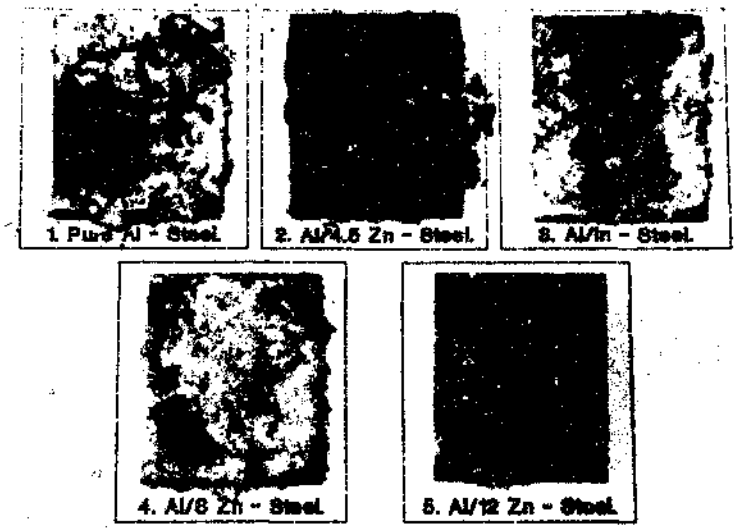


Figure 60 : Acetic acid salt spray coupons.

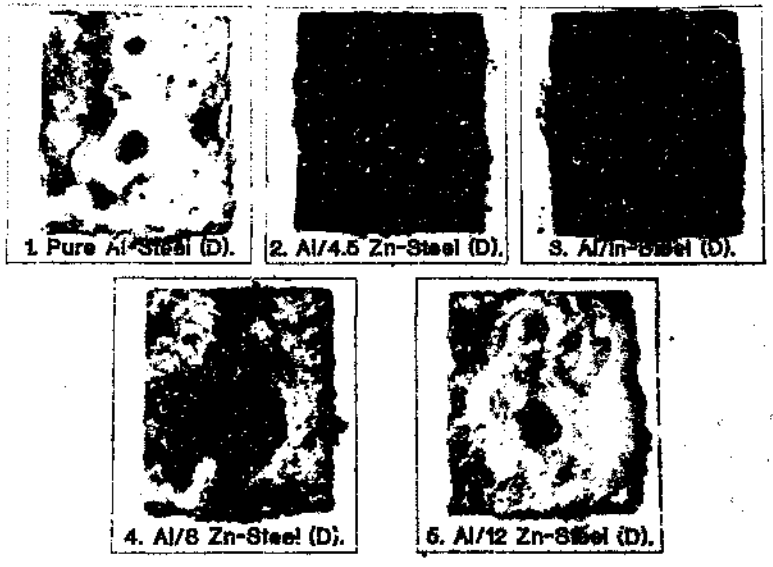


Figure 61 : Acetic acid salt spray coupons.

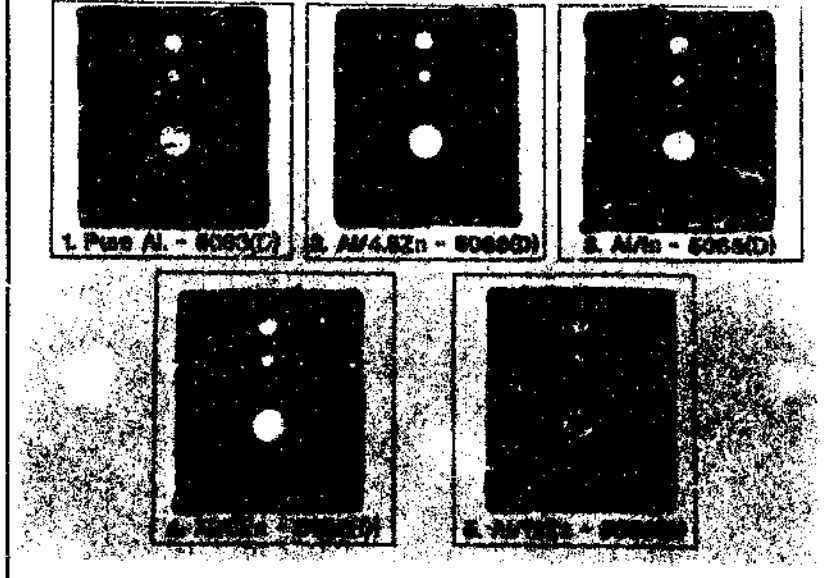


Figure 62 : Acetic acid salt spray coupons.

4.5.2 Alternate Immersion Trials

The purpose of alternate immersion is to try and simulate the wet/dry conditions encountered in many industrial applications. The apparatus was designed to hold the test coupons out of the various solutions for 50 minutes and in for 10 minutes, a ratio sufficient to allow complete wetting and drying. Thus a days cycle could theoretically be condensed into one hour.

4.5.2.1 Tap Water Trials

As was initially expected all the metal coatings showed a very high resistance to corrosion in the alternating wet/dry environment. This was especially noticeable in the relatively non-corrosive tap water solution. It was thus decided to terminate this trial after 1500 hours, realizing that to achieve any results the experiment would have to run for a inordinate length of time. An example of the extremely effective protection afforded by these coatings in the tap water environment is shown in the photograph below.

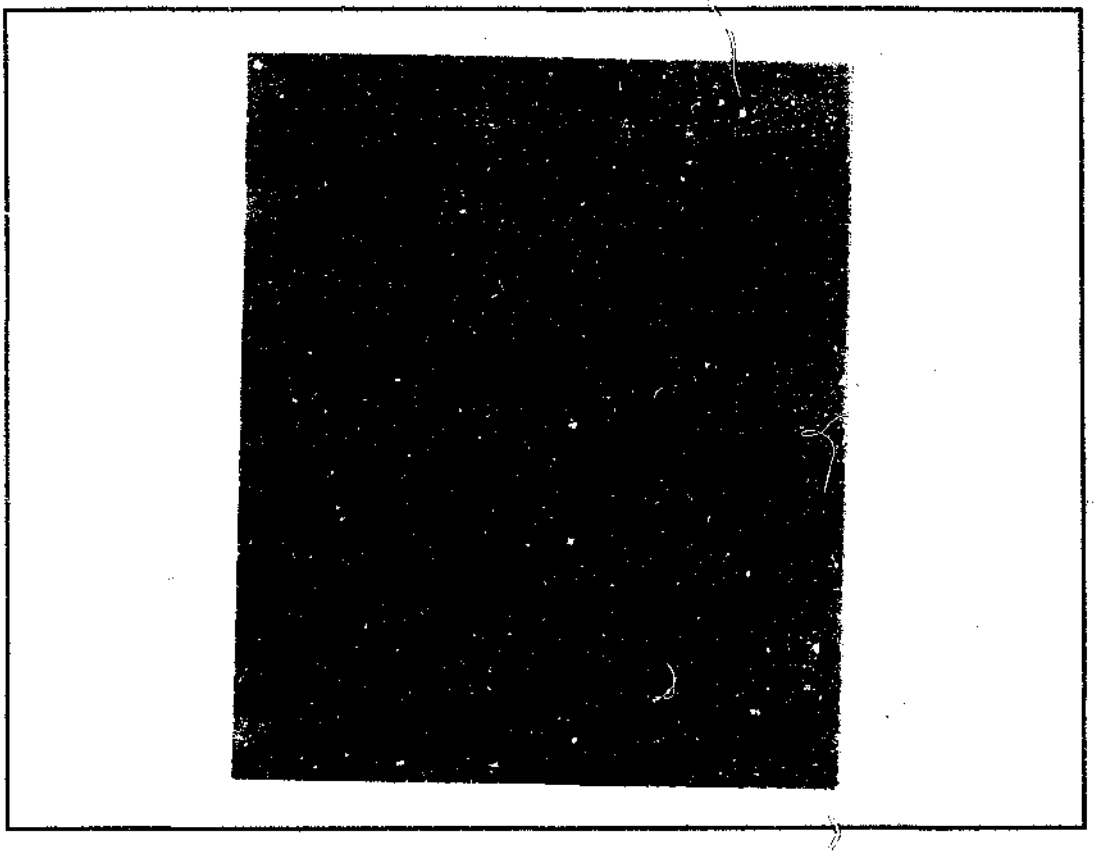


Figure 63 : Alternate immersion samples after 1500 hours.

The small amounts of corrosion product present appeared early in the trial and merely served to block any pores in the coating, thereby inhibiting any further corrosion.

4.5.2.2 Synthetic Mine Water Trials

(i) Water A (1000ppm Chloride/1000ppm Sulphate)

All the aluminium coated samples performed exceptionally well in all the test waters considered during the alternate immersion trials. Figures 64 to 70 on the following pages, which are representative samples after 5000 hours of exposure in water A, substantiate this observation. The corrosion product present is found largely on the edges of the coupons and can thus not be taken as representative of the overall coating behaviour. The photographs show how well the controlled defects are protected, with even the exposed mild steel only showing slight signs of rusting, as the close-up in the figure below illustrates.

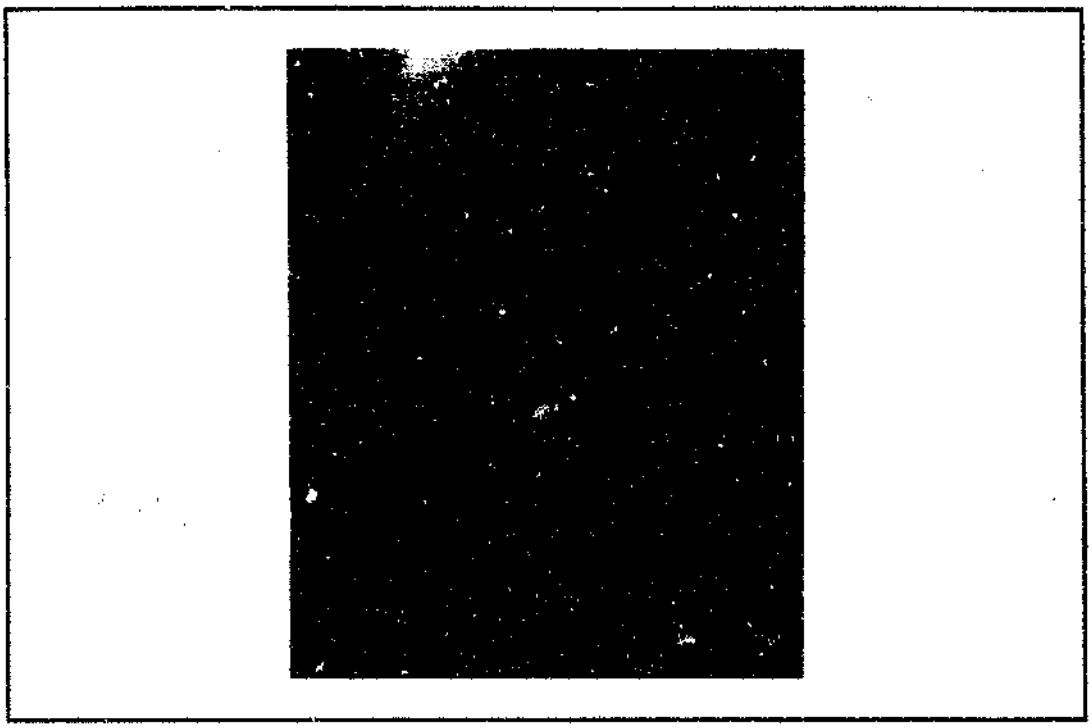


Figure 71 : Close-up of a coated mild steel coupon after 5000 hours exposure in water A.

It was in no way possible to determine the optimum coating for a particular substrate or to rank the coatings relative to one another, even after 5000 hours exposure. Thus, although coating lifetimes could not be predicted, the excellent performance in this accelerated trial and the ease with which the coatings can be re-sprayed demonstrates their suitability for alternate wet/dry conditions.

