BioZinalium®

THE RELIABLE COATING, MADE TO LAST

Complete pipeline solutions

PAM SAINT-GOBAIN

"84 % of the service life of a pipe is determined by its external coating* "

See page 20

Contents

• natural • DN 60 to 600

• blutop • DN 75 to 160

from 2014, BioZinalium® coating will gradually replace Zinalium® coating in the Natural® and Blutop® ranges.

The revolution....

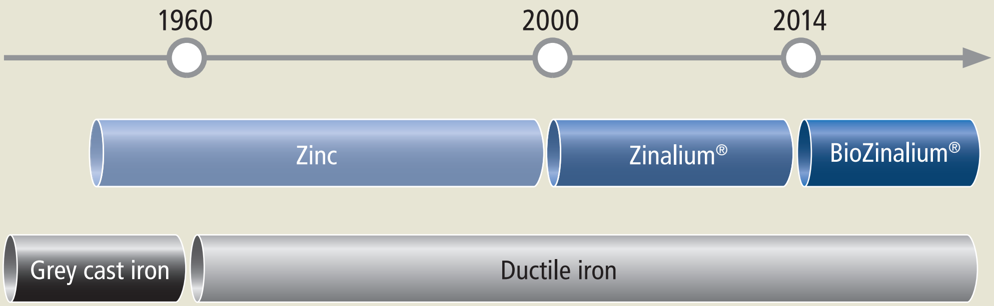
Always a coating ahead

Water authorities all around the world have to keep in mind the reduction of leakage rates and the respect of a defined budget frame work. These concerns have a direct influence on maintenance, renewal and extension programmes for water networks, as well as encouraging the choice of reliable and durable pipes.

BioZinalium® is Saint-Gobain PAM's practical response to the genuine concerns of water network investors, managers and operators.

Saint-Gobain PAM's research into zinc-based coatings has constantly helped to improve the protection of buried networks of iron pipes, which still supply the majority of capital cities.

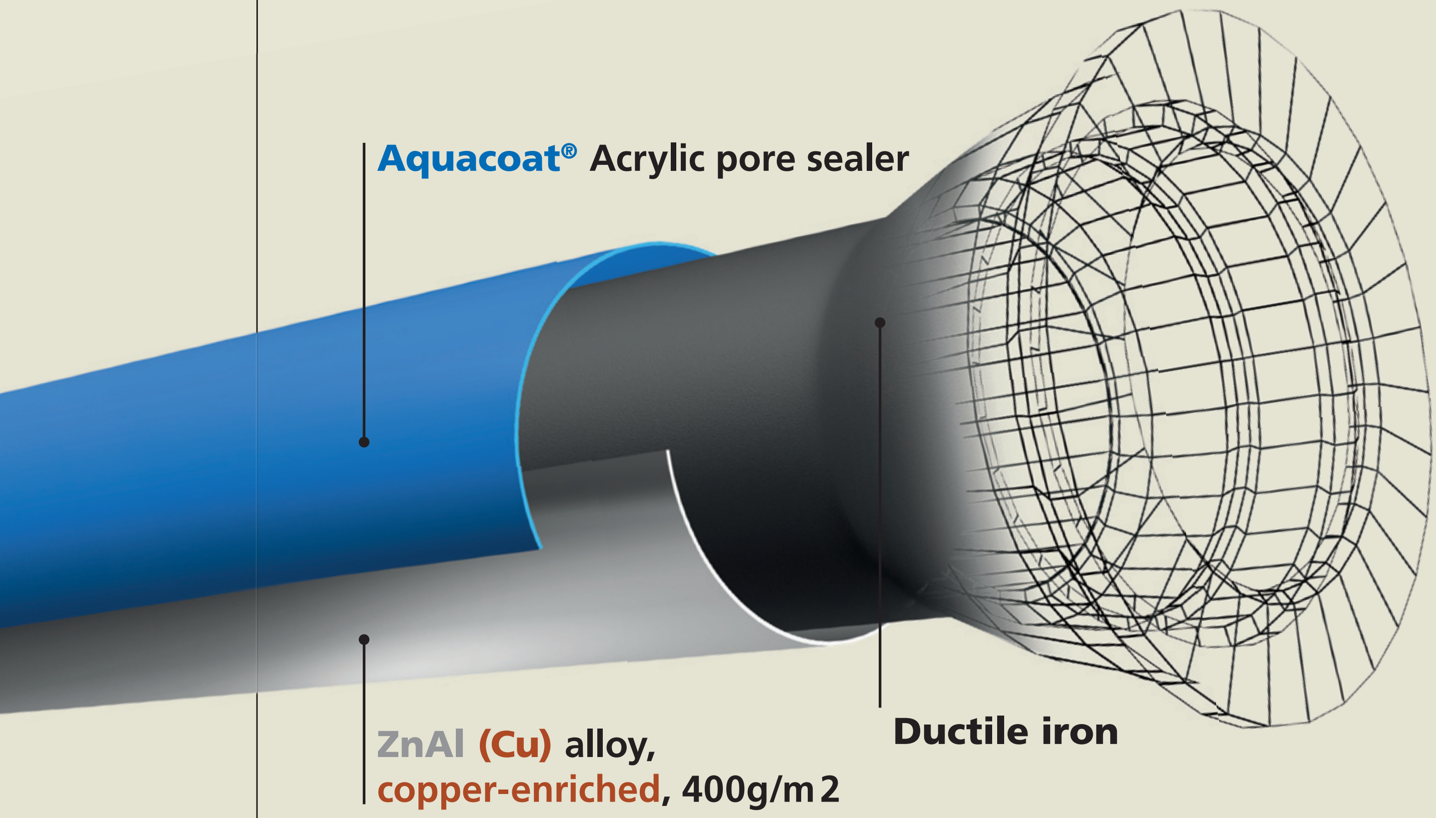
Saint-Gobain PAM, driving innovation



The answer to the Clients' expectations

BioZinalium®

ZINC-ALUMINIUM + COPPER + AQUACOAT®



The BioZinalium® coating consists of two layers:

A layer of zinc-aluminium 85/15 alloy, enriched with copper, with a minimum surface density of 400g/m², applied by spraying molten metal onto the surface of the iron, using an electric arc spray gun, from ZnAl (Cu) alloy wire.

