ZINALIUM® : revêtement des tuyaux en fonte ductile
ZINALIUM®: external coating of ductile iron pipes
ZINALIUM®: Äußere Beschichtung von Rohren aus duktilem Eisen

Gérard NOUAIL – Centre de Recherche et Développement SAINT-GOBAIN PAM
Gérard NOUAIL – Zentrum für Forschung und Entwicklung von SAINT-GOBAIN PAM

Les tuyaux en fonte ductile des gammes NATURAL® et BLUTOP®, pour l'adduction et le transport de l'eau, proposés par SAINT-GOBAIN PAM, sont équipés du revêtement extérieur ZINALIUM®. Ce revêtement bi couche est constitué d'un dépôt d'alliage de zinc à 15% d'aluminium, par projection thermique à l'arc électrique complété par une finition polymérique. Les mécanismes d'action de ce système de protection sont présentés. Les spécificités de l'alliage par rapport à d'autres couches métallisées sont illustrées au travers d'analyses métallographiques. Quelques essais, extraits de la caractérisation des comportements mécaniques et en corrosion de ce type de protection sont proposés. Le domaine d'utilisation préconisée du revêtement dans la majorité des sols est précisé, les quelques circonstances restrictives sont indiquées.

NATURAL® and BLUTOP® pipes from SAINT-GOBAIN PAM, dedicated to convey waters intended for human consumption are provided with ZINALIUM® external coating. It is a duplex coating comprising a first layer of an arc-sprayed true alloy of zinc with 15% of aluminium, and a finishing layer of a polymeric paint. The mechanisms of action of the protective system are presented. The specificity of the alloy compared to other metallic layers is illustrated by metallographic analyses. Some mechanical and corrosion tests results taken from the global evaluation of ZINALIUM-like coatings performances are provided. The recommended field of use of the coating is presented; its few limiting circumstances of use are indicated.

NATURAL® und BLUTOP® Rohre von SAINT-GOBAIN PAM, die dem Transport von Trinkwasser dienen, verfügen über eine äußere ZINALIUM® Beschichtung. Hierbei handelt es sich um eine Doppelschicht, die aus einer im Lichtbogen-Spritzverfahren aufgetragenen unteren Schicht (Zinklegierung mit 15 % Aluminium) und einer Polymer-Deckbeschichtung besteht. Die Wirkmechanismen des Schutzsystems werden vorgestellt. Die Spezifizität der Legierung im Vergleich zu anderen Metallschichten wird anhand metallografischer Analysen erläutert. Ferner werden einige Ergebnisse von Korrosions- und mechanischen Tests aus der globalen Evaluation der Leistung von ZINALIUM-ähnlichen Beschichtungen zur Verfügung gestellt. Der empfohlene Anwendungsbereich der Beschichtung wird unter Angabe einiger weniger Einschränkungen erläutert.

ZINALIUM®: external coating of ductile iron pipes

Gérard NOUAIL - Engineer - Centre de Recherche et Développement SAINT-GOBAIN PAM.

NATURAL® and BLUTOP® pipes from SAINT-GOBAIN PAM, dedicated to convey waters intended for human consumption are provided with ZINALIUM® external coating. It is a duplex coating comprising a first layer of an arc-sprayed true alloy of zinc with 15% of aluminium, and a finishing layer of a polymeric paint. The mechanisms of action of the protective system are presented. The specificity of the alloy compared to other metallic layers is illustrated by metallographic analyses. Some mechanical and corrosion tests results taken from the global evaluation of ZINALIUM-like coatings performances are provided. The recommended field of use of the coating is presented; its few limiting circumstances of use are indicated.

1. Introduction

As early as the beginning of 60's, the external protection of Pam® buried ductile iron pipes has been performed by a zinc based coating, progressively from small diameters, less than DN 250, up to DN 2000. It is a duplex coating comprising an arc sprayed layer of pure zinc completed by a finishing paint. This coating was recognized by an ISO standard in 1985 [1].

Due to increasing demands from customers to install pipes in more and more corrosive soils and to get longer service life, zinc coated pipes were laid with a complementary protection by PE sleeving in difficult ground conditions. For extremely corrosive soils, pipes have been equipped by barrier coatings, thick polyurethane by 1979 and thick extruded polyethylene by 1989, both being today proposed depending on pipeline project.

In order to improve the field of use of zinc coating and to avoid the drawbacks of PE sleeving on site, studies started in SAINT-GOBAIN PAM research centre by the end of 60's. Alloying zinc with other metals was an option followed to improve the corrosion resistance. Among solutions, DUNOIS alloy [2], alloyed zinc with 15% of aluminium, provided by VIEILLE MONTAGNE was analysed, first in laboratory tests (1969-71) then in field conditions (pipes samples buried in clay soil [1971] and in marine sludge [1972]). Good results from field tests proved the enhanced performance of DUNOIS alloy versus pure zinc for underground conditions. During 80's and 90's, complementary studies and characterisation have been performed in the laboratory, on field tests sites, to optimise the aluminium content in the zinc-aluminium alloy, to define a new external coating (now known as ZINALIUM®) and its field of use. A patent was issued in 1994 [3]. Together with these studies, developments on arc-spray process performances were achieved.

In year 2000 NATURAL® pipes range was introduced on the market, for carrying waters intended for human consumption. Progressively the diameter range extended from DN 60-300 to DN 600 (DN 1000). Recently launched BLUTOP® pipes are also coated with ZINALIUM®. (See www.pamline.com)

Since 2002 zinc-aluminium coatings as external protections of ductile iron pipes have been acknowledged in the European standard EN 545 regulating ductile iron pipes for water pipelines [4].

