

CORROSION AND CATHODIC PROTECTION

**A general view on corrosion and its' combatting
by means of cathodic protection.**

Practical applications

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CORROSION AND CATHODIC PROTECTION

1. CORROSION AND HISTORY

Corrosion is the degradation of a metal by its combination with a non-metal such as oxygen, sulphur etc. Generally this means a return of the metal to the form in which it originally existed as an ore, with complete loss of its metallic properties. Most naturally occurring ores are: oxides, sulphides and carbonates. Energy must be expended in converting these ores to metal.

Corrosion, the reverse process, requires no such supply of energy, so that the formation of the oxide, sulphide or carbonate occurs readily, or even spontaneously under certain conditions.

A man of importance in electrochemistry and corrosion was Faraday. He investigated, early nineteenth century, the correlation between the electrical and chemical phenomena. From the many corrosion experiments he carried out, he was able to derive his laws of electrochemical action which give the relationship between the electrical current flowing and the associated corrosion.

Nevertheless, towards the end of the eighteenth century electrochemical corrosion received little attention in practice.

An important paper was published by Evans in 1924 called "The New Electrochemical View on the Corrosion of Metals" describing several mechanisms which led to the establishment of corrosion currents on a single metal surface.

Evans and his colleagues continued their investigation work and in 1938 Horn published a discussion on the basic electrochemical theory of cathodic protection. In the meantime in 1936 in America the Mid-Continent Cathodic Protection Association was formed to discuss and exchange information on cathodic protection.

This association later became the foundation of the National Association of Corrosion Engineers, still known as NACE.

According to my information the first CP applied in the Middle East was in 1939 on behalf of loading pipelines at Bahrain.

From these early beginnings cathodic protection has developed rapidly. The technique is now established as an essential engineering service with a sound scientific background.

2. ELECTROCHEMICAL THEORY

To be able to well understand the theory and application of cathodic protection it is good to explain some basics in chemistry first.

2.1 Atoms

The smallest particle of an element still bearing the chemical properties of the element is called an atom. The atomic theory describes the atom as having a massive positively charged central nucleus surrounded by a cloud of negatively charged electrons.

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The atom in total is electrically neutral.

The cloud of electrons is divided into a series of shells; the inner ones are filled first and require 2, 8, 18 or 32 electrons ($2n^2$ in the n-shell) (see appendix 0).

When the electrons just fill the shells completely with no electrons left over, then the element is very stable.

Examples are the inert gasses Helium and Neon (see appendix 1).

2.2 Molecules

Usually however, the outer shell has insufficient electrons to fill it, and either has a few left over after filling the last completed shell or too few to complete the outer shell.

The atom tends to obtain a cloud of completed shells by gaining or loosing electrons.

This loss or gain tendency gives the element its chemical properties: a metal sheds electrons and a non-metal accepts electrons.

Thus metals and non-metals combine to form salts by the metal atom donating electrons and the non-metal receiving them. The particle so formed is called a molecule.

Examples are sodium-chloride (NaCl) and water H_2O (appendix 1A).

Again: the molecule is the smallest particle of that substance still bearing the chemical properties of the same.

2.3 Oxidation and reduction

Loosing electrons is called oxidation.

Gaining electrons is called reduction.

The common salt molecule consists of an atom of sodium which has given an electron to its associated chlorine atom. This produces a positively charged metal ion and a negatively charged chlorine ion.

If salt is dissolved in water these ions separate and the solution contains a mixture of sodium ions and chlorine ions.

The corrosion of a piece of iron may be summarized as the change from the metal to the metal ion or the loss of one or more electrons from the metallic atom.

Electrically this is written:



This equation indicates:

The iron atom looses 2 electrons and goes into solution as a ferrous ion.

Because the positively charged nucleus does not change and two negative electrons are lost, the ferrous ion is not electrically neutral anymore but receives a positive charge of 2^+ .

The piece of iron assumes a negative charge for the excess electrons that remain in it.

The passage of the metallic atom into the solution as an ion is thus the equivalent of a flow of electric current from the metal into the solution.

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3. ELECTROCHEMICAL CORROSION

3.1 Electrical double layer

Almost all metals placed in a watery environment have the tendency to go into solution more or less.

A number of metal atoms on the interface metal-electrolyte leaves the metal and goes into the liquid as a positively charged metal ion.

In the metal an equivalent amount of electrons remains as a result of which the potential of the metal with respect to surrounding electrolyte drops.

The potential difference between the metal and the electrolyte will increase as the amount of atoms going into solution per surface unity increases. In this way a so called "electrical double-layer" is formed: one negatively charged layer of electrons in the metal and one positively charged layer of metal ions in the liquid.

Both layers have an opposite polarity and thus attract each other (see appendix 2).

After some time a balance will be reached.

For iron this balance is reflected with the chemical reaction equilibrium : $\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}^-$.

3.2 Electrical force series

If iron is placed in its own salts with a concentration of 1 Mol Fe^{2+}/l , termed **normal concentration**, an iron half cell is formed having a Fe-typical potential.

In the same way all other metals in the solution of their own salts at normal activity have their own typical potential.

For standarization of all half cells the scientific standard is formed by the **standard hydrogen half cell**.

This half cell consists of a hydrogen film formed on a platinum electrode immersed in an electrolyte which has a normal activity of hydrogen ions.

The potentials of all other standard half cells can now be determined by comparison against the hydrogen electrode.

All metals can be classified in a table having the most negative metal K with -2,92 V at the top and the most positive metal Au with +1,42 V at the bottom.

This table of potentials is called **the electrical force series** and is listed hereafter:

Element	Ion	Potential w.r.t. H_2
Potassium	K^+	-2,92 V
Calcium	Ca^{++}	-2,76 V
Sodium	Na^+	-2,72 V
(continues on next page)		

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Element	Ion	Potential w.r.t. H ₂
Magnesium	Mg ⁺⁺	-2,34 V
Aluminium	Al ⁺⁺⁺	-1,67 V
Zinc	Zn ⁺⁺	-0,76 V
Chromium	Cr ⁺⁺⁺	-0,71 V
Iron	Fe ⁺⁺	-0,44 V
Cadmium	Cd ⁺⁺	-0,40 V
Titanium	Ti ⁺	-0,34 V
Nickel	Ni ⁺⁺	-0,25 V
Tin	Sn ⁺⁺	-0,135 V
Lead	Pb ⁺⁺	-0,125 V
Hydrogen	H ⁺	0,000 V
Copper	Cu ⁺⁺	+0,345 V
Mercury	Hg ⁺⁺	+0,80 V
Silver	Ag ⁺	+0,80 V
Platinum	Pt	+1,2 V
Gold	Au ⁺⁺⁺	+1,42 V

Potentials w.r.t. H₂ electrode at 25° Celcius.

3.3 Practical galvanic series

In practice the situation of equilibrium such as : $\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}$ at normal activity, in general does not occur however.

This makes the scientific electrical force series of no practical use.

Therefore a practical galvanic series has been arranged.

In this table the most relevant metals are classified in order of their metal/electrolyte potentials in neutral soils and seawater, measured against the common Cu/CuSO₄ reference electrode.

In this table, listed hereunder, magnesium is placed at the top with E = -1,75 V and carbon (coke) is placed at the bottom with E = +0,3 V.

Practical galvanic series in soil and water w.r.t. Cu/CuSO₄

Magnesium anodes (galvomag)	-1,75	V
Magnesium anodes (6% Al / 3% Zn)	-1,6	V
Zinc anodes	-1,1	V
Aluminium anodes	-1,05	V
(continues on next page)		

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Practical galvanic series in soil and water w.r.t. Cu/CuSO ₄		
Steel, clean and shiny	-0,5/0,8	V
Steel, rusted	-0,2/0,5	V
Cast iron	-0,5	V
Lead	-0,5	V
Steel in concrete	-0,2	V
Copper, bronze	-0,2	V
Carbon, graphit, coke	+0,3	V

3.4 Potential measurements

As we have learned in par. 3.2 in cathodic protection a "potential" means the electrical voltage between a metal surface and it's surrounding electrolyte. This potential can be determined by comparison with a reference electrode.

Such a reference electrode must have an absolute stable reference potential, independent to the composition of the liquid or soil in which the electrode is placed.

For scientific purposes the standard hydrogen reference electrode is used.

Along the platinum electrode the chemical equilibrium: $H_2 \leftrightarrow 2H^+ + 2e$ exists.

To this electrode the standard potential 0,000 has been ascribed.

For use "in the field" the hydrogen electrode is not suitable however and therefor one of the following practical reference electrodes are used:

The Calomel electrode (Hg/Hg₂Cl₂/HCL)

The Calomel electrode is a half cell made of a mercury/mercurous chloride mixture (Hg/Hg₂Cl₂) in contact with a solution of potassium chloride.

The solution contacts the soil through a porous plug.

Calomel electrodes are made of glass in most cases and are less rugged for field use.

They are commonly used in laboratories.

The reference potentials of Calomel electrodes are:

. 0,1 N Calomel (0,1 N KCl solution) : +0,334 V/H₂

. 1 N Calomel (1 N KCl solution) : +0,280 V/H₂

. Saturated Calomel (Saturated KCl) : +0,242 V/H₂.

The Silver/SilverChloride electrode (Ag/AgCl)

The Silver/SilverChloride reference electrode consists of a silver wire coated with silver chloride so that both silver and silver chloride are in contact with a chlorine ion electrolyte.

The potential of the half cell will depend on the chlorine ion concentration.

The electrode is used in marine applications.

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The reference potentials of Ag/AgCl electrodes are:

- . 0,1 N Ag/AgCl (0,1 N KCl solution) : +0,288 V/H₂
- . 1 N Ag/AgCl (1 N KCl solution) : +0,240 V/H₂
- . Ag/AgCl - seawater : +0,250 V/H₂ (see appendix 3).

The Copper/CopperSulphate electrode (Cu/CuSO₄)

The most common reference electrode in use for cathodic protection onshore is the Copper/CopperSulphate half cell.

This consists of an electrode of electrolytic copper placed in an, usually transparant, reservoir containing a saturated solution of copper sulphate.

The liquid has a bright blue colour and is saturated as long as undissolved chrystals are present. The reservoir is at the bottom side provided with a porous plug (commonly ceramic) for contact with the soil or water.

The electrode can easily be made to have a large current capacity, degreasing however with time due to the formation of copper sulphate chrystals and copper oxide on the metal. This implies that the cell needs to be cleaned frequently to restore its former value (two or three months is common).

Copper sulphate is an unpleasant liquid to handle as it will attack the clothes and stain the skin. If it leaks into the electrolyte, copper may come out of the solution and form small copper cathodes on the structure being measured.

The effect of this is serious as the corrosion is greatly increased at that spot.

The reference potential of Cu/CuSO₄ reference electrodes is : +0,316 mV/H₂.

Appendix 4 gives a picture of a standard Hommema Cu/CuSO₄ reference electrode.

3.5 Corrosion cell

Discussing the electrical double layer in par. 3.1 we have seen that a chemical equilibrium arises if the free electrons left behind in the metal would remain on their places.

This is not the case however!

The electrons are free to move in the metal and they will travel from anodic places, with a surplus of electron, to cathodic places with relatively little electrons.

At the anodic places the bond with a part of the positively charged ions is lost with the consequence that these ions are no longer being attracted towards the metal surface and disappear into the electrolyte (see appendix 5).

They must be considered as "lost".

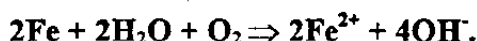
In that case the chemical reaction will move to the right, which means that the anodic reaction $\text{Fe} \Rightarrow \text{Fe}^{2+} + 2\text{e}$ will dominate.

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At the cathodic places the electrons will be used in one of the following **cathodic reactions**:

- . In an acidic environment ($\text{pH} < 4$) : $2\text{H}^+ + 2\text{e} \Rightarrow \text{H}_2$
- . In a neutral environment ($4 < \text{pH} < 7$) : $4\text{H}^+ + \text{O}_2 + 4\text{e} \Rightarrow 2\text{H}_2\text{O}$
- . In an alkaline environment ($\text{pH} > 7$) : $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e} \Rightarrow 4\text{OH}^-$

The total (gross) corrosion reaction is than:



3.6 Forms of corrosion

a. **Uniform corrosion**

This form of corrosion in general occurs with uncoated, bare steel structures in a homogeneous environment, e.g. a steel structure in seawater.

The corrosion cell in this case is formed as a result of small variations in potential over the surface of the metal caused by impurities in the metal. The whole surface of the metal may consist of a multitude of small cells, the anodes and cathodes being as small as the metal grain chrystals.

Anodic and cathodic places vary continuously with time so that a rough attacked surface occurs.

b. **Pitting**

A characteristic of pitting corrosion is the very local occurrence.

In general this type of corrosion is caused by a local failure of the coating..

Interference currents on well coated pipelines can lead to severe pitting at spots where the coating fails.

c. **Acidic corrosion**

This form of corrosion occurs in very acidic environments ($\text{pH} < 3$).

At the cathodic areas a strong generation of hydrogen gas will take place.

