

Corrosion layers on historic iron artefacts

Cathodic protection of iron artefacts during cleaning in acid solutions

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Abstract

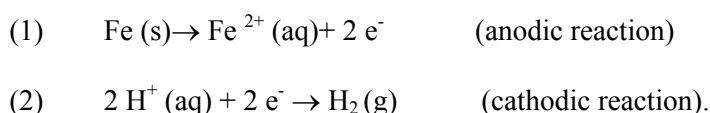
Cathodic protection has been studied as a method for protecting iron objects during cleaning in acid solutions. The effect of the type of acid, potential and distance between the anode and cathode were investigated. Iron sheets, polished and corroded, were immersed in 0.5 M citric, sulphuric, or ortho-phosphoric acid baths while cathodic protection was used. Applying a potential of -650 mV and -850 mV Ag/AgCl to the immersed samples successfully protected them. Some of the samples were only slightly etched and this was related to surface size of the anode. Both the geometry and distance between anode and cathode have a large influence on the cleaning and etching of the original surface. Unprotected iron sheets were strongly etched by the acids after an immersion of three hours. Cathodic protection thus appears to be a good technique for protecting iron objects during acid cleaning. 0.5 M ortho-phosphoric acid baths was considered to be the best electrolyte for practical considerations. However, further research is needed before this treatment can be safely carried out on objects.

Keywords: Historic iron, iron corrosion, electrolytic cleaning, acid, cathodic protection.

1. Introduction

In the conservation field chemical and mechanical techniques are commonly used to remove iron corrosion products on historical iron objects (Tomozei and Balta 1998). If the corrosion products are located in a position which is difficult to reach, for example, for engraved surfaces, these methods are not always feasible. In industrial processes acid baths are commonly used to remove iron corrosion layers (Berry 1993). However, this can result in the dissolution of iron. Industrially this dissolution is not a problem, but in conservation this kind of attack is unacceptable.

A possible solution for the problem of the dissolution of iron in acid is the use of cathodic protection. Cathodic protection is a technique to prevent corrosion of a metal in aqueous environments by lowering the potential of the object. For iron in acid solutions, this means suppressing the iron dissolution (anodic) reaction and promoting the hydrogen reduction (cathodic) reaction, that is



This technique is widely used in industry to protect iron and steel structures such as boats and buried pipelines (Jones 1996).

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The objective of this research project was thus to investigate the use of cathodic protection during the treatment of iron artefacts in an acidic environment so that corrosion products would be removed and the iron protected. Focus was placed on parameters which were considered to be important during treatment such as type of acid, potential needed for the cathodic protection, the required time for immersion, as well as the removal of the acid from the object (rinsing). Ethical and aesthetic issues concerning changes in appearance and the preservation of patina were also considered.

2. Experimental procedure

Three series of experiments were conducted in this research program. In series 1, the effect of the type of acid on the cathodic protection of polished steel sheet samples was investigated. In series 2, the use of cathodic protection during acid treatment of corroded material was tested. Finally, in series 3, a practical simulation was conducted to investigate the use of cathodic protection for objects with varying geometry.

Testing was conducted using samples cut from St. 37¹, sheet having a thickness of 1 mm. Specimen dimensions were 50 x 20 mm for test series 1 and 2. In order to vary the shape of the cathode in test series 3, specimens were bent into the form as shown in Figure 5 of the results section. Specimens for test series 1 and 3 were polished on one side with 500, 800, 1200, and 2500 grit abrasive paper. A shiny surface with fine grinding marks was the result. The corroded steel sheets used in test series 2 were cut from a large sheet of St. 37 which had been placed outdoors for 33 days to form a corrosion layer². The corrosion product was polished away on half of the surface of one side of the specimen, while the other half of the same side was left corroded. Photographs of all specimens were taken before and after the experiments with a standard camera and in the optical microscope. An identifying mark was made with a steel scribe to enable photographs to be taken at the same place before and after the experiment.