A protective layer of Aquacoat® (semi-permeable), a water-based blue acrylic of average thickness 80 microns applied using a spray gun.

Benefits

Durable, Reliable, Preventative

Overall corrosion protection

The BioZinalium® coating retains the "active" properties of the Zinalium® coating when in contact with the ground, i.e.:

- formation of an adhesive and stable all-round protective layer (zinc hydroxides, etc.) covering the entire surface of the buried pipe;
- restored continuity of this protective layer at points which have been slightly damaged (impacts during transportation, scrapes when backfilling).

The two-phase combination of aluminium and zinc in the ZnAl (Cu) alloy increases the strength of the overall protective layer. When compared to pure zinc, it extends the areas of use (or the service life) in highly corrosive soils as defined in European standard EN545 : 2010 (appendix D.2.2.).

Protection against localised bio-corrosion

The copper enrichment of the ZnAl (Cu) alloy helps, by leveraging the bactericidal properties of copper, to reduce the possible risk of localised bio-corrosion in the following situations:

- anaerobic soils (heavy soils, wet clay soils, etc.);
- soils rich in $SO4^{2-}$ sulphates and organic matter;
- damage to the coating.

BioZinalium® therefore provides a brand new way of reducing this possible risk and thus increasing the guarantee of longevity.

Sustainable development commitment

The finishing coat (pore sealer) of BioZinalium® is produced using an emulsion of water-based acrylic-PVDC resin, which contains neither organic solvents nor Bisphenol A (BPA).

It contributes to:

- reducing emissions of volatile organic compounds (VOCs) into the atmosphere,
- complying with sanitary recommendations for reducing the risk of exposure for the population and the environment to BPA.

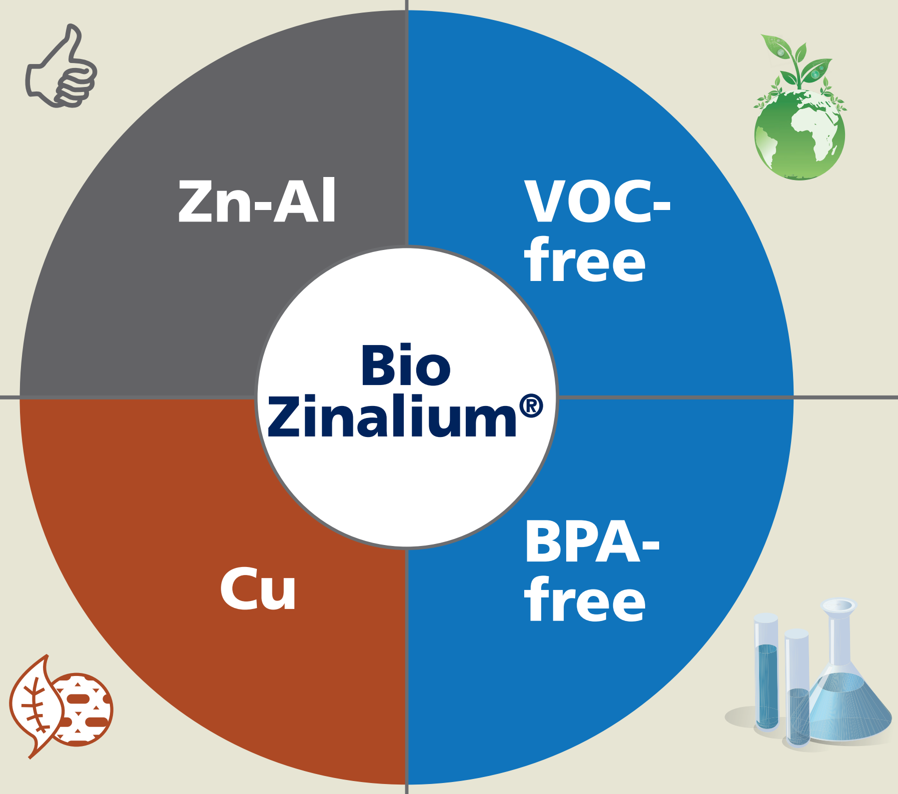
As an illustration, the move to acrylic paint in 2012 helped to reduce VOC emissions by 24 % in our Saint-Gobain PAM plants.

Benefits

Durable, Reliable, Preventative

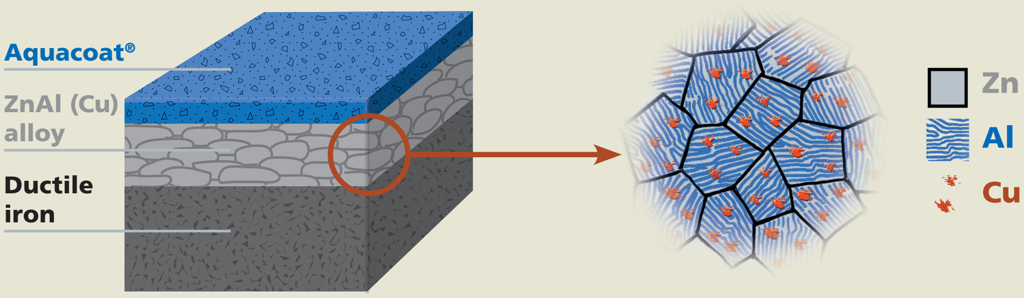
Durable protection against overall corrosion