The anodic areas are going into solution at a high rate.

d. **Pure chemical corrosion**

Pure, chemical corrosion does in fact not take a place in the different forms of electrochemical corrosion. We can find it in ovens and combustion chambers of engines.

It is a direct combination of metal and free oxygen under the influence of extreme high temperatures.

3.7 Factors, stimulating corrosion

a. **Conductivity of the electrolyte**

The corrosion rate increases with the electrical conductivity of the electrolyte. In fresh water corrosion may be low; in seawater, known as very conductive, corrosion is severe.

CORROSION AND CATHODIC PROTECTION**b. Galvanic cells**

Metals, in a galvanic connection with other dissimilar metals, will form a galvanic cell with those metals.

An example is a steel pipeline network provided with copper tie-in lines. The less noble metal, in this case the steel pipes, forms the anode which goes into solution i.e. corrodes; the most noble metal (in this case the copper pipes) form the cathodes which are more or less cathodically protected.

c. Differences in aeration

Differences in aeration of one and the same structure form aeration cells: the best aerated areas form the cathodes, the less aerated areas form the anodes and tend to corrode.

d. Dissimilarities of the electrolyte

Dissimilarities of the electrolyte in which the structure is situated lead to corrosion.

A pipeline, for example, crossing respectively clay and sand areas will tend to corrode in the low resistivity clay area while the section in the sand receives more or less protection.

e. Temperature

Corrosion increases strongly with an increase of temperature.

f. Sulphate reducing bacteria

Anaerobic (oxygenless) soils contain sulphate reducing bacteria, specially in water logged clays.

This condition can be recognized by the grey-blue colour of the clay as opposed to the rich yellow-brown of the aerobics clays.

Under these conditions rapid corrosion is encountered due to the reduction of sulphates to sulfides which provide an acceptor system for cathodic hydrogen. This leads to a powerful cathodic depolarizer allowing the corrosion current to flow almost unlimited.

The corroding metal becomes covered with a black slime of iron sulphide which is recognized by its characteristic odour and taste.

Cathodic protection is possible in the presence of these bacteria, applying a higher current and achieving a potential of 100 mV more negative compared to normal conditions.

4. COMBATTING CORROSION

Electrochemical corrosion can be combatted with the following measures.

a. Passive protection

In the form of an electrically insulating coating applied to the buried or immersed structure, e.g. a polyethylene coating on a steel pipeline or an asphalt/bitumen layer applied to buried tanks and vessels.

This measure will prevent contact between the metal and the electrolyte and thus prevent corrosion.

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b. Active protection

In the form of cathodic protection, which technic actively intervenes the electrochemical corrosion process.

Although a passive protection in the form of a good coating is an extremely effective weapon against corrosion it never will provide you with 100% protection.

Always several small coating defects will occur which can lead to severe pitting corrosion.

For this reason it is common to provide buried steel pipelines and vessels with a good coating and to provide them **additionally** with a cathodic protection system.

Exemption on this rule are the offshore structures such as platforms and sheetpiles, which are in general not coated and only provided with cathodic protection.

In the foregoing about electrochemical corrosion we have seen that a metallic structure in a corrosive environment has anodic and cathodic areas. It is noted that at the anodic areas, where the structure corrodes, current is flowing from the structure into the surrounding electrolyte. Likewise, where current is flowing from the electrolyte into the structure, this structure area is cathodic and does not corrode.

Having said this, it becomes obvious that if every part of the metallic structure could be made to collect current, it would not corrode because the entire surface would be cathodic. And this is exactly what cathodic protection does.

Direct current is forced to flow from an external source onto all surfaces of the structure.

When the amount of current is adjusted properly, it will over-compensate the corrosion current discharging from all anodic areas on the structure. The entire surface will be cathodic and the protection complete.

5. CATHODIC PROTECTION

5.1 Definition

Cathodic protection of a metallic structure is applying that much negative charge that the entire surface of the structure exclusively consists of cathodic areas.

5.2 Period of application

Because of side reactions on the metallic surface, negative charge is consumed continuously. This means that the supply of negative charge towards the structure also must be continuously, thus a CP-system has to be a permanent application.

5.3 Insulating of structures to be protected

For the effective application of cathodic protection to a structure it is necessary to avoid that negative charge will leak away to other structures (being no part of the object to be protected).

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It is a first requirement therefore, that the structure to be protected will be insulated completely from other (parasitic) structures (except in situations with "Hot Spot" cathodic protection; see further par. 6.3).

5.4 Range of application

The desirability to protect an object cathodically depends on the nature of the environment in which the object is situated.

In dry sandy soils electrochemical corrosion is negligible. In clayey and saline soils, and particularly in seawater, the corrosion rate is high.

The range of aggressivity of the environment with respect to electrochemical corrosion can be expressed in the specific resistivity.

The unity of specific resistivity is expressed in Ohm.cm (Ω .cm).

One Ohm.cm indicates the ohmic resistance of a cubical "block" of electrolyte having a length of 1 cm and a cross section of 1 cm².

Based on their spec. resistivities the corrosion promoting properties of various soils can be ranged as follows.

Spec. resistivity in Ohm.cm	Degree of aggressivity
< 10	strongly aggressive
10 - 20	very aggressive
20 - 50	moderate aggressive
50 - 100	little aggressive
100 - 250	hardly aggressive
> 250	not aggressive

Remark: seawater is approx. 25 Ω .cm!

According to the Dutch Standard for Cathodic Protection (NPR 6912) the application of CP is not required if all the following conditions are met:

- the spec. resistivity of the environment > 10.000 Ohm.cm
- degree of acidity (pH) > 6
- no presence of anaerobic bacteria
- interference smaller than accepted criteria.

5.5 Criterion of protection level

In the daily practice of cathodic protection the most widely used criterion of protection is the metal-electrolyte potential.

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The most common criterion for the cathodic protection of steel structures says that electrochemical corrosion is stopped completely if the potential to all areas of the structure to be protected is lowered till -850 mV or more negative relative to a copper/copper sulphate reference electrode.

When measuring the potential the reference electrode must be placed as close as possible to the structure; in theory directly across the interface steel-electrolyte.

For buried structures such as pipelines this is seldom feasible. In common practice the usual and closest approach is to measure the potential between the pipeline and the soil at the surface, directly above the pipeline.

A widely used method to measure the real potentials, eliminating IR-drops in the soil, is called the "instantaneous-OFF" method.

This method implies that the metal-electrolyte potential of a structure is measured immediately after switching off the CP-current source.

At that moment, while the CP current is zero, the IR-drop in the soil is zero and the real, polarized protection potential can be determined.

The max. time span "off" depends on the depolarization speed of the structure protected. The off-time should be shorter as the spec. soil resistivity is higher.

One should consider that the potential thus measured is the **average value** of the total structure.

5.6 Overprotection

It is not advisable to lower the potential of the structure more than necessary for the maintenance of the required protection level.

A further decrease of potential means lost energy that is consumed by chemical side reactions which do not contribute to the degree of protection.

What's more, if the polarized potential becomes more negative than -1200 mV/CuCuSO₄, one of these side reactions - the formation of hydrogen gas - can create a real risk with respect to the coating (disbonding) and with respect to the steel itself (hydrogen embrittlement).

5.7 Current density and current requirement

The current requirement of an object to be protected means the total protective current to be supplied by the CP-system to lower the potential to the required level.

The current requirement is determined to a great extent by the specific current density of that object; in other words: the average current required per surface unity.

The current density, expressed in mA/m², is mainly determined by the type of coating applied.

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The Dutch Standard for Cathodic Protection (NPR 6912 for onshore, the NPR 2727 for offshore structures) give the following practical current density figures. These figures are in the same order as BS 7361 and the Shell DEP.

Current density figures according to NPR 6912	
Type of coating	Current density $\mu\text{A}/\text{m}^2$
asphalt/bitumen	10 - 100
poly ethylene (PE)	1 - 10
butyl rubber coatings	50 - 100
epoxy coatings	variable

Current density figures according to NPR 2727 (bare steel)	
Area	Current density mA/m^2
North sea	90 - 150
Indonesia	65 - 85
Gulf of Mexico	65 - 85
Arabian Gulf	80 - 150
Nigerian Coast	85
Cook Inlet, Alaska	250
Steel in seabed	20 - 30

6. CATHODIC PROTECTION SYSTEMS

6.1 The sacrificial CP-system

A sacrificial CP-system consists of one or more so-called "galvanic" anodes which are placed in the same electrolyte as the structure to be protected. The anodes are electrically connected to the structure. They are made of a metal having a natural potential (in the electrochemical force series) more negative than the structure.

For onshore installations magnesium anodes are commonly used.

The potential of these anodes is approx. $-1600 \text{ mV}/\text{CuCuSO}_4$.

For offshore structures (platforms, sealines etc.) zinc and aluminium anodes are most popular; the potential of these anodes is approx. $-1050 \text{ mV}/\text{CuCuSO}_4$.

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Once these sacrificial anodes are electrically connected to the structure (commonly steel) on the combination a so-called "mixed potential" will occur. The level of this potential will be between the natural potentials of steel and the anode material.

The CP-system must be designed in such a manner that the mixed potential will be -850 mV/CuCuSO_4 or more negative.

The sacrificial anodes supply the required negative charge (electrons) to the steel structure, self going into solution gradually (they "corrode").

An example of a sacrificial CP-system on behalf of a buried tank is given in **appendix 6**.

Note: In onshore installations sacrificial anodes (mainly magnesium) are used with a prepacked chemical backfill to surround the anodes completely. The main reasons are:

- better current efficiency is promoted
- reduction of formation of passivating films (as carbonates)
- absorption of moisture
- reduction of anode-to-soil resistance.

An advantage of a sacrificial anodesystem is the small sensivity for failures and as a consequence the simple maintenance.

A disadvantage is that the anodes are consumed and have to be replaced with time.

A disadvantage of sacrificial anodes in onshore installations is the limited current capacity of them (dependent on the soil resistivity).

Some exeamples for offshore applications are given in:

- **Appendix 7** : Bracelet anode for sea pipelines.
- **Appendix 8 + 9** : Retrofit anodesystems for (existing) piles under jetties and platforms.
- **Appendix 10** : Monitoring anode.

6.2 Impressed current CP-system

An impressed current CP-system consists of one or more inert anodes installed on a central location, in the same electrolyte in which the structure is situated.

The anodes are electrically connected to the plus-output of an adjustable transformer rectifier. The minus is connected to the structure to be protected (the cathode).

The rectifier is adjusted in such a manner that the anodes discharge just enough current to the structure (through the soil) to achieve the required lowering of the potential (see **appendix 11**).

Impressed current CP-systems are used for the bigger structures such as pipeline systems, sheetpiling, jetties etc.

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In onshore installations the most popular anode is made of Silicon Iron. For offshore structures generally platinized or mixed metal coated titanium anodes are used (coated film 2,5 to 10 μm only).

Although these inert anodes in an impressed current system are extensively less sensitive for dissolving (corroding) than sacrificial anodes are, they suffer with deterioration as well. For Silicon Iron anodes the loss of material varies between 200 and 400 gram material per Ampere current discharge per year.

The wear-rate of platinized titanium anodes in fresh seawater is only 5 to 10 mg platinum per Ampere current discharge per year.

The great advantage of an impressed current CP-system is that such a system is fully adjustable and that its capacity is not limited in principle.

A disadvantage is its sensitivity for failure and as a consequence the need of a more frequent inspection of these systems.

6.3 Cathodic protection by means of Hot Spot

6.3.1 Principle

Although the principle of cathodic protection using the "Hot Spot" method does not differ fundamentally from that of a conventional CP system (either by means of sacrificial anodes or according to the impressed current method), the form of implementation is certainly completely different.

The operational principle of Hot Spot systems rests on the fact that the required metal-electrolyte potential difference is not sought by lowering the potential of the structure relative to the surrounding electrolyte, but is reached by **raising** the potential of the electrolyte relative to the structure.

In other words: when the potential of the structure cannot, or at least cannot sufficiently be made more negative since this structure is so "massively" earthed, the surrounding ground is locally made positive in such a way that the same result is achieved.

Influencing the ground potential is realised by installing a relatively large number of anodes at a relatively short distance from the structure to be protected. The number of anodes required and the distance demanded are mainly determined by the specific resistivity of the soil in which the structure is situated. The depth at which the anodes are placed is a very important aspect in this. As a rule, the specific resistivity of the soil (in the upper layer) decreases with depth, due, to a significant extent, to the presence of ground water, but also through the presence of other types of ground layer of lower resistance.

Anodes installed in a ground layer with a specific resistivity much lower than that of the layer in which the structure to be protected is located have less effect, since the protective current will mainly "seek out" the parasitic elements in the system and in so doing will not, or not sufficiently act upon the desired structure.

A thorough soil investigation must be undertaken before installing Hot Spot anodes. In addition, during the installation of the anodes, the ground resistance attained by the anodes in relation to the installation depth must be permanently supervised (see appendix 12).

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6.3.2 Protection criterion for Hot Spot cathodic protection

The most widely known and used protection criterion for conventional CP systems is the "Instantaneous Off" or "IR free" criterion.

