



MULTICLIENT RESEARCH PROJECT PROPOSAL

STUDY OF SPECIFIC APPLICATIONS OF CATHODIC PROTECTION

Project Leader: prof. Luciano Lazzari

Working Group:

- Dipartimento CMIC del Politecnico di Milano, Milan, Italy.
Researchers: F. Bolzoni, G. Fumagalli, M. Ormellese
- Laboratorio di Ricerche Marine MARECO (IENI- CNR, Bonassola, Italy).
Researchers: A. Benedetti

Milano, September 2007

File: Appendix 6 - PRGmultiSponsorCP-draft-07-09-07.doc

Sede Leonardo:

Piazza L. Da Vinci, 32 – 20133 Milano
Tel. ++39-02 2399.3200
Fax ++39-02 2399.3209

Cod. fisc. 80057930150
Partita IVA 04376620150
Sito web: www.chem.polimi.it

Sede Mancinelli:

Via Mancinelli, 7 – 20131 Milano
Tel. ++39-02 2399.3100
Fax ++39-02 2399.3180



CONTENT

1	INTRODUCTION.....	4
2	SPECIFIC APPLICATION OF CP	5
2.1	CP OF STAINLESS STEEL	5
2.2	CP IN SEAWATER: SUNLIGHT IRRADIATION EFFECTS.....	6
2.3	USE OF AL ANODES IN SOIL	6
2.4	USE OF AC TO ACTIVATE GALVANIC ANODES.....	7
2.5	CHEMICAL CORROSION OF METALS UNDER CP	7
3	STATE-OF-THE-ART	9
3.1	CP BY PASSIVITY OF STAINLESS STEELS	9
3.2	CP IN SEAWATER: SUNLIGHT IRRADIATION EFFECTS.....	10
3.3	USE OF AL ANODES IN SOIL	10
3.4	EFFECTS OF AC ON GALVANIC ANODES.....	11
3.5	CHEMICAL CORROSION OF METALS UNDER CP	12
4	RESEARCH PROGRAM.....	14
4.1	TARGETS OF RESEARCH PROPOSAL	14
4.2	RESEARCH PHASES	14
5	EXPERIMENTAL PROGRAM.....	15
5.1	CP OF STAINLESS STEELS.....	15
5.1.1	<i>Materials</i>	15
5.1.2	<i>Test conditions</i>	15
5.2	CP IN SEAWATER: SUNLIGHT IRRADIATION EFFECTS.....	16
5.2.1	<i>Materials</i>	16
5.2.2	<i>Test conditions</i>	16
5.3	ALUMINIUM ANODES ALLOY IN SOIL	17
5.3.1	<i>Materials</i>	17
5.3.2	<i>Test conditions</i>	17
5.4	AC-RELATED ANODE ACTIVATION	17
5.5	CHEMICAL DISSOLUTION OF METALS UNDER CATHODIC PROTECTION	18



MULTI-SPONSORS RESEARCH PROPOSAL

Study of specific applications of CP

5.5.1	<i>Materials</i>	18
5.5.2	<i>Test conditions</i>	18
6	RESEARCH PHASES AND TIME SCHEDULE	19
7	PARTECIPATION FEE	20
8	DISTRIBUTION (PROVISIONAL)	21

DRAFT



1 INTRODUCTION

Cathodic protection (CP) is widely applied for corrosion prevention on metallic structures in natural (marine or soil) and industrial environments. Although the applications of cathodic protection are considered as consolidated, some uncertainties exist for some specific applications. These applications should be better investigated to optimise the design and operating parameters.

The aim of these research is to carry out laboratory and field tests to solve the open questions in the five specific applications described below.



2 SPECIFIC APPLICATION OF CP

2.1 CP of stainless steel

CP can prevent localised corrosion of active-passive metallic materials, such as stainless steel. In such application it is not necessary to bring the potential of the material to the immunity condition, but it is sufficient, and much more convenient, to apply a low cathodic polarisation in order to reach the so called *cathodic protection by passivity*. If the CP is applied on metals in passive condition, i.e. before corrosion initiation, it is called *cathodic prevention*.