2. Constitution of ZINALIUM

Similarly to zinc coating, ZINALIUM® constitutes a duplex coating; it comprises a first metallic layer of a true zinc-aluminium alloy with 15% of aluminium [ZnAl 85-15], which is covered by a second layer: a blue finishing paint.

The weight of ZnAl 85-15 is at least 400 g/m² and the mean thickness of the paint is 120 µm when they are controlled following test procedures of EN 545 standard.

The metallic layer is arc-sprayed on the pipe wall surface from pre-alloyed wires. The process leads to specific microstructure and structure of the deposited layers. These typical layers are quite different from the ones that we obtained from our past studies on arc spraying associating one pure zinc wire and one pure aluminium wire. The metallographic examination of cross sections of layers deposited either from two pre-alloy wires or from two distinct wires illustrates (photos n°1 and n°2) the difference in the repartition of zinc and aluminium in the metallic sprayed layer.

Complementary analysis by EDAX [photos n°1; n°3 and n°4] emphases the homogeneity of the deposit from pre-alloyed wires both in terms of:

- its structure: regular piling-up of homogeneous true ZnAl 85-15 droplets,
- its microstructure: tiny scale mixing of a zinc-rich phase (light) and an aluminium-rich phase (dark): size less than 5 µm

It has not be possible to reproduce this peculiar pattern by co-deposition processes from separate wires of zinc and aluminium, either using the wires in the same gun or from two guns one for zinc and the other for aluminium. In both cases, the deposit gathered droplets of pure zinc and of pure aluminium, with some globules of various zinc alloys more or less aluminium-rich. (Photos n°5; n°6 and n°7)

The better corrosion behaviour of ZnAl 85-15 alloy versus pure zinc is explained by this specific dual microstructure of the true alloy arc-sprayed layer. The aluminium rich phase constitutes a skeleton that confines the zinc-rich phase, and then limits the zinc ions migration during ZnAl 85-15 conversion in soils. Due to the spontaneous formation of alumina on aluminium-rich phase, it offers a better corrosion resistance than the zinc-rich phase and thus maintains the aluminium-rich skeleton. Moreover it takes profit of some galvanic protection by zinc-rich phase.

Besides intrinsic properties of ZnAl 85-15, the polymeric nature of the finishing layer (cross-linked macromolecules, better ageing than previous bitumen varnishes) and its optimized thickness bring a significant contribution to the performances of ZINALIUM® by regulating the conversion of ZnAl 85-15 in soils.

3. Mechanisms of protection provided by ZINALIUM®

Three mechanisms provide the protection of external surface of ductile iron pipes when they are in soils, namely

- Formation of a protective layer of conversion products of the alloy
- Galvanic protection due to respective positions of iron and ZnAl 85-15 in the electrochemical scale
- Self-healing of coating damages that can occur during pipes handling and laying operations.

These mechanisms are similar to the ones met with the zinc coating [5-7]. Advantages of ZnAl 85-15 versus pure zinc are provided by the nature of the conversion products layer, its physical and chemical nature and also its structure. The presence of aluminium in ZnAl 85-15 slightly reduces the electronegativity of the alloy compared to pure zinc. However it is still enough low to ensure the galvanic protection of iron and the healing of damages.

The particular microstructure of pure ZnAl 85-15 alloy favours the formation of the long-term protective layer. The aluminium-rich phase withstands the aggressive condition of a large range of soils due the low solubility of alumina and aluminium hydroxide. Migration of the conversion products of zinc-rich phase towards the ground is restricted; it then make denser the transformation layers. Besides this action the finishing paint layer reduces the activity of corrosive species against the alloy. It thickness plays an important role: an optimum is to reach in order to sufficiently limit the access of soil electrolyte to ZnAl 85-15 without providing a mere close film hindering the galvanic effect and prone to blistering the paint, then enhancing corrosion.

4. Protective properties of ZINALIUM®

Duplex coatings based on ZnAl 85-15 have been evaluated comparatively to pure zinc based duplex coatings in a large range of corrosion tests both in laboratory and also in field sites. Photo n°8 illustrates the large improvement generally afforded by ZnAl 85-15. On ordinate axis we find the ratio of the corrosion rates of zinc and the alloy. On abscise axis the severity of test is reported: it has been defined as the magnitude of the corrosion rate of pure zinc duplex in the test normalised to a reference rate: its rate obtained in a field condition.

Out of these test results, three items are hereafter emphasised:

- Conversion layer of ZnAl 85-15
- Galvanic protection and healing of damages
- Resistance to concentration cell

a. Conversion layer of pure ZnAl 85-15

The photo n°9 shows the pattern of the transformation of the alloy after an electrochemical test: dissolution in sodium chloride solution under imposed current density of 350 µA/cm². The test is stopped before the entire transformation of the alloy. A cross section of the layer is then characterised by SEM and EDAX technics. X-ray cartographies illustrate the modification of the repartition of aluminium and zinc in the layer, due to the anodic polarisation. It leads to some depletion of zinc by migration in the upper part of the layer, but it is not complete as zinc conversion products form, which is revealed by the enriched presence of oxygen element. In fact these conversion products are confined within the network of the aluminium-rich phase, more enlighten in the transformed part of the layer as it relative concentration is higher.

b. Galvanic protection

Various types of testing procedures were used to evaluate this characteristic, such as:

- long-term evolution of the electrochemical potential
- protection of coating damages like scratches, impacted area, …
- macro-cell technics providing a galvanic cell between a small rod of bare ductile iron and a plate of coated ductile iron

The photos n°10 and n°11 present some examples of the devices used.