For Hot Spot CP-systems this criterion cannot, however, be used in all cases.

Without cathodic protection, the "natural potential" of the object to be protected is in fact the active corrosion potential of the combination: steel object + electrical earths + a great deal of concrete. In magnitude (bare surfaces), the latter parts will dominate and the corrosion potential of the combination will be determined only to a limited extent by the steel object itself. This means that after disconnecting the Hot Spot CP current, the compound potential of the combination will as a rule quickly return to its original value. For these reasons, the following protection potential criterion relating to Hot Spot CP systems, derived from the NACE, is normally used (see NACE Recommended Practice PR0169-92).

Cathodic protection by the Hot Spot principle is considered fully effective if at all places on the protected structure a potential drop of at least 300 mV is reached w.r.t. the original free corrosion potential of the structure.

The protection potential is measured w.r.t. a saturated Cu/CuSO₄ reference electrode placed as near as possible above, or alongside the protected structure, at constant, but maximum intervals of 5 m (see appendix 13 and 14).

Since as a rule the free corrosion potential of the steel structure itself cannot be measured due to contact with other types of underground conductors, this is set at -650 mV/Cu.CuSO₄.

The derived protection criterion for Hot Spot CP systems is then a protection potential of -950 mV/Cu.SO₄ or more negative at all points on the protected structure.

In cases of doubt, the free corrosion potential is determined with the aid of an insulated pin on which a bare steel point (sample) is mounted. This test probe is driven into the ground to the same depth and in close proximity to the structure to be protected. After the introduction of the test probe the corrosion potential of the steel point (sample) is measured. The value found then serves as the basis for determining the required protection potential.

6.3.3 Permanent IR drop-free reference electrode(s)

For a CP system applying the Hot Spot principle, it is further recommended that at least one permanent "IR drop-free" reference electrode is buried close to and at the same depth as the protected pipe/structure (see appendix 14A).

At the steel test coupon on this electrode it is possible to measure the spontaneous corrosion potential in the proximity of the structure, which can be used to set the minimum protection potential. After permanent connection of the terminal to the cathodically protected structure, the "IR drop-free" protection potential can be measured at any time without the need to disconnect the CP supply source. It is also possible to measure the polarised potential at the steel test coupon when this is temporarily disconnected from the protected structure.

CORROSION AND CATHODIC PROTECTION

6.4 Additional CP within casings

6.4.1 Plastic casings such as PVC, PE or GRE constitute a complete electrical screen from the product pipeline.

Within such casing, the effect of external cathodic protection (e.g. a magnesium anode or a rectifier and anode bed installed outside the casing) is zero.

The space between the casing and the product pipeline must be seen as a **fully isolated area** in which corrosion will certainly take place (if there is ground water in the space between the product pipeline and the casing) that cannot be measured or influenced from outside the casing. To prevent electrochemical corrosion in this area, additional cathodic protection must be introduced within the casing.

a. By means of magnesium ribbons

The most widely used cathodic protection method for pipes inside insulating casings is by means of magnesium ribbon anodes. Depending on the diameter of the product pipeline and the casing, one or more magnesium ribbon anodes are mounted on the product pipeline over the full length within the casing.

The number of ribbon anodes to be used depends on the resistivity of the groundwater as well as on the product pipeline diameter.

A good rule of thumb is that the distance around the pipe between the magnesium ribbon anodes be not greater than 700 mm, with a minimum of two ribbon anodes for each product pipeline.

The ribbon anodes must be mounted the same distance apart around the product pipeline, with one ribbon anode installed directly under the product pipeline. This is necessary to ensure that when only the underside of the product pipeline is in contact with the standing water level in the casing the CP (i.e. the lowest anode) will become active.

This requirement often poses a technical installation problem since insulators with a low stud height (sometimes only 25 mm) are often used which means that not enough space remains between the underside of the product pipeline and the casing to accommodate the lowest ribbon anode. There thus arises a fair chance of damage to the ribbon anodes when inserting the product pipeline into the casing.

Internal protection by means of ribbon anodes is illustrated in Figure 3.1 (see appendix 15).

In practice, the casing will often be **permanently and completely** under the level of ground water, in which case the position of the lowest ribbon anode is no longer critical and it can be mounted more to the side of the product pipeline (where there is usually more space).

CORROSION AND CATHODIC PROTECTION

b. By means of impressed current

Instead of sacrificial magnesium ribbon anodes, it is possible to use titanium wire anodes, with a thin layer of platinum or "mixed metal oxide", installed in perforated PVC pipes along the product pipeline and connected to a precisely regulated rectifier. In this case also, the wire anodes must not protrude from the ends of the casing.

The most widely used type of wire anode has a diameter of just 3 mm and a Platinum coating of approximately 2.5 mm.

Due to the small wire thickness, such a Pt/Ti wire anode can be installed in a much thinner perforated PVC pipe.

The lifetime of such a system is **many times longer than in the case of sacrificial ribbon anodes** and the replaceability of the wire anodes is much better.

6.4.2 Measurement of CP within casing

Since the space within insulating casings, eg. PVC, is completely isolated from the "outside world" potential measurements undertaken outside this area (at grade level for example) do not supply with any relevant information on the level of protection **inside** the casing.

To read the potential within the casing, at least one permanent reference electrode must be installed inside the casing at a distance of at least $2 \times D$ from the end of the casing. The reference electrode must be connected by means of an insulated cable to a test facility above ground, and must be connected to an individual test terminal.

The most widely used type of permanent reference electrode is the flat zinc reference electrode. This electrode should be mounted at the lowest point inside the casing, between two of the ribbon anodes.

7. INTERFERENCE

7.1 Introduction and example

When associated with cathodic protection, interference is understood to be: the undesired influence on the metal-electrolyte potential of underground metal structures (especially of pipelines) due to inflowing and outflowing "foreign" direct currents which balance themselves within the ground. The principal causes of interference are cathodic protection systems and direct current traction systems of tram and railway companies.

A situation where a steel pipeline is cathodically protected by means of a rectifier installation is illustrated in Figure 1.1 (see Annex 16).

The anode bed for this installation is located a short distance away from a "foreign" buried conductor. It is assumed that the anode bed has been installed at insufficient depth and the protective current is therefore discharged to the soil in the upper ground layers. The foreign conductor now finds itself in the positive voltage gradient of the anode bed, so that its potential at this point becomes more negatively charged. If the coating on the foreign conductor would be in perfect condition nothing untoward would happen.

CORROSION AND CATHODIC PROTECTION

The protective current of the CP system would not be able to enter the foreign conductor and would reach the pipeline to be protected along the "usual route", i.e. by spreading through the ground. In practice, of course, the coating on the foreign conductor will not be perfect and, both in the direct vicinity of the anode bed and the point much further away where the foreign conductor again runs close to the protected pipe, there will be greater or lesser contact between the foreign conductor and the ground. It should be apparent that this is bound to have an effect on the foreign conductor. A part of the CP current will now actually enter the foreign conductor in the vicinity of the anode bed and use this as a current conductor (since its electrical resistance is less than that of the ground) to the spot where the foreign conductor and the protected pipe come close together again.

In this area the CP current will leave the foreign conductor and, via a short path through the ground, ultimately enter the protected pipeline. At the spot(s) where the CP current leaves the foreign conductor, electrochemical corrosion may be expected to occur; there will be a positive shift in the potential of the foreign conductor. To a large extent the rate of this corrosion will depend on the local specific ground resistance.

If this is high, the interference current will find it difficult to balance itself; if it is low, then even for a slight potential difference, an interference current will start to flow.

7.2 Interference measurements

From the above it follows that interference can be determined by measuring the potential of the threatened conductor(s). These interference measurements are carried out after a time-switch has been placed at the output of the rectifier for the disruptive (interfering) CP system, which repeatedly switches the rectifier on and off.

In the Dutch standard for cathodic protection NPR 6912 the recommended switching times are 40 seconds "on" and 20 seconds "off".

The metal-electrolyte potential of the foreign conductor is now measured at all the points where the current entering and leaving is most likely. The difference in the potential measured immediately before the rectifier switches "off" and that measured at the end of the "off period", in conjunction with the specific soil resistivity forms the basis of the assessment of the acceptability of the interference in accordance with NPR 6912.

7.3 Interference criteria

In NPR 6912 interference is considered to be harmful if, on switching the CP system for the protected structure "on", the metal-electrolyte potential of the foreign conductor affected:

- 1st Undergoes a shift in the positive direction
for which the numerical value expressed in mV is more than:
 - a. Twice the specific soil resistivity (in ohm.m) for steel
 - b. Equal to the specific soil resistivity (in ohm.m) for lead

CORROSION AND CATHODIC PROTECTION

- 2nd Acquires a value w.r.t. a Cu/CuSO₄ reference electrode more negative than:
- a. -1200 mV for aluminium
 - b. -1500 mV for lead
 - c. -800 mV for saponifiable paints
 - d. -2500 mV for thick and impermeable types of coating

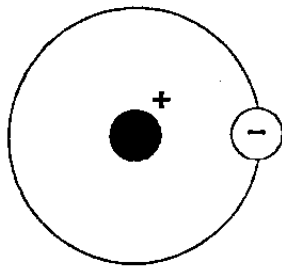
7.4 Measurement of the specific soil resistivity

The specific soil resistivity "Rho" must, of course, be measured as close as possible to the location of the interference. The most practical method for determining Rho (at depth) is by means of a ground sample measurement.

TABLE OF APPENDICES

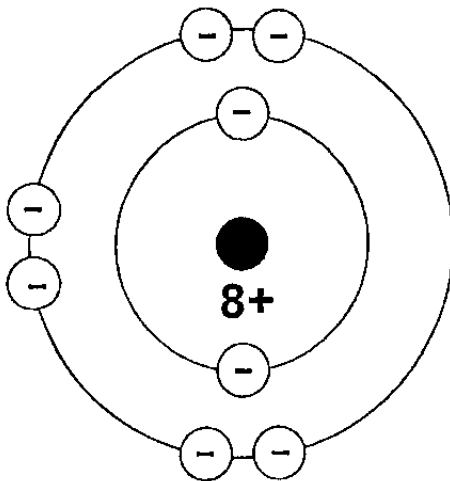
- 0. Atoms**
- 1. Inert gas configuration**
- 1A. Water molecule**
- 2. Schematic outline of electrical double layer**
- 3. Ag/AgCl reference electrode**
- 4. Cu/CuSO₄ reference electrode**
- 5. Galvanic cell**
- 6. CP tank with sacrificial anode**
- 7. Bracelet anode for sea pipeline**
- 8. Retrofit anode system (front view)**
- 9. Retrofit anode system (cross section)**
- 10. Monitored sacrificial anode**
- 11. Impressed current CP-system**
- 12. Hot Spot CP-system**
- 13. Potential graph Hot Spot (on commissioning)**
- 14. Potential graph Hot Spot (after polarization)**
- 14A. IR-drop free reference electrode**
- 15. Internal CP in casing**
- 16. Schematic outline of interference**
- 17. Current distribution of a deepwell grounded**