Since nowadays CP is applied during the laying of the pipes, i.e. the pipe is passive, the cathodic prevention (CPrev) conditions has to be investigated.

A specific application of CPrev, with both practical and economical important implications, is the internal protection of low grade stainless steel pipes used for seawater transportation or anti-firing system; for examples, nowadays on the North Sea platforms the use of titanium (an expensive) has replaced carbon steel (with a corrosion allowance) and cupro-nichel alloys due to the higher reliability.

In the presence of stagnant natural sea water, pitting or crevice corrosion occur if PREN (Pitting Resistance Evaluation Number = %Cr + 3.3%Mo, simplest formulation) of stainless steel is lower than 30, and it has an high probability when PREN is close to 35, above all if temperature is higher than 30°C.

The application of CPrev to stainless steel pipes with iron anodes seems appealing for many reasons: (a) is cheap; (b) brings the stainless steel to potential in the range of -0,5/-0,6 V SCE, with no risk of initiation of pitting corrosion; (c) is easy to install into the pipes, along one generatrix of the pipes.

The practical problem is to verify if the CPrev on stainless steel is able to prevent pitting corrosion in stagnant condition in the presence of a biofilm, when the protection potential is the one obtained by the protection with iron galvanic anodes (-0,5/-0,6 V SCE).

From a practical point of view, if this application is effective, a significant saving of money is achieved due to the possibility to use low grade stainless steel.



2.2 CP in seawater: sunlight irradiation effects

CP is positively affected by the formation of the so called "calcareous deposit". This mineral layer is made basically by CaCO_3 and $\text{Mg}(\text{OH})_2$, and its precipitation depends on alkalinity forming at the metal-seawater interface once a cathodic potential is imposed in seawater.

An application that is not well studied is represented by shallow photic seawaters. The sunlight irradiation can induce cyclic variations on parameters like protection current.

Thus, it is reasonable to argue if sunlight irradiation is able to determine daily and seasonally:

- direct effects on cathodic reactions (oxygen reduction and hydrogen evolution) as a function of the three bands composing the photoactive spectrum (UV-B, UV-A, PAR) in presence of calcareous deposit on metal-solution interface;
- indirect effects on the precipitation of calcareous deposit mediated by metabolic cycles of colonizing biofilm as influenced by sunlight cycles.

The aim of the research is to understand the mechanisms of sunlight irradiation on cathodic processes in seawaters.

2.3 Use of Al anodes in soil

While aluminium anodes are widely used in sea water, they are not specified for soil applications, because of their tendency to passivate in environments with low chloride content. However, there are chloride contaminated soil where aluminium bracelet anodes could be of interest. Few studies are present in literature about the behaviour of aluminium anodes in these environments.

The aim of the research is to study:

- the effectiveness of aluminium anodes as a function of soil composition, namely chloride and sulphate concentration;
- anodic efficiency of galvanic anodes.

The advantage taken from the research is due to the possibility to use aluminium anodes, less expensive than magnesium ones.



2.4 Use of AC to activate galvanic anodes

Galvanic anodes for industrial applications are fabricated with alloys of aluminium, magnesium and zinc, in order to avoid the tendency to passivation that the pure metals show in neutral environment: aluminium and magnesium tend to become passive, i.e. get covered with a hydroxide or oxide film, as soon as they are forced to be anodic; zinc is active, but tends to be passive in the presence of impurities, such as iron. Therefore, pure metals are not suitable as anodic materials, and specific anodic alloys are set up. Zinc alloys work in active conditions, while aluminium and magnesium alloys work in pitting conditions.

Results of a 4 years research program, carried out by our research team, dealing with the effect of AC on corrosion and protection of metallic materials (carbon steel, stainless steel, aluminium and zinc), point out that the AC interference on passive metals tends to induce localised corrosion attacks, due to the breakdown of the passive layer.

On this basis, we think to the possibility to use an AC signal to activate anodic alloys, for applications in which they tend to become passive, such as the aluminium alloys in environment with low chlorides content. It is possible to continuously apply an AC interference on the anodic alloys, by means of a remote grounded, in order to maintain active the anodic alloy that otherwise will tend to become passive.

