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Environmentally Friendly Solutions For Industry

MEXEL® 432 ANTI CORROSION IMPACT

1. Preamble

Power Plants water cooling circuits are equipped with Condensers, Heat exchangers and various equipment made from various metals and/or alloys (copper, stainless steel, mild steel, titanium …).
Corrosion of condenser tubes is source of condenser tubes leaks, which generates pollution of Boiler water with subsequent corrosion of Boiler tubes and deposit on Steam Turbine blades. These problems are source of high maintenance costs, unavailability of the Plant, and reduction of plant residual life which has a direct incidence on Plant financial costs
Corrosion of components installed on water cooling circuit, including Condenser and auxiliary heat exchangers, pumps filters, valves… is source of high maintenance cost due to corrosion
Protection of these materials against corrosion is required to improve Plant availability factor, and increase residual life of components which have a direct incidence on Plant maintenance costs and Plant financial costs

2. Anti-corrosion properties of Mexel® 432

Chemical analysis of Mexel® 432 makes the product to be not an oxidant.
In addition, from its activity, the MEXEL Process offers anti-corrosion properties. Such anti-corrosion properties are delivered by the two following activities of Mexel® 432:
- Dispersion of biological film offering a reduction of corrosion generated by bacteria,
- Protection of the metal offered by the film created at surface, which provides a barrier between metal and water.

Corrosion reduction has been observed on numerous applications of MEXEL process.

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In addition, corrosion inhibition has been demonstrated by several laboratory tests, on various metals and alloys.

2.1. Corrosion inhibition on brass in fresh water

Conditions of laboratory Test made: Test is made on 4 samples in brass, immerged in (Seine) river fresh water at pH 4 and 7. Two samples are not treated and two samples are fully covered with Mexel® 432 by brush application. All samples are maintained in water under continuous stirring, during 25 days. The following up of potential is made using a calomel electrode. The test demonstrates (Bardet):
- Samples without Mexel® 432, show potentials higher by about + 60 mV compared to the ones protected with Mexel® 432,
- Samples in a pH = 4 solution have an average potential which is higher than the ones immerged in a natural solution of pH = 7,
- Samples without Mexel® 432 present a stable potential versus time,
- Sample in pH = 4 solution and protected with Mexel® 432, smoothly moves to potential of natural metal without any protection. Sample in pH = 7 solution and protected with Mexel® 432 shows low stable potential,
- Only the surface protected with Mexel® 432 and immerged in pH = 7 solution does not present any corrosion and shows initial aspect at issue of 25 days test (Cf. Slide 1).

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Slide 1 : Corrosion inhibition of a sample in brass, protected with Mexel 432 at pH 7.

In addition, when protected by Mexel® 432, the brass polarization curve immerged in river (Seine) fresh water moves to cathodic potentials. This indicates that corrosion speed of the metal without any Mexel® 432 protection is about 100 times higher (Cf. figure 1).

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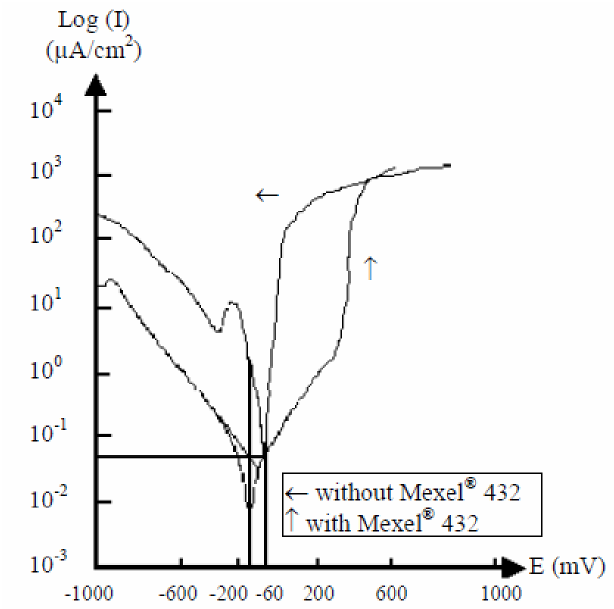
Figure 1 : Brass sample polarization curve after brush application of Mexel® 432 (Bardet)



Similarly, same test made on the field on a brass tube shows an anti-corrosion effect generated by Mexel® 432 injection, illustrated by the decreasing of potential by 40 to 50 mV, followed by potential stabilization.