Atoms



H-atom

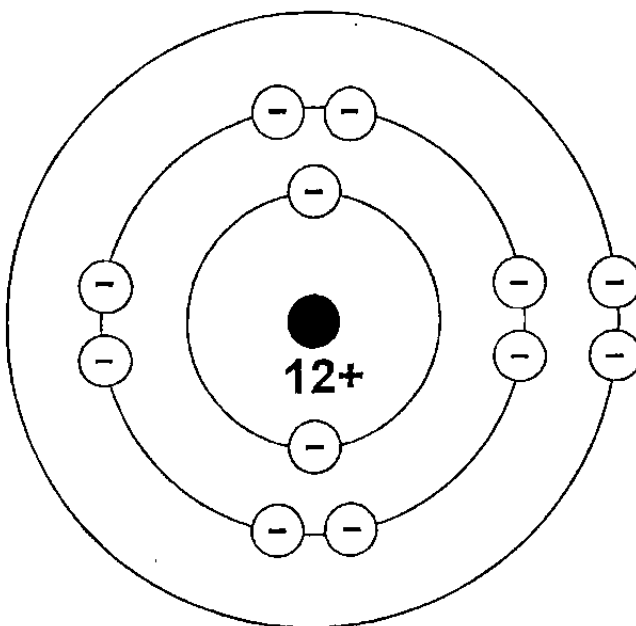
1 shell, 1 electron



O-atom

1st shell: 2 electrons

2nd shell: 6 electrons



Mg-atom

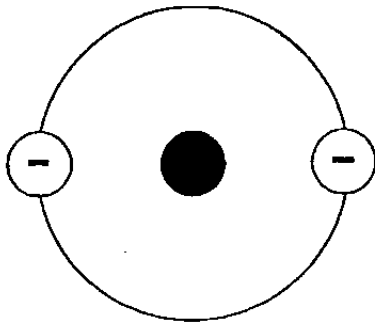
1st shell : 2 electrons

2nd shell : 8 electrons

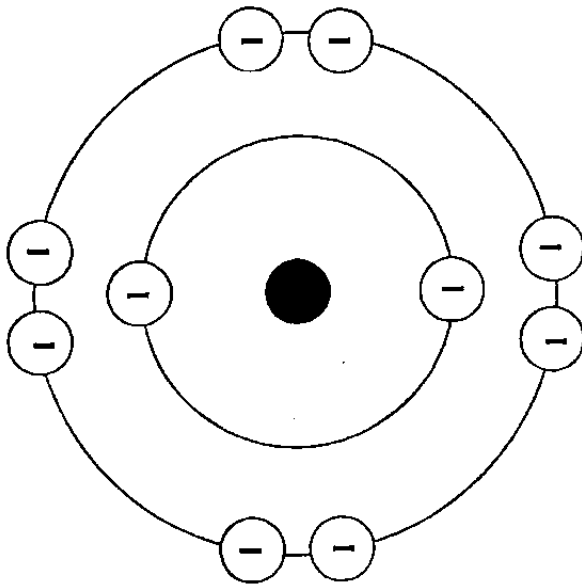
3rd shell : 2 electrons

n^{th} shell: $2n^2$ electrons

Inert gas configuration



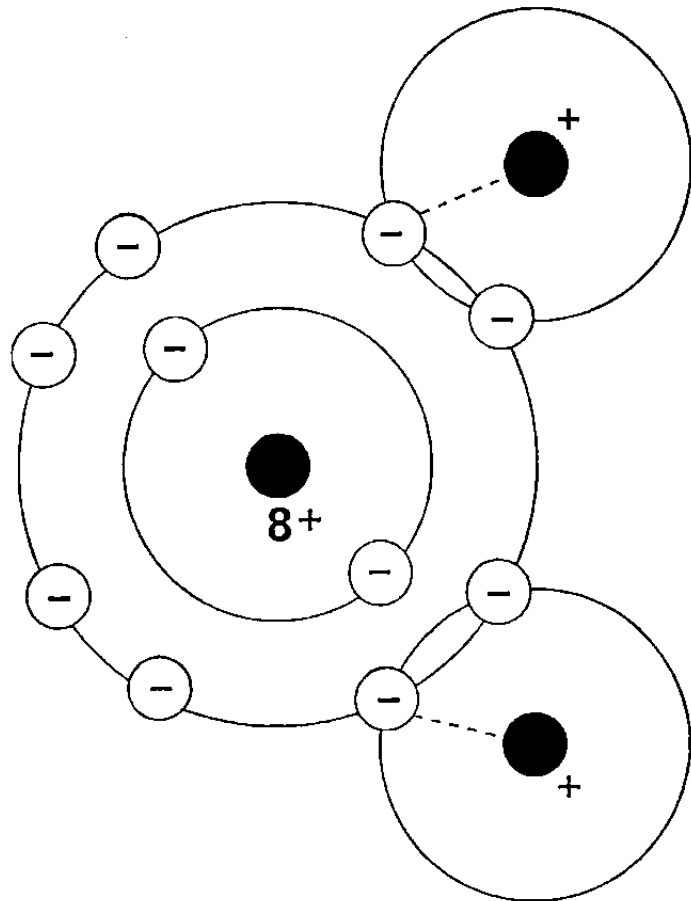
atom Helium
1 shell, 2 electrons



atom Neon
1st shell: 2 electrons
2nd shell: 8 electrons

**Inert gasses are chemically stable:
they do not form chemical combinations**

Water molecule



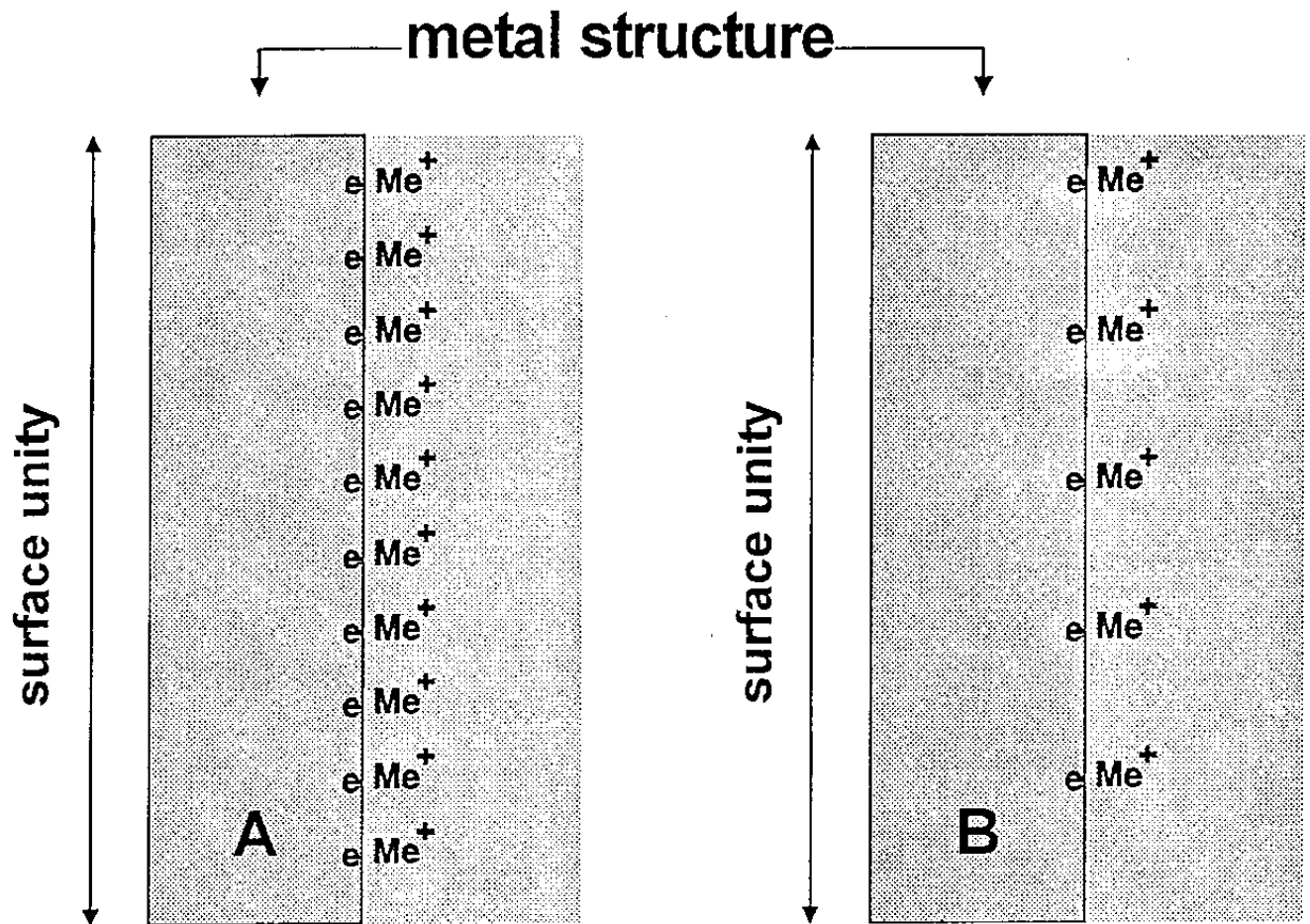
Formula: H_2O

All atoms seem to have an inert gas configuration:

H has 2 electrons

O has 8 electrons (in the outer shell)

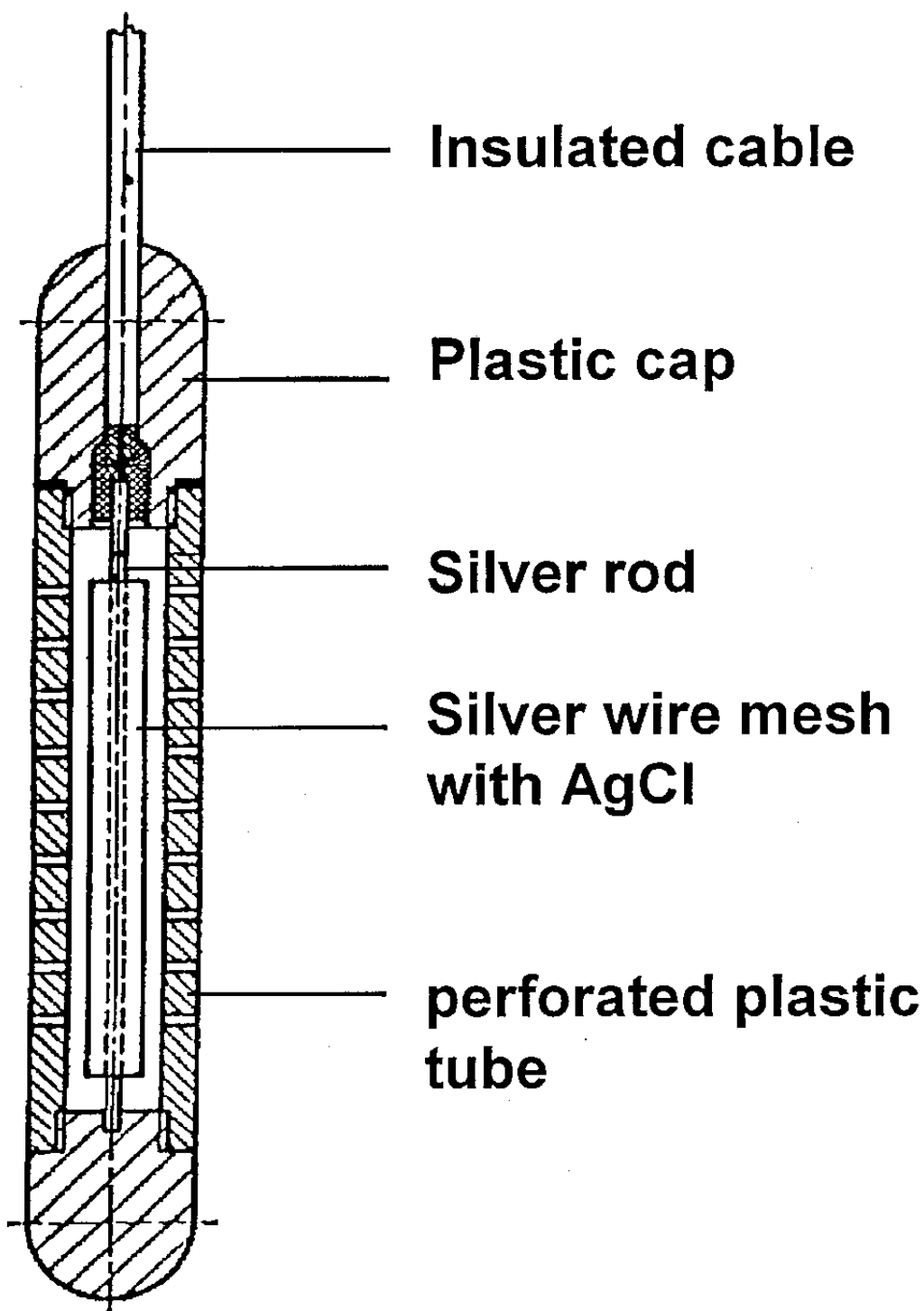
Schematic representation electrical double layer



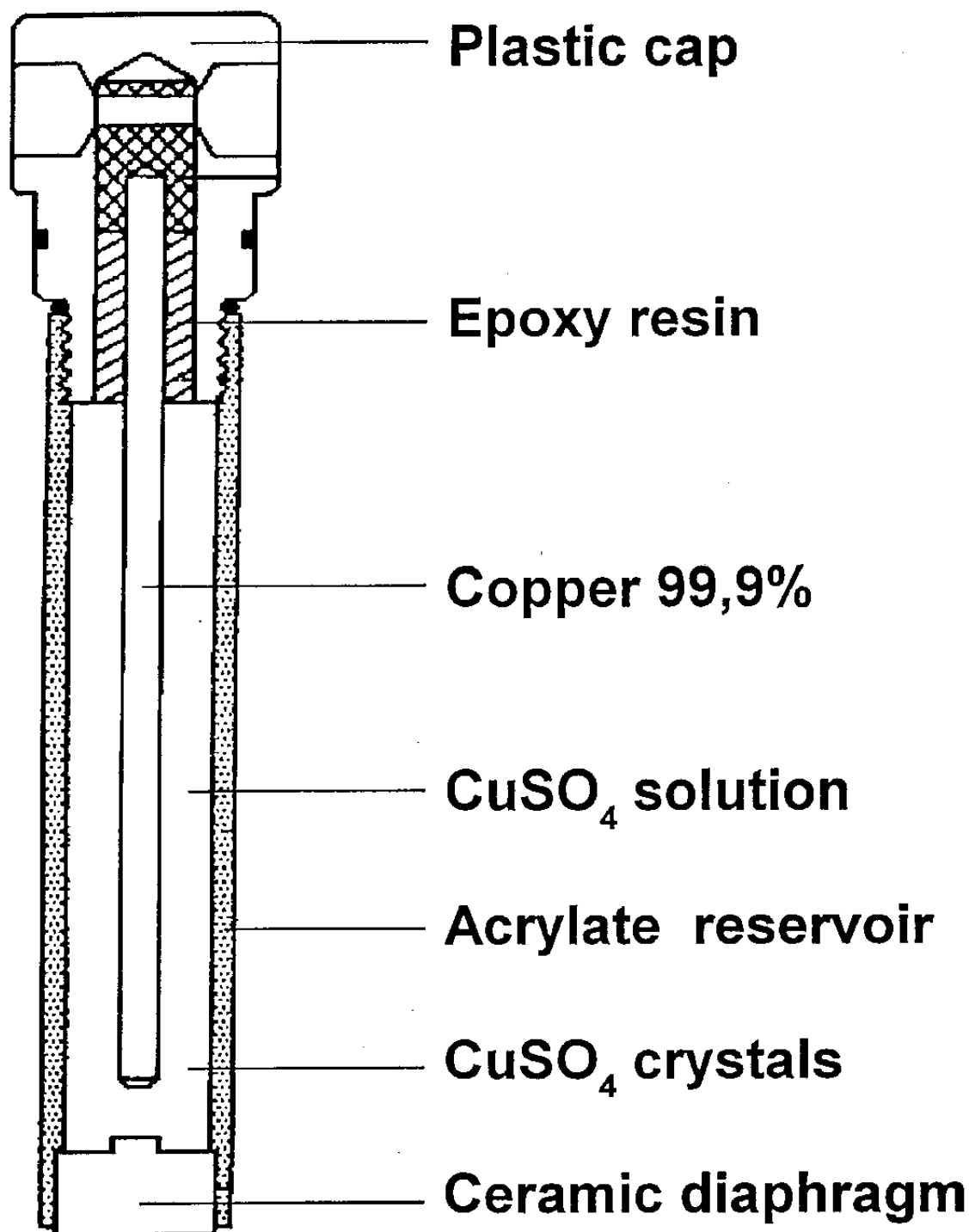
Potential difference metal to electrolyte
of A is bigger than B

