

**CEOCOR DRESDEN – SECTOR A**

**Paper n. 08**

**POTENTIOSTATICALLY AIDED SACRIFICIAL  
ANODES  
CATHODIC PROTECTION SYSTEMS**

Andrea Bergo \* , Ranieri Cigna \*\* , Osvaldo Fumei \*\* , Giancarlo Raoli \*\*\*

\* *Università di Roma La Sapienza, Italy*

\*\* *Isproma, Mazzin (TN), Italy*

\*\*\* *Global Engineering, Roma, Italy*

## **Abstract**

A cathodic protection system using the sacrificial anodes technique may fail, even if well designed, whenever some conditions sensibly vary; at the design stage it is possible to forecast the use of an additional cathodic protection system. Two cases histories are reported in the paper concerning the addition of unexpected metallic components and the soil resistivity sharp increase. In both cases it has been demonstrated that the delivery of a supplementary current by means of a potentiostat helps the operation of the sacrificial anodes without giving any inconvenient implicit in the use of the impressed current techniques.

The driving voltage is of the order of hundreds of millivolt and the relevant current intensities are of the order of tens of milliampères.

## **Introduction**

Buried structures are designed to have a lifetime of about 30 to 50 years. For this purpose, to protect pipelines and other buried carbon steel structures against external corrosion, they are usually coated and cathodically protected [1].

The majority of the cathodic protection systems are based on the impressed current technique, which, having a large driving voltage, may be used to protect large structures in high resistivity environments; moreover, the voltage may be easily tuned to control the performance of the system.

However there are several cases where the sacrificial anode technique may be considered more convenient or definitely mandatory, in particular when:

- there is a risk of reaching overprotection conditions, e. g. in presence of steel prone to hydrogen embrittlement;
- there is a risk of sending current to other buried structures not connected to the main system;
- there is a need of a huge number of isolating joints;
- there are particular safety conditions, e. g. when sparkling has to be avoided.

In such cases the design, which leads to the calculation of the number of anodes of a given weight and to their distribution, will take into account the geometry and the surface area of the buried structure to be protected, as well as the soil resistivity and the presence of earthing systems.

However, during operation it may happen that either due to incorrect design or because new environmental conditions have arisen, the desired value of the protection potential is non achieved. Therefore, the design must be revised since an increased current is needed and the scope may be reached by adding a certain number of anodes, often with high costs due to excavation, connection, etc.

## ***Experimental***

### **Preliminary test**

In the area of a petrochemical plant in Northern Italy more than fifty above ground tanks have been cathodically protected with magnesium sacrificial anodes. The tanks are rather old and the corrosion risk is mainly due to the presence of a circular earthing system made of a tinned copper, which causes the formation of macrocells and potential extensive damage to the carbon steel tanks [2]. The spontaneous potentials were, without protection, within the range  $-300 \div -400$  mV vs. Cu/CuSO<sub>4</sub> sat. reference electrode; therefore there was a great danger of corrosion for the tanks bottom. Following the indications of Ashworth, after a preliminary campaign of measurements (potential, potential gradient, resistivity, cathodic protection trials), and using a mathematical model, a defined number of magnesium anodes were located around the tanks in order to reach at least the potential of  $-700$  mV corresponding (see Table 1) to conditions of spontaneous corrosion/moderate protection; this value of potential was decided since with the galvanic anodes in some cases, due to the particular configuration of the tanks bottoms and the high soil resistivity it was considered impossible to reach the complete protection potential of  $-850$  mV.

The installation scheme is shown in Fig. 1.

During the first year after completion of the installation of the anodes the potential was in all cases, with the exception of two, more negative than  $-700$  mV and often more negative than  $-850$  mV. The current delivered by the anodes was almost constant, but in some cases it was much lower than that predicted at the design stage.

Table 1 - Relationship between potential and the possibility of corrosion and cathodic protection of bare steel [1]

| Potential vs. Cu/CuSO <sub>4</sub> sat. | <i>Corrosion state</i>      |
|---|-----------------------------|
| $-0.6$ volt $\div$ $-0.7$ volt          | Freely corroding            |
| $-0.7$ volt $\div$ $-0.8$ volt          | Some protection             |
| $-0.8$ volt $\div$ $-0.9$ volt          | Zone of cathodic protection |