Tests performed in different media, either saline solutions or artificial soils indicate that ZINALIUM-like coatings provide the galvanic protection of ductile iron, and that ZnAl 85-15 ensures the self-healing of damages.

Photos n°12 and n°13 show the results observed after roughly ten years of two duplex coatings, one with pure zinc the other with ZnAl 85-15, same weight of metal and thickness of the finishing layer.

Both in synthetic sea water and ground water, galvanic protection of bare iron rods of the macro-cells lasted for years. Few signs of red rust are only detected at the end of the test.

c. Self-healing of damages

Photo n°14 illustrates, for instance, the ability of ZnAl 85-15 to scar small scratches affecting the coating down to ductile iron. Three damages due to saw cut, widths of 1.0; 2.0 and 3.5 mm are present on pipe coupons immersed in 2,500 ohm.cm sodium sulphate solution. After 15 months, the two coatings, either with pure zinc or ZnAl 85-15 succeeded in healing of the damages. It can be observed that the duplex coating with zinc exhibit a larger amount of conversion products than the one with ZnAl 85-15 due to the specific microstructure of the latter. It results from a smaller area of the coating liberating zinc ions as intermixed networks of zinc-rich phase and aluminium-rich phase reduce the migration and diffusion of species.

Similar tests were performed in sodium chloride solutions at various concentrations and ground water confirming this observation.

d. Resistance to concentration cell

Two examples of concentration cell tests excerpted from several others performed comparing duplex coatings based on pure zinc and ZnAl 85-15 are presented.

Photo n°15 (graph on left) shows the evolution the current exchanged between two square plates of coated ductile iron placed in a synthetic sandy ground (0-2 mm) partly logged with a ground water (1,400 ohm.cm; pH 7.6). One plate is above the water level, the other under, and they face themselves. The quantity of current exchanged after 1,200 days in the concentration cell is roughly ten times higher with pure zinc than with ZnAl 85-15. The evolution curves show a quite long period of time before the large increase of the current developed with zinc coating. The delay comes from the slow ageing of the finishing layer and the medium aggressiveness of the ground water.

Photo n°15 (graph on right) illustrates the behaviour of duplex coatings when submitted to the effect of a fluctuating water table in a peat soil. A 1,000 ohm.cm sodium chloride solution flooded the peat during three weeks, the three following weeks the water level is lowered to a middle level. Then the cycle starts again. Specimens are DN 100 pipe sections, 100 mm length arranged to constitute a vertical concentration as described in reference [8]. A very large influence of the aeration of peat during periods of low level of the water table is observed on the evolution curve of the current in the cell with pure zinc based duplex coating. The quantity of current exchanged during the 500 days of test appears as high as twelve time the one of ZnAl 85-15.

The benefits of the typical microstructure of ZnAl 85-15 appear clearly in its better resistance than pure zinc in such situations of concentration cell. Other tests performed in various conditions confirm the improvement even if the ratios of quantities of current are somewhat less. (Photo n°16) [9]

e. Field test results

First results obtained from samples buried in years 1971 and 1972 (see photos n°17 and n°18) have been confirmed by more recent campaigns of characterization in ground conditions.

After 14 years in marine sludge of Mont Saint Michel bay, ZINALIUM® proves its better resistance than a zinc coating as defined by EN 545 especially for differential aeration cell. Galvanic protection and self-healing of damages made before burying the samples have been completed (Photo n°19).

Examination of cross sections of externally duplex coated pipe wall reveals the preserved integrity of the layers and slight conversion of ZnAl 85-15 after ten years in these very aggressive soil conditions (Photo n°20)

In gypseous marls (resistivity around 500 ohm.cm) less conversion products were formed on duplex coating with ZnAl 85-15 than with pure after 13 years (photo n°21). Only a superficial oxidation of the alloy was observed on EDAX analysis of ZINALIUM® (Photo n°22)

5. Mechanical properties

Resistance of ZINALIUM® to damages that can occur when handling and laying ductile iron pipes was established from laboratory tests, such as adhesion of the coating evaluated either by pulling-off test (ISO 4624) and cross-cut test (ISO 2409) or impact test (based on ISO 6272) [10-12] .

ZINALIUM® offers good adhesion both of the epoxy and ZnAl 85-15 layers, with a mean adhesion value of 10 MPa. (Photo n°23) It ca n sustain impacts of energy up to 100 joules, leading to no damage in 32 cases out of 52, the overall mean damage area being of 0.7 mm² (Photo n°23).

6. Field of use of ZINALIUM®

The development of a mathematical modelling of soils distribution and associate corrosion rates of ZnAl 85-15 and ductile iron deduced from soil surveys performed during decades together with the numerous laboratory tests and long-term site trials, permitted to optimize the weight of ZnAl sprayed over the pipe wall to allow the expected service life in the vast majority of soils of our countries. However very few circumstances, leading to too high transformation rates of ZnAl 85-15 exist, such grounds with very low resistivity (seashore, estuary, soil with marine water table, …), acidic soils (peats, saline marsh, ..) and polluted grounds (chemical, electrical or agricultural pollution). Annex D from EN 545-2010 indicates limits of ZnAl 85-15 coating and type of protection to use in these cases.

