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# Monitoring cathodic protection of buried pipeline by means of a potential probe with an embedded zinc reference electrode

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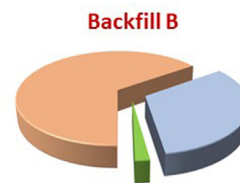
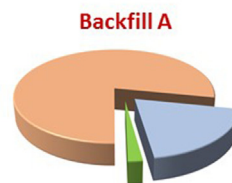
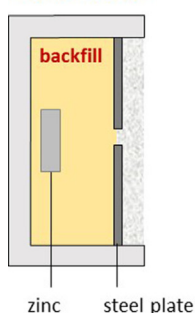
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## HIGHLIGHTS

- A potential probe with a Zn reference electrode embedded in a proper backfill is proposed to monitor cathodic protection
- The probe allows measuring potential eliminating the ohmic drop contribution, as requested by international standard
- Backfills are based on a mixture of gypsum, bentonite and cellulose in order to retain water and reduce mass loss
- Backfills avoid shrinkage and guarantee a good electrolytic contact between zinc electrode and carbon steel plate

## GRAPHICAL ABSTRACT

### Potential Probe



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## ABSTRACT

According to international standard, cathodic protection efficiency is controlled by monitoring IR-free potential. Nowadays commercial probes are available to perform correct potential reading, eliminating the ohmic drop contribution. In this paper, a new probe with a zinc reference electrode embedded in a proper backfill is proposed. Zinc is a promising material due to the low overvoltage in active condition and the high exchange current density. Laboratory tests were performed to select a stable backfill, in order to avoid any risk of shrinkage and mass loss. Sixteen mixtures based on gypsum, clay and other additives were considered. Gypsum, specifically sulfate ions, were used to maintain zinc in active condition; bentonite, absorbing humidity from the surrounding soil, guarantee a constant proper level of water content. Four additives, pure cellulose, an air-entraining agent, expanded glass granules and silica-based sand, were added to study the effect on water absorption, mass loss and electrical conductivity. Two of them were selected to prepare two probe prototypes with incorporated zinc electrode in order to verify the stability of both backfill and zinc during continuous cathodic protection monitoring.

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## 1. Introduction

Cathodic protection (CP) is an electrochemical technique used to prevent and control corrosion of buried carbon steel pipelines [1,2]. The plants are designed according to ISO 15589-1 [3] and EN 12954

standards [4], based on past experience and, in the last decades, using finite element methods to simulate the electrical field [5,6], above all in the case of complex structures immersed in soil suffering high level of stray current. The criterion used to assess CP condition is based on the IR-free potential measurement, in compliance with the protection

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criteria provided by international standards. As reported by ISO 15589 [3] and EN 12954 [4], the IR-free potential is defined as the structure-to-electrolyte potential measured without the voltage error caused by the ohmic drop in the electrolyte due to the any current circulating in soil.

According to the scheme in Fig. 1, structure-to-soil potential measurement is carried out by placing a reference electrode in contact with the soil surrounding the structure and using a high impedance voltmeter. Negative pole is connected to the reference electrode, while positive pole is connected to the metallic structure. Metals most used as reference electrodes for soil application are copper, zinc, stainless steel and mixed metal oxide activated titanium.

The potential reading is reliable if stable reference electrodes are used. Stability rely on electrochemical properties of the metal used as electrode [7–8]: active metals, with high exchange current densities and low overvoltages, such as copper or zinc, are more stable than passive metals, such as stainless steel or activated titanium, which have very high anodic overvoltage. Such active metals are also less polarizable during reading. Indeed, during a potential measurement, a current flows between the monitored structure and the reference electrode due to the driving voltage (i.e., the potential difference) between them. This current increases decreasing the voltmeter impedance and could cause the polarization of the reference electrode if the current density at the electrode surface exceed the exchange current density or the passive current density, for active and passive metals, respectively. To reduce electrode polarization, voltmeter with high internal impedance are recommended [3,4]: 1 M $\Omega$  is suggested for active metals, more than 1 G $\Omega$  for passive ones.

The measured value, the so-called “on-potential”,  $E_{on}$ , is the sum of three contributions (Fig. 1):

$$E_{on} = E_{eq} + \eta + IR \quad (1)$$

where  $E_{eq}$  is the metal equilibrium potential,  $\eta$  is the overvoltage with respect the equilibrium potential and  $IR$  is the ohmic drop in soil, which depends on the reference electrode position, the soil resistivity and the circulating current.