(ii) Water B (2000ppm Chloride/500ppm Sulphate)

Once again this trial was stopped prior to some of the others to make way for the use of a more corrosive media. Thus, after 2000 hours the samples were removed. The coupons, although not looking as good as those from the tap water trial, were still in excellent condition. Even the exposed mild steel remained shiny with slight corrosion only taking place in the centre of the larger defects, as is evident in the photograph below.

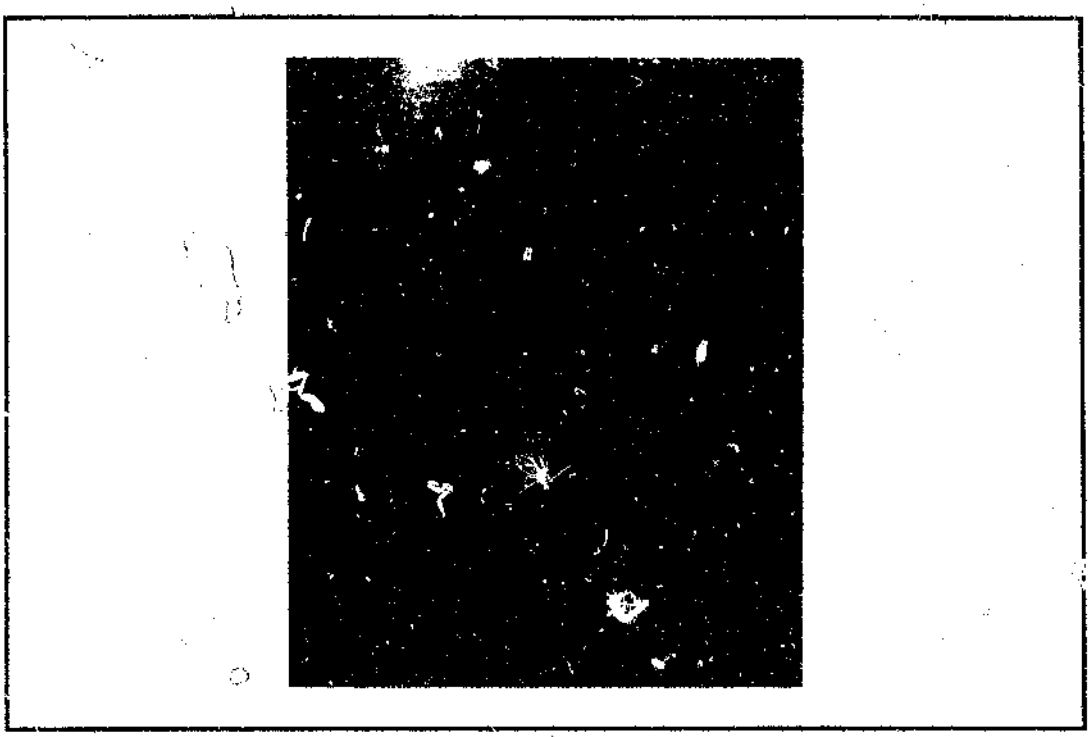


Figure 71 : Close-up of a coated mild steel coupon after 5000 hours exposure in water A.

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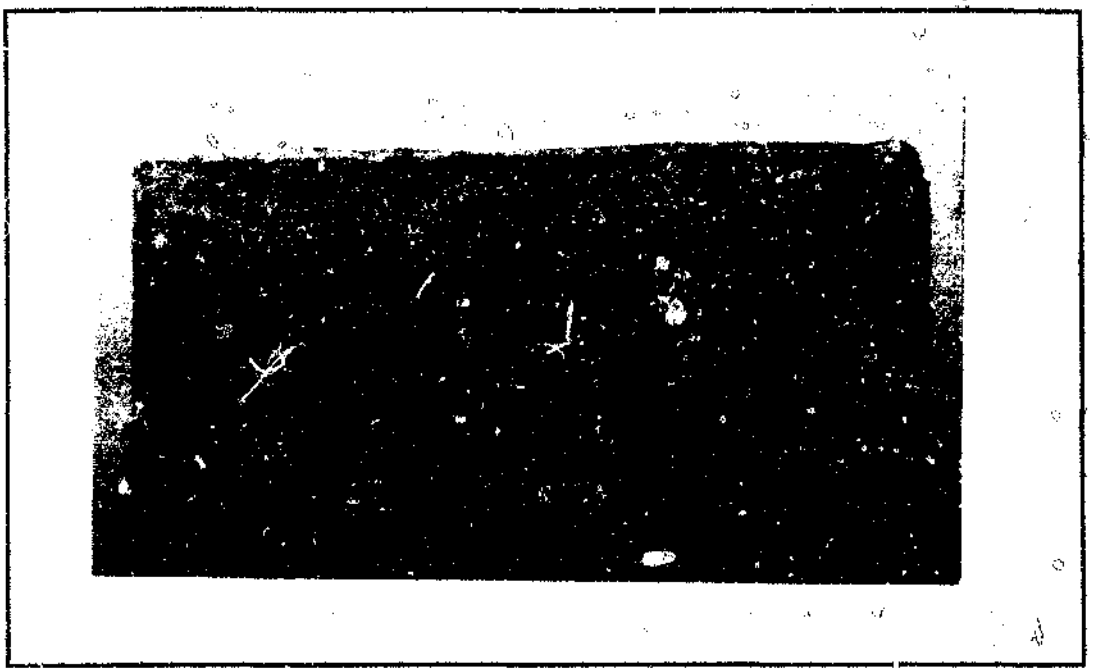

Figure 72 : A coated mild steel alternate immersion coupon after 2000 hours exposure.

The rusting only takes place in the centre of the defect as that is the region furthest from the sacrificial coating indicating that the "throwing power" of the sprayed aluminium is not quite good enough to protect such a large defect.

(iii) Water C (500ppm Chloride/2000ppm Sulphate)

Although this trial ran for 5000 hours, 3000 hours more than in trial B, the results achieved were very similar. All the coated coupons were in a very good condition with only slight discolouration and small amounts of corrosion product being found on the coupon surfaces. Once again it was not possible to select an optimum coating for a particular substrate due to the good condition of all the coating/substrate combinations.

Figure 64 : Mine water A alternate immersion coupons.

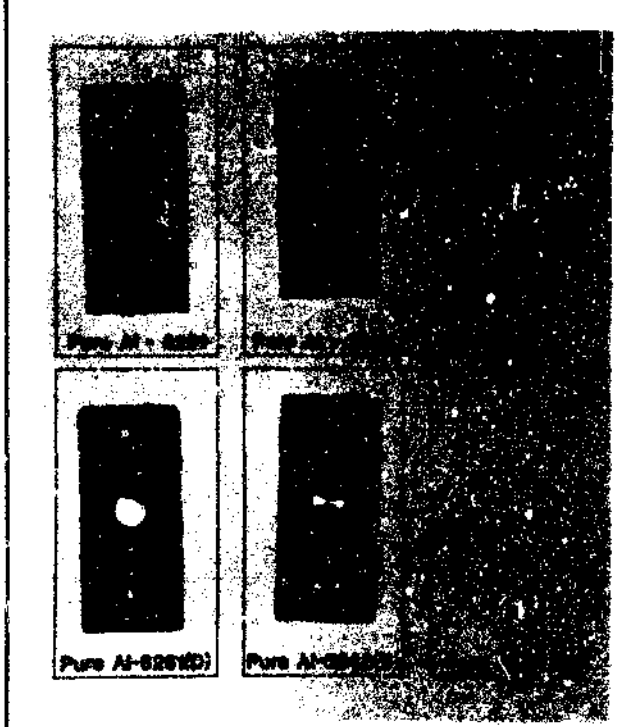

Figure 65 : Mine water A alternate immersion coupons.

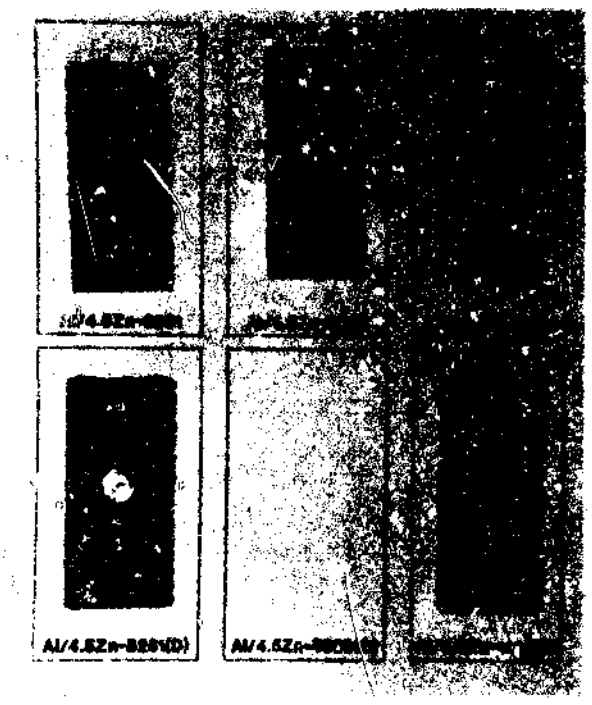

Figure 66 : Mine water A alternate immersion coupons.

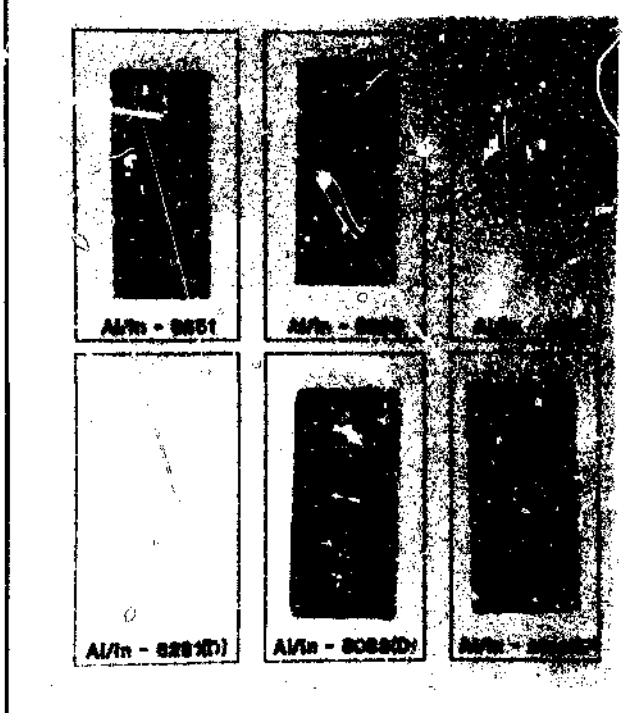

Figure 67 : Mine water A alternate immersion coupons.

Figure 68 : Mine Water A alternate immersion coupons.

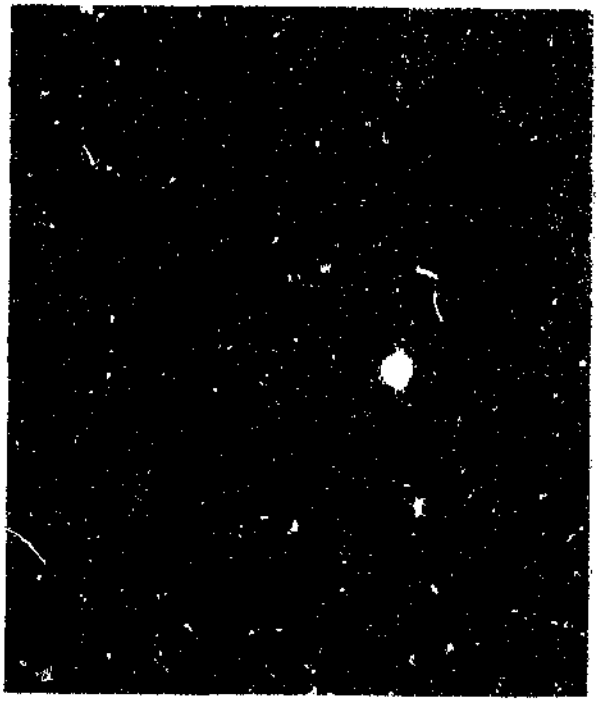

Figure 69 : Mine water A alternate immersion coupons.