7. Conclusion

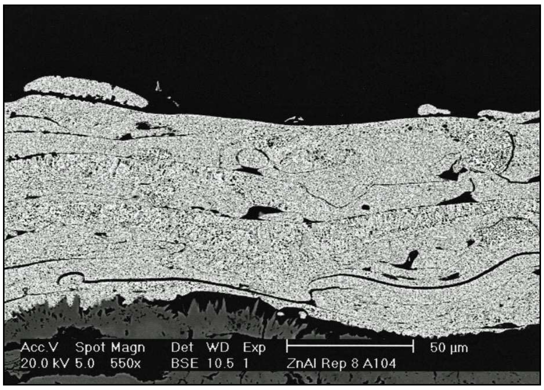
Compared to zinc coating defined in EN 545, ZINALIUM® provides an extended field of use of NATURAL® and BLUTOP® new ranges of ductile iron pipes from SAINT-GOBAIN PAM, and a largely enhanced life expectancy in the domain of application of conventional zinc coating. It comes from optimized choices of the zinc-aluminium alloy: ZnAl 85-15, the weight of the layer deposited (400 g/m²), and of the polymeric nature and thickness of the finishing layer (today 120 µm of epoxy paint) replacing the old bituminous varnish.

8. References

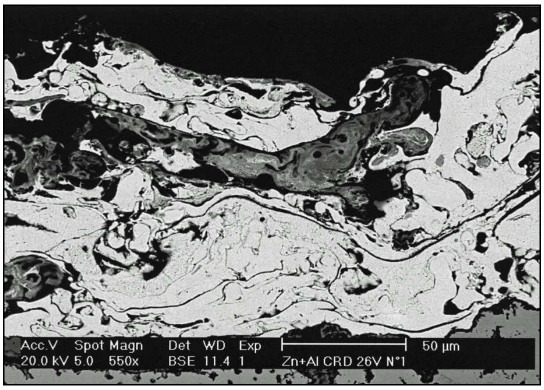
1- **ISO 8179** - Ductile iron pipes - External zinc coating - First edition 1985-04-01.
2- Private letter – 02/01/1969
3- **European patent** EP0686246 - Piping element for buried conduit, corresponding buried conduit, and method for manufacturing said element.
4- **EN 545** - Ductile iron pipes, fittings, accessories and their joints for water pipelines. - Requirements and test methods.
5- **Paris M.** - Zinc based coating for protecting buried grey and ductile iron pipes against corrosion. 1st International Conference on the Internal and External Protection of Pipes. September 9-11, 1975.
6- **Marchal R.** - Protection of Buried Ductile Iron Pipelines with zinc Based Coating – Healing Power of Coating Damage. 4th International Conference on the Internal and External Protection of Pipes. September 15-17, 1981.

7- **Nouail G.** - **Mailliard J.** - Zinc Based External Protection For Ductile Iron Pipes. 9th International Conference on the Internal and External Protection of Pipes. September 1991.
8- **Nouail G.** - A new coating for ductile iron pipes based on Zinc-Aluminium 85-15 alloy. 3R International (40) Heft2-3/2001 – pp120124.
9- **Nouail G.** - Revêtements protecteurs pour canalisations en fonte ductile. GWA 6/2011 – pp411-416.
10-**ISO 4624** - Paints and varnishes - Pull-off test for adhesion.
11-**ISO 2409** - Paints and varnishes - Cross-cut test.
12-**ISO 6272** - Paints and varnishes - Falling weight test.

Photos n°1 and n°2: Cross-section of ZnAl 85-15 layers; true alloy and pseudo-alloy

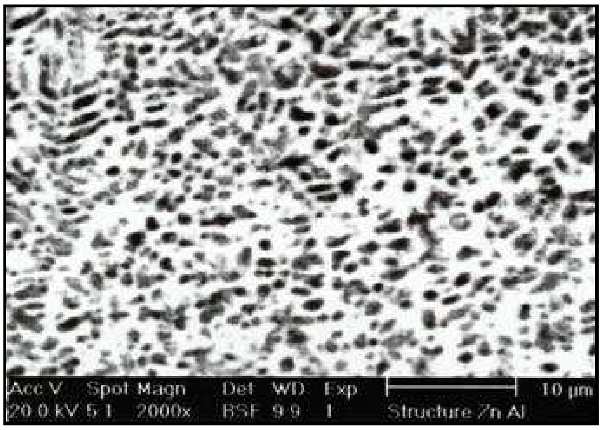


Arc sprayed layer of true alloy
from pre-alloy wires

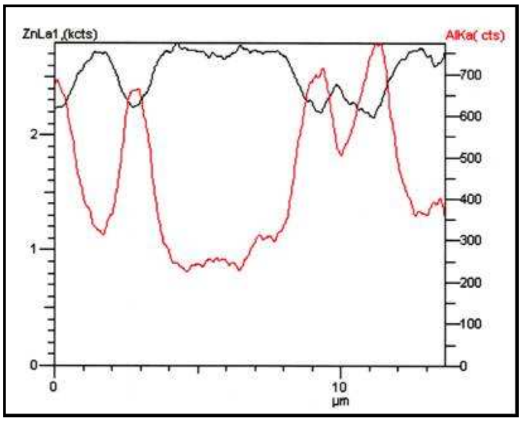


Arc sprayed layer of pseudo-alloy
from one Al wire and one Zn wire

Photos n°3 and 4: Microstructure of ZnAl 85-15 layer obtained from true alloy



Microstructure of ZnAl 85-15



EDAX characterisation

Photo n°5: EDAX characterisation of ZnAl 85-15 alloy layer
arc sprayed from true alloy wires