i.o.: A is more negative than B
 A is less noble than B

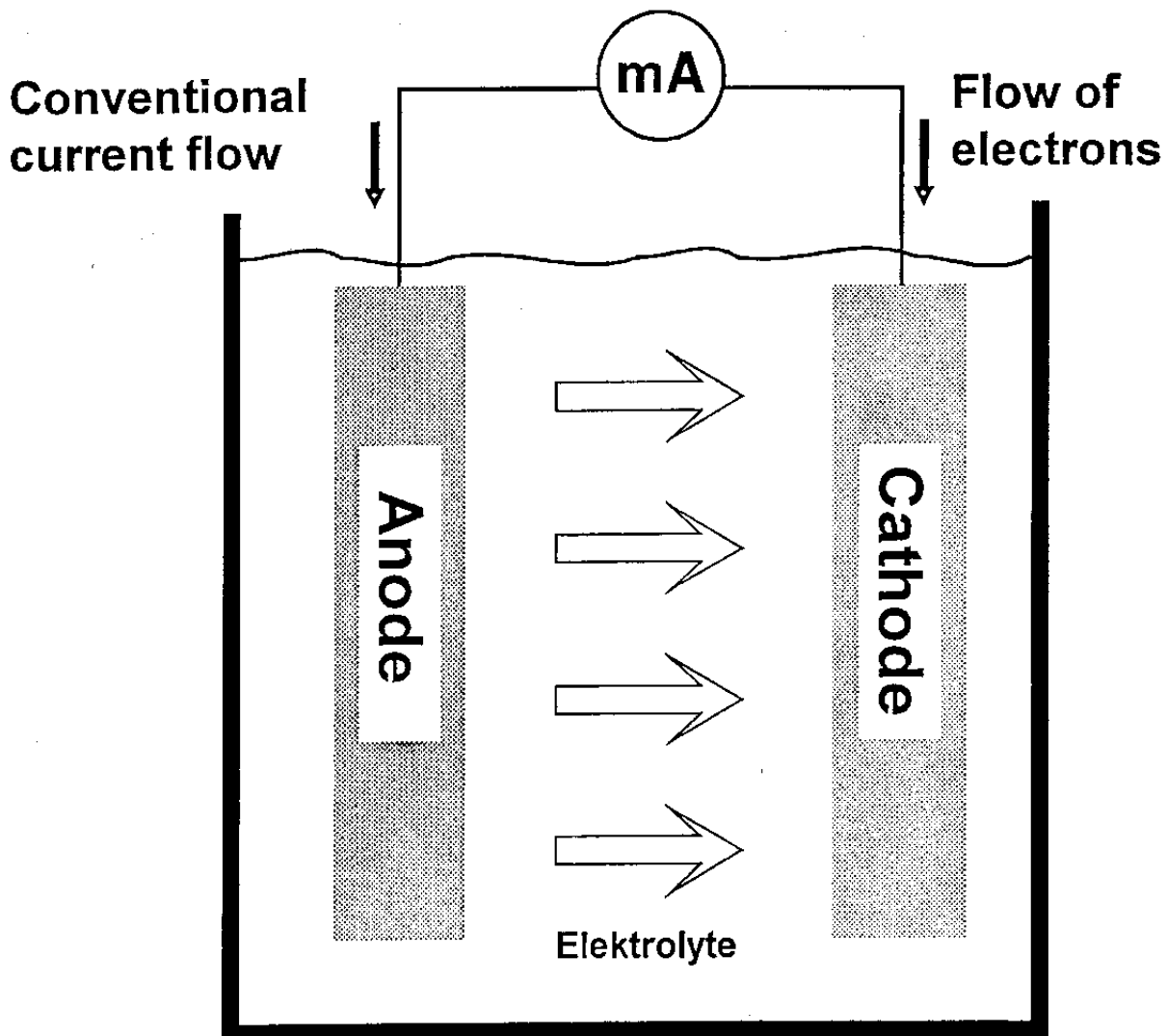
Silver/Silverchloride reference electrode



Cu / CuSO₄ Reference-electrode



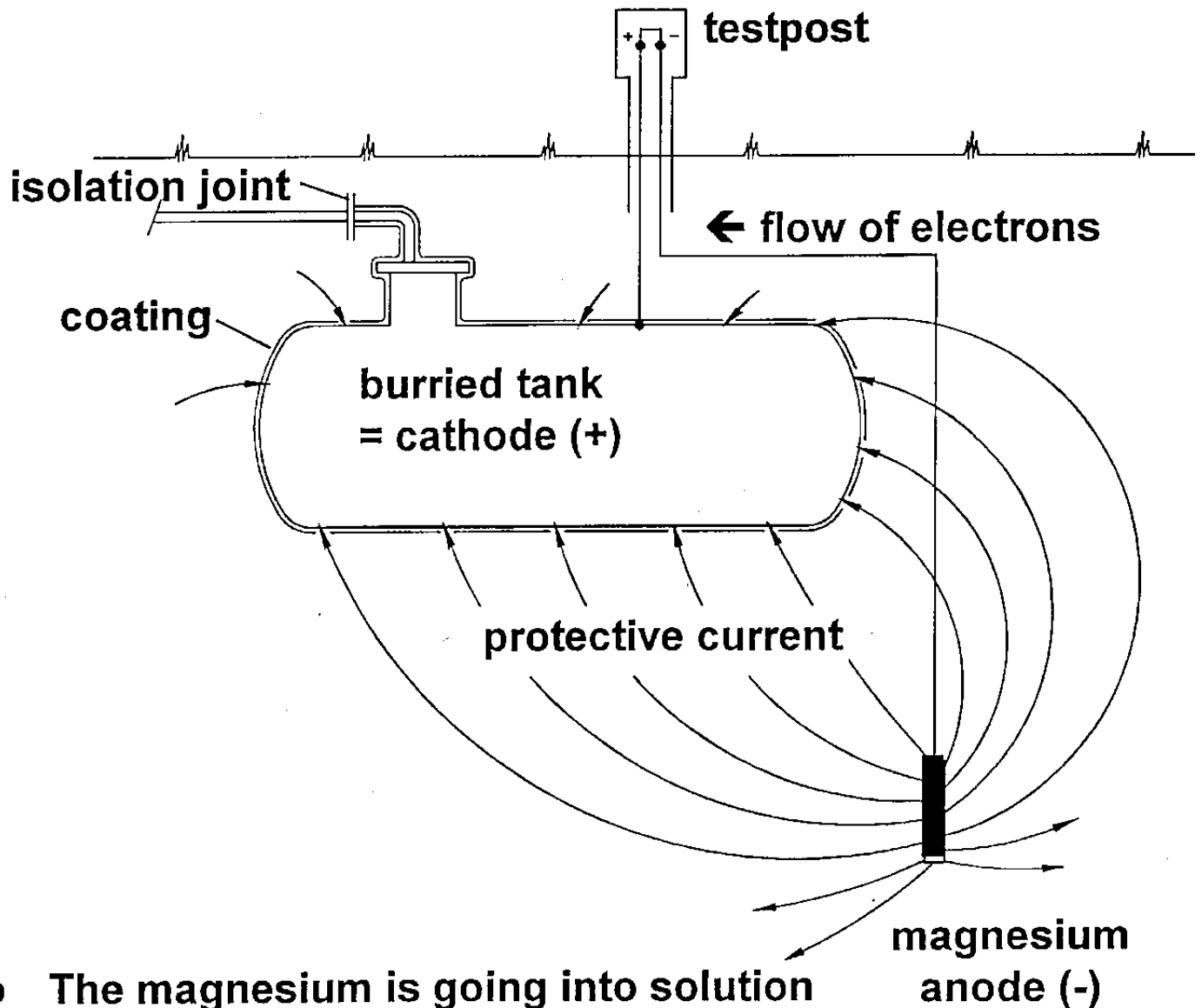
Galvanic cell



Anode: where current flows from the metal into the electrolyte

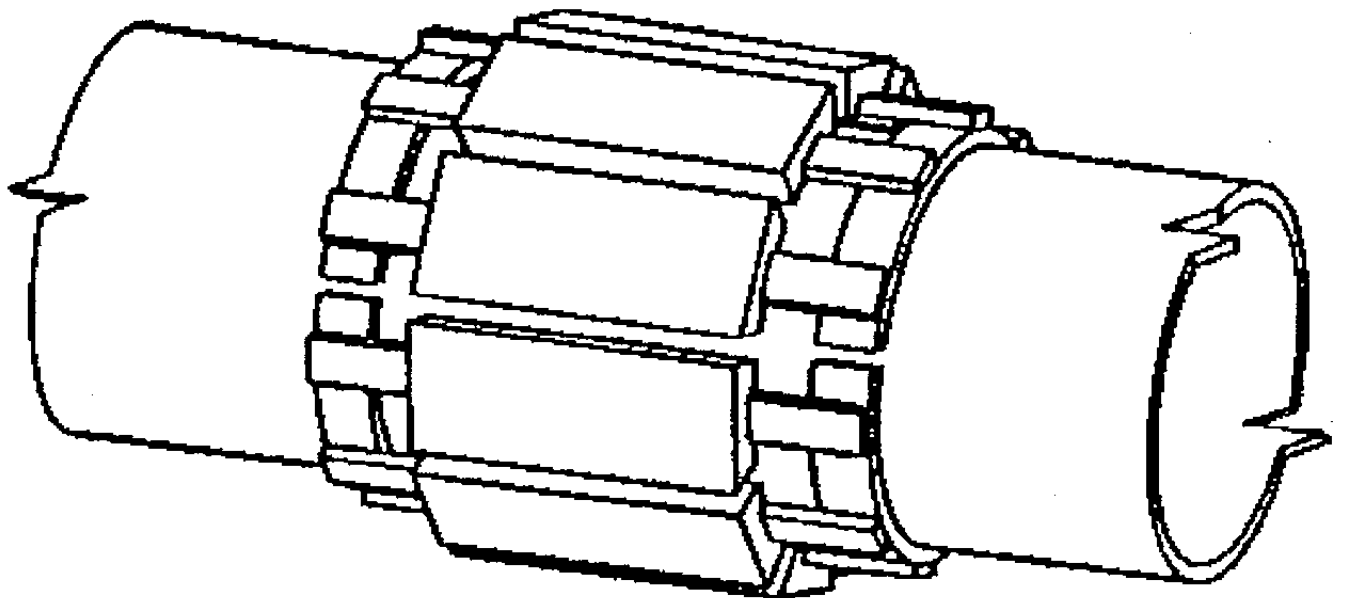
Cathode: where current flows from the electrolyte to the metal