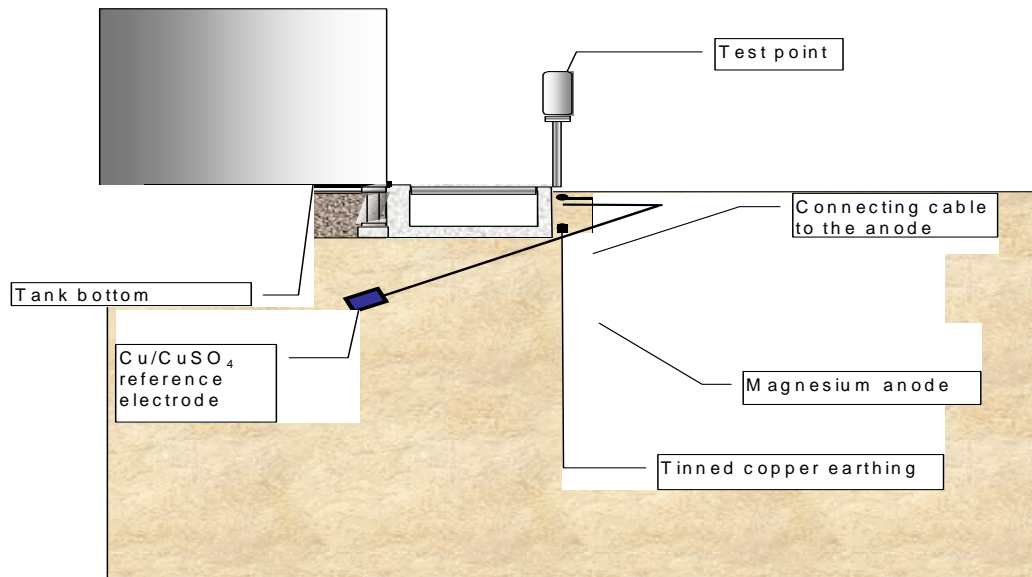


Fig. 1 - Installation scheme of sacrificial anodes to protect an above ground tank

During the second year of operation something happened and for ten tanks the potential measured was less negative than  $-700$  mV; inspections showed that in some cases other metallic components had been added (earthing network, antifire water pipes), while in other cases the very hot summer of 2003 had made the resistivity of the soil much higher and the water table much lower than it was at the beginning.

The necessary revamping of the cathodic protection system could be realized through the location of additional anodes, but this would be very difficult, since the anodes were already very close each other and also the mathematic model showed that since the anodes have a very marked reciprocal influence there would not have much progress in doubling the number of the anodes in each of the tanks where there were problems of protection.

Therefore, the idea that a potentiostatic help could be given to the anodes, in order to make them operate "more anodically" and make the potential of the structure more negative.

By means of a particular power supplier, of the type used for the cathodic protection of buried pipelines, it has been possible to obtain the polarization curves of the tank bottom and of the anodes by imposing potentiostatically the value of the potential to the tank and determining the correspondent current flowing in the circuit and the potential of the magnesium anodes; the result of the experiment is shown in Fig. 2.

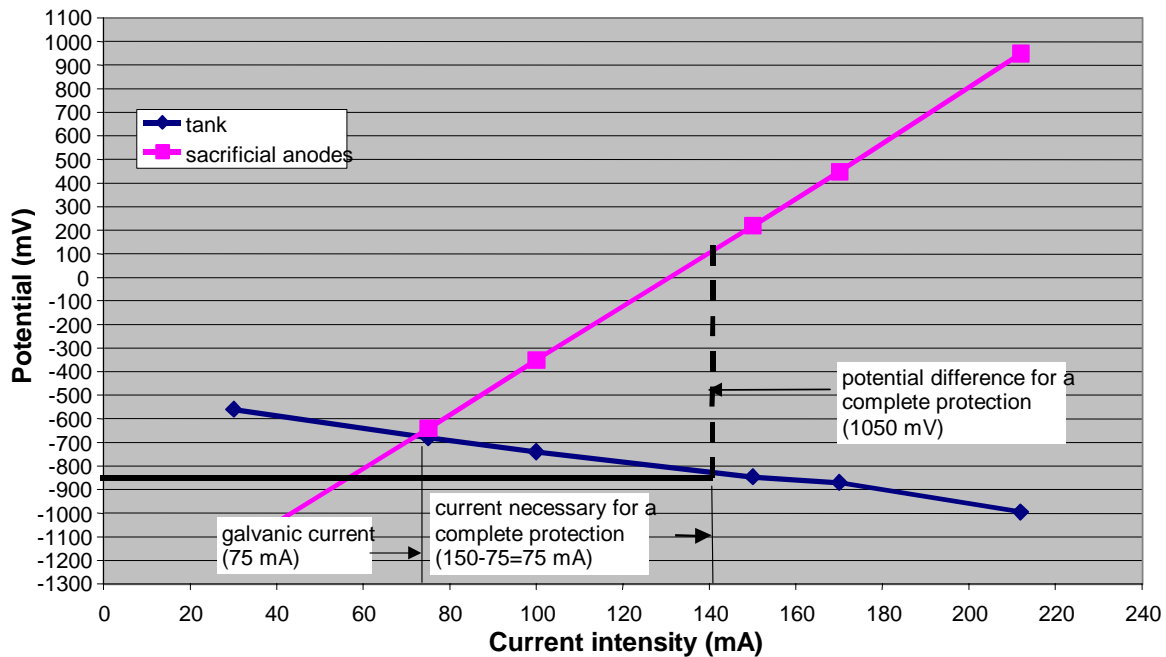


Fig. 2 - Polarization curves obtained with a potentiostatic device

It must be observed that the potential of the tank (working electrode) is realistic, since the reference electrode is rather close to its bottom; besides the potential of the magnesium anodes (counter electrode) is certainly untrue, since a very high ohmic drop is included in the measurement. This does not affect the result of the test, which shows that with a very low external driving voltage (1 V approximately) it is possible to bring the potential of the tank at a value of -850 mV with an additional current, delivered by the anodes, of only 75 mA.