Citric acid, sulphuric acid and ortho-phosphoric acid were tested as electrolytes. A pH between 0 and 1 was used based on experience with industrial baths for the removal of corrosion on steel at Corus Group in IJmuiden, The Netherlands³. By using concentrations of 0.5 M these pH values were attained. All three acids were tested in series 1. The results, to be discussed later, showed that 0.5 M ortho-phosphoric acid was the best candidate for cathodic protection and was therefore used for testing in series 2 and 3. Testing was carried out in a fume-hood at room temperature. The solutions were not stirred. After immersion the samples were rinsed shortly with tap water and acetone and then dried with compressed air.

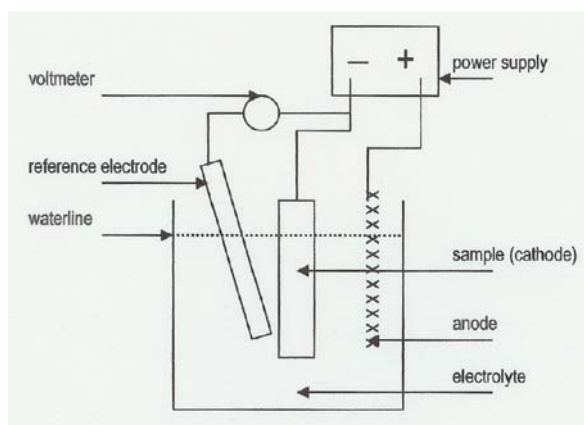


Figure 1, Schematic drawing of test system.

¹ St 37 is an alloy of steel which contains: C ≤ 0,12%, Mn ≤ 0,60 %, P ≤ 0,045 %, S ≤ 0,045 % and Fe ≤ 99 %, staalmarkt Den Bosch, the Netherlands.

² from 16-01-03 until 18-02-03, in the garden of the Netherlands Institute for Cultural Heritage, Gabriël Metsustraat 8, Amsterdam, the Netherlands.

³ Private communication, Dr. Ir. H. van der Weijde, Corus Group, IJmuiden, the Netherlands.

The testing system is shown in Figure 1. For cathodic protection, a stainless steel mesh⁴ was used as the anode and a DC power supply⁵ for the supply of electrons. The anode was connected to the positive terminal of the power supply and the sample (the cathode) was connected to the negative terminal. An Ag/AgCl (silver/silver chloride) reference electrode⁶ and a digital multimeter⁷ were used to measure the cathodic potential. The power supply with the required potential was switched on before the sample came in contact with the acid electrolyte. The samples were immersed in such a way that the electrical connections to the sample remained above the waterline.

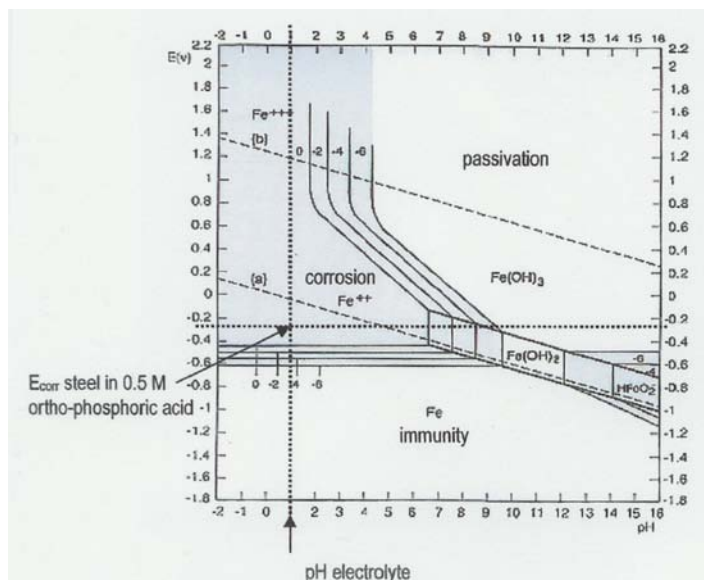


Figure 2, Pourbaix diagram for the iron/water system. E_{corr} for steel in 0.5 M ortho-phosphoric acid has been indicated (-295 mV SHE). When lowering the potential to a more negative value the immunity area is being reached and the steel will be cathodically protected (adapted from Jones 1996).