The benefit of this research is that one may use galvanic anodes also in not suitable environment (for example in conditions in which an impressed current system should be preferred) with the use of an alternate impressed current system (not expensive and easy to manage) for the activation of the anodes. It is important to underline that an AC system is not dangerous as regard corrosion induced by AC interference.

2.5 Chemical corrosion of metals under CP

Cathodic reactions which take place on a metallic structure in CP (oxygen reduction and hydrogen development) cause an increase of pH at the metal-solution interface, so that pH may reach values above 12.

In case of high protection current densities (10 A/m^2), which can be locally measured in the presence of low-dimension defects in the coatings of pipes, the pH may locally rise even to



MULTI-SPONSORS RESEARCH PROPOSAL

Study of specific applications of CP

values of 14 or more. Considering the Pourbaix diagram for iron, the thermodynamically favoured reaction, in those conditions of pH and for a potential equal to the protection potential, is the dissolution of iron to ferrite. Since iron corrosion was observed even under CP, both in laboratory experiments and in field applications, a purely chemical, and not electrochemical, corrosion mechanism can be proposed. Therefore, tests will be performed in order to whether confirm or exclude the onset of an electrochemical mechanism.

DRAFT



3 STATE-OF-THE-ART

3.1 CP by passivity of stainless steels

CP of active-passive metals, known as *cathodic protection by passivity*, is generally applied from the very beginning of the structure lifetime (the use of such a technique to stop an already acting localized corrosion is becoming more and more uncommon): therefore, it is more appropriate to refer to it as *cathodic prevention* (CP_{prev}).

The cathodic protection by passivity has an extremely sound theoretical background, which was introduced by Pourbaix and afterwards confirmed by numerous practical applications. It was P. Pedferri, the founder of our research group, who invented the *cathodic prevention*, specifying the cathodic protection conditions necessary to maintain in a passive state a passive metal when no localized corrosion is acting.

CP applied to stainless steels in seawater is typically protection by immunity, rarely cathodic protection by passivity or cathodic prevention. The main reason for this behaviour is that cathodic protection is achieved by the use of Al and Zn galvanic anodes, which bring the potential in conditions of immunity (below the iron protection potential, which is more negative than that of the main three alloying elements, Cr, Ni and Mn).

Cathodic prevention for stainless steels in seawater is efficient at a relatively positive potentials, with respect to the immunity condition in the case of cathodic protection. As a practical example, let's consider the pitting potential (below which no localized corrosion can start) for an AISI 304: its value is -0,2 V SCE, well above the -0,8 V SCE, which is the immunity potential for this material (-0,9 V SCE in case of an anaerobic environment). Working at so positive potential values is very uncommon for a practical reason, that is, no galvanic anodes work at those potentials; moreover, for impressed current cathodic protection, it stands to reason that more negative or less negative potentials can be chosen indifferently. Therefore, in general the immunity condition, or conditions close to it, are applied (another reason for that concerns the poor knowledge available about the cathodic protection by passivity).



Study of specific applications of CP

As for the definition of the conditions for the protection of stainless steel pipes carrying seawater through iron anodes, no definite answer has been found yet: the current research is aimed at finding a definitive solution.

3.2 CP in seawater: sunlight irradiation effects

Literature works dealing with the behaviour of cathodic protection in photic shallow seawaters weren't found on the basis of a preliminar bibliography research.

Preliminary short-time investigations on carbon steel showed that cathodic current density enhances under direct sunlight irradiation. Calcareous deposit precipitation controls the photo-electrochemical effect but does not eliminate it (temperature was demonstrated to play a secondary role both in presence and absence of calcareous deposit)¹.

This topic is interdisciplinary and involves different research fields for which literature do exist:

- calcareous deposit precipitation on cathodically polarized metal
- relations between cathodic processes and biofilm
- photochemistry and semiconduction
- photo-electrochemistry

3.3 Use of Al anodes in soil

Typical materials for galvanic anodes are aluminium, zinc and magnesium, used for cathodic protection of carbon steel. In general, soils are characterised by a low chloride concentration and pH close to neutrality, these conditions favour the passivation of aluminium and its alloys, limiting their efficiency as galvanic anodes.