Figure 70 : Mine water A alternate immersion coupons.

Results and Discussion

4.5.2.3 Tap Water Trial

Of all the waters used in the alternate immersion tanks the Rand Water Board water was the least corrosive. Not surprisingly, considering the results discussed above, the coupons were in perfect condition on completion of the 2000 hour trial period. The test was stopped prior to some of the others to make way for a synthetic sea water mixture, this being a more corrosive media.

4.5.2.4 Synthetic Sea Water Trial

As figures 73 to 79 illustrate the corrosion taking place on these coupons does not follow any distinct trend. Thus, the only observation that can really be made is that, considering that the test was run for 4000 hours, most of the coatings performed very well. From the photographs the improved corrosion resistance obtained by coating the aluminium and steel alloys is once again clear. Figure 79 exemplifies the protection offered as all the coated MMC coupons remain in excellent condition. Where corrosion is considerable it is thought to be largely due to edge effects or some other fault in the coating, rather than the intrinsic corrosion resistance of the coating itself.

Figure 73 : Sea water alternate immersion coupons.

Figure 74 : Sea water alternate immersion coupons.

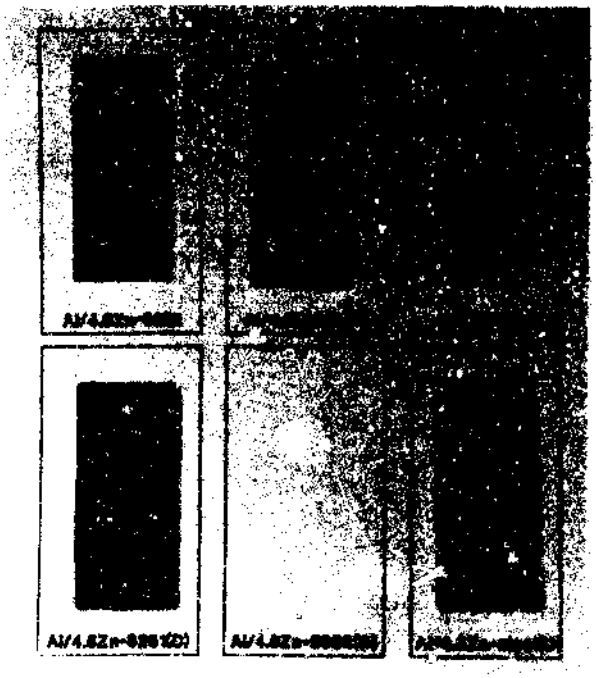

Figure 75 : Sea water alternate immersion coupons.

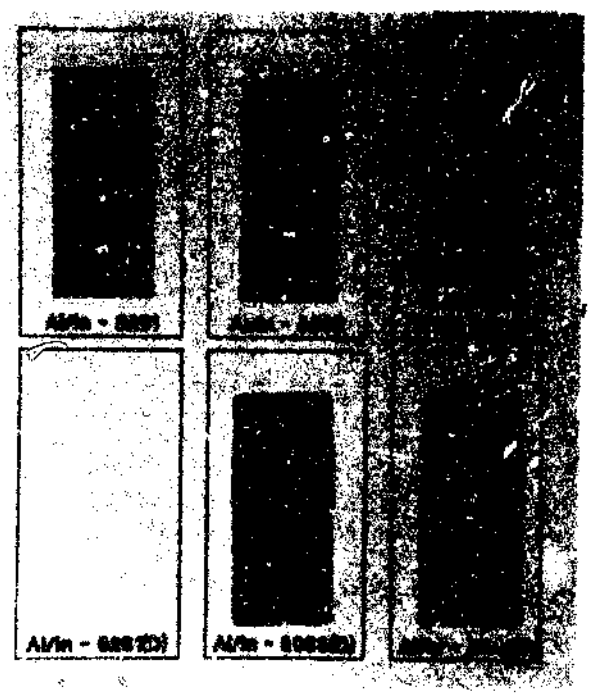

Figure 76 : Sea water alternate immersion coupons.

Results and Discussion

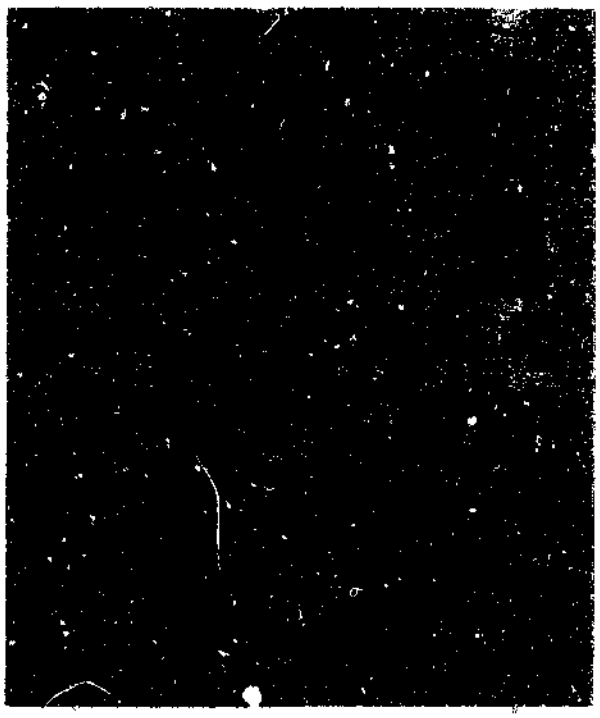

Figure 77 : Sea water alternate immersion coupons.

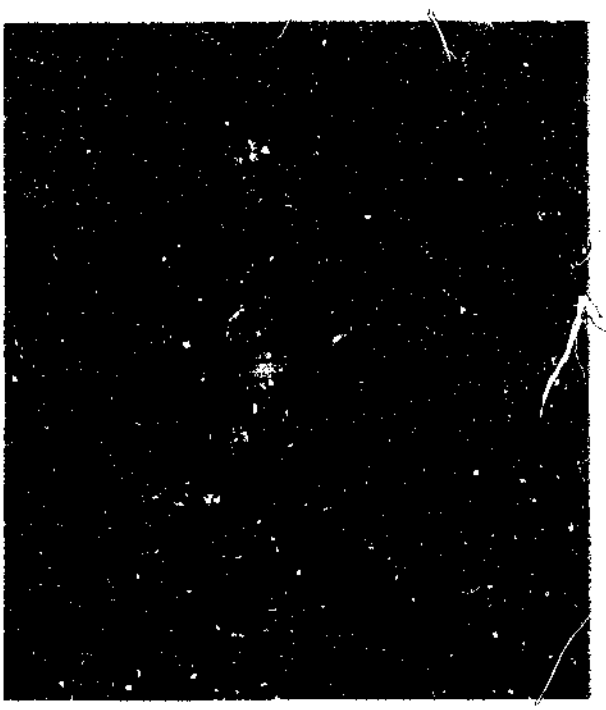

Figure 78 : Sea water alternate immersion coupons.

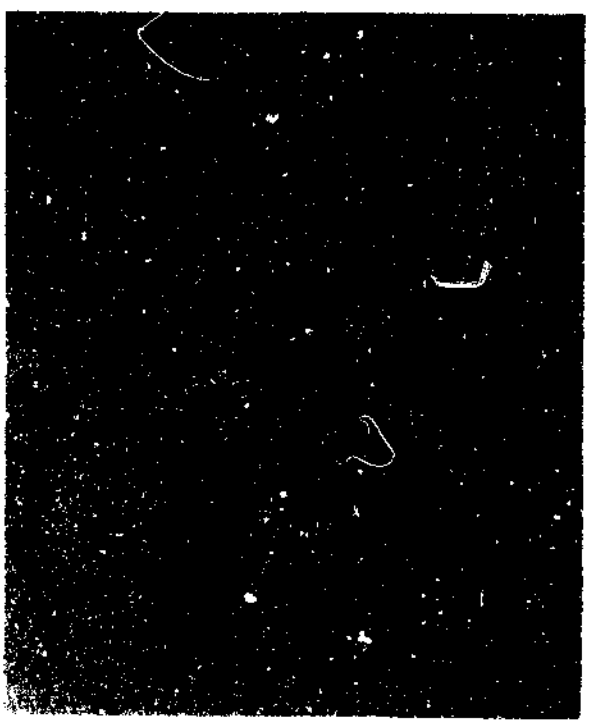

Figure 79 : Sea water alternate immersion coupons.

4.5.2.5 Sulphuric Acid Trial

After 2000 hours, having achieved no conclusive results from the trial conducted in mine water B, it was decided to replace it with a more corrosive solution. 0.1 Normal sulphuric acid was selected and placed in the alternate immersion tank. Photographs of the coupons after 1000 hours exposure are shown on the following pages.

It is clear that the pure aluminium coatings out-performed all the others irrespective of the substrate alloy. The reason for this is that the pure aluminium is far less anodic and hence less sacrificial than those coatings to which zinc is alloyed. This means, as was proven by the electrochemical work, that the potential difference between substrate and coating decreases as the percentage zinc is decreased. As the photographs show, large areas of coating have corroded away, leaving areas of bare substrate exposed. The photograph below shows this effect more clearly.

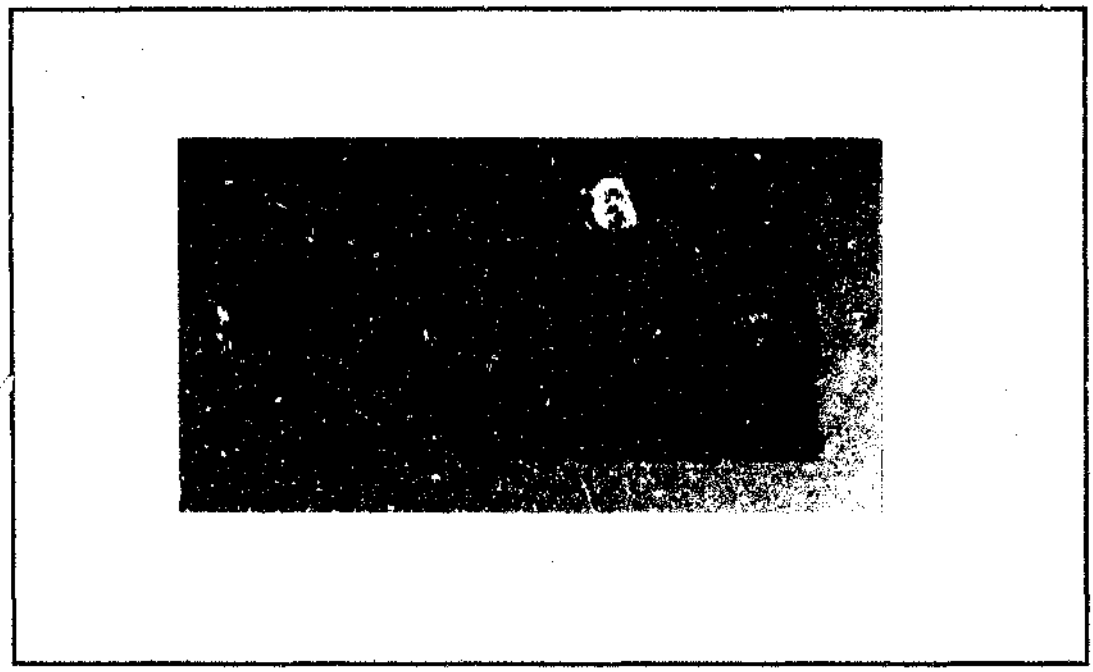

Figure 87 : A corroded steel sample after the 0.1N H_2SO_4 alternate immersion trial.