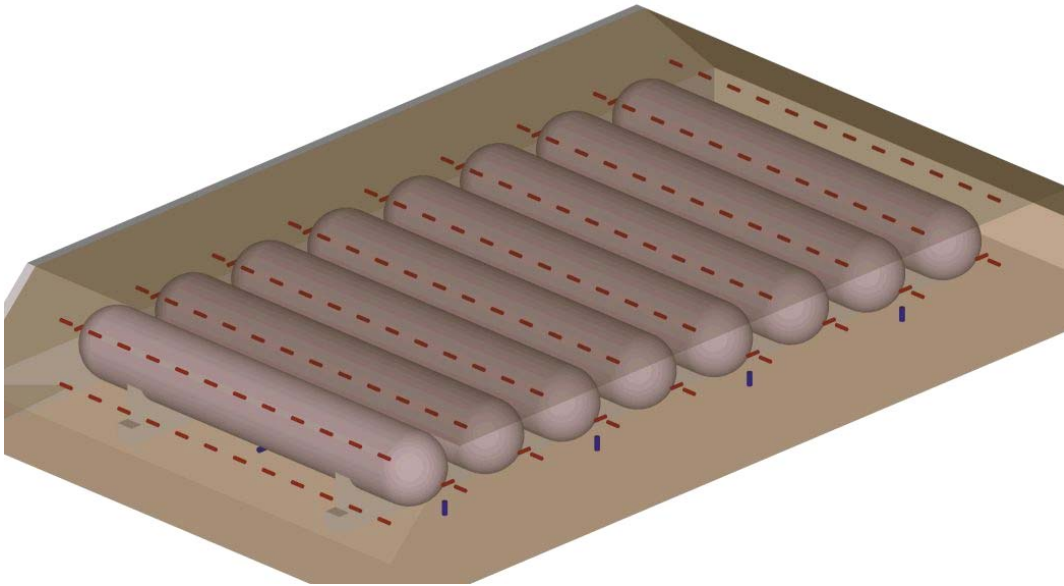
### Real scale test

The result obtained in the preliminary experiment needed a confirmation and a more careful way of operation, in order to understand the real behaviour of the whole system.

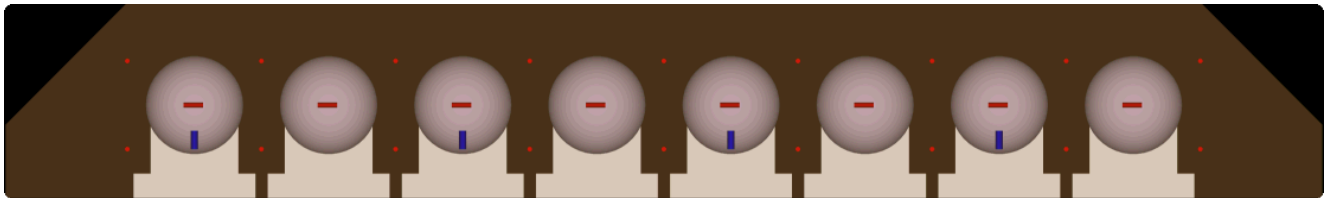
Therefore, a second test has been carried out in another plant (Fig. 3), where eight longitudinal cylindrical tanks, 24 m long, 4 m in diameter, set apart 1 m from each other, were installed over reinforced concrete saddles isolated from them by means of Teflon sheets [3,4].

The tanks were coated with 4 mm thick bitumen, as well as the pipelines connecting them.

The mound supporting the tanks was made of natural bentonite, which showed a resistivity of approximately  $80 \Omega \cdot \text{m}$ .

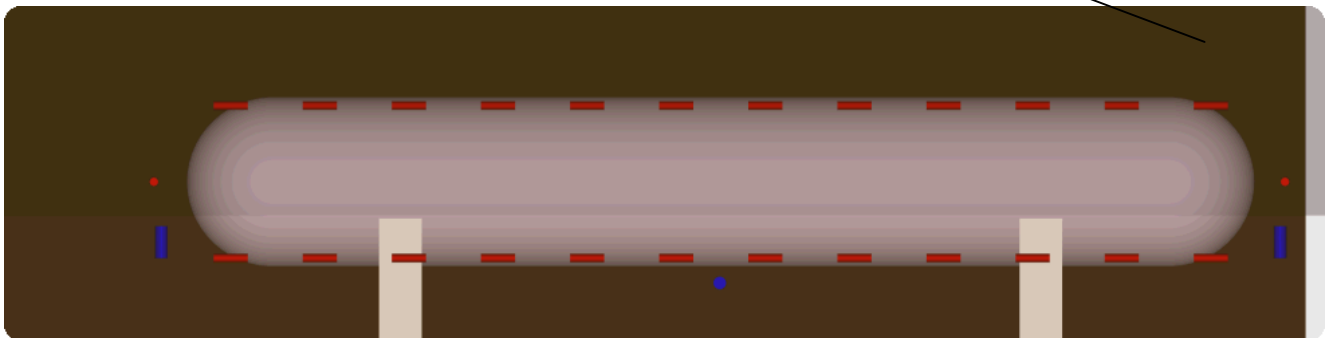


a)



b)

Concrete wall



c)

Fig. 3 - Distribution of the eight tanks, the sacrificial anodes (red) and the reference electrodes (blue)

a) isometric view

b) frontal view

c) side view

A reinforced concrete wall was erected on one side of the tanks, while soil was on the other side.