Low environmental impact



Protection against localised bio-corrosion

Solution to public health concerns

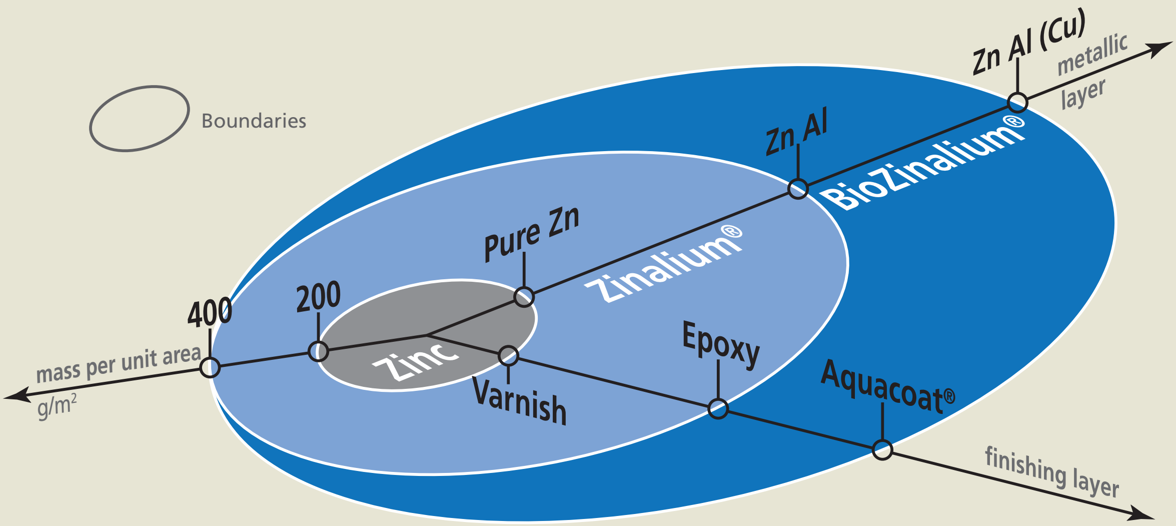


Performance

Pushing back the boundaries

Key features of BioZinalium®

The active nature of the metal layer + the surface density applied + the properties of the finish layer are the 3 aspects which contribute to the effectiveness of zinc-based coating systems.



Compliance with standards

The BioZinalium® coating complies with European standard EN545 : 2010 and International standard ISO 2531.
The BioZinalium® coating is suitable for the majority of soils, as defined in appendix D.2.2 of standard EN545 : 2010, apart from:

- soils located beneath the level of the marine water table whose resistivity is less than 500 Ω·cm;
- peaty and acidic soils;
- soils containing waste, ash, slag or contaminated with certain industrial wastes or effluents.

Performance

Pushing back the boundaries

The **advantage** of BioZinalium®

PERFORMANCE / CRITERIA	ZN	Zinalium®	BioZinalium®
Overall corrosion protection: Resistivity greater than: 2500 Ω.cm beneath the water table 1500 Ω.cm above the water table (see standard EN 545: 2010 D.2.1)			
Resistivity greater than: 500 Ω.cm beneath the water table (see standard EN 545 : 2010, D.2.2)			+
Regeneration of the coating protection when damaged			
Protection against localised bio-corrosion: Wet clay soils, soils containing sulphates, organic material, damage to the coating			+
VOC-free **(volatile organic compounds)**			+
BPA-free **(Bisphenol A)**			+

- Copper enriched, BioZinalium® reduces the random risk of localised bio-corrosion in the following situations:
- anaerobic soils (heavy soils, wet clay soils, etc.);
- soils rich in $SO4^{2-}$ sulphates and organic matter ;
- damaged coating.

The BioZinalium® coating has received sanitary compliance certificates which confirm its suitability for contact with potable water.

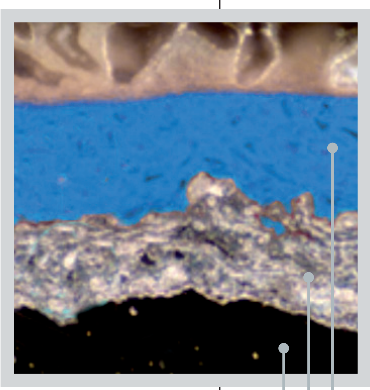
Zinc-Aluminium alloy
Global effect against overall corrosion

Overall corrosion

Overall corrosion refers to the uniform and well distributed corrosion which develops across the whole surface of the pipes and the attacks caused by the many differences in the soil (wet areas, mixture of backfill, variable oxygenation between sands and clays, etc.) and of the pipe (combination of different materials).

As soon as it is in contact with the soil, the zinc and aluminium alloy generates an outer protective layer which, together with the electrical cut-off capability of the elastomer gaskets, creates a true shell for buried ductile iron pipes.

The active properties of zinc



Cross-section of the coating

The BioZinalium® coating retains the "active" properties of the Zinalium® coating when in contact with the ground, i.e.:

- **formation of an adhesive and stable all-round protective layer** (zinc hydroxides, etc.) covering the entire surface of the buried pipe;
- **restored continuity of this protective layer** at points which have been slightly damaged, through the galvanic effect between the exposed iron and the zinc around the damage (e.g. impacts during transportation, scrapes when backfilling).