The anode used for test series 1 and 2 was flat while the anode used for test series 3 was placed around the cathode. The cathodic potentials used in the experiments were selected based on the Pourbaix diagram for the iron/water system, see Figure 2. The corrosion potential, E_{corr} , for steel in 0.5 M ortho-phosphoric acid was determined to be -295 mV SHE (Standard Hydrogen Electrode). If the potential is shifted to a more negative value which corresponds to the immunity area, the steel will be protected. This cathodic potential is dependent on the concentration of the Fe-species in solution. This is given by lines labelled 0, -2, -4 and -6 in Figure 2, representing areas where the concentration of Fe-species are 10^0 M, 10^{-2} M, 10^{-4} M and 10^{-6} M respectively. It can be seen that this cathodic potential lies between -450 and -600 mV/SHE or -650 mV and -800 mV Ag/AgCl. This is close to the value given by Mattsson (1996) needed for the protection of steel and iron at low pH values, < -950 mV Cu/CuSO₄ (-850 mV Ag/AgCl). It should be noted that cathodic protection in an acidic environment is rarely used in industry for economic reasons. A high current is needed which is too expensive for providing permanent protection (Jones 1996).

In test series 1, a cathodic potential of -650 mV Ag/AgCl was used based on the Pourbaix diagram. For the other experiments a cathodic potential of -850 mV Ag/AgCl was used based on the literature. An immersion time of three hours was used for the polished steel sheets used in test series 1 and 3. For series 2, the immersion time was that required to remove all of the corrosion products.

3. Results

⁴ XRF analyses for main elements: 15% Cr, 11% Ni, 3% Co, 2.6 % Mn and 67 % Fe

⁵ type: EA-PS-3016-10, Schöne Edelmetaal, Amsterdam, the Netherlands.

⁶ type: 6.0733.100, Metrohm, Eco chemie, Utrecht, the Netherlands.

⁷ type: DVM 850 BL, Velleman, Muco Amsterdam bv., Amsterdam, the Netherlands

The results of the first series of tests indicate that all specimens were protected by cathodic protection regardless of the type of acid, compare micrographs in Figure 3. After an immersion time of three hours at a cathodic potential of -650 mV/Ag/AgCl no etching could be seen visually and in the stereo-microscope except for slight etching at the waterline. Total immersion of the sample would avoid this etching. The unprotected specimens on the other hand, were etched and had a dark grey colour after three hours. The unprotected specimen in sulphuric acid and ortho-phosphoric acid were more strongly etched.

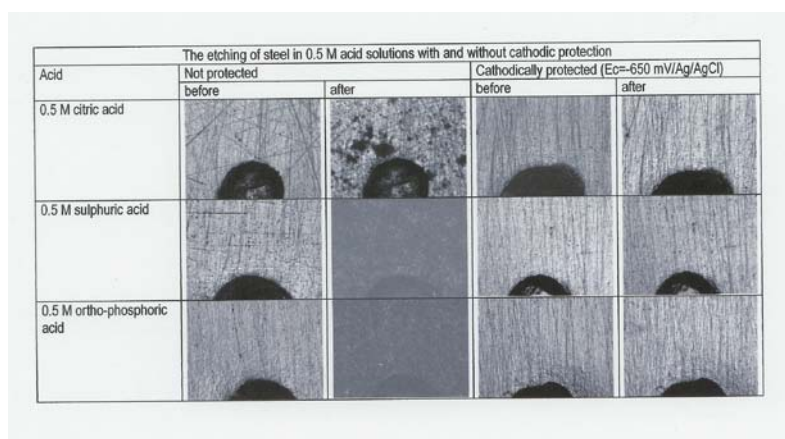


Figure 3, Surface of steel sheet specimens before and after testing in 0.5 M acid solutions with and without cathodic protection (test series 1). The dark half circles in the micrographs are the identifying marks ($\varnothing \sim 1$ mm).