The surfaces of carbon steel and copper earthing were respectively  $2600 \text{ m}^2$  and  $50 \text{ m}^2$ ; therefore, the protection current was estimated at  $4.3 \text{ A}$ , using a value of  $1.25 \text{ mA/m}^2$  for the protection current density of coated carbon steel and  $20 \text{ mA/m}^2$  for copper.

Assuming that the magnesium sacrificial anodes, selected for the cathodic protection, could give a current intensity of approximately  $20 \text{ mA}$  each, and taking into account the geometry of the system, the total amount of anodes is 232.

Clearly, the anode chains, 18 of 12 elements along the tanks and 2 of 8 elements in front of the bottoms, were installed progressively, as the artificial soil was distributed for the mounding.

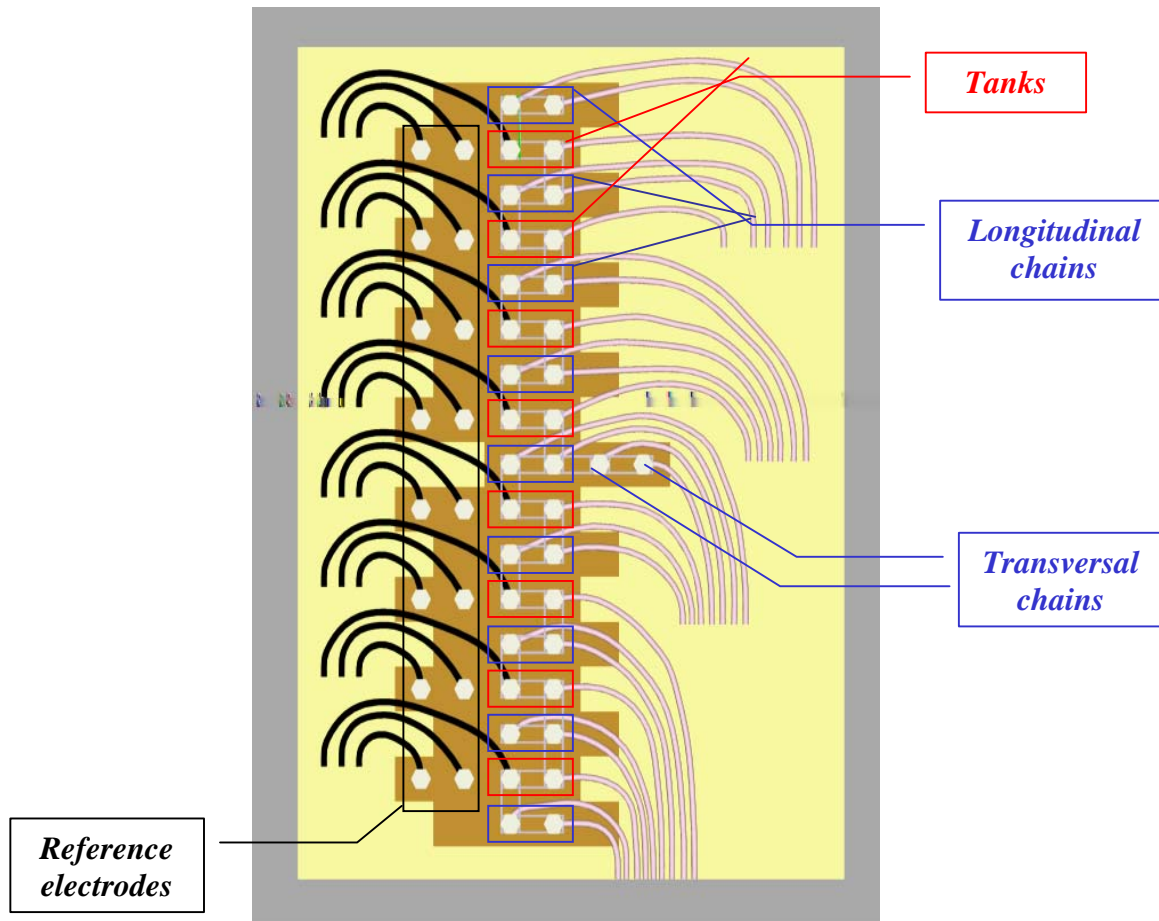


Fig. 4 - Schematic arrangement of the connections among the tanks, the anodes and the reference electrodes

Two fixed reference electrodes (copper/saturated copper sulphate) were positioned for each tank: one located immediately aside the bottom of each tank and the other at one of the extremities. Because of construction reasons, the position of the latter reference electrodes was alternate, the first at the soil side, the second at the wall side, and so on. This position should be kept in mind, as the results of the corrosion potential measurements turned out to be different.

In Fig. 4 the connecting box designed for the measurement of the protection potential and current independently for each chain and reference electrode is shown.

During commissioning, after approximately one and a half year and two and a half years, the potential of each tank, versus the two fixed reference electrodes (Table 2) was measured.

Examining the values of the potentials measured with the cathodic protection system completely ON, it can be observed that while the potential measured vs. the references electrodes placed under the

tanks and vs. those located at the extremity of the tanks 1, 3, 5, and 7 are very negative, as predicted, the potential measured vs. the references electrodes placed at the extremity of the tanks 2, 4, 6, and 8 are less negative than - 850 mV.

The less negative values of potentials at the wall side has been explained "in situ" observing that, contrary to the original design, in that area other metallic elements were joined to each tank; moreover, there is also metallic contact with the reinforcement of the concrete wall. The increased amount of metal to be protected caused evidently the situation highlighted by the measures.