Cathodic protection with sacrificial anode

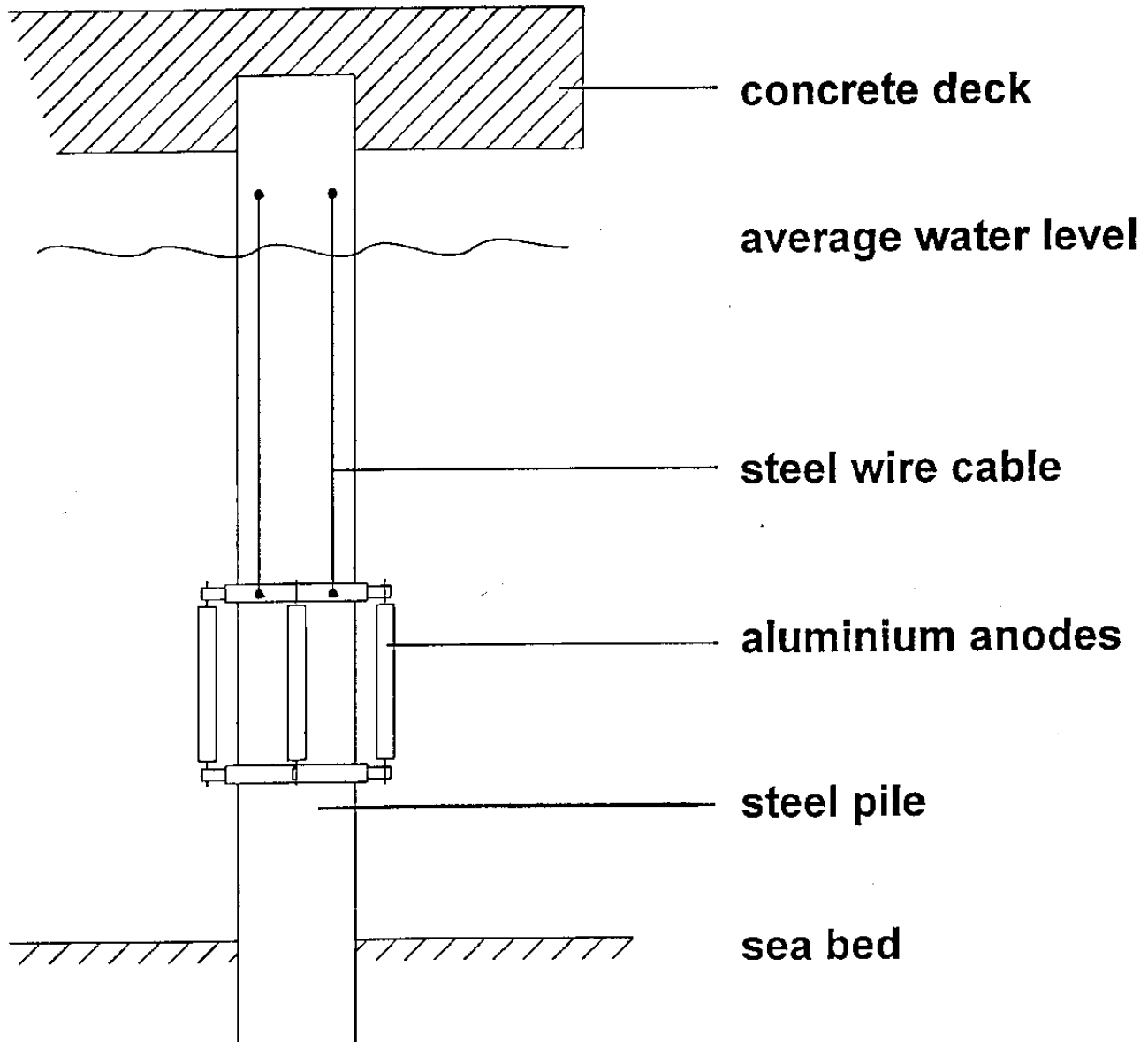


- o The magnesium is going into solution
- o The free electrons flow to the tank
- o The tank becomes more negative
- o Collecting current = cathodic protection

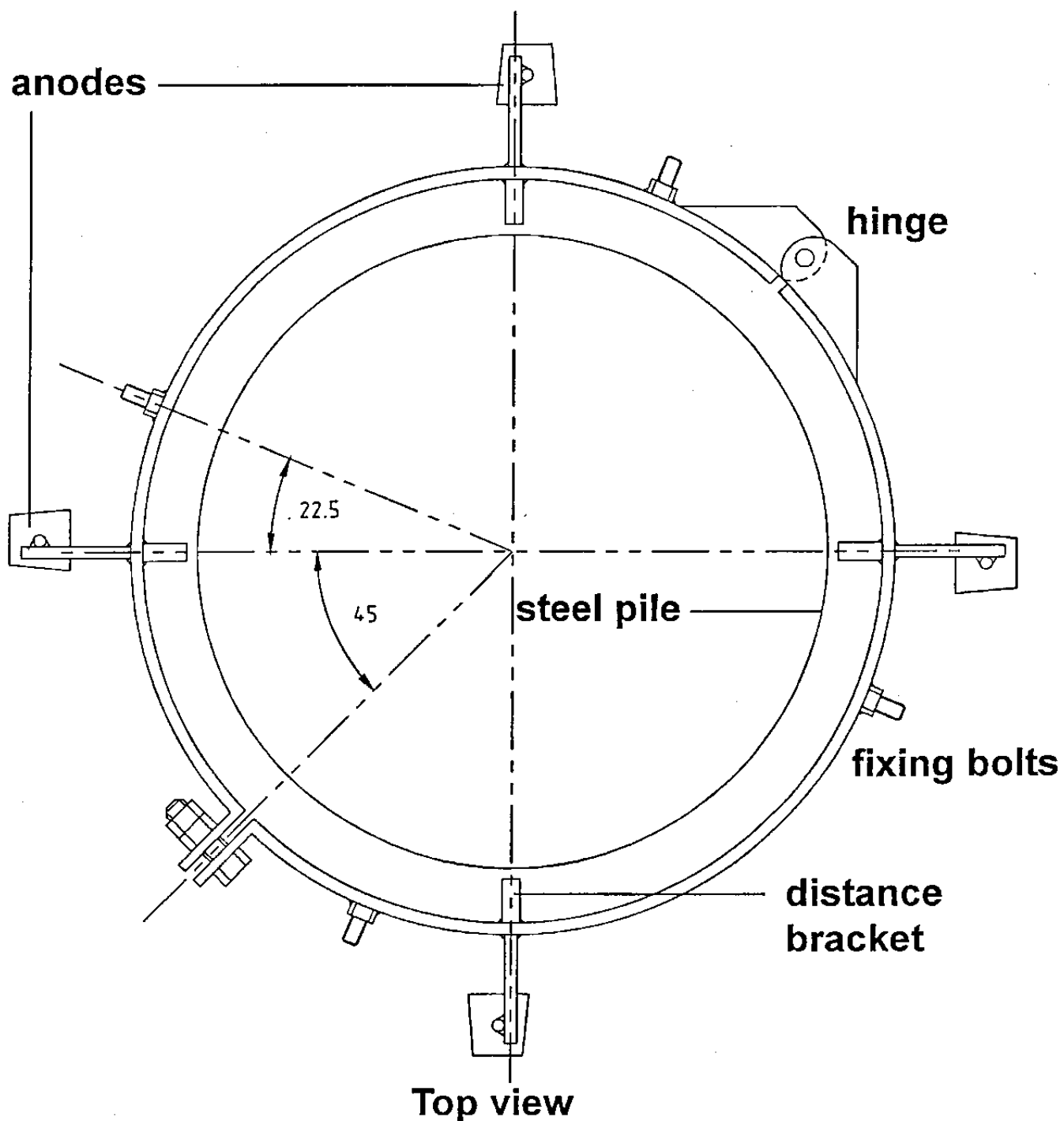
Bracelet anode for sea pipelines

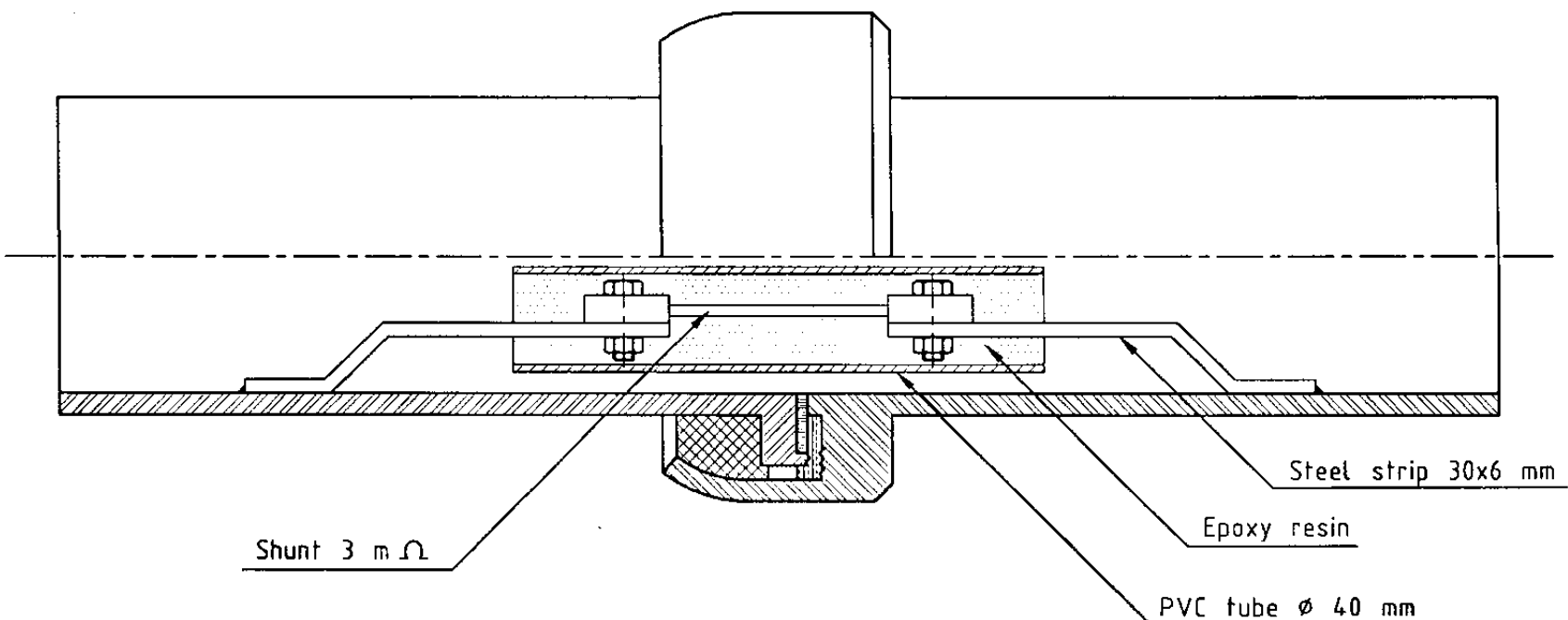


Retrofit anode system

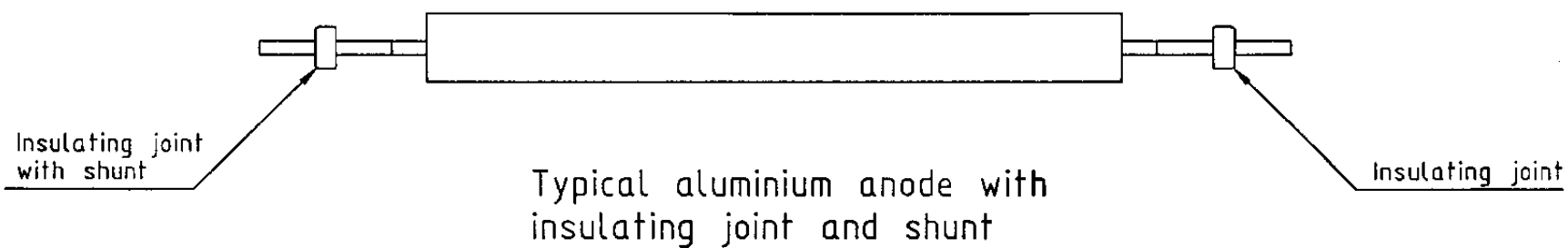


Aluminium anode for offshore applications (Retrofit-system)