¹ A.Benedetti, E. Chelossi, M. Faimali, L. Magagnin, G. Montesperelli, F. Passaretti, proc. of Seventeenth International Offshore (Ocean) and Polar Engineering Conference ISOPE – 2007, Lisbon, Portugal; July 1-6 2007, paper n. jsc365



MULTI-SPONSORS RESEARCH PROPOSAL

Study of specific applications of CP

It is well known that the behaviour of aluminium alloys employed as galvanic anodes depends on several factors: the environment (temperature, pH, chloride concentration), exposure time, anodic current density and chemical composition. Few literature data have been presented and can be summarised as follows:

- the Al-Zn-In alloys in a 1,000 ppm SO_4^{2-} without chlorides show a typical active-passive behaviour. The addition of chlorides, ranging from 0.001 M (35 ppm approximately) to seawater concentration, provokes localized corrosion;
- free corrosion potential and galvanostatic tests (0.5 to 5 A/m^2) in 0.5 Na_2SO_4 solutions (equivalent to 48,000 ppm sulphate) show that
- Al-Zn-In alloys in SO_4^{2-} containing solutions was not activated with 1,000 ppm chlorides and activate in chloride concentration higher than 5,000 ppm;

These results can be explained if the inhibiting effect of SO_4^{2-} on the pitting corrosion of aluminium alloys is taken into account. This effect has been studied in literature.

Some preliminary tests performed by the authors of this proposal showed that²:

- in potentiodynamic tests in solution free of sulphates, the aluminium anodes are active even in a 300 ppm chlorides solution; on the other hand, the aluminium anodes show passive behaviour in sulphate containing solutions, in absence of chlorides;
- it was possible to reach the protection conditions in soil saturated with seawater, eventually diluted (2,000 to 19,000 ppm chlorides).

3.4 Effects of AC on galvanic anodes

As reported in §3.3, in certain conditions, galvanic anode alloys may passivate, and become unable to supply the protection current.

² F. Bolzoni, G. Contreras, L. Lazzari, E. Perez and A. Benedetti *Behaviour of Aluminium Galvanic Anodes in Soil*, Eurocorr 2006, Maastricht, 25–28 September, page 1–7



MULTI-SPONSORS RESEARCH PROPOSAL

Study of specific applications of CP

Possible solution to this practical problem is the activation of the anodes by the application of an AC signal, of a sufficient intensity, so that the anodes may supply continuously the protection current.

No data are reported in scientific literature as regard this specific topic.

This idea grew up on the basis of the experimental results of an ongoing research (performed in our laboratories) dealing with the study of the effect of AC on corrosion and protection of metals. Tests carried out on anodic alloys, as well as on metallic materials with an active-passive behaviour, both in freely corrosion and CP conditions, point out that:

- corrosion of commercial galvanic alloys (aluminium, zinc and magnesium) increases as the AC current density increases, also in environment with a chlorides content lower than the critical threshold to initiate localised corrosion in free corrosion condition; in the presence of an AC density of 10 A/m^2 a significant corrosion is observed³;
- on active-passive metals, localised corrosion attacks were observed when AC density was higher than 30 A/m^2 , in the presence of a chlorides content lower than the critical one⁴;
- in CP condition, galvanic anode efficiency decreases due to the higher corrosion of anodic alloys in the presence of AC.

As a consequence, the possibility to activate passive galvanic anodes by the application of an AC signal could be possible; the values of the AC density, the duration of the interference and the efficiency of the activation has to be investigated.

3.5 Chemical corrosion of metals under CP

No researches or publications are available in the literature which specifically refer to the dissolution (corrosion) of iron in chemical and physical conditions identical to those occurring when CP is applied.