Table 2 - Potential values of each tank, measured with all anode chains short-circuited, vs. the copper/saturated copper sulphate reference electrodes (mV).

| Position of the reference electrode | Under the tanks |         |         | Aside the bottom |         |         |
|-------------------------------------|-----------------|---------|---------|------------------|---------|---------|
|                                     | Date            | Nov. 01 | Apr. 03 | Feb. 04          | Nov. 01 | Apr. 03 |
| 1                                   | -               | -       | -       | -1197            | -1168   | -1085   |
| 2                                   | -               | -       | -       | -790             | -738    | -707    |
| 3                                   | -1191           | -1103   | -984    | -1251            | -1153   | -1116   |
| 4                                   | -1269           | -1175   | -1092   | -767             | -698    | -660    |
| 5                                   | -1328           | -1211   | -1173   | -1277            | -1193   | -1154   |
| 6                                   | -1381           | -1250   | -       | -721             | -675    | -654    |
| 7                                   | -1285           | -1268   | -1224   | -1246            | -1142   | -1110   |
| 8                                   | -1214           | -910    | -816    | -831             | -716    | -707    |

As already done in the preliminary test, using in this case a laboratory potentiostat, in principle able to carry out potentiodynamic curves with instant-off semi-continuous device, the polarization curve of the system tank/anodes was obtained (Fig. 5). Unfortunately, probably because of the large dimensions of the system, the instant-off device did not work, and therefore the real potential of the magnesium during the potentials in Fig. 5 include the ohmic drop.



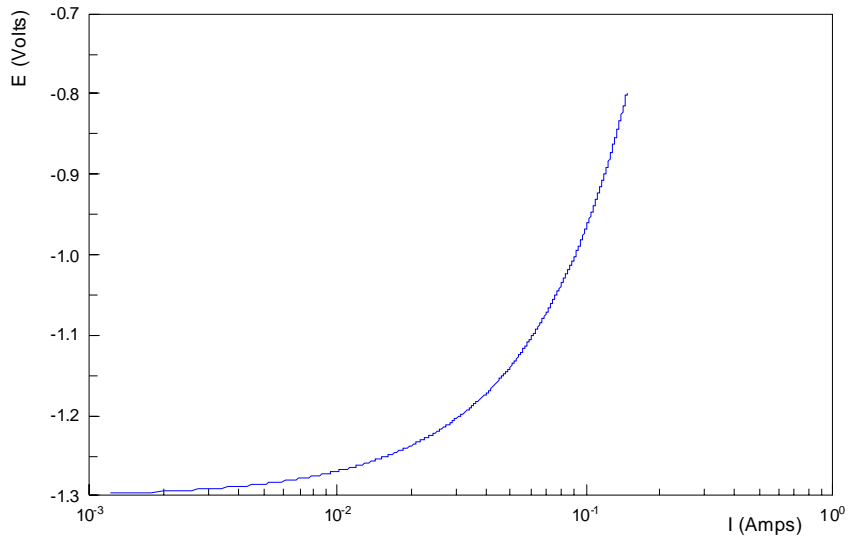


Fig. 5 - Polarization curve of the magnesium anode

A further attempt has been made by polarizing the system with increasing current intensities, from 0 to 300 mA, and measuring the corresponding potential values. For each step the current was "manually" interrupted and the potentials immediately after the interruption were recorded.

Table 3 - Results of the polarization test with current interruption

| I (mA) | E <sub>Mg-On</sub> | E <sub>Mg-Off</sub> | E <sub>Fe-On</sub> | E <sub>Fe-Off</sub> |
|--------|--------------------|---------------------|--------------------|---------------------|
| 0      | -1184              | -1284               | -404               | -404                |
| 50     | -1107              | -1250               | -384               | -411                |
| 100    | -915               | -1192               | -448               | -414                |
| 200    | -564               | -1168               | -558               | -416                |
| 250    | -389               | -1144               | -617               | -419                |
| 300    | -217               | -1117               | -677               | -422                |

The results, reported in Table 3 and Figure 6, clearly show that there is no particular meaning in these measures, since both electrodes (tank and magnesium anode) seem to be almost completely depolarized after the current interruption. This fact demonstrates that this experiment is not reliable, since the ohmic drop in proximity of the tank should be very low, nearly null.