2.2. Brass corrosion inhibition in sea water

Several tests regarding brass corrosion inhibition on tubes samples delivered by CPT Le Havre, have been carried out by EPI company (Bonnet, 1998, 1999a,b,c,d). This company is equipped with an instrumented mini-exchanger offering a following up of the corrosion on a tube sample in brass ($CuZn_{22}Al_2$) under thermal stresses. Water used for the test is a synthetic sea water (according to ASTM standard).

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2.2.1. Mexel® 432/0 product efficiency

Mexel® 432 product study under conditions similar to the ones met in Industry show than use of Mexel® 432 offers:
- to reduce average corrosion speed from 283 Dm/year to a value in the range of 58,3 to 95,7 Dm/year (Table 1).
- improve the formation of a passive coating,
- improve the thermal exchange capacity, in addition to the one generated by cleaning action of Mexel® 432.
An average concentration of 5 mgL_{-1} of Mexel® 432 offers to provide a protective film. This film is maintained for a concentration down to 2,5 mgL_{-1}.

Table 1 : Brass corrosion inhibition in sea water offered by Mexel® 432, compared to a treatment using sodium hypochlorite and ferrous sulphate (Bonnet, 1999,a,b)

Treatment conditions	Duration (hour)	I^{corr} ($\mu A/cm^2$)	$V^{I/E}_{corr}$ (μm/year)	V^{m}_{corr} (μm/year)
Test 1 : without treatment	120	9	172	283
Test 2 : 7 mgL^{-1} Mexel during 1 hour	150	2.4	45.9	95.7
Test 3 : alternated treatment 5 mgL^{-1} / 0,5mgL^{-1}	460	1.0	19	75
Test 4 : filming at 5 mgL^{-1}, followed by 2.5 mgL^{-1}	280	1.0	19	58.3
Test 5 : 0.1mgL^{-1} ferrous sulphate treatment	165	7	134	209
Test 6 : 0.1mgL^{-1} ferrous sulphate treatment + 1 mgL^{-1} chlorine	170	2.1	40	75

I^{corr} : corrosion current calculated from potential curve,

$V^{I/E}$: corrosion speed calculated from potential curve,

V^{m} : average corrosion speed during test duration, measured from weigh loss.

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2.2.2. Mexel® 432/0 efficiency compared with others treatments

Under same test conditions, compared to witnessing sample, ferrous sulphate treatment improves protection against both erosion and corrosion aluminum brass (Table 1). However, ferrous sulphate treatment efficiency is quite lower than the one of Mexel® 432:
- Higher corrosion effect,
- surface is object of a strong erosion,
- No passivation effect is observed on the surface treated using ferrous sulphate.

Simultaneous injection of chlorine improves ferrous sulphate treatment efficiency as well as the formation of an alumina coating underneath the ferrous film, as illustrated by:
- Increasing of aluminum and oxygen content measured at surface,
- Joint evolution of potential and resistance to polarization.

Ferrous sulphate treatment efficiency looks to be very dependant of redox potential of the system. Mechanism of formation of a protective coating, using ferrous sulphate treatment looks to require the formation of colloidal hydroxides particles under action of electrostatic forces (zeta potential), which shall deposit on brass surface to provide a protective film. The kinetic of coating formation looks then very dependant of the redox potential of the system; which makes the ferrous sulphate treatment questionable:
- How to guarantee a minimum redox potential, in case of polluted waters, for which chlorine demand is variable?,
- If test shows positive impact of chlorine injection in case of aluminum brass application, it appears that some local corrosions effects are developing. This fact has been observed for brass, and also for AISI 316. The electro-chemical activity looks to be highly affected by ferrous sulphate treatment, as demonstrated a following up of potential made in parallel on a witnessing sample installed in the test circuit. Numerous transient potentials characterizing phenomena’s of amorcing – re-passivation typical to pitting corrosion have been observed.