³ S. Goidanich, L. Lazzari, M. Ormellese, MP. Pedeferrri, *Effect of AC on CP of carbon steel in soil simulated conditions*, Eurocorr 2006, Maastricht, September 25–28, page 1–8

⁴ P. Carpentiers, R. Gregoor, A. Pourbaix, *AC corrosion: detection, investigations and mechanisms*, Proc. Int. Conf. Eurocorr 2003, Budapest, September 28 – October 2, paper 307



Study of specific applications of CP

Nevertheless, works belonging to the Russian school are well known (Tomashov, Frumkin and Kolotyrkin), as well as James' review⁵ where a lot of examples related to the corrosion, exhibiting a chemical mechanism, of multiple valence metals in acidic environments are given. Recently, a review has been published by D.M. Drazic⁶ where analogous examples are reported.

The dissolution of iron in conditions of cathodic overprotection seems to show a tendency to chemical dissolution (with amphoteric reaction characteristics) similar to those reported in literature.

⁵ W.J. James, Anodic Dissolution of Metals - Anomalous Valence in *Advances in Corrosion Science and Technology*, Vol. 4 M.G. Fontana and R. W. Staehle, Eds., Plenum Press, New York, 1974, pp. 85-147

⁶ D.M. Drazic e J.P. Popic, Anomalous dissolution of metals and chemical corrosion, *J. Serb. Chem. Soc.* 70 (3) 489-511 (2005) UDC 620.123.4:546.72:546.76, JSCS-3284



4 RESEARCH PROGRAM

Lab and field tests will be worked out in order to give answers to all questions raised up on the applications of CP illustrated in previous paragraphs.

4.1 Targets of research proposal

Main targets of the research program are the following:

- up-date the state of the art on all mentioned CP applications;
- obtain valuable results from each set of experiments to validate or confirm the proposed applications;
- propose or validate the related mechanism of the proposed applications.

4.2 Research phases

Main phases of the research program are the following:

- preparation of the detailed research program to be discussed and accepted by the sponsors;
- bibliographic research and up-dated state-of-the-art for each applications;
- laboratory and field tests as per detailed research program.



5 EXPERIMENTAL PROGRAM

5.1 CP of stainless steels

5.1.1 Materials

Low grade stainless steels will be used. Candidate compositions will be:

- AISI series 200 (Mn stainless steels with low nickel content) 201 and 204;
- AISI 304;
- AISI 420 (weldable 13 to 17 Cr content);
- 9Cr - 1Mo or equivalent.

Samples will be of cylinder shape taken from tubes.

As galvanic anode, pure iron and carbon steel with low carbon content (less than 0.2%) taken from commercial rebars (or equivalent).

Copper will be used to verify feasibility. The advantage of copper is based on possible antifouling effects.

5.1.2 Test conditions

Tests will be performed in natural seawater. CP will be obtained by pure iron galvanic (sacrificial) anodes and by potentiostat at room and higher temperature (e.g., 25°C; 40°C; 60°C). The higher temperature tests simulate stagnant conditions achieved when pipes are exposed to sun light in tropical areas.

Potential, current and bacteria count are parameters periodically measured. At end of testing a visual inspection will be carried out.

For comparison purposes, a control test in aerated seawater will be also performed.



5.2 CP in seawater: sunlight irradiation effects

5.2.1 *Materials*

Pipeline carbon steel will be used as cathode; some test will be eventually carried out on stainless steel (AISI 304).

Aluminium or zinc alloys will be used as anodes.

5.2.2 *Test conditions*

Cathodic polarizations will be performed in natural seawater (biologically active and non active) and, for comparison purpose, in NaCl 3.5%.

Applied cathodic potential will be -0.85 V SCE (typical protection potential) and a lower value, where hydrogen evolution is predominant. Protection current will be monitored.

Tests will be performed in marine sea station MARECO of the IENI-CNR. Electrochemical cells will be exposed inside the laboratory or on the roof of the laboratory, where natural sunlight irradiation occurs and photosynthetic processes are allowed. The use of different solutions allow the separation of contributes depending on:

- light/temperature,
- light/temperature + calcareous deposit
- light/temperature + calcareous deposit + biofilm

The tests will last from short time (days) to long (months).

Laboratory tests will be performed also exposing the electrochemical cells at the three bands composing the photo-active spectrum (UV-A, UV-B, PAR). Time scales will be in the range of hours.