Tank n. 4

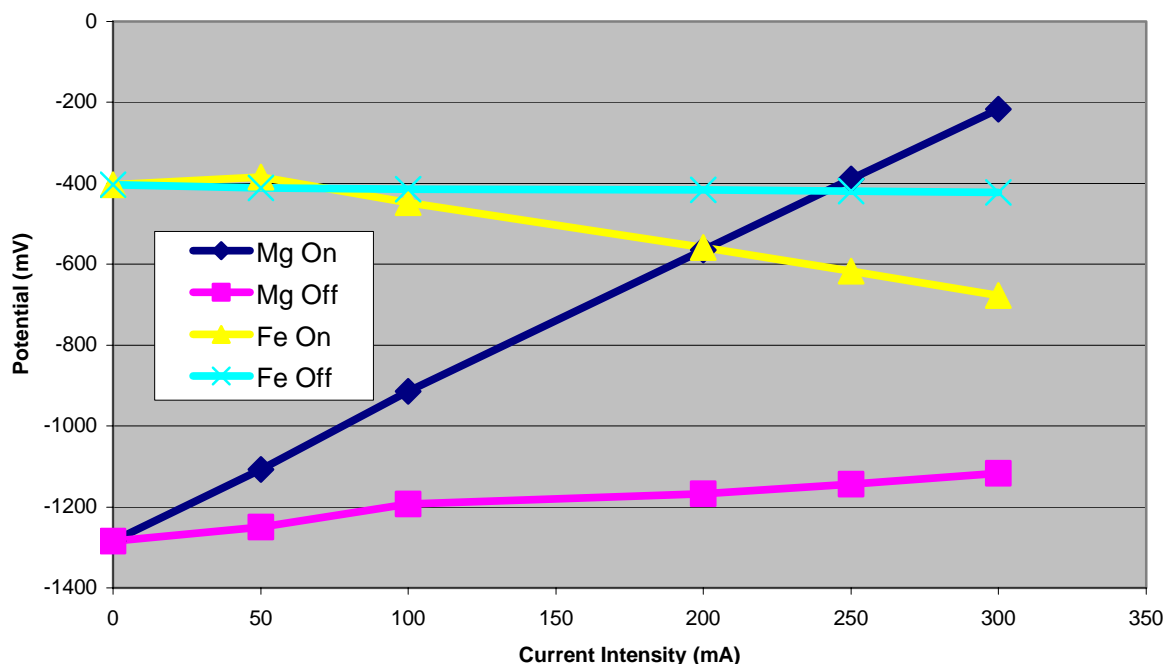


Fig.6 - Results of the polarization test with current interruption

### Field test

Finally, it has been decided to make an appropriate test in field in order to find out which is the "true" potential of the magnesium anode while the cathodic protection system is ON and the electrode is polarized.

The test has been programmed in field and not in laboratory, in order to reach results as close as possible to those obtainable in real scale experiments.

The arrangement of the experimental test is shown in Fig. 7.

The equipment used for the polarization is very simple: a common battery with a variable resistance has been connected to the two electrodes, a carbon steel structure buried in the soil and a magnesium anode and its backfill, also buried in the soil at a distance of approximately 4 m.

Two SCE reference electrodes have been buried very close to the steel structure and to the magnesium anode.

A common battery in series with a rheostat has been used in order to vary the current flowing in the circuit and polarize the steel at the desired value.

Firstly the battery was not inserted in the circuit and the resistance of the rheostat was varied, by discrete steps in the range  $100 \Omega - 0 \Omega$  (short-circuit).

Successively, the battery has been put in the circuit, in series with the rheostat, according to the scheme of Fig. 8. The cathodic protection current was so increased and the steel was polarized to values more negative than the short-circuit potential. During

these steps the potential of the steel structure and of the magnesium anode, and the current flowing in the circuit were recorded and are reported in Table 4 and Fig. 8.