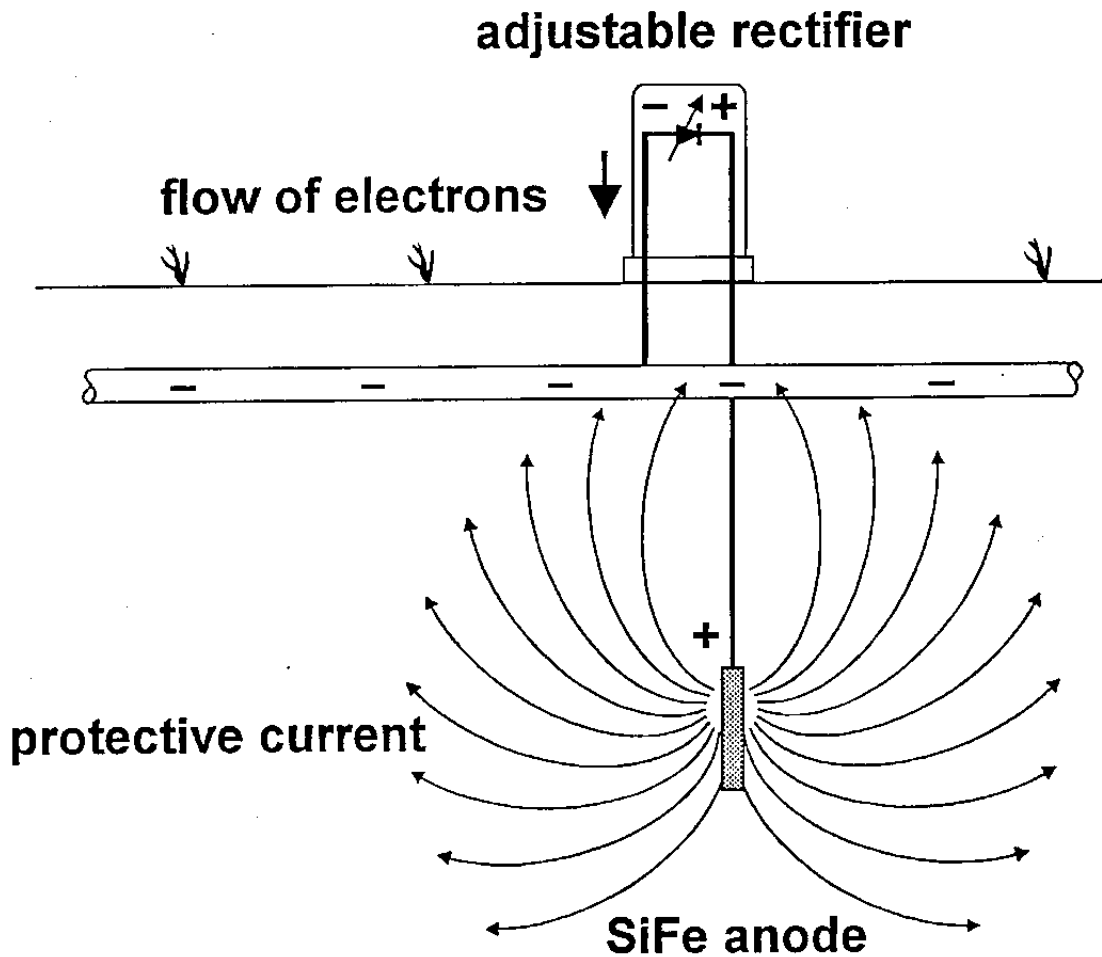


Insulating joint with shunt



Typical aluminium anode with insulating joint and shunt

Cathodic protection with impressed current



Potable water
reservoir

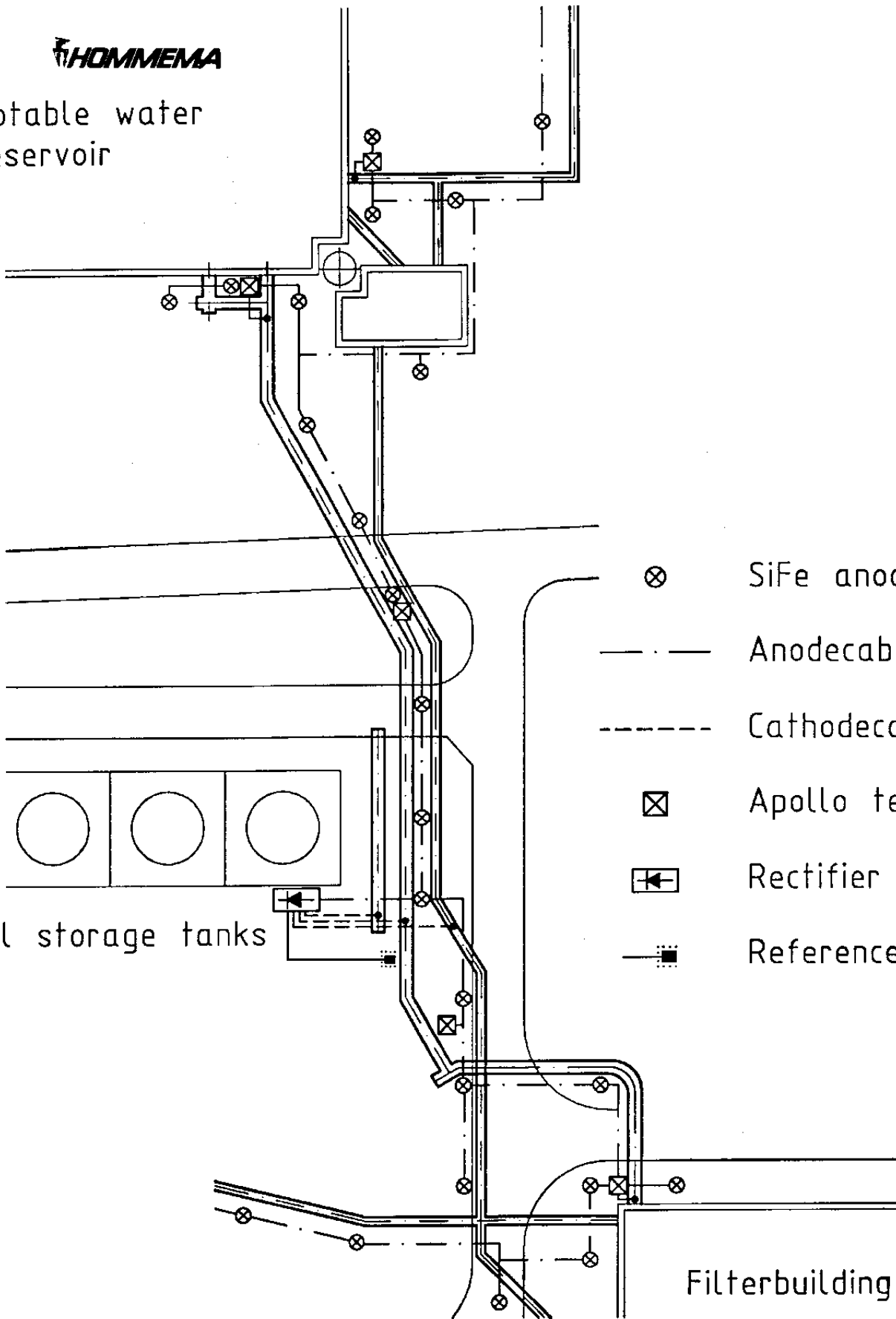
Oil storage tanks

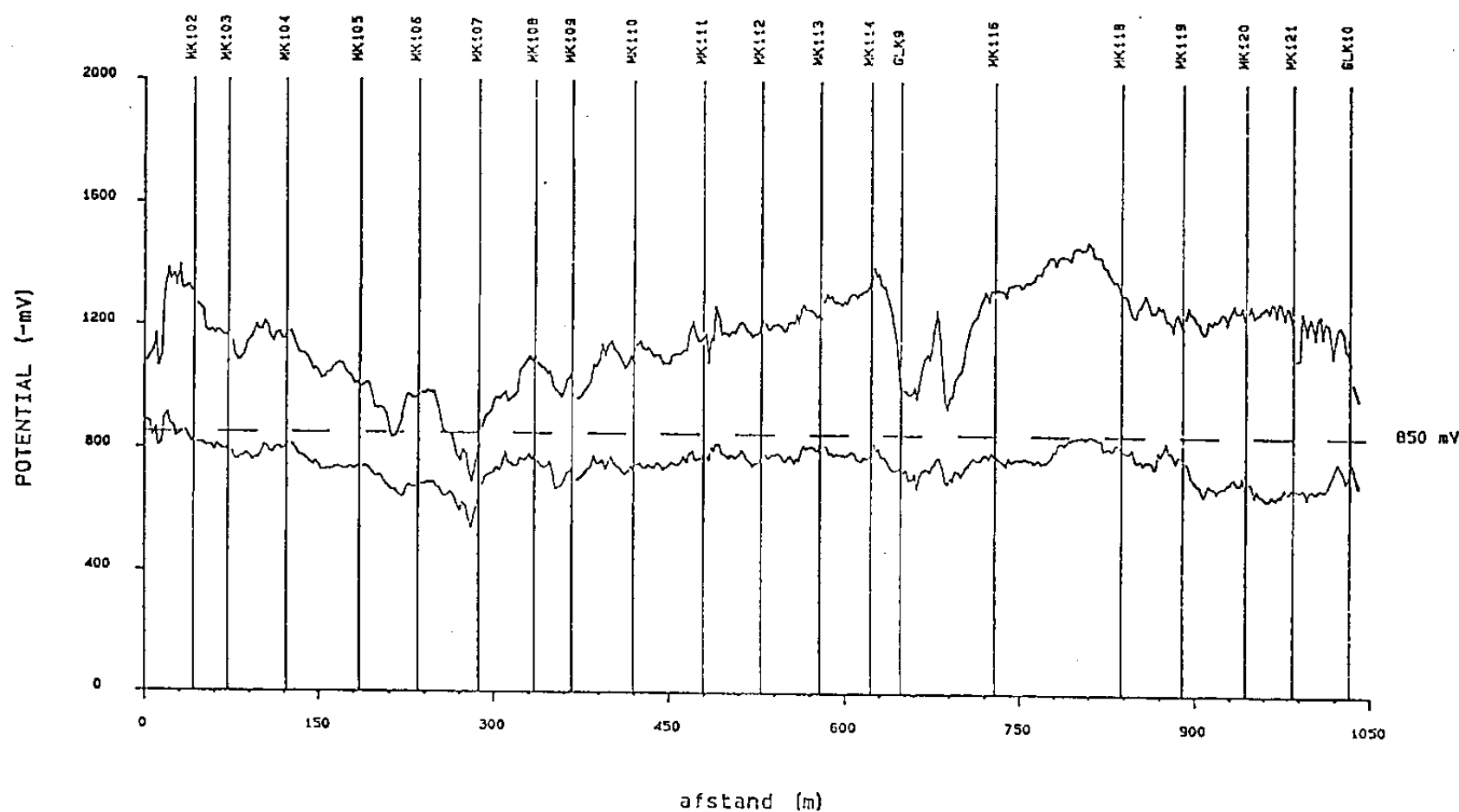
Filterbuilding

- ⊗ SiFe anode
- Anodecables
- - - Cathodecables
- ⊠ Apollo testbox
- ⏏ Rectifier
- ■ Reference electrode

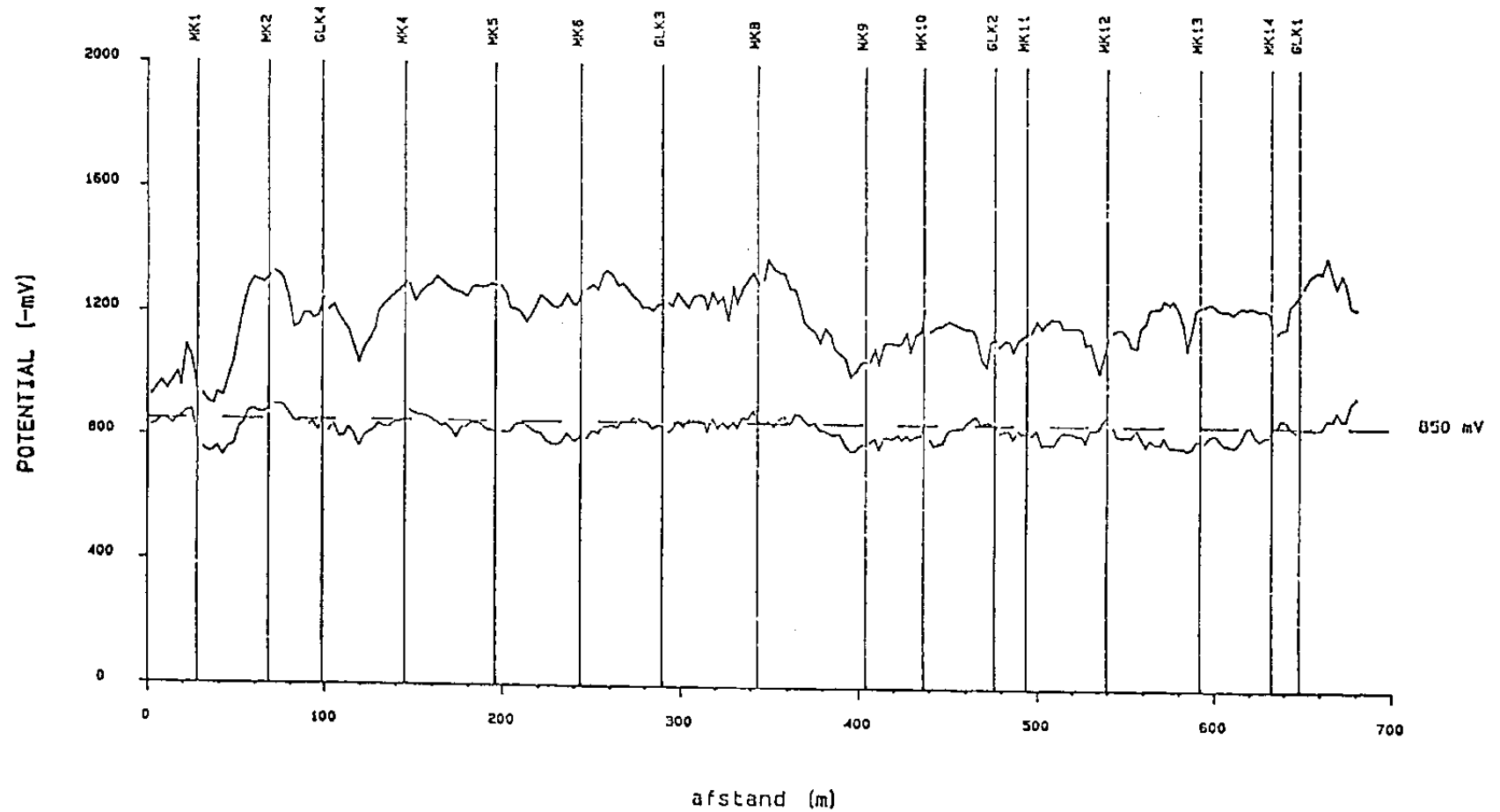
HOT SPOT C.P. SYSTEM

(EXAMPLE)





Definitieve eindoplevering Gelijkrichters 1 t/m 10 in bedrijf Aan/uitpotentialen t.o.v. Cu/CuSO4 Hommema wo. nr: 421032/19 Grafieknr: 0001	DATE : 12 maart 1993 SCALE : ZIE GRAFIEK DRAWN : AA SUPV : AA PASSED : APPR :	
		Kath. Bescherming/Hot-Spot
		C200/D200/D300
		HOMMEMA KATH. BESCHERMING B.V.
INPUT FILE MC110393.FMT.		