The sum ( $E_{eq} + \eta$ ) is defined the “IR-free potential”,  $E_{IR-free}$ :

$$E_{IR-free} = E_{eq} + \eta = E_{on} - IR \quad (2)$$

Second Ohm's law defines the ohmic drop contribution,  $IR$ , as:

$$IR = \rho \cdot i \cdot d \quad (3)$$

where  $\rho$  is soil resistivity (assuming soil homogeneous),  $i$  is the average current density flowing in soil and  $d$  is the distance between the reference electrode and the pipeline.

Combining Eqs. (2) and (3), the IR-free potential,  $E_{IR-free}$ , is obtained:

$$E_{IR-free} = E_{on} - \rho \cdot i \cdot d \quad (4)$$

Ohmic drop contribution may reach tens of millivolts up to few volts in low or high resistivity soils, respectively [9]. Then, to assess the cathodic protection condition, ohmic drop should be eliminated.

Several methods to measure the IR-free potential are available. They are based on the reduction of the distance,  $d$ , between reference electrode and structure (local or fixed reference electrode, Luggin capillary and potential probes with an internal reference electrode), or on the interruption of the circulating current (on-off technique in impressed current CP systems). The description and some applications of each technique are available in the specific literature [10–22]. It should be pointed out that IR-free potential is undoubtedly provided by reduction of the distance reference electrode-to-structure, then by the use of potential probes with internal reference electrode or by a reference electrode placed in a Luggin capillary or in a buried plastic conduit, which ends close to a steel coupon. These techniques allow measuring the IR-free potential by placing a reference electrode very close to a coupon connected to the pipeline [10–17]. Compared to other systems, the use of potential probes offer greater durability. Conversely, on-off technique is based on the experimental evidence that when the protection current is interrupted, the ohmic drop vanishes in very short time (in the order of  $10^{-6}$  s) while the concentration overvoltage of oxygen reduction reaction is eliminated in a longer time (from a few seconds up to a few days) being a diffusion controlled reaction [1–2]. The standard ISO 15589 [3] reports that the potential measured within one second after the interruption of the protection current is usually sufficiently accurate. The drawback in the on-off reading is the inability to detect overprotection condition, the no-applicability in the presence of galvanic coupling and stray current [18–22].

Existing commercial potential probes consist of a circular carbon steel coupon connected to the structure with an incorporated reference electrode located close to the coupon, as schematically shown in Fig. 2. Steel coupon is manufactured from a material similar to the pipeline; the coupon is coated leaving a defined bare area, according to ISO 15589-1 [3]. The coated steel coupon is intended to simulate a coating defect.

Many commercial potential probes use an internal copper reference electrode immersed in a saturated sulfate solution. Although the electrode is very stable due the low electrochemical activation of copper, this potential probe has the drawback of lasting only few years, often less than 5 years, because the sulfate solution dries out or it is polluted due to the ingress of chloride and calcium ions from soil. Different and more durable reference electrodes were proposed, such as the mixed metal oxide activated titanium (Ti-MMO) embedded with the steel coupon in a solid alkaline mortar [23]. Despite the high capability to eliminate the ohmic drop contribution and the long lasting due to the presence of a solid electrolyte (the mortar) which avoid the risk of

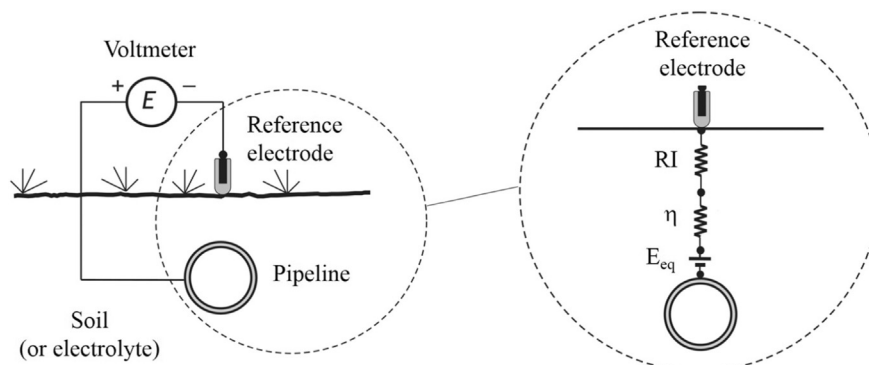


Fig. 1. Potential measurement and its electrochemical interpretation.

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