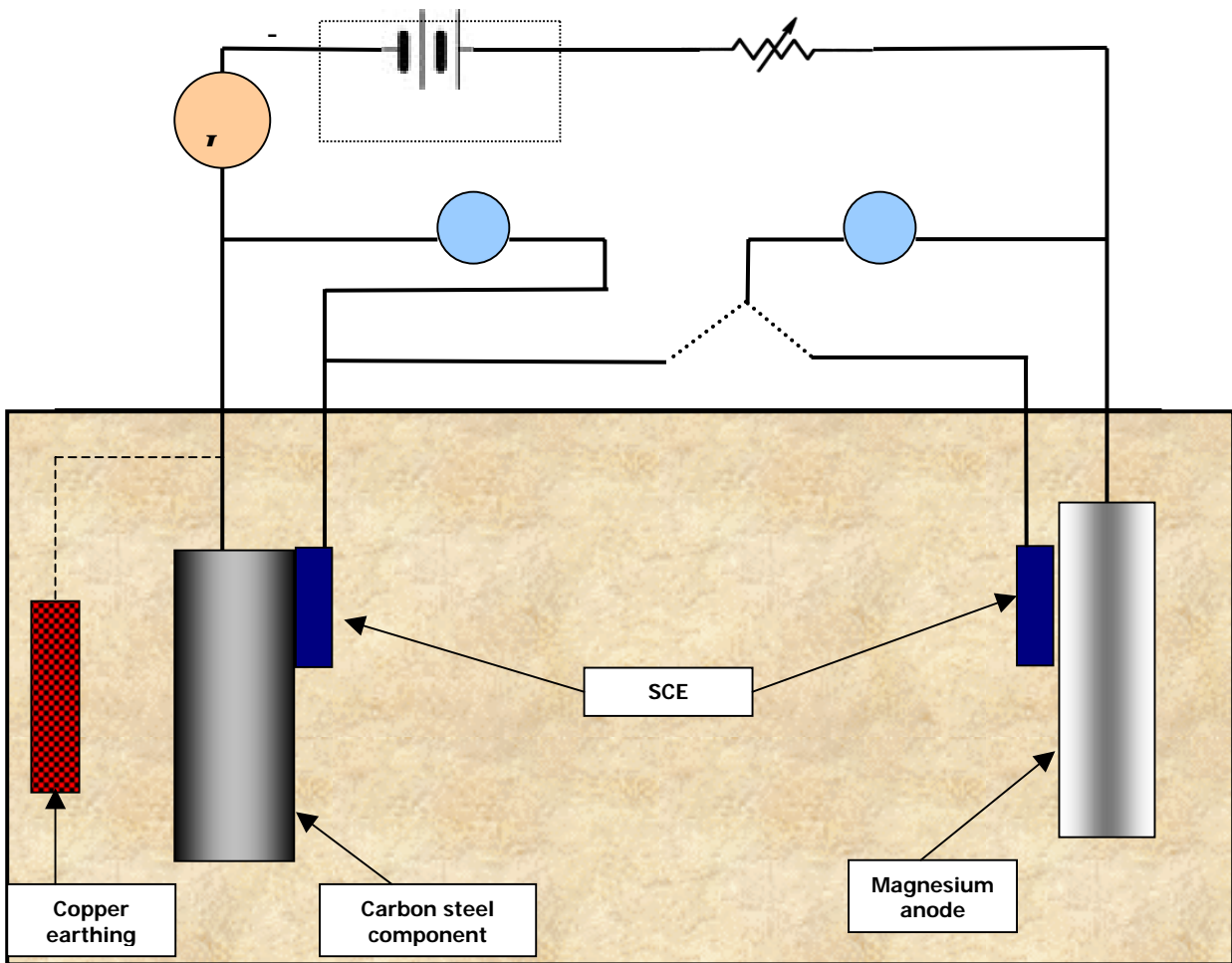


Fig. 7 - Schematic arrangement of the experimental test

It has been observed that the "true" potential of the magnesium during the galvanic coupling is much more negative than the one read in correspondence of the reference electrode close to structure to be protected (which is the usual situation in practice).

Table 4 - Results of the test in field (without earthing)

| I (mA) | E <sub>Fe</sub> (Ref near Steel) | E <sub>Mg</sub> (Ref near Steel) | E <sub>Mg</sub> (Ref near Mg) |
|--------|----------------------------------|----------------------------------|-------------------------------|
| 0      | -0.675                           | -1.525                           | -1.525                        |
| 3.6    | -0.833                           | -1.187                           | -1.303                        |
| 4.2    | -0.855                           | -1.127                           | -1.269                        |
| 6.2    | -0.929                           | -0.929                           | -1.155                        |
| 7.4    | -0.982                           | -0.797                           | -1.087                        |
| 9.8    | -1.092                           | -0.533                           | -0.936                        |
| 11.5   | -1.200                           | -0.368                           | -0.849                        |

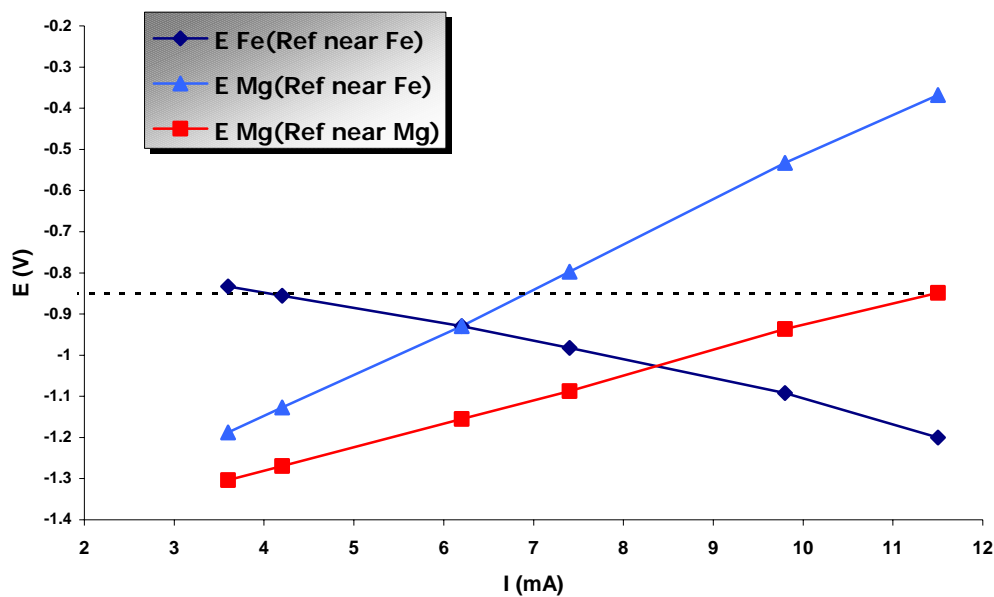


Fig. 8 - Results of the test in field (without earthing)

In order to better differentiate the behaviour of the magnesium, the test has been repeated putting in contact with the carbon steel structure a copper earth cable, which represents a common situation in the protection of buried tanks. The results are shown in Table 5 and Fig. 9.

### **Discussion and conclusions**

API recommended practice [5,6] suggests that the galvanic systems minimize interference problems and are most safe in areas where safety aspects are predominant.

Sometimes, however, it may happen that the galvanic anodes alone are not able to supply, in particular circumstances, the current necessary for the complete protection of the structure to be protected.

To think of an "hybrid" cathodic protection system may be a very good idea whenever it is almost mandatory to have a sacrificial anode solution.