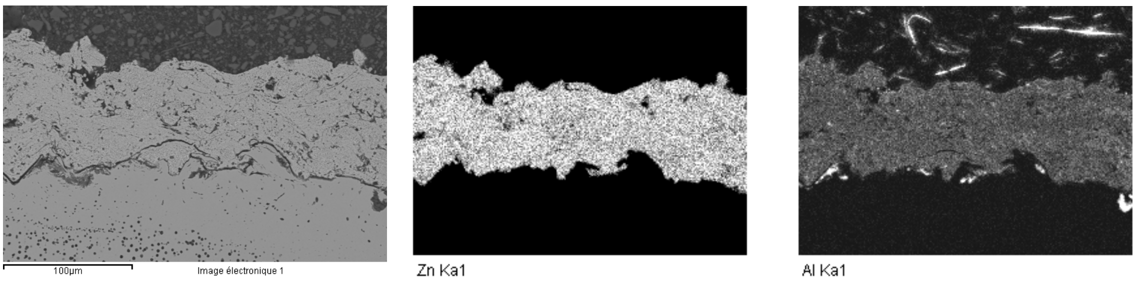


Photo n°6: EDAX characterisation of ZnAl 85-15 pseudo-alloy layer
arc sprayed from a Zn wire and an Al wire

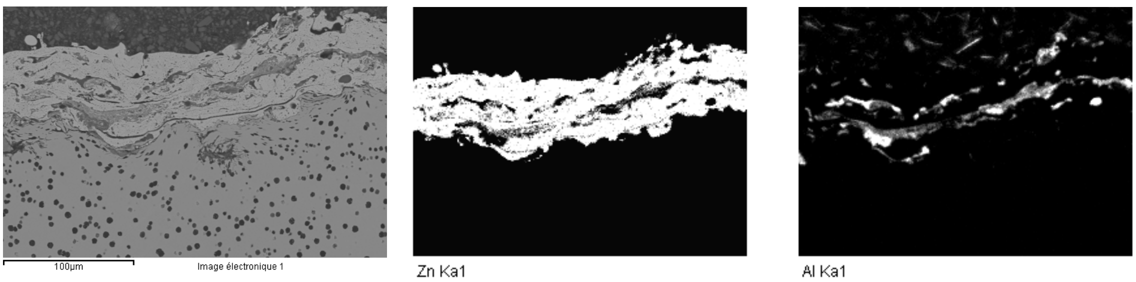


Photo n°7: EDAX characterisation of ZnAl 85-15 pseudo-alloy layer arc sprayed from two guns, one with Al wires the other with Zn wires

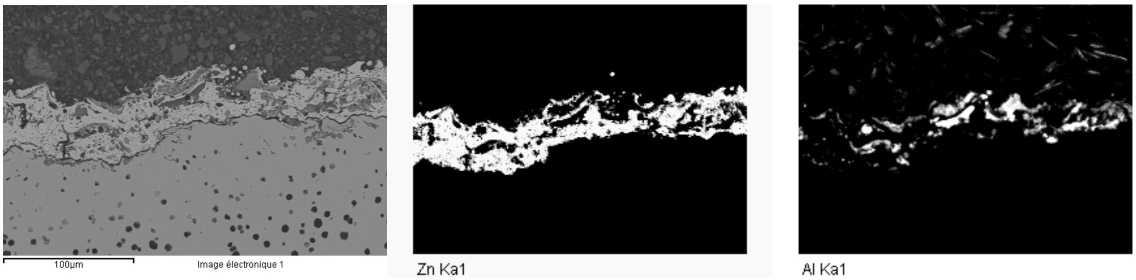


Photo n°8: Comparative evaluation of zinc and ZnAl 85-15 based coatings in laboratory tests

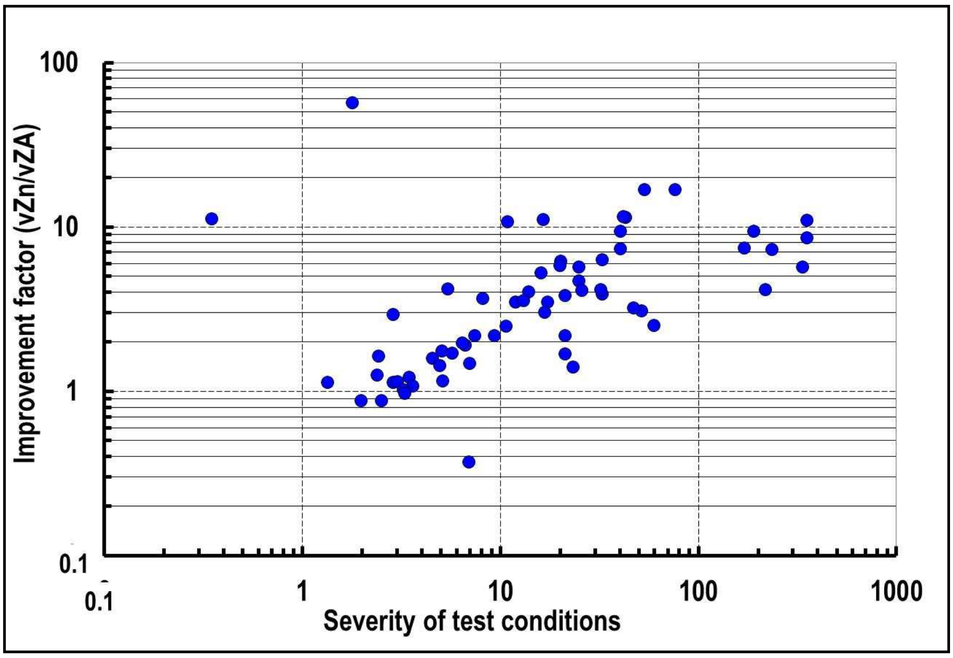


Photo n°9: EDAX analysis of an arc sprayed ZnAl 85-15 layer after controlled dissolution under 350µA/cm² in NaCl 5 gL^{-1}