Service life three times longer *

* see pages 11 & 20

Zinc-Aluminium alloy

Global effect against overall corrosion

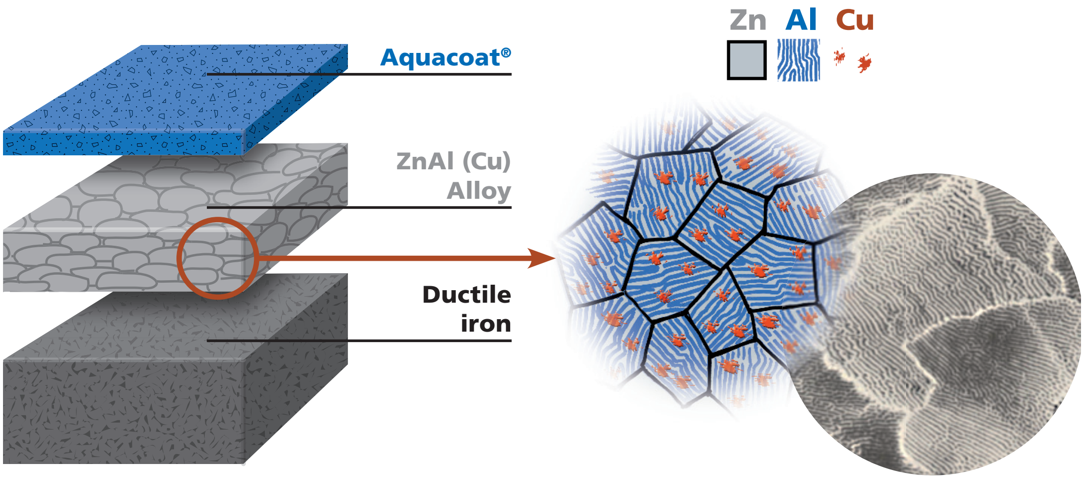
Aluminium, hand-in-hand with zinc

The two-phase combination of aluminium and zinc in the ZnAl (Cu) alloy considerably increases the strength of the outer protective layer.

In BioZinalium®, the transformation sequence is driven by 2 factors:

- the semi-permeable paint layer which limits, without preventing, transfers with the moist surrounding soil;
- the two phase structure of the 85/15 ZnAl alloy, which helps to slow the conversion of the zinc rich phase and thereby improves its quality.

The aluminium rich phase "traps" the zinc rich phase, slowing down the rate of conversion of the zinc ions and keeping them inside the metal layer.



The 85 % zinc, 15 % aluminium composition gives the optimum effect.

The ZnAl (Cu) alloy extends the areas of use (or the service life) in highly corrosive soils as defined in European standard EN545: 2010 (appendix D.2.2.).

BioZinalium® is suitable for the majority of soils, apart from:

- soils located beneath the level of the marine water table whose resistivity is less than 500 Ω·cm;
- peaty and acidic soils;
- soils containing waste, ash, slag or contaminated with certain industrial wastes or effluents.

Zinc-Aluminium alloy

Service life three times longer*

Comprehensive long-term studies on real sites

Saint-Gobain PAM has used the Mont-Saint-Michel site to test the coatings of its pipes since 1932.

A large-scale trial involved burying pipes under real conditions in the marine sands of the Saint-Gobain PAM test site in Mont-Saint-Michel, France and unearthing them **14 years later** (source: Saint-Gobain PAM internal report). rapport interne - Saint-Gobain PAM).

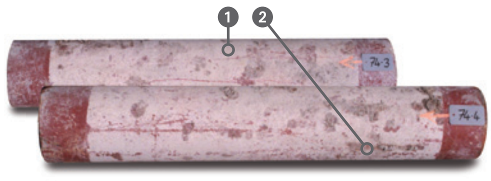
The conditions were particularly aggressive:

- sand of resistivity of **100 Ω.cm;**
- laid at a depth of 1.2 m;
- pipes buried vertically and horizontally.

The test was used to compare the behaviour of the 200 g/m² zinc + 80 µm bituminous paint coating and the 400 g/m² ZnAl 85/15 + 100 µm epoxy coating.

Results for the horizontally-laid pipes, unearthed after 14 years:
on the 2 coatings, a whitening of their original colour could be observed, a sign of the transpiration of the zinc components and therefore successful formation of the protective layer ❶.
The initial damage to the coating had also been protected and healed ❷.

200 g/m² zinc + 80 µm bituminous paint coating

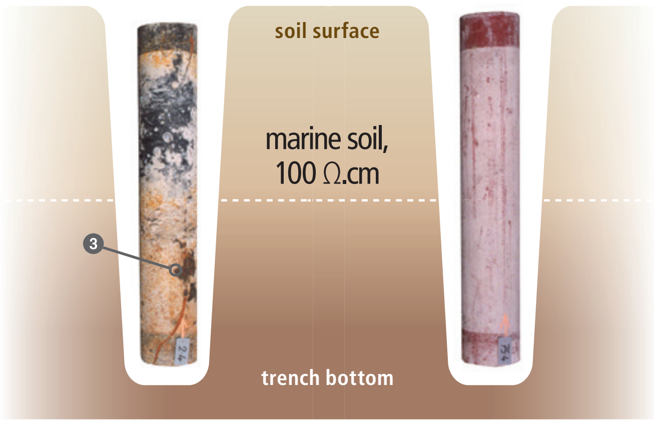


ZnAl 85/15 400 g/m² + 100 µm epoxy coating

Results for the horizontally-laid pipes, unearthed after 14 years

With the pure zinc coating, the beginnings of a corrosive attack ❸ can be seen, corresponding to the part furthest away from the soil surface (differential aeration phenomenon)

No signs of an attack are detectable on the pipe coated with the ZnAl 85/15 alloy



200 g/m²zinc + 80 µm bituminous paint coating

ZnAl 85/15 400 g/m² + 100 µm epoxy coating

Zinc-Aluminium alloy

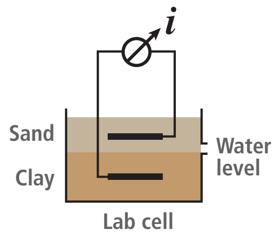
Service life three times longer*

Speed of attack reduced by a factor of 3

This very severe test involves recreating a situation frequently encountered by buried pipes: differential oxygenation between the upper and lower parts of the trench (due to the depth or the presence of **water tables**) which can intensify the corrosive effect of the soil. This is known as a "**geological cell**".

These geological cells have been recreated in instrumented laboratory cylinders, with 4 types of soil (sand, limestone, clay and peat) while simulating a fluctuating water table.