The results of the treatment of the half-corroded specimens, test series 2, are shown in Figure 4. During these experiments, the time for complete removal of the corrosion product was measured. The corrosion product was completely removed from the unprotected sheet in 110 minutes. The cleaned surface was dark grey in colour. On the protected sheet, the corrosion layer was removed after 70 minutes. The cleaned surface was a lighter grey except at one edge and the water line where it was dark grey. The polished side of the sheet remained shiny. No corrosive attack could be found by optical microscopy.

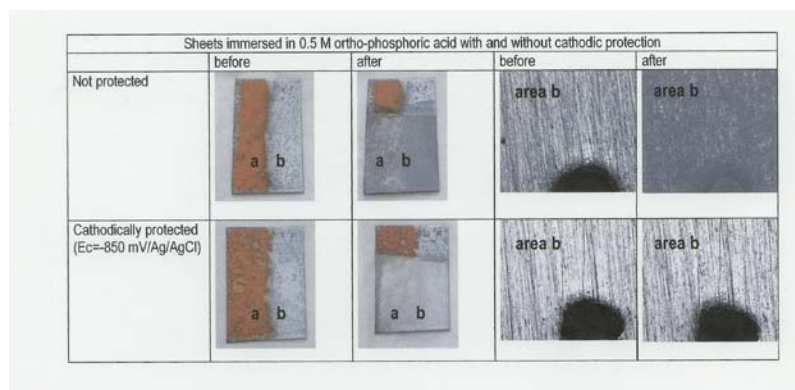


Figure 4, Surface of half-corroded steel sheet specimens before and after cleaning treatment in 0.5 M ortho-phosphoric acid with and without cathodic protection (test series 2).

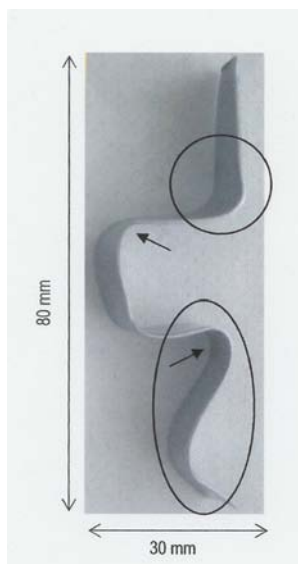


Figure 5, Bent steel sheet used in test series 3. The circles indicates the areas where etching has occurred with an anode-cathode distance of 2,5 cm. The sheet was less etched with an anode-cathode distance of 7 cm as indicated with the two arrows.

The third series of tests with the bent specimens showed uneven protection after immersion for three hours in 0.5 M ortho-phosphoric acid. The differences in protection can be seen in Figure 5. A specimen tested at a distance of approximately 2.5 cm from the round anode (as measured from the end of the specimen) was etched at both sides of the lower part of the sheet and at a higher position. These areas are indicated with circles. During another test where a specimen was hung 7 cm from the round anode, the electrolyte became yellow around the anode during immersion for 3 hours. However, after immersion, the sheet showed much less etching than the specimen which was closer to the anode. These areas are indicated with an arrow.

4. Discussion

The results of this program indicate that cathodic protection is effective in protecting iron objects from etching during cleaning in acid solutions. The immersion time is also shortened when an object is cathodically protected. The development of hydrogen helps the cleaning effect. This was demonstrated in test series 2, where the removal of the corrosion product on the unprotected corroded sheet took 110 minutes, while it only took 70 minutes for the cathodically protected materials. The treatment time also depends on the thickness of the corrosion layer on the object. When the corrosion layer is thick the immersion time is longer as a result. This was shown in supporting experiments performed on corroded iron pipes.

Cathodic protection appears to work regardless of the type of acid. All steel sheets were protected after 3 hours of immersion. However, further experiments indicate that ortho-phosphoric acid is a better choice for the acid bath based on practical considerations. Citric acid dissolves iron corrosion more slowly than sulphuric or ortho-phosphoric acid. This means that the treatment for an object immersed in citric acid would take longer. The time for the object to be immersed in an acid should be as short as possible to avoid problems that could occur with a power interruption or in the absence of the conservator. Rinsing is also very important when an acid is being used in the case where a residue can cause corrosion. Sulphuric acid cause serious corrosion when a residue is left behind (Wilthew 1985). The residue of ortho-phosphoric acid is, on the other hand, a stable iron phosphate which does not cause further corrosion (Galjaard and Van Leeuwen 1969).