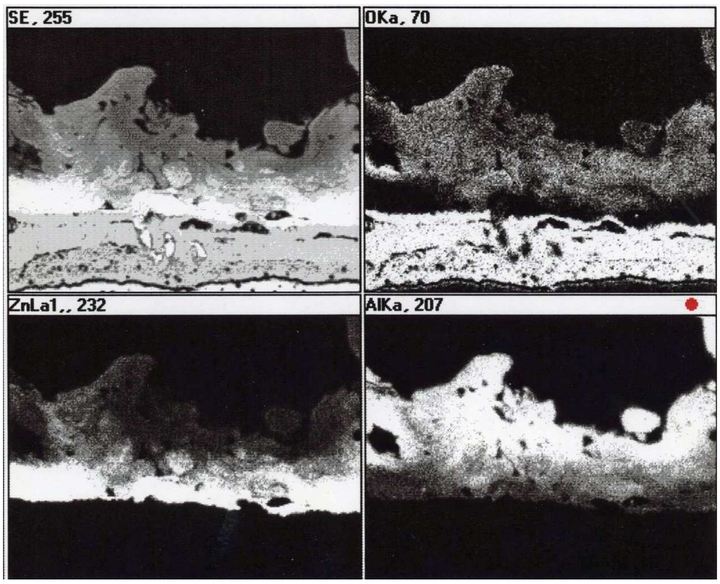
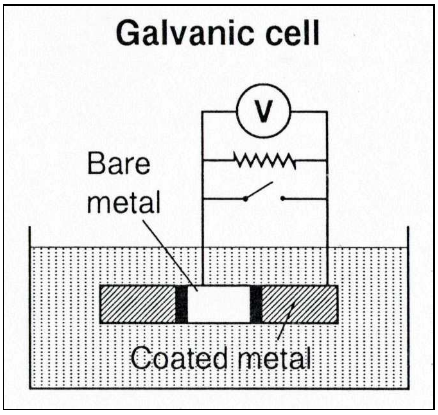


Photo n°10: Example of macro-cell devices



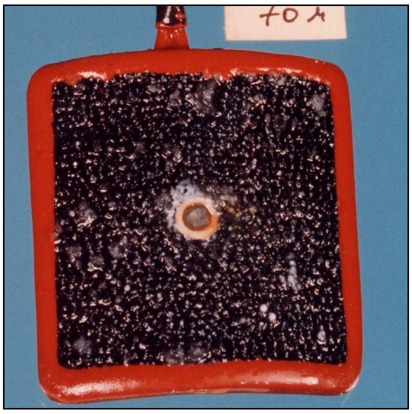
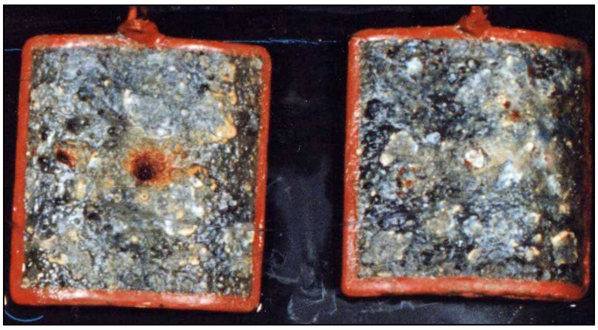
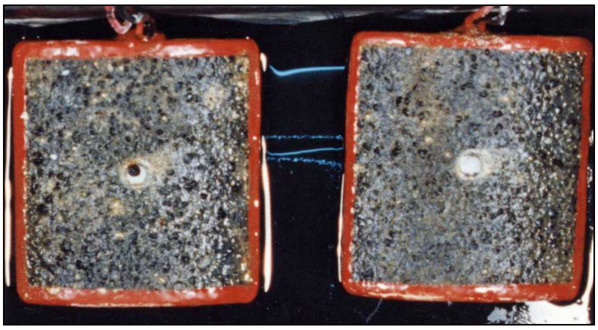


Photo n°11: Example of damaged coating by saw cutting on sample

Photo n°12: Zinc and ZnAl 85-15 coatings after 10 years in synthetic seawater



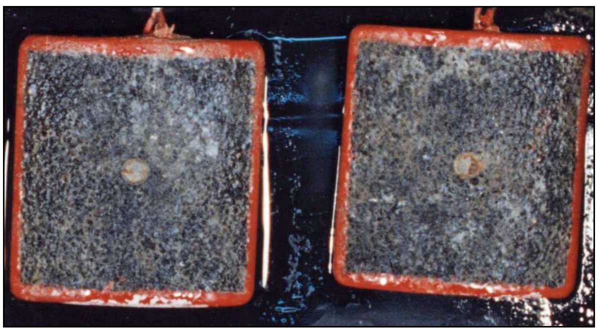
Zinc 600 g/m²+Finishing paint



ZnAl 85-15 600g/m²+ Finishing paint

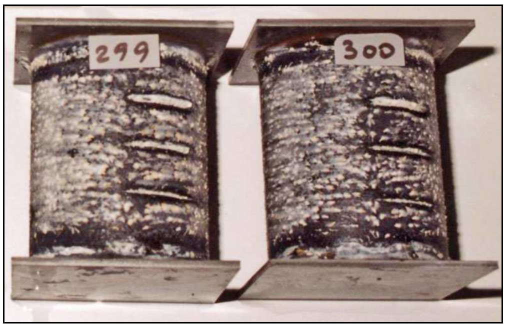
Photo n°13: Zinc and ZnAl 85-15 coatings after 10 years in ground water