5.3 Aluminium anodes alloy in soil

5.3.1 *Materials*

Commercial aluminium alloys (at least two alloys) and, for comparison purpose, zinc alloy will be tested. Pipeline carbon steel (like X52) will be used as cathode. The cathode/anode area ratio is around 50.

5.3.2 *Test conditions*

Tests will be performed in solution or saturated soil. Solutions with salinity ranging from low (less than 1,000 ppm) to high (35 g/L, seawater salinity). Molar ratio chloride/sulphate from 0.2 to 16 (corresponding to synthetic seawater according ASTM D-1141). Most significant testing will be repeated in natural seawater, eventually diluted.

The performed tests will be:

- electrochemical characterisation by means of potentiodynamic tests (ASTM standard)
- cathodic protection tests: anodes will be coupled with carbon steel. Surface area ratio between cathode and anode surfaces will be suited to reach practical anode current density (between 1 and 5 A/m²); protection potential and current, anode efficiency will be evaluated;
- galvanostatic tests as reported in DNV standard.

5.4 AC-related anode activation

5.4.1 *Materials*

Commercial aluminium anode composition and pure aluminium alloys will be tested. Samples will be of cylinder shape. Anodes will be coupled with carbon steel cathode. Surface area ratio between cathode and anode surfaces will be suited to reach practical anode current density (between 1 and 5 A/m²).

5.4.2 *Test conditions*

Tests will be carried out in solution and in water saturated sand. Different chlorides and sulphates content will be considered (chloride and sulphate content less than 100 ppm).



Study of specific applications of CP

Different AC density will be used to identify a threshold for anode activation.

Duration of the test will range from 1 week to months.

The following parameter will be monitored: anode working potential, efficiency, output of the anode duration of activation, corrosive effects induced by the AC.

5.5 Chemical dissolution of metals under cathodic protection

5.5.1 Materials

Iron (carbon steel), lead, tin and aluminium will be considered to tailor laboratory tests to prove the chemical dissolution mechanism.

5.5.2 Test conditions

Test conditions will be studied and selected to prove the chemical dissolution mechanism it is thought to occur on carbon steel structures under CP in presence of AC. Amphoteric conditions for metals considered (with different nobleness) under cathodic polarisation will be investigated. Weight loss results will be compared to theoretical value from Faraday's law.



6 RESEARCH PHASES AND TIME SCHEDULE

Duration of research project will be 24 months.

Lab tests will be carried out at CMIC Department of Politecnico di Milano and MARECO laboratory (IENI-CNR, Bonassola, Italy, Liguria sea).

Research leader: L. Lazzari.

Working group: L. Lazzari, F. Bolzoni, G. Fumagalli, M. Ormellese (Polimi)
A. Benedetti (CNR)

Table 1. Schedule time (bimonthly)

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
1	■											
2	■	■										
3		■	■	■	■	■						
4			■	■	■	■	■					
5			■	■	■	■	■	■	■	■	■	■
6						■	■	■				
7									■	■	■	
Riunioni	■		■		■		■			■		■
Relazioni			■				■			■		■

Phase 1 Preparation of a detailed research program

Phase 2 Update of the state-of-the-art

Phase 3 CP of stainless steels

Phase 4 Photo-electrochemical effects on CP

Phase 5 Al anode tests in soil

Phase 6 AC-related activation of galvanic anodes

Phase 7 Chemical corrosion mechanism under CP conditions

Periodical meeting and Reporting at Politecnico di Milano.



7 PARTECIPATION FEE

Budget for the execution of the research program is €180.000,00=.

Fee per sponsors for 6 (six) sponsors is € 15.000,00=/each per year (for a total two year testing).

DRAFT



8 DISTRIBUTION (PROVISIONAL)

This research program proposal has been distributed to:

APCE (Italy)

Eni – E&P (Italy)

Eni – G&P (Italy)

ENEL (Italy)

EDISON (Italy)

ITALGAS (Italy)

SNAMRETEGAS (Italy)

BP (USA)

Gaz de France (France)

Total (France)

Repsol (Spain)

Statoil (Norway)