This photograph shows that, although the coating is partially corroded away, it is still able to protect the regions immediately adjacent to it.

4.5.2.5 Sulphuric Acid Trial

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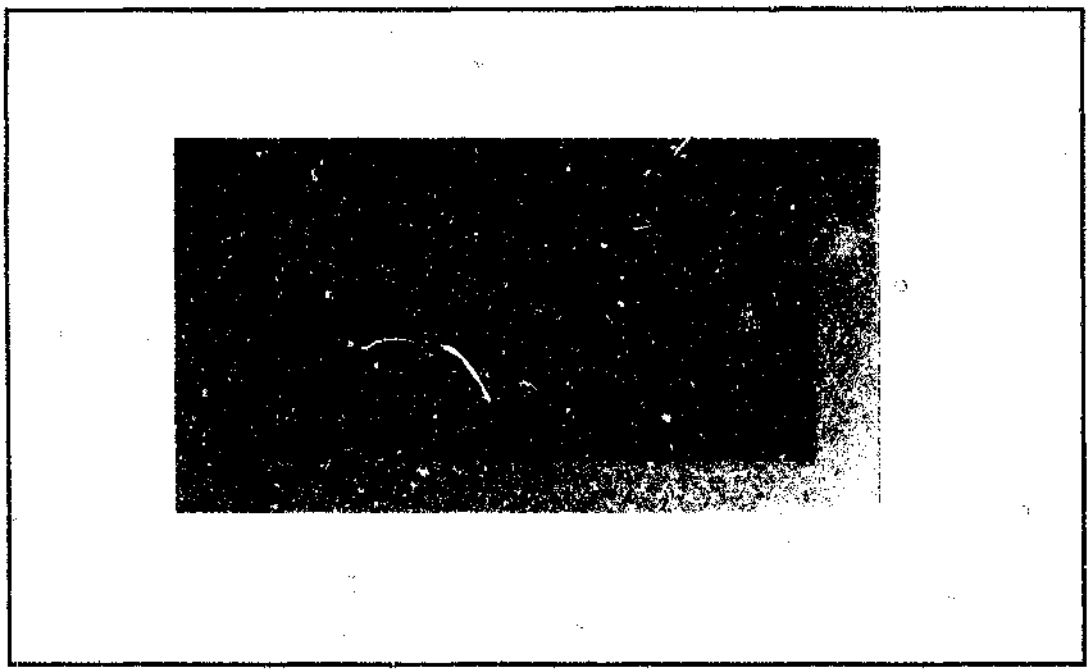

Figure 87 : A corroded steel sample after the 0.1N H_2SO_4 alternate immersion trial.

This photograph shows that, although the coating is partially corroded away, it is still able to protect the regions immediately adjacent to it.

Although the pure aluminium coated panels provided the best results, their controlled defects are completely rusted over. This suggests that even though the aluminium/zinc coatings corrode too fast, if intact they would protect holes in the coating far more effectively, due to their more anodic nature. Thus when selecting a coating for a specific medium it would be best to choose the one that generates the highest possible potential difference between coating and substrate, while ensuring that the coating would last the required life of the component.

Figure 80 : 0.1N H_2SO_4 alternate immersion coupons.

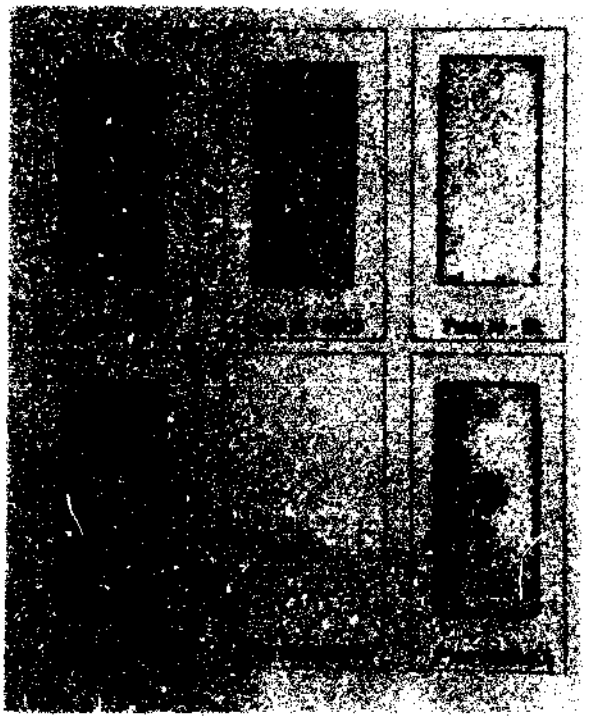

Figure 81 : 0.1N H_2SO_4 alternate immersion coupons.

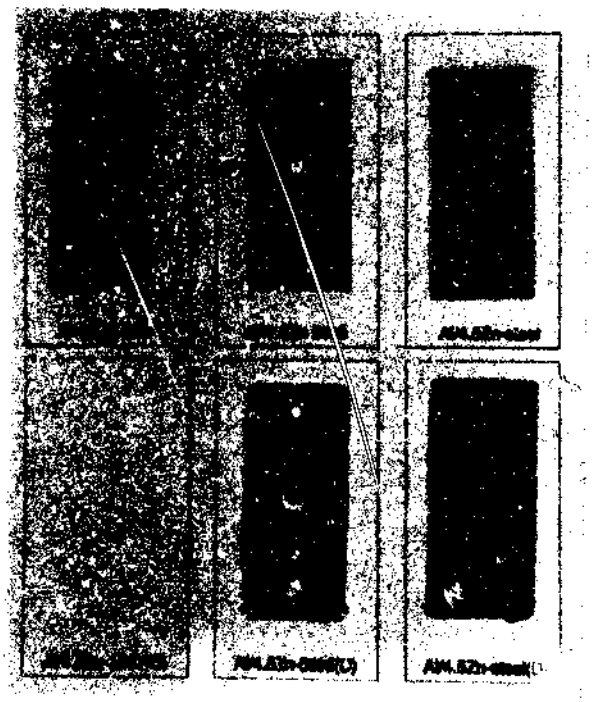

Figure 82 : 0.1N H_2SO_4 alternate immersion coupons.

Figure 83 : 0.1N H_2SO_4 alternate immersion coupons.

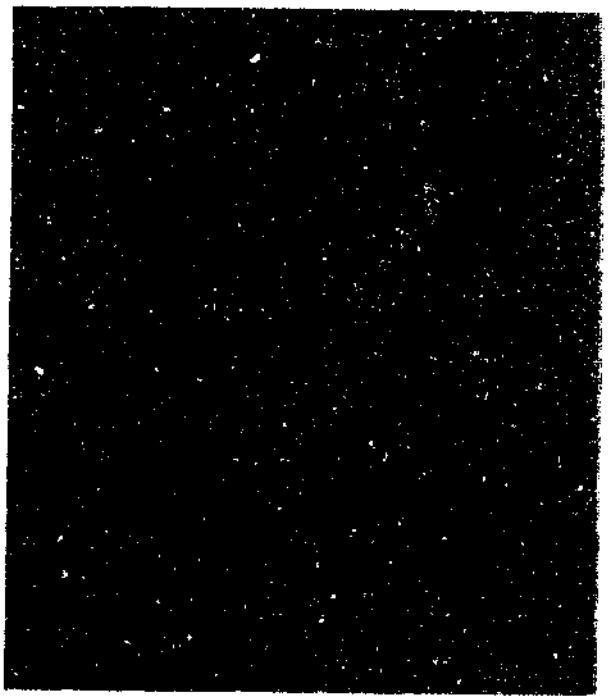

Figure 84 : 0.1N H_2SO_4 alternate immersion coupons.

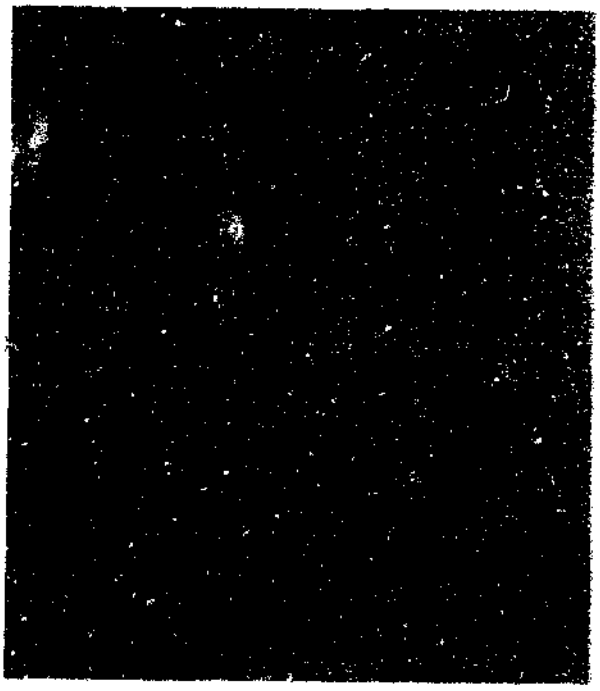

Figure 85 : 0.1N H_2SO_4 alternate immersion coupons.

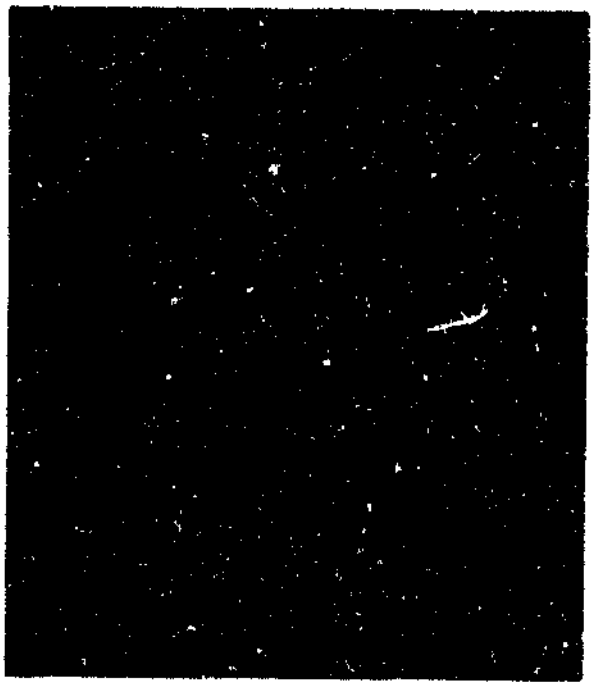

Figure 86 : 0.1N H_2SO_4 alternate immersion coupons.

Results and Discussion

4.5.3 Complete Immersion Trials

4.5.3.1 Synthetic Mine Water Trials

All the complete immersion coupons were suspended vertically in tanks containing the four test waters for a period of 5000 hours, ie. roughly seven months. The reason for this lengthy trial period was once again to try and rank the performance of the various coating/substrate combinations. Photographs of representative test coupons taken from water A, the most aggressive of the synthetic mine waters, are shown on the following pages.

As the photographs illustrate, it is impossible to establish any consistent differences between the various combinations of coating and substrate. The coupons, although slightly discoloured, all performed exceptionally well. Comparing the uncoated mild steel coupon in figure to all the coated steel specimens, the high degree of sacrificial protection becomes apparent. The exposed steel on the coated samples has in fact hardly rusted at all, behaviour similar to that found in the alternate immersion trials. The presence of the white corrosion product, as previously mentioned, must not be misinterpreted as deleterious, as it is in many ways beneficial as it seals off any pores in the coating.

The coupons exposed to the other two, less corrosive synthetic mine waters, not surprisingly, showed even fewer signs of corrosion and were in fact hardly affected at all.

The performance of the test specimens in all three of the above stated waters serves to confirm their suitability in mine water environments. From these tests it is not possible however to select the optimum coating for a specific substrate. This selection would require either a longer exposure period or the evaluation of the coating/substrate combinations in more aggressive environments.