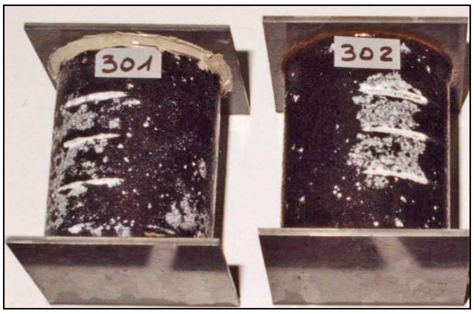
Zinc 600 g/m²+Finishing paint



ZnAl 85-15 600g/m²+ Finishing paint

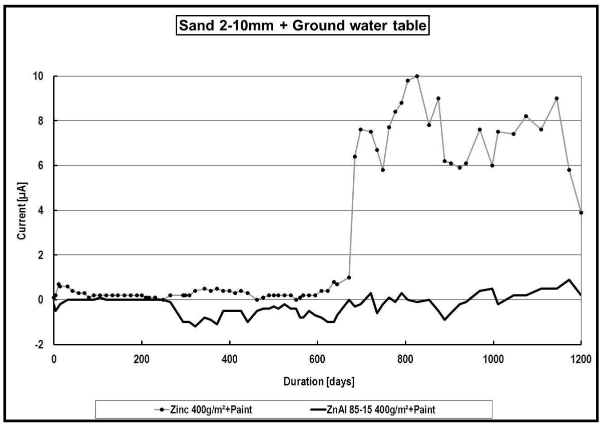
Photo n°14: Pattern of zinc coating and ZnAl 85-15 coating after 15 months in Na_2SO_4 - 2,500 ohm.cm





Zinc 400 g/m²+Finishing paint | ZnAl 85-15 400g/m²+ Finishing paint

Photo n°15: Examples of current evolution in concentration cells



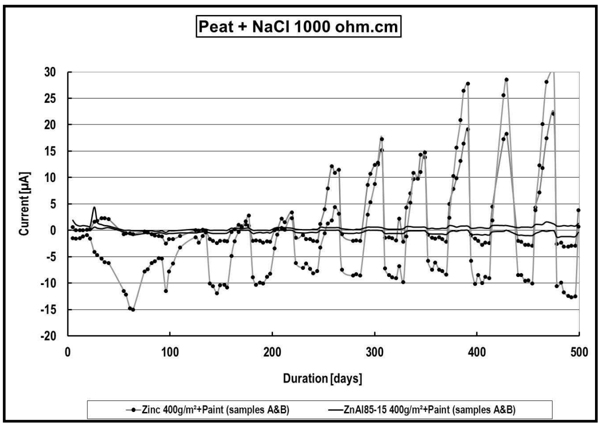


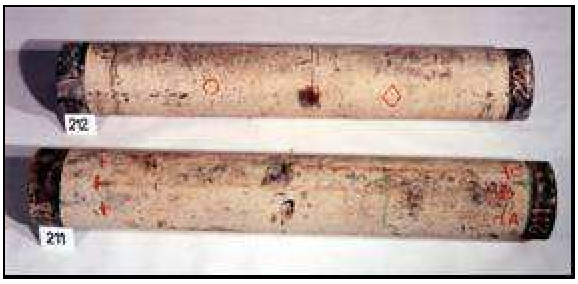
Photo n°16: Aspects of different concentration cells

Zinc 400 g/m²+Finishing paint | ZnAl 85-15 400g/m²+ Finishing paint

Photo n°17: Coatings after 19 years in Lesmesnils clayey soil (1971-1990)

Zinc 200 g/m²+Finishing paint | ZnAl 85-15 200g/m²+ Finishing paint

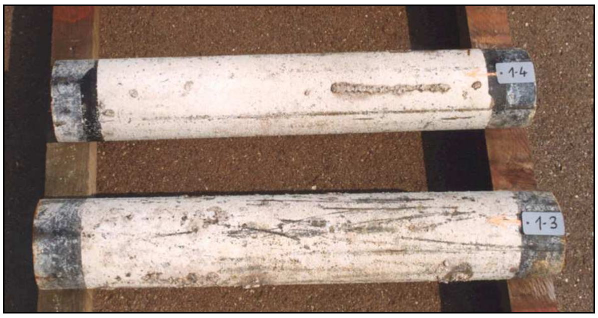
Photo n°18: Coatings after 10 years in soil of Mont Saint Michel Bay (1972-1982)



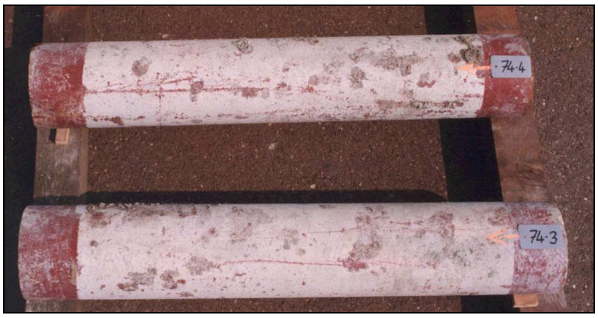
Zinc 200 g/m²+Finishing paint

ZnAl 85-15 200g/m²+ Finishing paint

Photo n°19: Coating after 14 years in soil of Mont Saint Michel Bay (1982-1996)