To summarize, according to tests, both types of treatment, respectively chlorine + ferrous sulphate and Mexel® 432, show similar corrosion speed, including, in case of chlorine + ferrous sulphate treatment, formation of a passive coating rich in alumina at surface of brass.
However, chlorine + ferrous sulphate treatment shows a fouling at surface of the tube, as well as the development of local corrosion.
This test demonstrates the possibility to cancel chlorine + ferrous sulphate treatment if the circuit is treated using MEXEL process.

2.3. Stain less steel corrosion inhibition in fresh water

As observed for brass, a field study (thermal plant condenser) shows that Mexel 432 treatment generates a decreasing of potential by about 10 mV followed by a stabilization of potential (Bardet).

2.4. Mild steel corrosion inhibition in sea water

The injection of Mexel® 432 at a concentration of 10 mg/l, made in laboratory, in sea water (Micromer, 1993) offers a reduction of micro-fouling in the factor range from 300 to 900.000 (Tableau 1) on treated surfaces. Without Mexel® 432, E 36 mild steel potential moves rapidly to values of – 710 mV/ECS. When treated using Mexel® 432 at a concentration of 10 mg/l, this potential stabilizes at a value in the range of – 572 et – 603 mV/ECS, that is 100 mV higher to value recorded without Mexel® 432.

Table 2: Evolution of total heterotrophe micro Flore (Cells/cm²) in presence of Mexel® 432 at a concentration of 10 mg/l

Metal	Aquatic Milieu		Surface	
	Witness	Mexel®432/0	Witness	Mexel®432/0
316 L	$2.\ 10^6$	$2.\ 10^5$	$9.\ 10^6$	10
E 36	$2,1.\ 10^6$	$4.\ 10^4$	$9,7.\ 10^5$	$3.\ 10^3$

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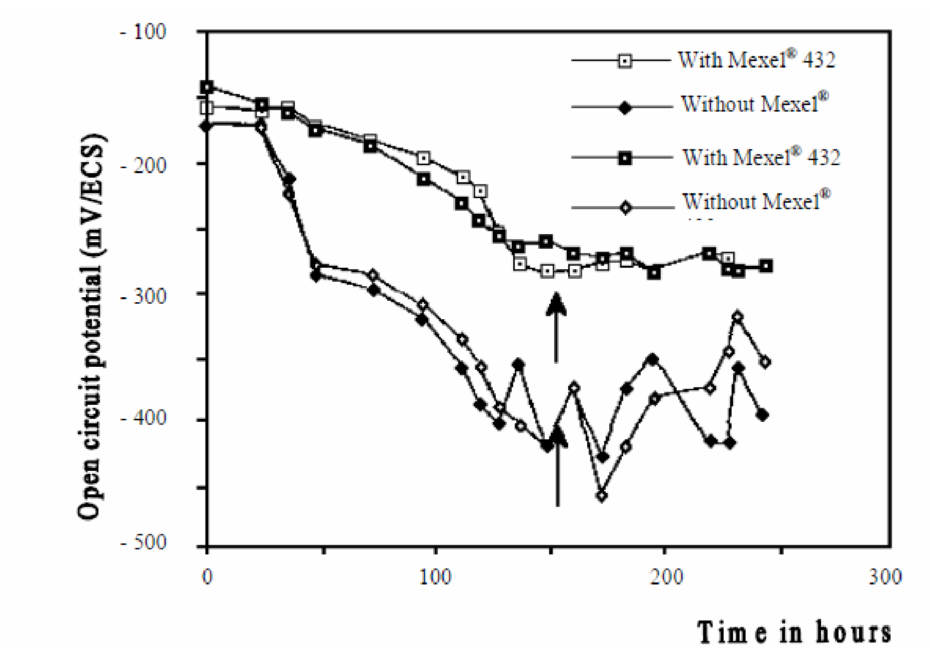
Under such condition, polarization curves recorded within cathode domain, at issue of respectively 4 and 15 days of treatment, show presence of a zone of oxygen diffusion.
Corrosion currents calculated based on transfer resistance measured, are respectively 0,494 mA/cm2 in presence of Mexel® 432 and 1,27 mA/cm2 without Mexel® 432.
Filming impact of Mexel® 432 is demonstrated by observation of corrosion inhibition in marine ambient. The formation of an organic film at surface of mild steel (The University of Tennessee Knoxville, Micromer, 1993) keeps its potential to a value closed to – 600mV/ECS after one week test. That is a gap of about + 100 mV compared to sample without any treatment placed in same marine ambient (Micromer, 1993). This filming impact is also observed on polarization curves (Micromer, 1993), as well as on impedance diagrams.
This film is stable during several days (The University of Tennessee Knoxville). This stability is maintained by a regular regeneration of Mexel® 432 coating. If this regeneration is not maintained, a corrosion is initiated induced by the progressive removal of Mexel® 432 protective film.
A regular addition of Mexel® 432 maintains a protective film at surface, which offers corrosion inhibition.