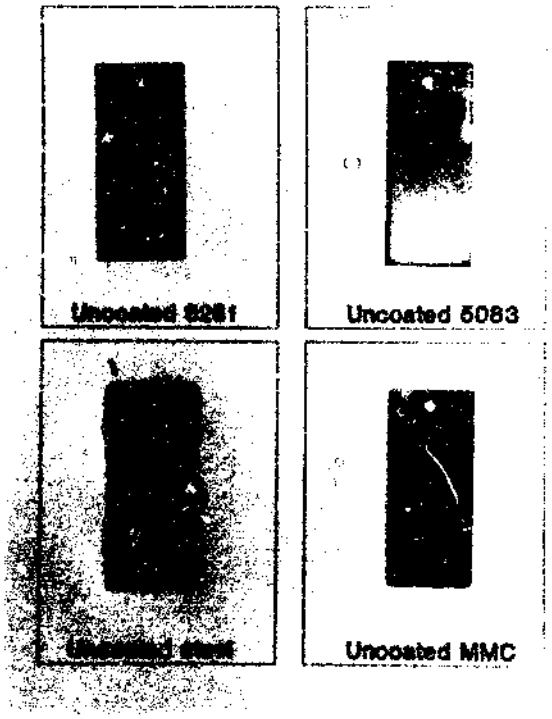

Figure 88 : Mine water A complete immersion coupons.

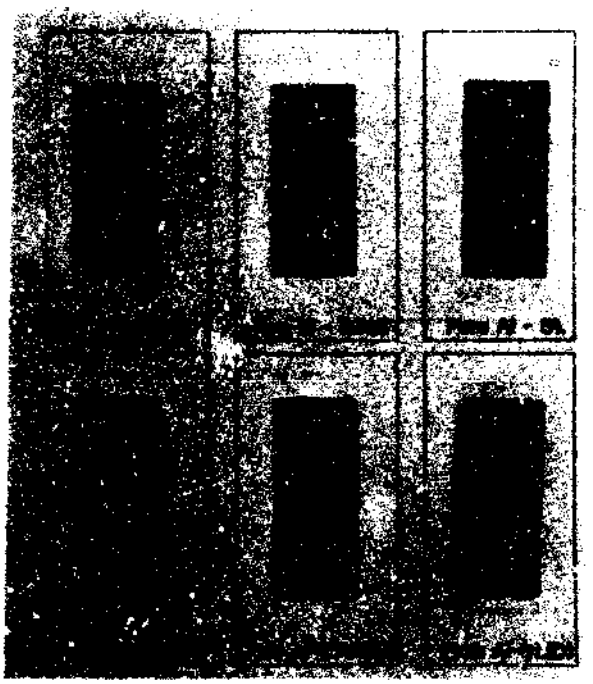

Figure 89 : Mine water A complete immersion coupons.

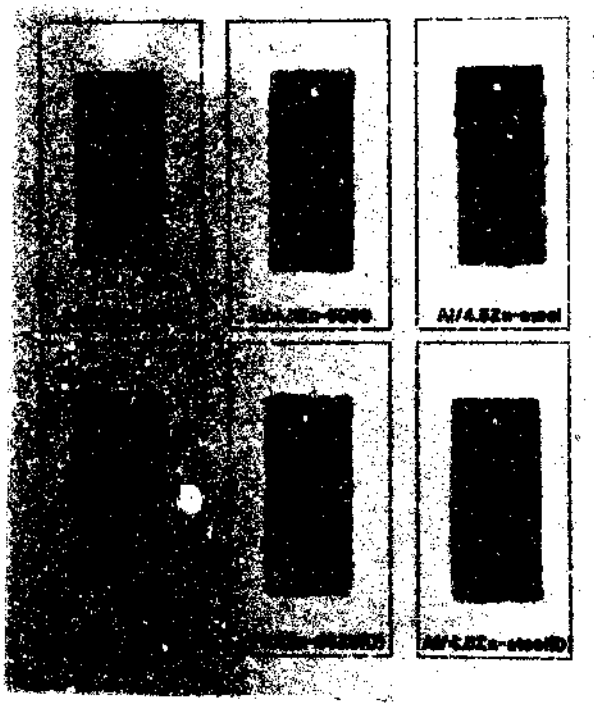

Figure 90 : Mine water A complete immersion coupons.

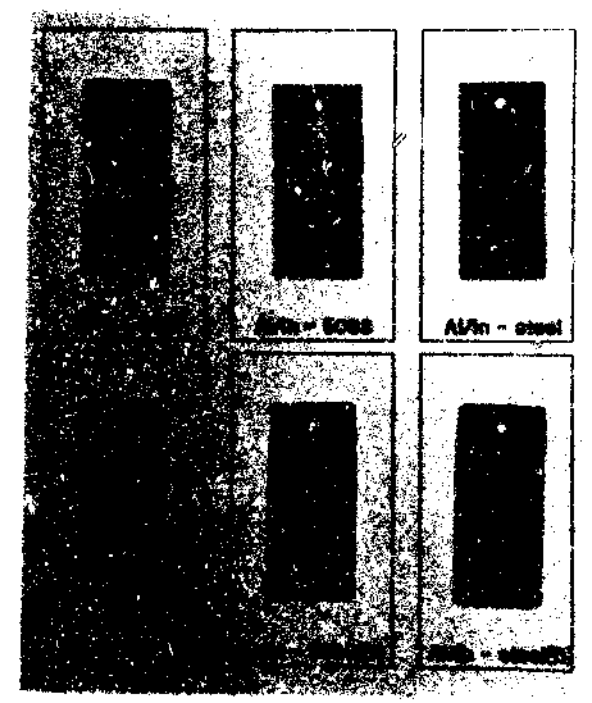

Figure 91 : Mine water A complete immersion coupons.

Figure 92 : Mine water A complete immersion coupons.

Figure 93 : Mine water A complete immersion coupons.

Figure 94 : Mine water A complete immersion coupons.

Results and Discussion

4.5.3.2 Tap Water Trial

As with the above mine water trials, no conclusive results could be drawn from this series of tests. The innocuous nature of the tap water meant that the test specimens, with the exception of the uncoated mild steel coupons, suffered very little corrosion. The exposed areas of substrate, resulting from the controlled defects, were once again well protected, with the coating adjacent to the holes providing the sacrificial protection. This protection by sacrificial means is illustrated in the photograph below.

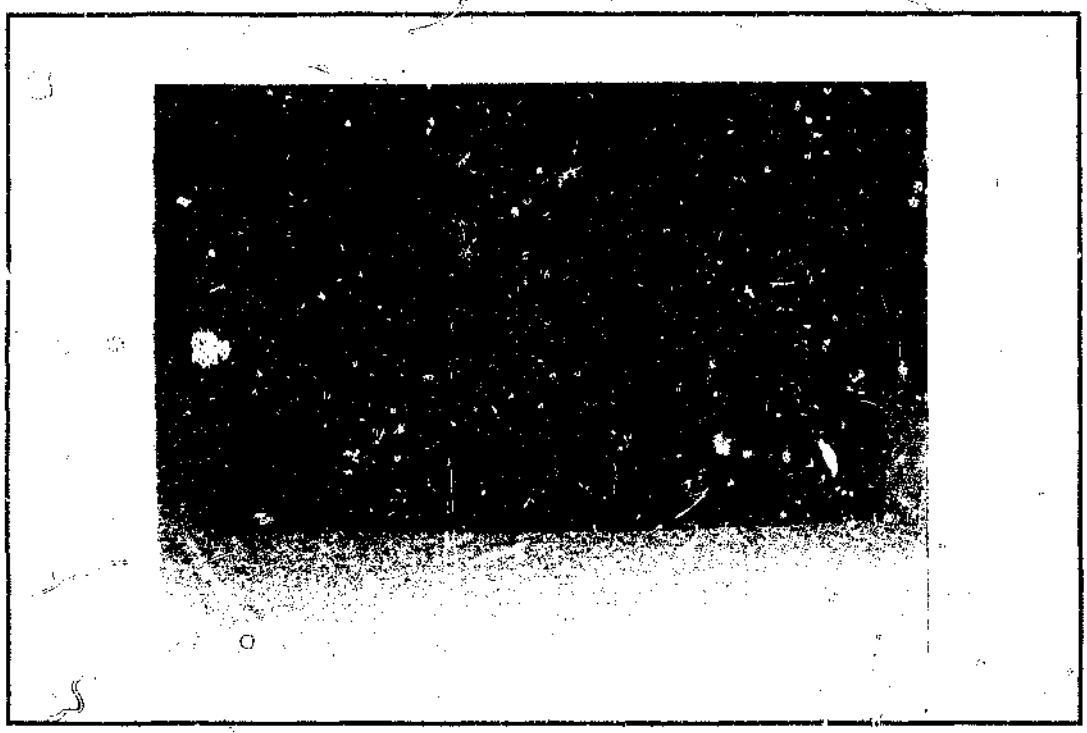

Figure 95 : A coated mild steel complete immersion coupon after 5000 hours exposure in Rand Water Board water.

The regions adjacent to the holes have been corroded, as clearly shown by the black discolouration in these areas, while the rest of the coating remains completely intact.

4.5.4 Weight-Loss Measurements

Prior to the commencement of any of the trials it was decided to limit the weight-loss evaluations to the undamaged complete and alternate immersion test coupons. The salt spray samples were not considered as they were suspended at roughly 15° to the vertical, so the one side corroded far more than the other. The masking off of the samples with controlled defects also precluded their use as weight-loss coupons.

Before measuring the loss in weight, the coupons were cleaned to remove the corrosion product, using the techniques explained in the experimental procedure. For those coupons, both continuously and alternately immersed in the synthetic mine waters and the tap water, the results achieved were largely meaningless. The weight-losses were inconsistent and in many cases there were no losses at all; in fact in a few instances the coupons even gained weight. These inconclusive results can be attributed firstly to the resistance of the coatings to the environments. Secondly any corrosion that did take place resulted in a blocking of the pores with corrosion product, thus slowing the corrosion rate down and making the corrosion product very difficult to remove.

The only test that yielded meaningful results was the alternate immersion trial carried out in 0.1 normal sulphuric acid. The reason this trial differed from the others was firstly that the solution was more corrosive and thus attacked the samples more aggressively, and secondly that the corrosion product dissolved into solution rather than adhering to the sample surface (as a result of the low pH). The chart below shows the results achieved for this trial. Clearly, as predicted by the visual examination conducted in section 4.5.2.4, the weight-loss increases as the percentage zinc is increased. As previously explained this is directly linked to the potential difference between coating and substrate.