Zinc 200 g/m²+Finishing layer



ZnAl 85-15 400 g/m²+epoxy layer

Photo n°20: Optical examination of cross-section of zinc and ZnAl 85-15 coatings after 10 years in marine sludge of Mont Saint Michel Bay (1982-1992)

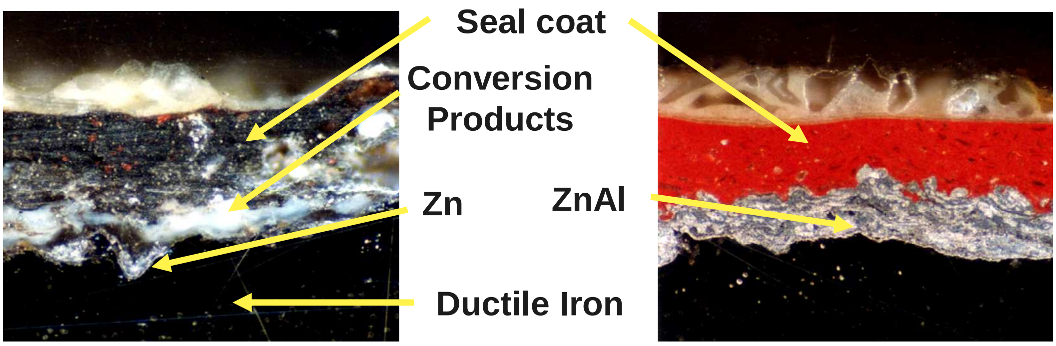
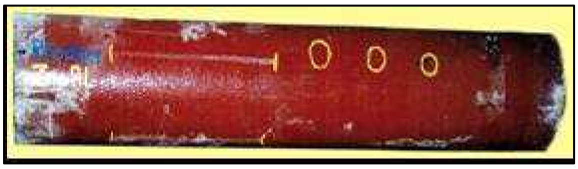


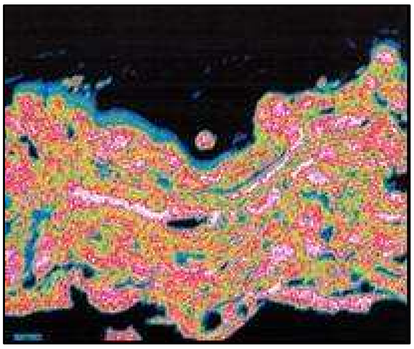
Photo n°21: Coatings after 13 years in gypseous marls (1985-1998)

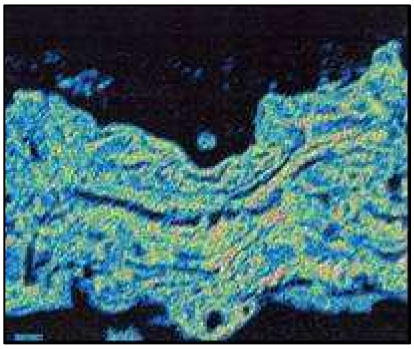
Zinc 400 g/m²+Epoxy paint



ZnAl 85-15 400g/m²+ Epoxy paint

Photo n°22: EDAX analysis of ZnAl 85-15 coating after 13 years in gypseous marls (1985-1998)


Zinc element


Aluminium element

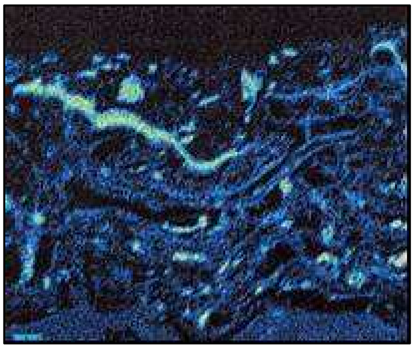
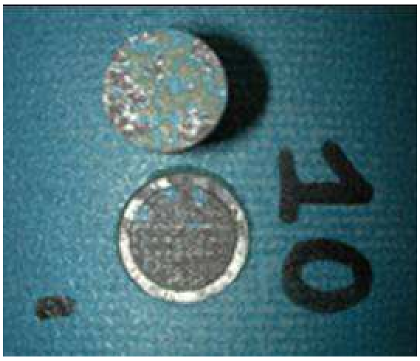
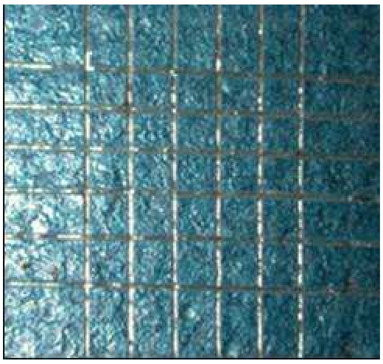
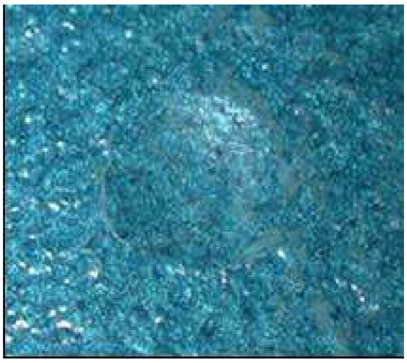

Oxygen element

Photo n°23: Illustrations of ZINALIUM® mechanical resistance



Pull-off test
Adhesion = 10MPa


Cut-cross test


Impact test
Energy = 100 joules