2.5. 304 L stainless steel inhibition in sea water

The study of evolution of 304 L stainless steel potential (The University of Tennessee Knoxville) in artificial sea water open circuit (D1141) containing *Vibrio natriegens* shows that after 24 hours, potential decreases rapidly, and moves to a value in the range of – 420 mV/ECS, at the issue of the test. This demonstrates a local corrosion initiation as expressed by local passivation-repassivation cycles. Against, if treated by Mexel® 432, at a concentration of 10 mg/l during 1 hour offering the formation of a protective film, and maintained during 7 days at a residual concentration of 1 mg/l, the potential of the open circuit decreases slowly and stabilizes at a value around - 250 mV/ECS (Fig 2).

Fig 2: 304 L stainless steel potential evolution in artificial sea water, in presence of *Vibrio natriegens.*



At issue of day 7 (refer to arrow in Fig 2,), addition of Mexel® 432 solutions together with stirring is stopped in order to generate the formation of a bio-film. No potential modification is observed in presence of Mexel® 432. Against, without Mexel® 432, open circuit potential moves considerably.

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2.6. 316 L stainless steel corrosion inhibition in sea water

Test made in laboratory, in marine ambient (Micromer, 1993), without Mexel 432, the free potential of samples increases slowly after 4 days test. Against, in presence of Mexel 432 at a concentration of 10 mg/L, potential are stabilized at a value in the range of - 200mV/ECS to – 250mV/ECS.
Potential stability is offered by the cleanliness of the surface, including lack of any biologic coating as well as any biologic activity on the surface, as delivered by Mexel 432/0.
The formation of a biological coating on any surfaces placed in natural milieu generates an increasing of potential to more anodic values, according to mechanism mainly bond to surface colonization or by a bio-film (enzymatic catalyze of oxygen reduction reaction etc.).
Impedance curves recorded after 1, 4 and 7 days show similarly the formation of a film.
In addition, the study of anti-corrosion impact of Mexel 432, made at a concentration of 10 mg/l during 17 days with 316 L stainless steel, compared to the one of glutaraldehide at a concentration of 10 mg/l, and to soda hypochlorite ($HCLO_3$) at residual concentration of 3 mg/l, shows (The University of Tennessee Knoxville) :
- in sterile sea water (ASTM D 1141), potential is not widely modified and are in the range of + 20 et – 80 mV/ECS for all products tested,
- in sea water containing *Deleya marina*, potential decreases in systems containing glutaraldehide, soda hypochlorite as well as only bacteria. This positive decreasing, which is higher than 300 mV/ECS, in case of solutions containing hypochlorite de sodium or glutaraldehide, shows the initiation of corrosion at the surface. Againsts, in presence of Mexel 432, the system is not widely modified.

In presence of Mexel 432, *D. marina* colonization on stainless steel does not present corrosion inhibition, and the open circuit potential is maintained at a constant level, and prevents any corrosion. The oxygen and pH at interface between bio-film and substrata are maintained constant. Test carry out with hypochlorite and glutaraldehide generate a potential fluctuation of open circuit showing passivation - repassivation cycles at stainless steel surface.

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3. References

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