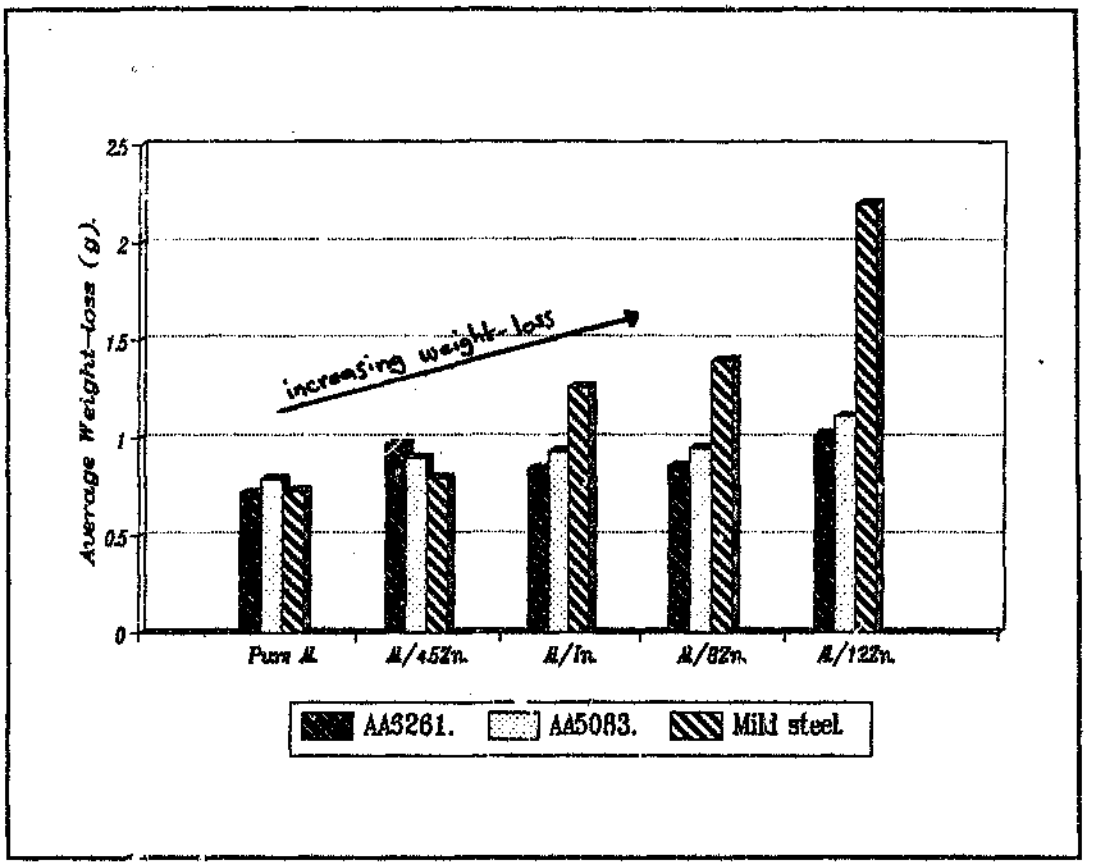

Figure 96 : Weight-loss measurements for the coupons alternately immersed in 0.1N H_2SO_4.

4.5.5 Scanning Electron Microscopy

The EDAX facility was used to determine the elements present on the surface of both uncorroded and corroded samples. Some of the typical plots found are shown in the figures below. Figure 73 was achieved having scanned an area of a mild steel coupon coated in aluminium / 8% zinc, prior to any corrosion testing.

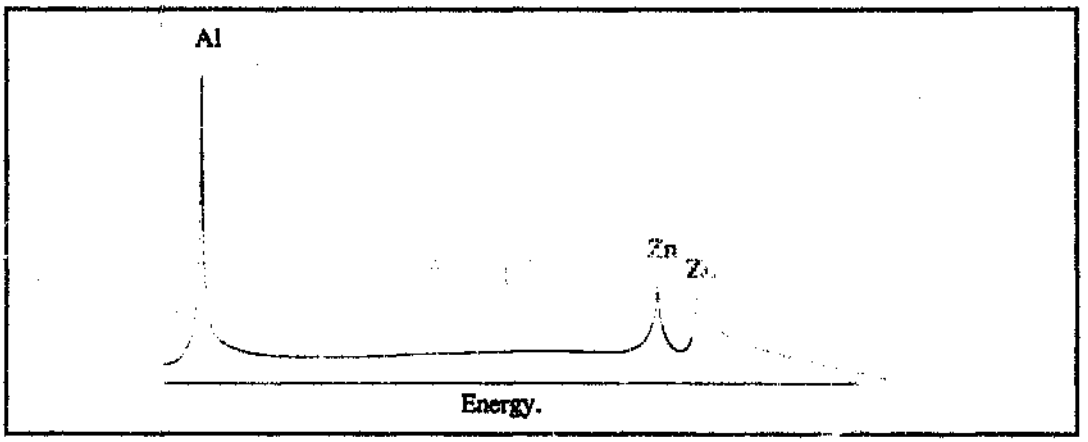

Figure 97 : EDAX of corrosion coupon prior to testing.

This coupon was then placed in the salt spray cabinet and exposed for 1000 hours to the synthetic mine water A. Figure 74 shows an EDAX taken across an area of this surface.

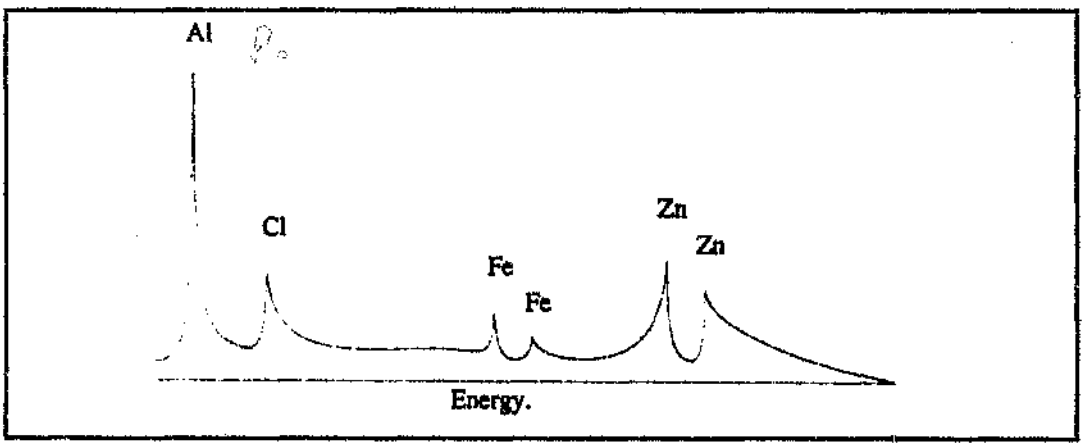

Figure 98 : EDAX of corroded surface.

The small iron peaks serve to prove that the coating has been penetrated at certain regions of the coupon. Also, as expected, the high salt concentration in the water results in the

precipitation of chloride containing corrosion products on the sample surface.

The next EDAX was taken across the surface of an alternate immersion specimen (still coated in Al/8%Zn) exposed to water B, the high chloride containing synthetic mine water. The clearly evident calcium peaks prevail due to the evaporation of the water on the coupon surface as it is removed for 50 minutes from the water bath.

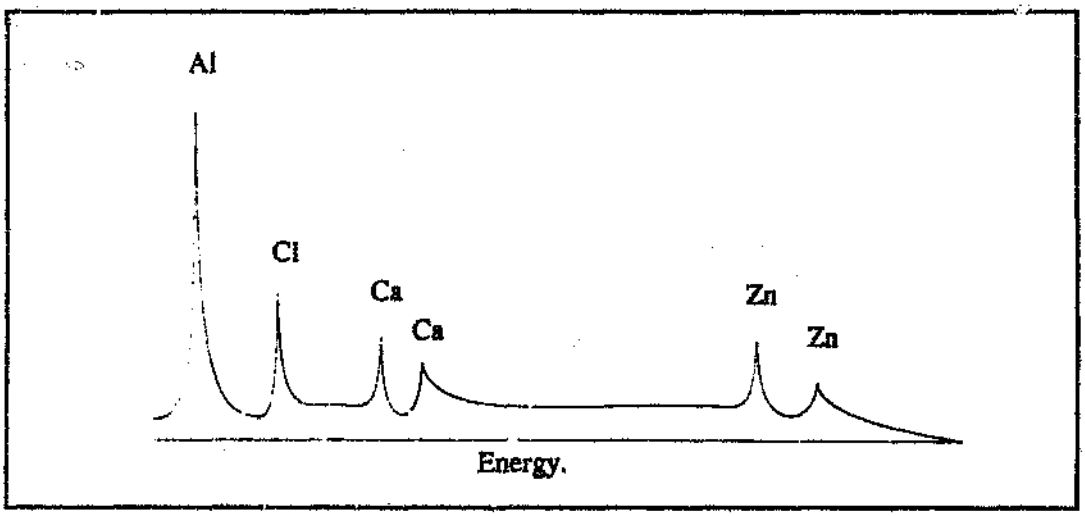

Figure 99 : EDAX of a panel taken after 1000 hours in the alternate immersion machine.

Finally an EDAX of the corrosion product found on the surface of another alternate immersion specimen was carried out. (The material having been scraped off the coupon surface.) The sample was exposed to water A, thus explaining the high sulphur and chlorine peaks. The calcium, although not corrosion product, was present as a result of its precipitation during the drying cycle and could be deleterious as it may result in crevice corrosion. The proof that corrosion of the coating is in fact taking place comes in the form of the aluminium and zinc peaks, which are clearly evident in the corrosion product.

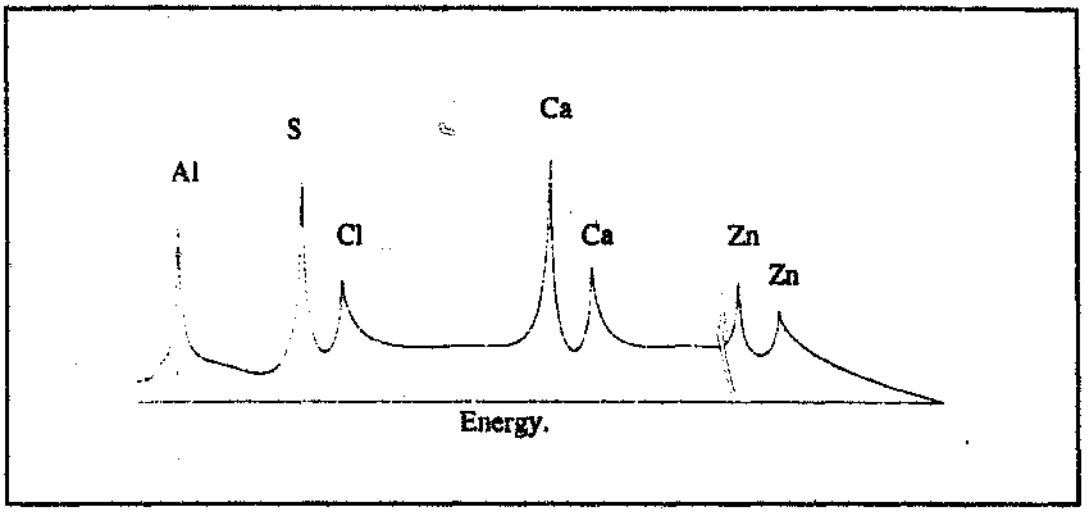

Figure 100 : EDAX of the corrosion product scraped off an alternate immersion specimen.

4.6 Surface Roughness Evaluation

The important figures gained from the analysis of the surface roughness were the following :

(i) **The arithmetic mean roughness value :** This being the average value of all absolute distances of the roughness profile R from the centre-line within the measuring length l_m. This is demonstrated in the figure below.

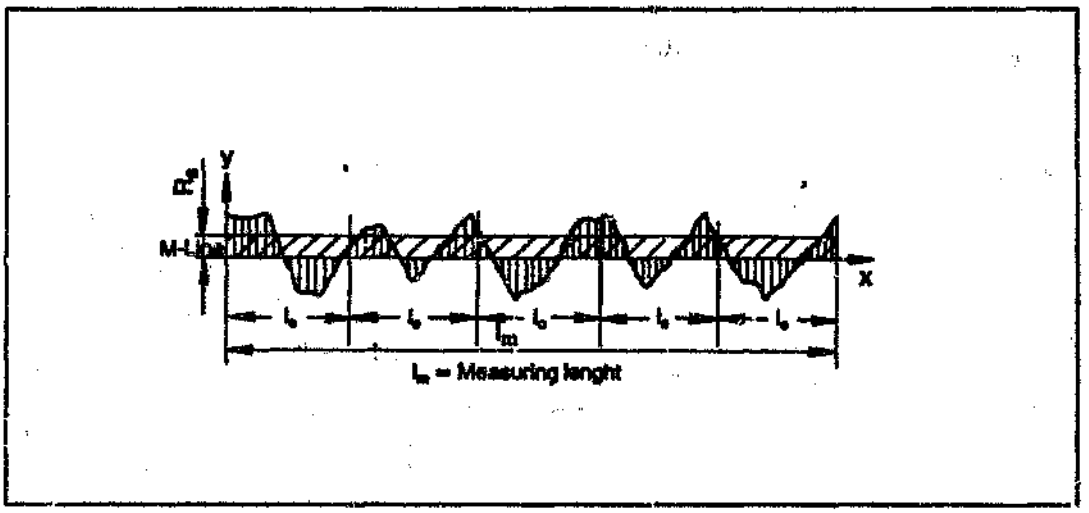

Figure 101 : Arithmetic mean roughness value parameters.