Source : Source: a new coating for DI pipe based on Zinc-Aluminium 85-15 alloy/Gérard Nouail – SGPAM/3R international-n°40/2001



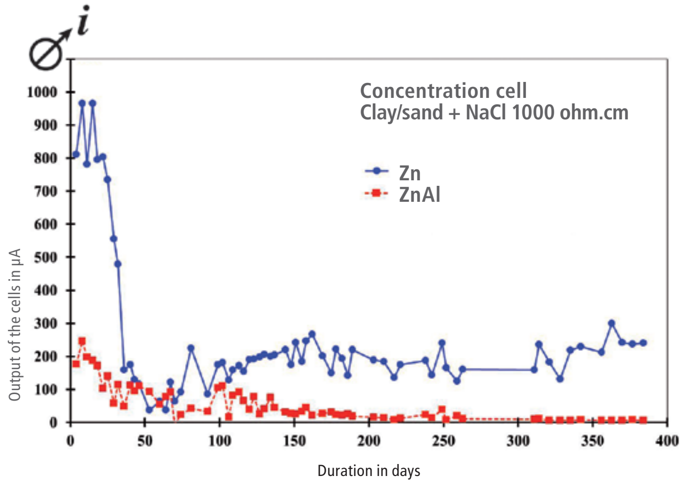
Recreations of 6 geological cells in the laboratory

Example on a clay/sand geological cell over 13 months

- Clay 200 Ω. cm + sulphates, sand 0-2 mm, saline solution
- Pure zinc 400 g/m2 and ZnAl 85/15 400 g/m2 applied to pipe samples (25x25cm)

By measuring the current exchanged between the 2 cell elements, we observe that the ZnAl 85/15 alloy is much less converted than the zinc.

The ZnAl 85/15 alloy has reduced the corrosion rate by a factor of 3.

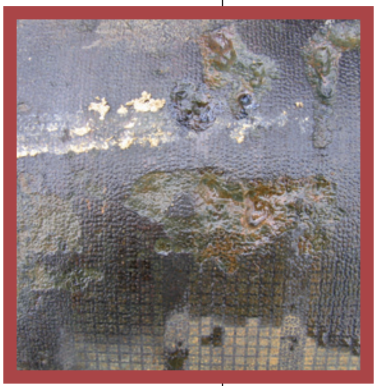


* see pages 11 & 20

Copper

Targeted impact on bio-corrosion

Localised bio-corrosion



Example of localised bio-corrosion

Corrosion of exposed iron in soils is an electrochemical reaction which, in simple terms, is similar to the iron being "dissolved" in the soil:

Fe (in wall) $\xrightarrow{\text{dissolution}}$ **Fe^{2+}** (in the soil) **+2 electrons** (electrical current)

Various micro-organisms, present locally in the soil, sometimes increase the electrochemical corrosion process by promoting the capture of the electrons released by the oxidation of the iron to "feed". This is called "bio-corrosion".

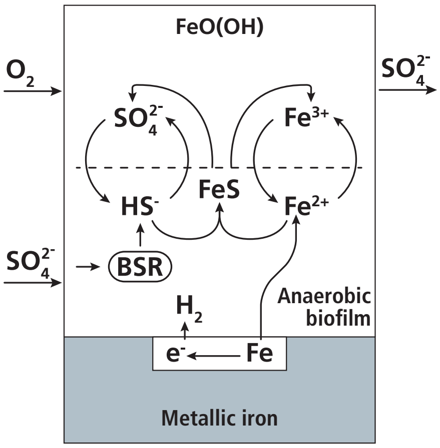
It is most commonly observed in anaerobic conditions, such as wet clay soils. It involves sulphate-reducing bacteria (SRBs) which "take these electrons" to "feed" by reducing the sulphates commonly found in the natural environment. The sulphides formed react with ferrous ions.

$4Fe^{2+} + S^{2-} + 6OH^{-}$ -> FeS (sulphide film) **+ 3 $Fe(OH)^{2}$**

The growth of these bacteria can be detected by the formation of a film of iron sulphide and a biofilm on the surface of the pipe.

Favourable conditions for localised bio-corrosive attacks are:

- anaerobic environments (heavy, clay and wetsoils);
- "nourishing" soils(containing sulphates $SO4^{2-}$, organic matter);
- the presence of iron (e.g. damage to the coating).



Source: "rôle des bactéries sulfurogènes dans la corrosion du fer" (role of sulphidogenic bacteria in the corrosion of iron) article/R. Marchal/revue IFP/54-1999-5

Protection against localised bio-corrosion

Copper
Targeted impact on bio-corrosion

Copper, a powerful bactericide

Copper is a material that is part of our everyday lives: containers, water pipes for sinks, coins (from ancient times to the present day).

Copper is an active component in many products to kill or inactivate pathogenic bacteria, moulds and viruses: in agriculture, the marine environment, the food production chain and domestic hygiene. It is recommend in hospitals for restricting hospital-acquired infections (e.g. handles and handrails).

The US American Environmental Protection Agency (EPA) officially registered copper as an anti-bacterial agent in 2008.

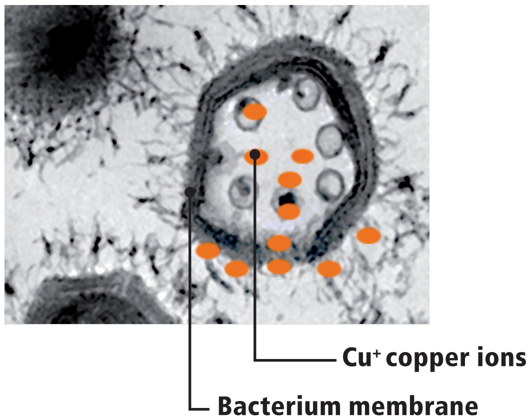
Copper is also a vital trace element in the human diet.

Copper affects bacteria in two stages:

- perforation of the cell membrane by Cu+ ions (short-circuit or oxidation),
- then penetration and invasion of the cell, thereby blocking the enzymes it requires for metabolism and killing it.

The copper included in the ZnAl(Cu) alloy remains in place and is not consumed by the metabolism of the bacteria. It only modifies the electrochemical processes. The antibacterial effect of ionic copper begins immediately by completely eradicating bacteria within a few hours. Oxidation of the copper does not diminish in any way its bactericidal ability.

Saint-Gobain PAM engineers and researchers have ascertained the right amount of copper to achieve the optimal bactericidal effect of around 0.5 %.