The experiments also revealed a number of practical aspects which must be considered when working with cathodic protection. When a normal DC power supply is used as was the case for this project, the cathodic potential can fluctuate ($\sim \pm 50$ mV) during the treatment due to the change in the surface condition of the corroded samples. During test series 2 with corroded samples, the cathodic

potential was not stable and had to be readjusted every 20 minutes. It should be noted that it is therefore important to use a reference electrode when setting and readjusting the cathodic potential. In any case, the conservator must be present to keep the cathodic potential at a constant value. To solve the problem of the fluctuation of the cathodic potential a potentiostat could be used. This computer controlled power supply automatically keeps the potential at pre-set values. It is much more expensive than a normal power supply and not available in most of the conservation laboratories. However, it is standard equipment in corrosion research laboratories.

The results of test series 3 show that protection varies over the surface of an irregularly shaped object. It appears that the distance to the anode is important, since there was more attack at a distance of approximately 2.5 cm than there was at 7 cm. However, the surface area of the anode used for the first specimen was three times smaller than the anode used for the second specimen. The difference in surface area of the cathode and the anode thus appears to be a more important parameter for the treatment to succeed. The geometry of the object will also be important. The etching on two areas on the second sheet with larger anode-cathode distance is located in the position where hydrogen bubbles can be trapped. It may be a reason that the protection has failed on these specific locations.

In test series 3, the electrolyte became yellow around the anode. This is due to the dissolution of the stainless steel anode. To avoid this dissolution an inert anode such as platinum should be used. However, these materials are more expensive than stainless steel.

Cathodic protection also produces hydrogen (reaction 2 in the introduction). The potential used for the cathodic protection in test series 1 was taken from the Pourbaix diagram for the iron-water system (-650 mV Ag/AgCl). For all other experiments, the more negative potential of -850 mV Ag/AgCl was used based on literature evidence that this value is better for low pH solutions (Mattsson 1996). However, at this more negative cathodic potential more hydrogen is developed. It is known that hydrogen embrittlement can be induced in steels during cathodic protection. However, this is generally only of concern for objects which are mechanically loaded after treatment, and is more a problem for high strength steels than iron and low carbon steels. Since the objects will not be mechanically loaded the effect of hydrogen embrittlement was not studied.

Ethical issues are also an important consideration in the cleaning of iron objects, with or without cathodic protection. The surface changes in an important way before and after the treatment. Acid treatment will remove any corrosion products. However, underneath the corrosion product, the surface is already damaged and after cleaning this can be seen. A light grey surface is the result. The corrosion pattern can still be recognised. This could be seen on iron pipes cleaned as part of this research project. The corrosion product was present as stripes. After treatment, this pattern could still be recognised on the cleaned surface. When a layer of microcrystalline wax was applied, the appearance of the surface became more homogeneous. Finally, it should be noted that the procedure described in this communication is not applicable for composite objects since some materials do not resist acids. The corrosion potential (E_{corr}) will also be very different for each metal.

5. Conclusion

A research project was conducted to determine the feasibility of using cathodic protection for protecting iron artefacts during treatment in acidic environments. The results of the experiments show that cathodic protection of iron in acid solutions can be used to protect objects during cleaning. Only a few of the samples showed slight attack. This is related to the area relationship and the distance between the anode and the cathode (object).

Further research is needed before this treatment can be routinely and safely carried out on objects. A better understanding of the relationship between the distance of anode and cathode, as well of the relation of the difference in surface size of the cathode and the anode, on the cathodic protection required. The use of a corrosion inhibitor in the acid solution may provide additional safety should cathodic protection fail. The use of a more conductive electrolyte may provide higher currents at the cathodic potential, resulting in better protection. Ethical aspects of the treatment must also be considered, since the treatment completely removes the corrosion layer which is not always desirable.

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