(ii) **The ten point height :** This being the average height difference between the five highest peaks and the five lowest valleys over a single sampling length.

(iii) **The maximum peak to valley height.**

The actual results achieved are summarized in the table below.

Table 14 : Results of the surface roughness evaluation.

Sample description	Arithmetic mean roughness value (μm)	Ten point height (μm)	Maximum peak to valley height (μm)
5083 alloy / pure Al coating	8.73 (long) 7.71 (trans)	58.01 57.53	62.54 70.38
5083 alloy / Al/4.5%Zn coating	6.84 (long) 6.98 (trans)	48.90 50.16	56.20 63.82
5083 alloy/Al/4.5%Zn /160ppm In coating	8.71 (long) 9.49 (trans)	63.84 60.18	69.88 71.50
5083 alloy / Al/8%Zn coating	9.53 (long) 8.02 (trans)	63.57 54.70	68.68 62.58
5083 alloy / Al/12%Zn coating	7.21 (long) 6.85 (trans)	50.20 53.05	57.08 62.34
6261 alloy / pure Al coating	6.45 (long) 6.78 (trans)	45.14 48.27	49.58 58.04
6261 alloy / Al/4.5%Zn coating	7.12 (long) 6.40 (trans)	50.11 50.33	53.36 58.12
6261 alloy / Al/4.5%Zn /160ppm In coating	6.89 (long) 7.08 (trans)	52.20 57.08	59.87 63.40
6261 alloy / Al/8%Zn coating	7.45 (long) 7.36 (trans)	65.09 63.21	67.75 68.97
6261 alloy / Al/12%Zn coating	6.69 (long) 7.32 (trans)	46.35 47.52	57.30 63.94
Mild steel / pure Al coating	5.95 (long) 5.25 (trans)	53.85 35.37	61.94 39.86
Mild steel / Al/4.5%Zn coating	7.79 (long) 6.67 (trans)	54.64 47.37	63.42 52.76
Mild steel / Al/4.5%Zn /160ppm In coating	4.58 (long) 4.96 (trans)	29.69 36.01	32.60 38.52
Mild steel / Al/8%Zn coating	5.94 (long) 5.78 (trans)	34.86 38.36	36.26 50.70
Mild steel / Al/12%Zn coating	4.27 (long) 4.30 (trans)	32.84 38.60	39.60 45.20

SABS 1391 and BS 1134 both specify that the average peak to valley height should lie between 50 and 100 μm for the best coating adhesion. The above table thus demonstrates the suitability of the substrates for metal spray purposes. The table also shows that after blasting the mild steel surfaces were not as rough as those of the aluminium alloys. This can be attributed to the higher hardness of the steel, making the alumina blasting slightly less effective, although still adequate.

4.7 Coating Thickness Measurements

The ultrasonic film thickness instrument used was only effective for the aluminium coated mild steel specimens. (The ultrasonic beam could not pick up the interface of the sprayed aluminium and the aluminium substrate). The average thicknesses achieved are tabulated below.

Table 15 : Coating thickness measurements.

Coating.	Ave.thickness µm.	Min.measured µm.	Max.measured µm.
Pure Al.	127.4	65.6	190
Al/4.5%Zn.	88.7	42.0	149
Al/In.	118.8	55.4	157
Al/8%Zn.	95.8	63.5	169
Al/12%Zn.	98.2	54.6	153

Note : The testing was carried out on three random samples from each batch, with a minimum of twenty measurements being taken from each specimen.

Although SABS 1391 recommends a range of coating thicknesses depending on the coating alloy and the environment, it was attempted in this research to keep all the thicknesses the same. A thickness of 100 µm was aimed for, this value being the minimum recommended thickness for a pure aluminium coating. The above table shows how the average thicknesses are around this mark.

4.8 Coating Adhesion Measurements

The coating adhesion tests were conducted in accordance with ASTM C633, with five specimens being tested to ensure reproducibility. All the coatings were pulled completely off the substrate, thus testing the physical bond between coating and substrate. Table 16 shows the average of the five adhesive strengths achieved for each coating/substrate combination.

Table 16 : Adhesive strengths of the coatings.

Coating Alloy	Adhesive Strength, MPa		
	AA6261 substrate	AA5083 substrate	Steel substrate
Pure aluminium	3.4	3.4	3.7
Al/4.5% Zn.	3.7	3.7	4.1
Al/4.5% Zn/ In.	3.5	3.6	5.1
Al/8% Zn.	3.5	3.3	3.6
Al/12% Zn.	3.6	3.9	3.6

SABS 1391, the standard specification for thermally sprayed coatings, recommends that for satisfactory performance, the adhesion of a flame sprayed aluminium coating, when coated onto steel, should be at least 3.5 MPa. The above table illustrates clearly that the preparation procedure followed in this research of cleaning, grit blasting and spraying creates coatings that adhere more than adequately to the surface. The metal sprayed onto the aluminium alloys, although not adhering as well, is still well within the limits of acceptability.

Conclusions and Recommendations

5.1 Conclusions

A range of especially formulated experimental aluminium-based alloys were sprayed onto the various substrates and tests conducted to ensure that the physical and mechanical properties were adequate. It was thereby possible to conduct all the corrosion testing assuming that the only difference between one test coupon and another was the composition of the coating and/or the substrate. Thus, assuming all else to be equal, meaningful conclusions could be drawn from the various tests.

5.1.1 Electrochemical Test Work

Referring back to Figure 41, which shows the trends established from the potentiodynamic test work, two factors become clear. Firstly, an increase in the percentage zinc in the aluminium-based coating decreases the corrosion current. This means that, relative to a given substrate, the coating becomes more anodic with increasing zinc content. Secondly, the higher the zinc level the greater the corrosion current. The superimposed scans in Figures 31, 32 and 33 demonstrate how a marked difference is noted in this current, especially considering the fact that the X-axis is a log scale. The current density is directly related to the corrosion rate and one can thus see how by increasing the amount of zinc, the coating will corrode at a much higher rate.

Conclusions drawn from the potentiodynamic test work can be further substantiated by the results of the E_{corr} versus time tests. Although these trials merely monitor the free corrosion potential as a function of time, the decrease in potential, and hence the increase in potential difference between coating and substrate, is clearly evident as zinc levels are raised. This is of significant importance as it quantifies the effect of zinc on the free corrosion potential and allows for the accurate measurement of the potential difference between coating and substrate.

Thus, using the electrochemically achieved potential difference readings, together with the results obtained from exposure trials, one could predict an optimum difference in potential between coating and substrate. This would, in future, make it possible to design a coating having a specific free corrosion potential that would best protect any substrate in a certain environment. It must be borne in mind however, that electrochemical testing alone cannot rank any of the coatings in terms of performance in any media, but can merely measure and rank the potentials at which they operate.

The effect on the coating's corrosion potential and corrosion current by the addition of small amounts of indium is also clear from the electrochemical work. The dissolution of the indium definitely makes the alloy more anodic when compared to the same indium-free alloy. Once again, however, the actual performance of the coating relative to the others cannot be established from these tests.

Thus, this series of tests, although not establishing all the trends did allow the determination of the following :

(i) The corrosion potentials and corrosion currents of the various coatings and substrates
(ii) The potential difference between coating and substrate
(iii) The effect of zinc on the corrosion potential and current
(iv) The effect of indium on the corrosion potential and current
(v) The effect of exposure time on the free corrosion potential of the coating.

5.1.2 Accelerated Corrosion Test Work

5.1.2.1 Salt Spray Testing

This form of testing, in comparison to the others, creates an environment closest to an actual underground mining environment. The test carried out in mine water A served to demonstrate clearly the suitability of these coatings for underground use. The water was highly aggressive, with 1000ppm sulphates and chlorides, but still hardly damaged the coatings during the exposure time. Particular success was noted for the coated aluminium coupons which far outperformed the coated mild steel specimens. This improved performance was a result of the better corrosion resistance of the aluminium substrates themselves, a factor that makes the use of coated aluminium combinations ideal for many mining applications. This conclusion was further substantiated by the synthetic sea water and acetic acid tests, after which the coated aluminium coupons were still in an excellent condition.

5.1.2.2 Alternate and Complete Immersion Testing

The up to seven months exposure period in many of these trials failed to enable the ranking of the range of coating/substrate combinations. With particular reference to the "less-corrosive" environments very little corrosion took place at all and any that did merely served to block any pores in the coating, thus improving the performance with time. This lack of a conclusive behavioral trend is good on the one hand, as it establishes all these aluminium-based sprayed coatings as excellent performers under complete and alternate immersion conditions in this range of enviro[illegible]ts. On the other hand, the optimum coating/substrate system in each solution still remains unknown and thus further testing would be required if the maximum possible component life is to be determined.

The one test that did conclusively rank all the coating/substrate combinations was the 0.1N H_2SO_4 alternate immersion trial. This was by far the most aggressive solution used, thus making the best possible sacrificial protection essential. As discussed in sections 5.1.3 however the creation of the largest possible potential difference between substrate and coating does not always make for the best combination. The relative success of the weight-loss

measurements are directly attributable to the corrosivity of the environment. Unlike all the other solutions in which tests were conducted, the sulphuric acid not only attacked the coupons but also dissolved the corrosion product, thereby reducing the protection further.

5.1.3 Coating Optimization

The determination of the best sprayed coating for a particular substrate in a certain environment hinges around three main factors, namely :

1. The potential difference between substrate and coating
2. The size and extent of defects or exposed substrate to be protected
3. The expected life of the system.

Increasing the potential difference, ie. improving the sacrificial nature of the coating, will protect larger regions of exposed substrate, especially in higher resistivity media, but will lead to rapid removal of the coating. Conversely, a smaller potential difference between coating and substrate, although increasing the coating life, will not protect exposed areas as well. Ideally a balance must thus be found, with each of the above factors being taken into account, so that the potential difference can be maximized whilst still enabling the coating to last the required time-span. In so doing the coating will protect the exposed areas as best as possible for a particular set of circumstances. When considering these variables it must always be borne in mind during the development of a new coating, that the process of grit blasting and re-spraying is an operation that can be carried out in the field.

5.2 Recommendations

- With regard the suitability of these coatings for underground mining applications it is recommended that test coupons be placed on-site at various mines across the country. This would serve to substantiate the conclusions drawn from this research, prior to the actual usage of the coating systems.

- The positive effects of indium found in only the one alloy should be further investigated using a range of zinc additions.

- The success of the sacrificial protection offered by these coatings meant that in some cases, especially in the less corrosive environments, the holes drilled in the coatings were not large enough to determine the coating's "throwing power". A larger number of holes and ones with sharp corners should be used in further test work.

- The sealing of the successful coating options needs to be examined as in most practical applications this is part of the system.

- More tests in a wider range of situations need to be conducted since as the pool of data on the numerous coating/substrate combinations in the many environments grows it may become possible to determine an optimum potential difference between coating and substrate. Thus a coating could be designed for a particular substrate material in a certain environment.

- This research has shown just how well aluminium-based metal sprayed coatings perform in a range of environments. This system must be compared to other coating techniques such as cladding, painting, duplex systems, etc.