The copper perforates the membrane of the bacterium then invades it and blocks its metabolism (the interpretation most commonly given by scientists).

Copper

Protection against localised bio-corrosion

From metallurgy to biology

Saint-Gobain PAM Research Centre

The Saint-Gobain PAM Research Centre has developed a testing methodology with the support of the bacteriology laboratory of the University of Clermont-Ferrand (France).

The tests focused on samples of cast iron coated with ZnAl 85/15 and ZnAl(Cu), exposed to 2 different inoculants, containing respectively:

- an aerobic strain: Pseudomonas Aeruginosa (ATCC 27853),
- an aerobic strain: désulfovibrio désulfuricans (ATCC 27774).

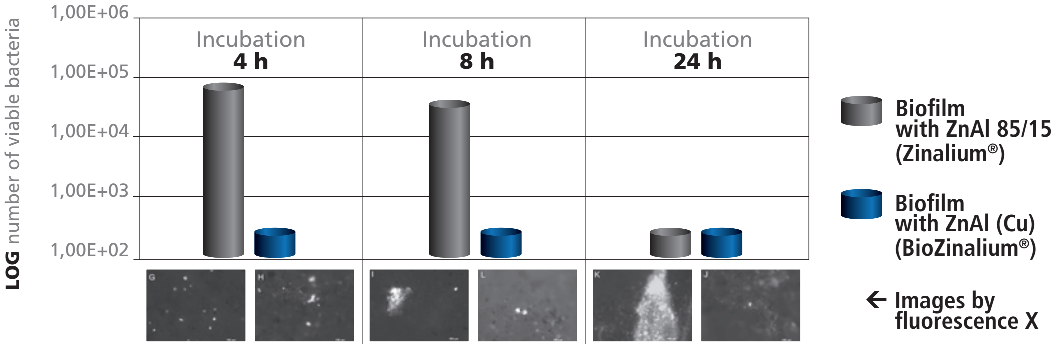
Each sample was exposed to the inoculant for 4, 8 and 24 hours at 35 °C. The biofilm which develops on the surface is then recovered via sonication and incubated on nutrient agar to allow the surviving population to grow.

Rapid action of copper

The biocidal power is assessed in the presence of strains of Pseudomonas Aeruginosa.

The breakdown below shows that the bacterial activity on the surface of the ZnAl(Cu) coated sample stopped within 4 hours, whereas it continued up to 24 hours for a sample coated with ZnAl.

Fluorescent observation of the sample surfaces reveals the surfaces which have been colonised by living bacteria (clear surfaces) and quantifies them. Extensive bacterial colonisation on the surface of the ZnAl layer can be observed, much greater than the traces of colonisation on the surface of the BioZinalium® ZnAl (Cu) layer.



Copper

Protection against localised bio-corrosion

EFFECTIVENESS VERIFIED DURABILITY

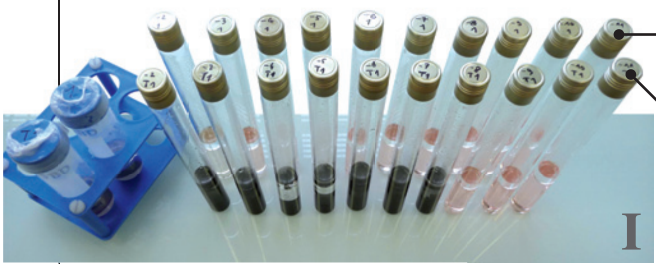
Effectiveness of Copper

Bacterial activity is measured in the presence of Desulfovibrio Desulfuricans strains (SRBs).

The samples of coated cast iron (2x2 cm^2 pieces) are processed in several stages:

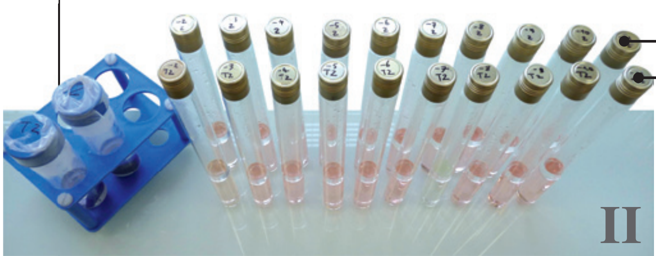
- inoculation and accelerated weathering (in solution) to trigger the reaction between iron, bacteria and copper;
- recovery of the biofilm via sonication and washing;
- incubation of the biofilm for 14 days at 30 °C, with different dilutions.

Finally, count the surviving population in the incubated biofilm, using the MPN (Most Probable Number) technique.
A dark colouration highlights bacterial activity, a clear colouration indicates the absence of any bacterial activity. The dilution level corresponds to the change in colour and provides information about the effectiveness of the biocide.

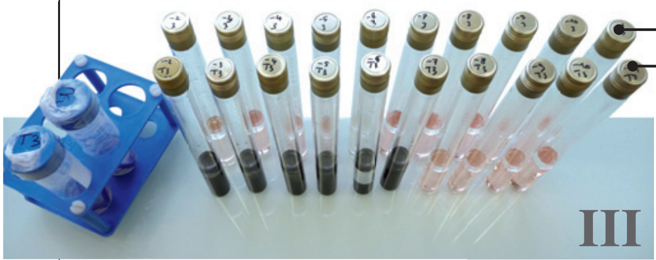


A Row with Biofilm on ZnAl (Cu) (BioZinalium®)

B Row with Biofilm on ZnAl 85/15 (control)



A
B



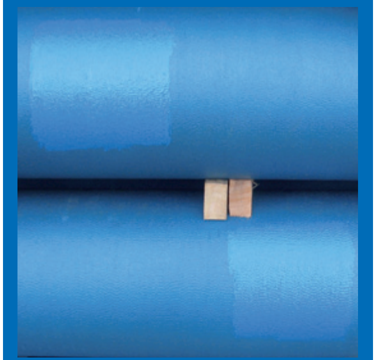
A
B

The comparative test is conducted 3 times (I, II, III). The following observations can be made from the series of test tubes opposite:

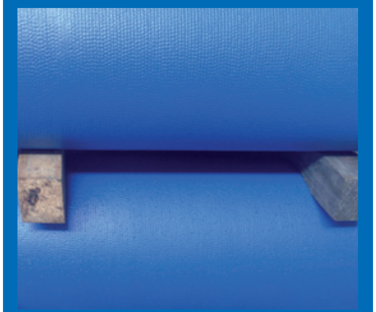
- Rows **(A)** with biofilm on ZnAl (Cu) (BioZinalium®): **no surviving bacteria**, in all 3 cases **(I, II and III)**.
- Rows **(B)** with biofilm on ZnAl (control): **surviving bacteria remain**, in 2 out of 3 cases **(I and III)**, estimated at $2.5x10^5$ bacteria per cm^2, using the MPN method.

Aquacoat®

Benefits of water-based protection



Repair on Epoxy



Repair on Aquacoat®

Hard-wearing...

Aquacoat®, the pore sealer for BioZinalium® is a single component paint made from a copolymer acrylic-PVDC (polyvinylidene chloride) resin in a water-based emulsion.

The film is applied by physical drying (evaporation of water at 50 °C) and irreversible coalescence of the organic particles.

The particles "agglomerated" in this way form a uniform, stable and adhesive protective film, with an average thickness of 80 µm, resistant to atmospheric conditions (stockyards) and to the soil.

Its mechanical and chemical properties are compatible with the increased resistance of the ZnAl (Cu) alloy.

... And ease of application

Aquacoat is a single component acrylic-PVDC paint, with the following practical advantages:

In the workshop: it removes the risk of incorrect mixtures, thereby eliminating potential visual defects (variable colouring), performance defects (quality of the film) or sanitary compliance faults.

On site: Unaffected by the moisture content of the substrate and easy drying, it is well suited to repair conditions following transport and on site.

A repair made using bi-component epoxy paints is frequently visible, but virtually invisible when a single-component acrylic paint is used.

Numerous tests have been conducted to verify the resistance of the BioZinalium® acrylic pore sealer. The table of results opposite shows that its performance when implemented with buried pipes is at least equivalent to that of the Zinalium® epoxy pore sealer.

The ecological and healthy choice

Aquacoat®

Benefits of water-based protection

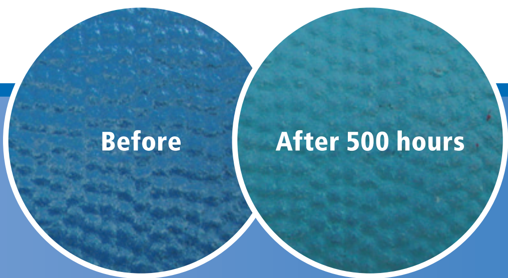
Remarkable durability

Parameters tested	Methodology	Criteria	Comparative Results	
			Epoxy pore sealer	**Aquacoat® pore sealer**
Cross-cut test	NF EN ISO 2409	adhesion score	**positive**	**positive**
Falling backfill	55 x 10 kg of gravel (2-14 mm) falling from a height of 2.50 m	no perforation of the pore sealer	**positive**	**positive**
Temperature of the water in the pipe	NF EN 545 : 2010	≤ 50 °C	**yes**	**yes**
Water absorption	in-house methodology	absorption of ionised water at 20 °C on clear film	**≈ 0 %**	**≈ 3 %**
Contact with drinking water	ACS methodology		**yes**	**yes**
Action on the galvanic effect of ZnAl	Zn Al + pore sealer 50 °C saline solution 100 Ω.cm	> 150 days	**> 400 days**	**> 400 days**
Artificial weathering and exposure to artificial radiation	NF EN ISO 11341	(500 hours of exposure/500 W/m²/ Dry air temp 55 °C - Method No. 1/ cycle A)	**see below***	**see below***
	NF ISO 7724-3	change of colour DE	**DE = 13.7**	**DE = 4.9**
	NF EN ISO 2813	loss of gloss at 60°	**74,8 %**	**17,6 %**
Drying properties	kiln drying	speed of drying	**40 min at 70 °C**	**12 min at 60 °C**

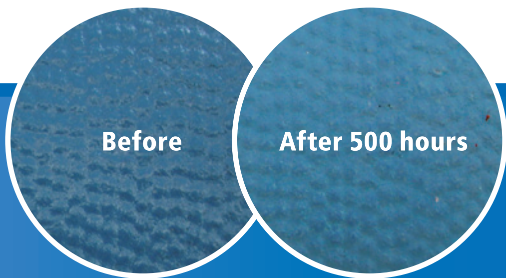
* **Details of the accelerated weathering test (500 hours of UV exposure)**

- the new epoxy is glossy and then takes on a clear matt appearance over time (whitening),
- the new acrylic is satin finish and retains the colour over time.

Epoxy



Aquacoat® (Acrylic)



Aquacoat®

The ecological and healthy choice

VOC-free (volatile organic compounds)

Definition and sources

Put simply, VOCs are gases emitted by the combustion of fuels or evaporation of solvents contained in certain materials and products. Their common factor is that they evaporate more or less quickly at ambient temperature and are found in the air. Today there are more than 300 different types.

Their sources can be natural (forests, meadows) or man-made (e.g. transport, industry).
There are numerous man-made sources, including the following industrial processes: chemistry, degreasing of metals, painting, printing, glues and adhesives, oil refining, etc.

Examples of well-known VOCs include:

- paint solvents (e.g. xylene, toluene),
- solvents in inks.

Toxic effects on health and the environment

The effects of VOCs vary considerably depending on the type of pollutant concerned. They range from an unpleasant smells to mutagenic and carcinogenic effects (e.g. benzene, certain HAP), as well as various irritations and a reduction in respiratory capacity. The symptomatology related to VOCs is complex and nonspecific.