Definitieve eindoplevering
 Galijkrichters 1 t/m 10 in bedrijf
 Aan/uitpotentials t.o.v. Cu/CuSO4
 Hommema wo.nr: 421032/16 Grafieknr: 0001

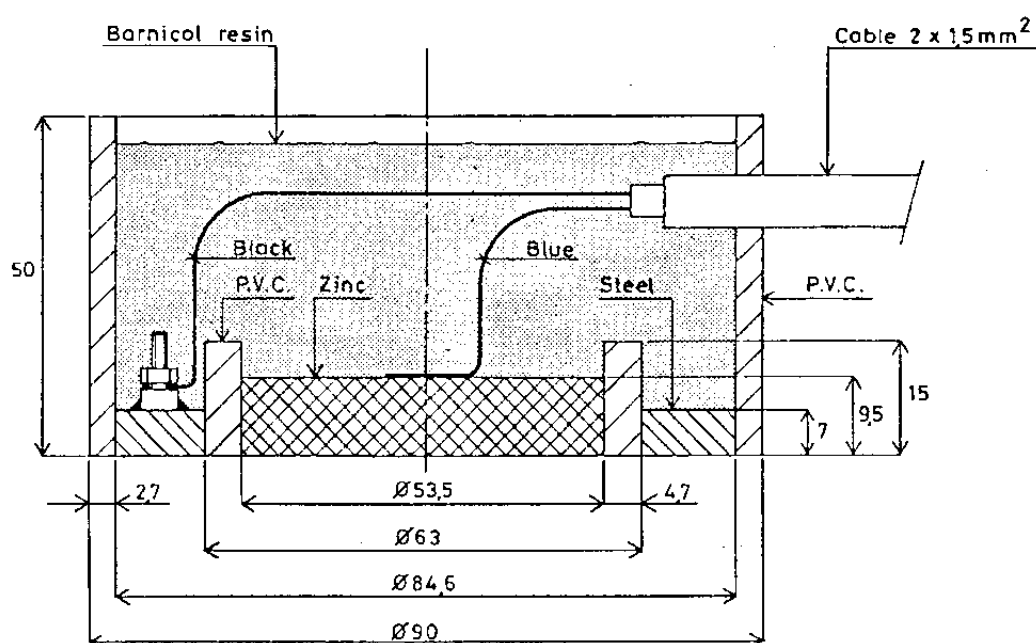
DATE : 12 maart 1993
 SCALE : ZIS GRAFIEK
 DRAWN : AA
 SUPV : AA
 PASSED :
 APPR :

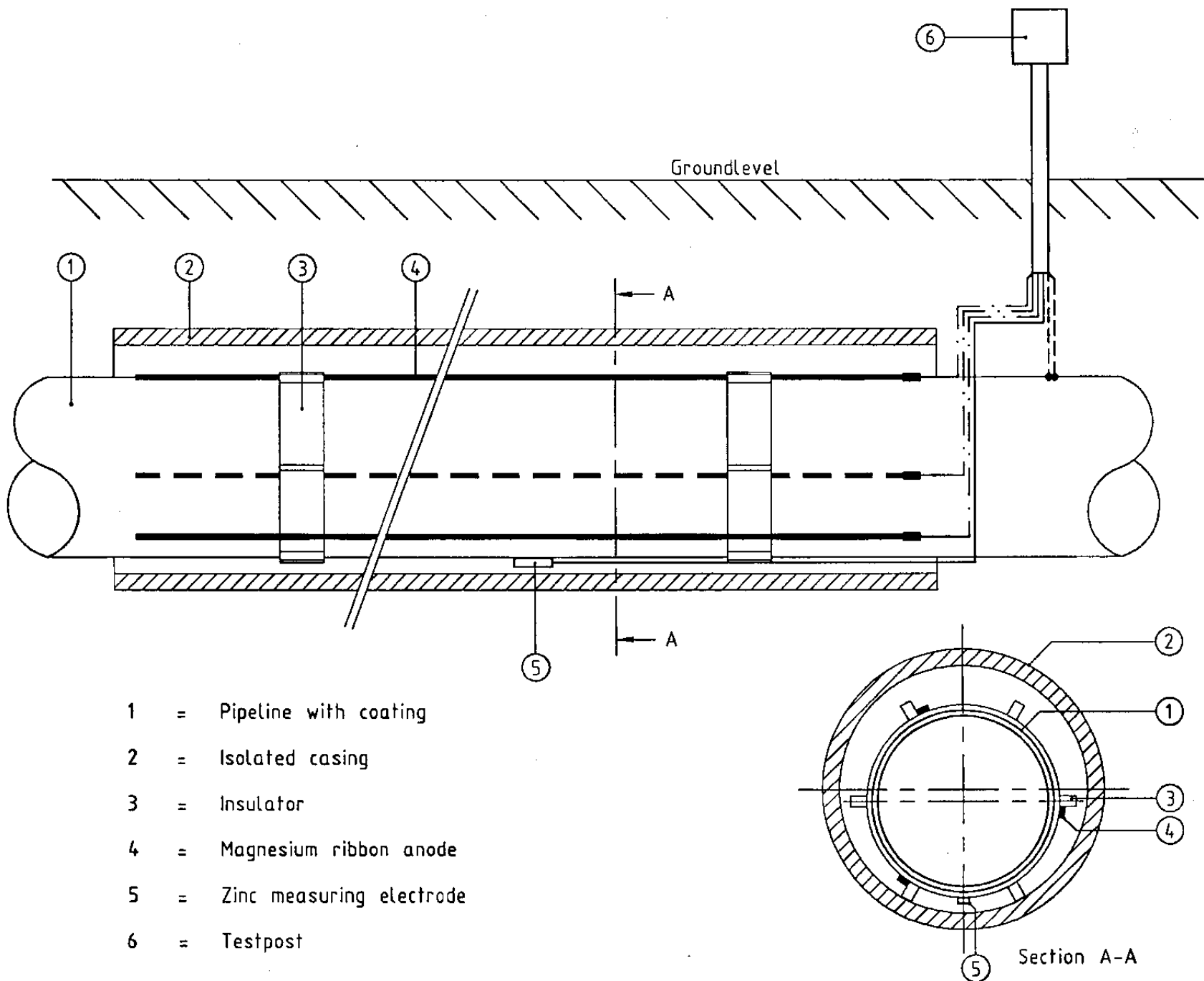
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Kath. Bescherming/Hot-Spot

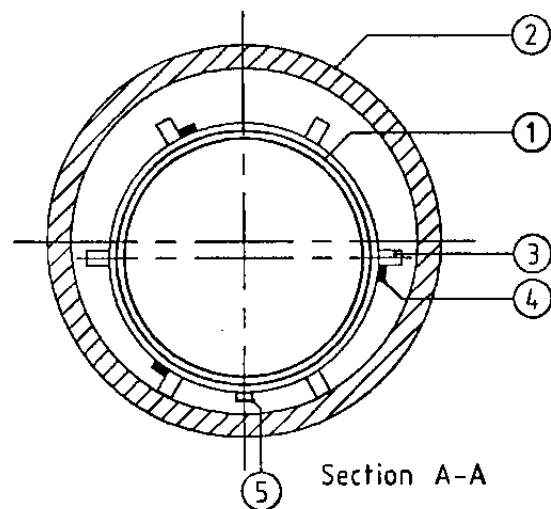
Straat A/B

HOMMEMA KATH. BESCHERMING B.V.





- 1 = Pipeline with coating
- 2 = Isolated casing
- 3 = Insulator
- 4 = Magnesium ribbon anode
- 5 = Zinc measuring electrode
- 6 = Testpost



Object: INTERNAL PROTECTION IN
PLASTIC CASING BY MEANS
MAGNESIUM RIBBON ANODES

Nr.:
Appendix 15

Dpdr. geveert:

blad van

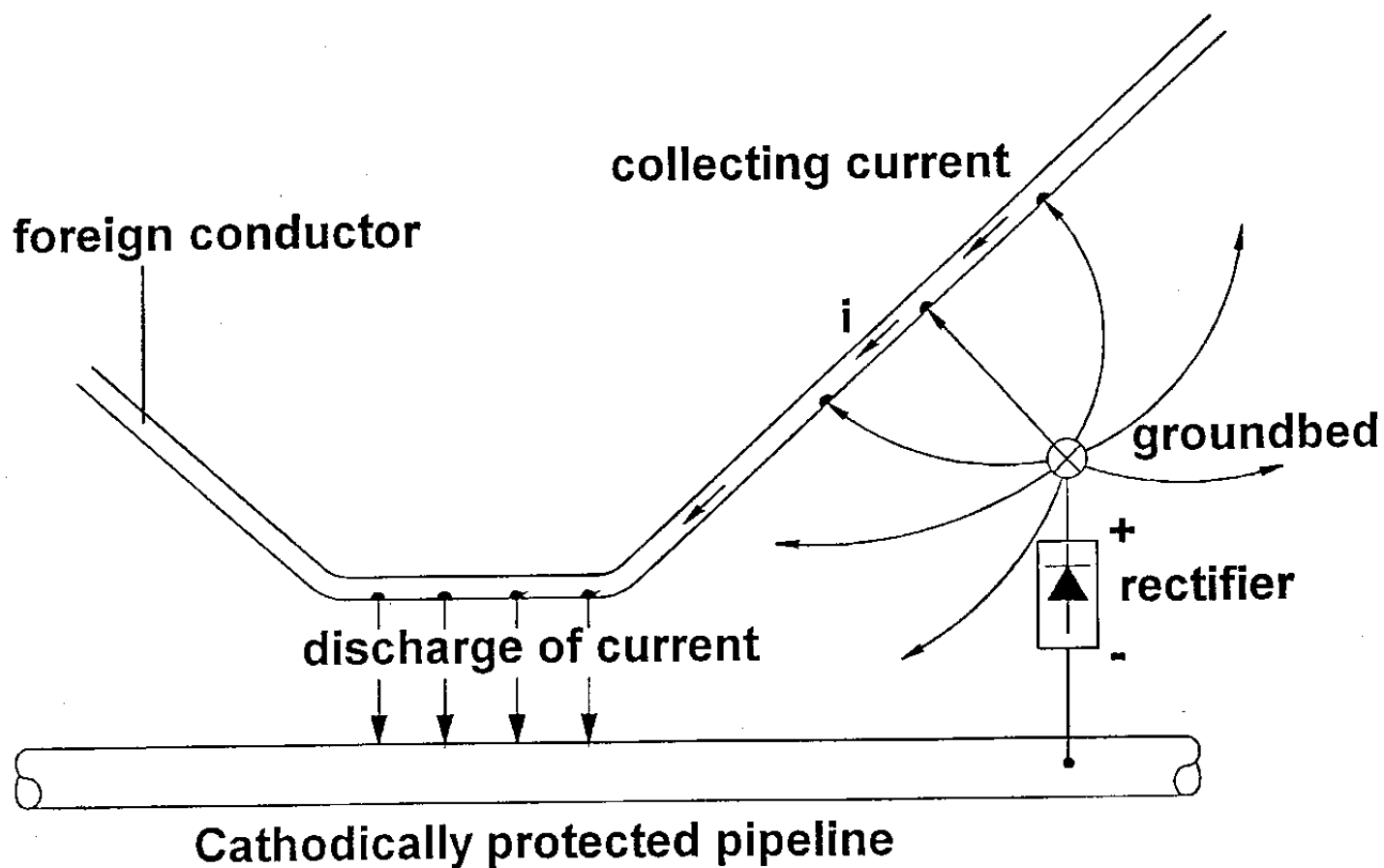
schaal: ----

get.: R.v.W.

datum: 1-3-'94

goedgekeurd G.G.

Interference



Uniform current distribution of a deepwell anode groundbed