References

1. Rogers, T.H., "**Marine Corrosion,**" George - Newnes Limited, London, 1968.

2. Franklin, J.R.. "**The Surface Coating of Materials,**" Materials and Design, Vol.6, No.3, June/July, 1985, pp.131-133.

3. Schmitt, R.J. and Rigo, J.H., "**Corrosion and Heat Resistance of Aluminium Coated Steel,**" Materials Protection, April, 1966, pp.46-52.

4. Klinge, R., "**Sprayed Zinc and Aluminium Coatings for the Protection of Structural Steel in Scandinavia,**" Eighth International Thermal Spray Conference, Sep./Oct., 1976, pp.203-213.

5. Carter, V.E., "**Metallic Coatings for Corrosion Control,**"Newnes - Butterworth, London, 1977.

6. Fontana, M.G., "**Corrosion Engineering,**" McGraw - Hill International Editions, Third Edition, Tokyo, 1988.

7. Uhlig, H.H., "**Corrosion,**" Vol.6, 1950, pp.29-33.

8. Diamant, R.M.E., "**The Prevention of Corrosion,**" Business Books Limited, London, 1971.

9. Callaghan, B.G., "**The Performance of Metallic Coatings in South Africa,**" Corrosion and Coatings South Africa, June, 1982, pp.9-18.

10. Haywood, D.M., "**Thermal Spraying , from Art to Science,**"FWP Journal, December, 1987, pp.21-32.

11. Korb, L.J., (Ed), "**Metals Handbook,**" Ninth Edition, Volume 13 : Corrosion, ASM, Ohio, 1987.

12. Haywood, D.M., "**Flame Spraying in Southern Africa,**" Metal Fabrication, Finishing and Protection, Nov./Dec., 1971, pp.3-7.

13. Carter, V.E., "**Metallic Coatings for Corrosion Control,**"Newnes - Butterworth, London, 1977.

14. Kubel, E.J., "**Thermal Spraying Technology : From Art to Science,**" Metal Progress, No. 2, 1987, pp.69-80.

15. Haywood, D.M., "**Surface Preparation for Thermal Spray Coatings,**" Corrosion and Coatings South Africa, December, 1979, pp.11-23.

16. Duligal, E.A., "**Evaluation and Requirements of Surface Preparation for Metal Sprayed Coatings,**" Fourth South African Metal Spraying Symposium, Rand Afrikaans University, October, 1979.

17. Sedriks, A.J., "**Corrosion of Stainless Steels,**" Wiley - Interscience, New York, 1988.

18. Ballard, W.E., "**Metal Spraying and Sprayed Metal,**" 3rd Edition, Charles Griffin and Company Limited, London, 1949.

19. Chapman, B.N. and Anderson, J.C., (Eds.), "**Science and Technology of Surface Coating : A NATO Advanced Study Institute,**" Academic Press, London, 1972.

20. Callaghan, B.G., "**The Performance of Metallic Coatings in South Africa,**" Corrosion and Coating South Africa, June, 1982, pp.9-18.

21. Campbell, H.S., "**Sprayed Aluminium and Zinc Protect Against Corrosion by Aqueous Solutions,**" Anti - Corrosion, August, 1982, pp.10-13.

22. Rogers, T.H., "**Marine Corrosion,**" George Newnes Limited, London, 1968.

23. Carter, V.E., "**Metallic Coatings for Corrosion Control.**" Newnes - Butterworth, London, 1977.

24. Davies, C. and Hanford, N.J., "**Metallic Coatings for the Protection of Mild Steel from Corrosion at Ambient Temperatures,**" Anti - Corrosion, July, 1970, pp.20-22.

25. Shaw, B.A., Liemkuhler, A.M. and Moran, P.J., "**Corrosion Performance of Aluminium and Zinc - Aluminium Thermal Sprayed Coatings in Marine Environments,**" Testing of Metallic and Inorganic Coatings, ASTM STP 947, Harding and Di Bari, (Eds.), ASTM, Philadelphia, 1987, pp.246-264.

26. Gartland, P.O., "**Atmospheric Corrosion of Aluminium Coated Steel in Sea Water,**" Materials Performance, June, 1987, pp.29-36.

27. Stanton, W.E., "**Sprayed Aluminium Coatings - Why, When, How ? "** Eighth International Thermal Spray Conference, Sep./Oct., 1976, pp.449-455.

28. Kain, R.M. and Baker, E.A., "**Marine Atmospheric Corrosion Museum Report on the Performance of Thermal Sprayed Coatings on Steel,**" Testing of Metallic and Inorganic Coatings, ASTM STP 947, Harding and Di Bari, (Eds.), ASTM, Philadelphia, 1987, pp.211-234.

29. Tolley, G., "**The Protective Action of Sprayed Aluminium Coatings on Steel,**" Journal of the Iron and Steel Institute, August, 1949, pp.377-384.

30. Snodgrass, J.S., "**Development of Aluminium Alloy Sacrificial Anodes,**" source unknown.

31. Campbell, H.S., "**Sprayed Aluminium and Zinc Protect Against Corrosion by Aqueous Solutions,**" Anti - Corrosion, August, 1982, pp.10-13.

32. Davies, C. and Hanford, N.J., "**Metallic Coatings for the Protection of Mild Steel from Corrosion at Ambient Temperatures,**" Anti - Corrosion, July, 1970, pp.20-22.

33. Fischer, K.P., Thomason, W.H. and Finnegan, J.E., "**Electrochemical Performance of Flame - Sprayed Aluminium Coatings on Steel in Seawater,**" Corrosion, September, 1987, pp.35-39.

34. Ballard, W.E. and Mansford, R.E., "**Sprayed Metal Coatings for Immersed Conditions,**" First International Congress on Metallic Corrosion, London, April, 1961.

35. Holroyd, N.J.H., Hopples, W. and Scamans, G.M., "**Protection of Al-Zn-Mg Welds Against Exfoliation and Stress Corrosion Cracking Using Aluminium Based Metal Spray Coatings,**" International Conference Exposition on Fatigue, Salt Lake City, USA, 1985.

36. Scott, D.J., "**Aluminium Sprayed Coatings : Their Use for the Protection Aluminium Alloys and Steel,**" Corrosion, December, 1979, pp.111-122.

37. Carter, V.E. and Campbell, H.S., "**The Prevention of Exfoliation Corrosion of Aluminium Alloys by Sprayed Metal Coatings,**" Journal of the Institute of Metals, Vol.89, 1960-61, pp.472-475.

38. Carter, V.E. and Campbell, H.S., "**Protecting Strong Aluminium Alloys Against Stress Corrosion with Sprayed Metal Coatings,**" British Corrosion Journal, Vol.4, January, 1969, pp.15-20.

39. Reboul, M.C., Gimenez, P.H. and Rameau, J.J., "**A Proposed Activation Mechanism for Aluminium Anodes,**" Corrosion, Vol.40, No.7, July, 1984, pp.366-370.

40. Vesely, V. and Horky, J., "**Electrochemical and Corrosion Properties of Thermally Sprayed Coatings of Aluminium Alloys,**" Eighth International Thermal Spraying Conference, Sep./Oct., 1976, pp.430-435.

41 Champion, F.A. and Walkiden, G.W., Chemistry and Industry, Vol.76, 1956.

42. Townsend, H.E. and Zoccola, J.C., "**Atmospheric Corrosion Resistance of 55% Al-Zn Coated Steel Sheet : 13 Year Test Results,**" Materials Protection, October, 1979, pp.13-20.

43. Bland, J., (Ed.), "**Corrosion Tests of Flame - Sprayed Coated Steel : 19 Year Report,**" American Welding Society, Florida, USA, 1974.

44. Lyall, R.A., "**Eskom's Paint Exposure Programme - Concluding Report,**" Eskom's Engineering Investigations Division, Johannesburg, July, 1990.

45. Porter, F.C., "**Sprayed Aluminium for the Protection of Steel,**" The Aluminium Development Association, The Aluminium Courier, No.58, June, 1962.

46. Sakano, T., Toda, K. and Hanada, M., "**Tests on the Effects of Indium for High Performance Aluminium Anodes,**" Materials Protection, December, 1966, pp.45-50.

47. Chavarin, J.U., "**Electrochemical Investigations of the Activation Mechanisms of Aluminium,**" Corrosion, June, 1991, pp.472-479.

48. Webb, N.C., "**A Statistical Approach to Thickness Measurement of Metal Sprayed Coatings,**" Fourth South African Metal Spraying Symposium, Johannesburg, 1979.

49. Ogburn, F., "**Thickness of Metallic Coatings,**" Testing of Metallic and Inorganic Coatings, ASTM STP 947, Harding and Di Bari, (Eds.), ASTM, Philadelphia, 1987, pp.123-128.

50. Wiktorek, S. and Bradley, E.G., "**Studies of Physical Properties of Hot Sprayed Aluminium Metal Coatings to Steel Substrates,**" Anti - Corrosion, September, 1986, pp.4-9.

51. Di Bari, G.A., "**Technical Overview on Mechanical and Physical Property Measurements on Coatings,**" Testing of Metallic and Inorganic Coatings, ASTM STP 947, Harding and Di Bari, (Eds.), ASTM, Philadelphia, 1987, pp.4-10.

52. Bland, J., (Ed.), "**Corrosion Tests of Flame - Sprayed Coated Steel : 19 Year Report,**" American Welding Society, Florida, USA, 1974.

53. Friel, J.J., "**Atmospheric Corrosion Products on Al, Zn, and Al-Zn Metallic Coatings,**" Corrosion, Vol.42, No.7, July, 1986, pp.422-426.

54. Godard, H.F. et al., "**The Corrosion of Light Metals,**" John Wiley and Sons, New York, 1967.

55. Hunter, M.S. and Fowle, P., Journal of the Electrochemical Society, Vol.30, No.9, September, 1956.

56. Buchan, A.J., "**Corrosion of Aluminium Alloys in Static and Recirculating Mine Waters,**" MSc Thesis, University of the Witwatersrand, Johannesburg, 1988.

57. Foley, R.T., "**Localized Corrosion of Aluminium Alloys - A Review,**" Corrosion, Vol.42, No.5., May, 1986.

58. Aylor, D.M. and Kain, R.M., "**Assessing the Corrosion Resistance of Metal Matrix Composite Materials in Marine Environments,**" Recent Advances in Composites in the USA and Japan, ASTM STP 864, Philadelphia, 1985, pp.632-647.

59. Carter, V.E., "**Metallic Coatings for Corrosion Control,**" Newnes - Butterworth, London, 1977.

60. Lyall, R.A., "**Eskom's Paint Exposure Programme : Concluding Report,**" Eskom's Engineering Investigations Division, Johannesburg, July, 1990.

61. Bland, J., (Ed.), "**Corrosion Tests of Flame - Sprayed Coated Steel : 19 Year Report,**" American Welding Society, [illegible], USA, 1974.

62. Buchan, A.J., "**Corrosion of Aluminium Alloys in Static and Recirculating Mine Waters,**" MSc Thesis, University of the Witwatersrand, 1988.

63. Higginson, A. and White, R.T., "**A Preliminary Survey of the Corrosivity of Water in Gold Mines,**" Mintek, Report No.M65, South Africa, January, 1983.

64. Higginson, A., "**The Effect of Physical and Chemical Factors on the Corrosivity of a Synthetic Mine Water,**" Mintek, Report No.M140, South Africa, April, 1984.

65. Damm, O.F.R.A., "**The Design and Construction of a Laboratory-Scale Semi-Continuous Casting Facility for Aluminium Alloys,**" University of the Witwatersrand, Department of Metallurgy, September, 1984.

66. "**Hot Dip Galvanizing : A Practical Reference for Designers, Specifiers, Engineers, Consultants, Manufacturers and Users,**" The Galvanizers Association of Australia, Eleventh Edition, June, 1985.

67. Higginson, A., "**The Effect of Physical and Chemical Factors on the Corrosivity of a Synthetic Minewater,**" Mintek, Report No. M140, April, 1984.