Being highly volatile, VOCs they can spread considerable distances from where they are emitted. They contribute to photochemical reactions in the lower atmosphere, thus causing an increase in the concentration of ozone in the troposphere. VOCs are therefore greenhouse gases with an indirect effect on health.

Legislation

On 1st December 1999, the United Nations Economic Commission for Europe (UNECE) obtained a commitment from 26 European countries, including France, as part of the Gothenburg protocol, to comply with limits on emissions of harmful gasses (including VOCs) in order to reduce the impact of atmospheric pollution on health and the environment.

In France, work to reduce volatile organic compounds is part of a national initiative by the Inspection des Installations Classées (French Inspectorate of Classified Installations). In the sectors where solvents are used (e.g. printing, painting), the aim was to reduce emissions by 50% in 2010.

Aquacoat®

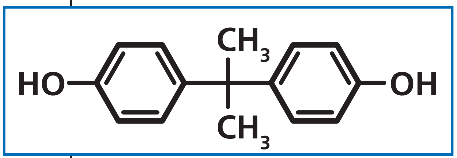
The ecological and healthy choice

VOC-FREE APPROVED BPA-FREE

BPA-free (Bisphenol A)

Definition and sources

Bisphenol A (BPA) is a chemical compound formed from the reaction between two equivalents of phenol and one equivalent of acetone.



BPA is a synthetic chemical substance which has been used for more than 50 years. It is found as a residue from the synthesis of plastics such as polycarbonates and epoxy resins. It is easily leachable, especially at high temperatures.

Toxic effects on health and the environment

BPA is on the list of endocrine disruptors.

The toxicity of BPAs is related to:

- its effects on the reproductive system and the mammary glands,
- its effects on metabolism and obesity,
- its effects on the brain and behaviour.

The extent of Bisphenol A toxicity and ecotoxicity and, indirectly, the "acceptable daily intake", are still the subject of scientific and social debate, reflecting the complex nature of the problem and the difficulty of understanding them.

Nonetheless, as a precautionary measure, countries are gradually putting legislation in place to reduce the risk of exposure of the population (particularly pregnant women and infants) through their diet (e.g. materials in contact with food) or from handling them in the workplace (e.g. thermal paper from cash registers).

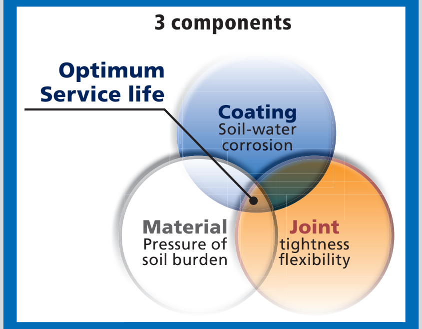
Initiatives across the world

Timeline:

- 2007, AESA report stipulating the acceptable daily intake (ADI),
- 2008, FDA (Food and Drug Administration) report recommending limiting exposure,
- 2011, ANSES (Agence Nationale de Sécurité Sanitaire, French health protection agency) on the health effects of BPA,
- 2012, French law prohibiting the manufacture, import and marketing of any packaging for food purposes containing BPA (effective from end 2015).

+++Durability

Contribution of the coating to the service life



The optimum service life is achieved when the 3 components - material, coatings and assemblies - are completely reliable.

For the pipe manufacturer, the service life depends on the performance of the following 3 components:

- **the material:** resistant to mechanical stresses (hydraulic pressure and weight of earth),
- **the coatings:** resistant to chemical attack (from water and soil),
- **the assemblies:** maintain watertightness in all circumstances (excess pressure or movement of the ground).

Saint-Gobain PAM has therefore developed an original and rational approach to individually assess the contribution of the coating to the service life:

their researchers have been working with a mathematical forecasting model, the only one of its kind in the world (in-house software). It is based on an algorithm which calculates cumulative probabilities, capable of assessing the risk of perforation, taking account of:

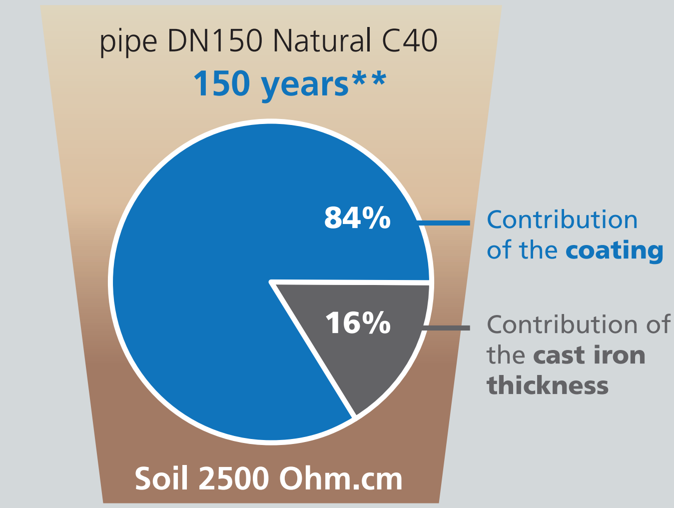
- the laws of cast iron corrosion (rate of attack depending on the environment);
- the performance of the coatings in the different soil types encountered;
- the geological distribution of the soils and their blends;
- the vagaries of installation.

Taking into account these numerous variables, the probabilistic model can be used to assess the "life expectancy" of a pipe by adding the zinc/aluminium alloy conversion time, the delay in the passive conversion of the hydroxide layer of the alloy and the cast iron corrosion time.

**With this model, the life expectancy of a DN150 Natural C40 EN 545 : 2010 pipe buried in soil of resistivity of 2500 Ω.cm is estimated at 150 years.

The software has been calibrated from an analysis of around one hundred samples taken from existing networks.

Contribution of the coating to the life expectancy of a buried pipe



Your challenges — BioZinalium® solutions

Your challenges	BioZinalium® solutions
Your investment	☑ Service life three times longer
Failure rate	☑ Insurance against bio-corrosion
Water quality	☑ BPA-free
Environmental impact	☑ VOC-free

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