Table 5 - Results of the test in field, with the copper earth cable connected to the carbon steel

| I (mA) | E <sub>Fe(Ref near Steel)</sub> | E <sub>Mg(Ref near Steel)</sub> | E <sub>Mg(Ref near Mg)</sub> |
|--------|---------------------------------|---------------------------------|------------------------------|
| 0      | -0.5                            | -1.55                           | -1.55                        |
| 5,3    | -0.61                           | -1.12                           | -1.21                        |
| 8,3    | -0.65                           | -0.87                           | -1.07                        |
| 10,5   | -0.68                           | -0.68                           | -0.95                        |
| 15,0   | -0.75                           | -0.35                           | -0.75                        |
| 19,0   | -0.80                           | -0.07                           | -0.61                        |
| 22,8   | -0.85                           | 0.20                            | -0.47                        |
| 26,5   | -0.90                           | 0.46                            | -0.33                        |
| 30,0   | -0.95                           | 0.70                            | -0.20                        |
| 35,4   | -1.02                           | 1.07                            | 0.00                         |

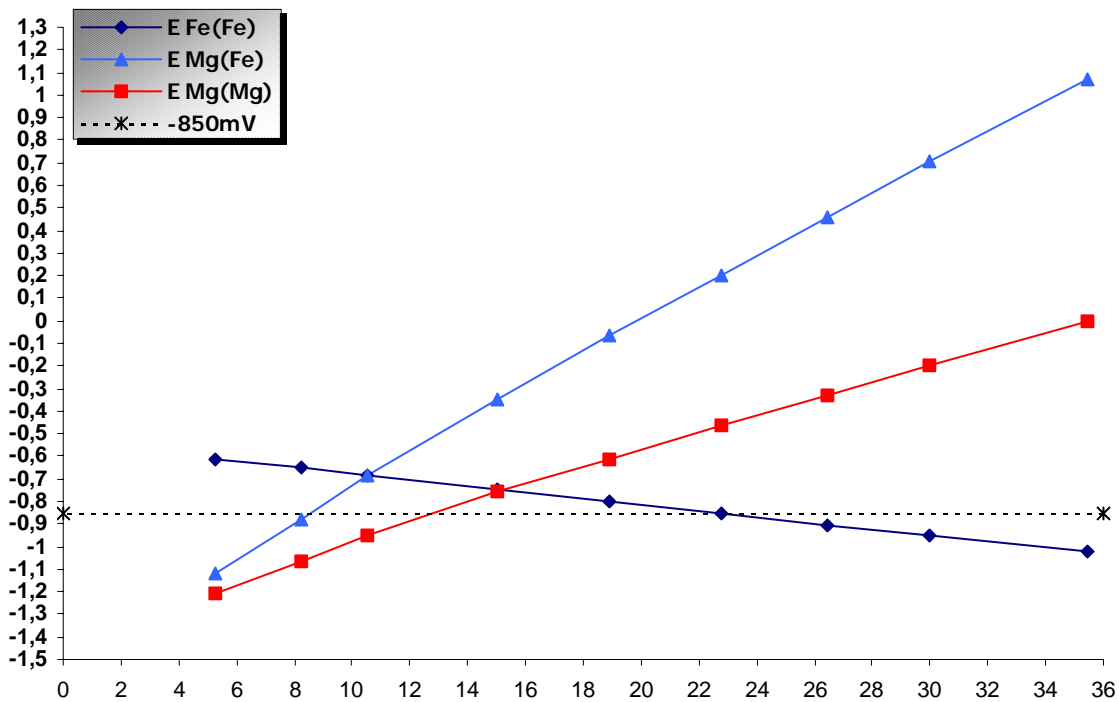


Fig. 9 - Results of the test in field, with the copper earth cable connected to the carbon steel

The experimentation described in this paper demonstrates that it is possible, in these circumstances, to "help" the galvanic anodes with an external energy source, without reaching the characteristics of an impressed current systems.

It has been in fact shown that the "true" potential of the anode, even with an external driving voltage, can remain below the potential of the carbon steel. In any case, the inversion of

polarity is very light and the currents involved are of the same order of magnitude of those obtained simply short-circuiting the anodes and the structure to be protected. Thus, the driving force, very low indeed, is just needed to win the ohmic drops. The above assessment may be rather important when cathodic protection has to be applied in hazardous areas where a risk of fires, explosion, etc. is present.

## **References**

- [1] V. Ashworth, C.J.L. Booker Eds., Cathodic protection: theory and practice, Ellis Horwood, Chichester (1986)
- [2] R.Cigna et al.- "Protezione catodica di un parco serbatoi atmosferici in un sito industriale", Proc. Convegno sulla corrosione in raffineria, nel petrolchimico e stato attuale di applicazione della PED, NACE, Gela, 19-20 giugno 2001, p. 2. togliere
- [3] O. Fumei, G. Raoli, R. Cigna, M. Di Bernardino - Cathodic protection of LPG mounded storage systems - EFC event nr. 254 "Cathodic protection and associated coatings", Aix en Provence 6-7 June 2002
- [4] O. Fumei, G. Raoli, R. Cigna, M. Di Bernardino - Monitoring of cathodic protection in LPG mounded storage systems - 6<sup>th</sup> Conf. CEOCOR, Giardini Naxos, 13-16 May 2003
- [5] API RP 651, Cathodic protection of aboveground petroleum storage tanks
- [6] API RP 1632, Cathodic protection of underground petroleum storage tanks and piping systems