

# Evaluation of Corrosion Inhibitors for Cooling Water by Physico-Chemical Methods

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## **Summary**

A combined approach to the development of corrosion inhibitors for industrial applications based on electrochemical measurements along with standard corrosion tests has been developed. The synthesis of standard engineering corrosion tests based on weight loss evaluation and scientific electrochemical laboratory methods combines the advantages of both techniques while avoiding their inherent shortcomings at the same time. Electrochemical measurements (corrosion potentials, voltammetry, capacitance measurements, polarisation resistance) are used to assess the relevant physical properties of new corrosion inhibitors. A variety of short-time corrosion tests on the laboratory scale is then used to determine performance and application parameters under different environmental conditions. Subsequent full-scale corrosion tests can be limited to already pre-optimised formulations. This development concept is exemplarily described for new ecologically compatible inhibitor systems.

## **Background**

The development of new inhibitor systems for industrial applications presents a constant challenge as products are optimised and prospective raw materials screened with regard to performance, environmental and economic viability. Within

this context, a fast response to customer needs and demands is essential. The flexibility of R&D required thus can only be ensured by state-of-the-art testing procedures.

Standard corrosion tests based on weight loss evaluation alone are very time-consuming and provide only limited information. For a systematic optimisation of formulations, a combined approach comprising both electrochemical methods and corrosion tests offers a sizeable advantage for the development process, as the design of experiments for full-scale corrosion tests up to pilot plant scale is optimised. A key element within this concept is the identification of electrochemical parameters with direct significance for inhibitor performance under application conditions.

## **Experimental Considerations**

**Materials and Sample Preparation.** Panels of low-carbon steel (AISI 1010) were used as the test specimen. Generally, the panels were treated with a pickling solution based on hydrochloric and nitric acid, rinsed with de-ionised water and acetone and subsequently dried at 70°C prior to corrosion testing. Different synthetic water qualities were employed reflecting different relevant application conditions, e.g. with respect to hardness and pH.

**Electrochemical Instrumentation.** Electrochemical measurements were performed with computer controlled potentiostats (Zahner IM5d for polarisation resistance measurements and voltammetry, AGEF II research instruments for high-resolution voltammetry and capacitance measurements). For all experiments, a Duran glass cell was used in standard three-electrode configuration. All potentials cited herein are with respect to SHE.

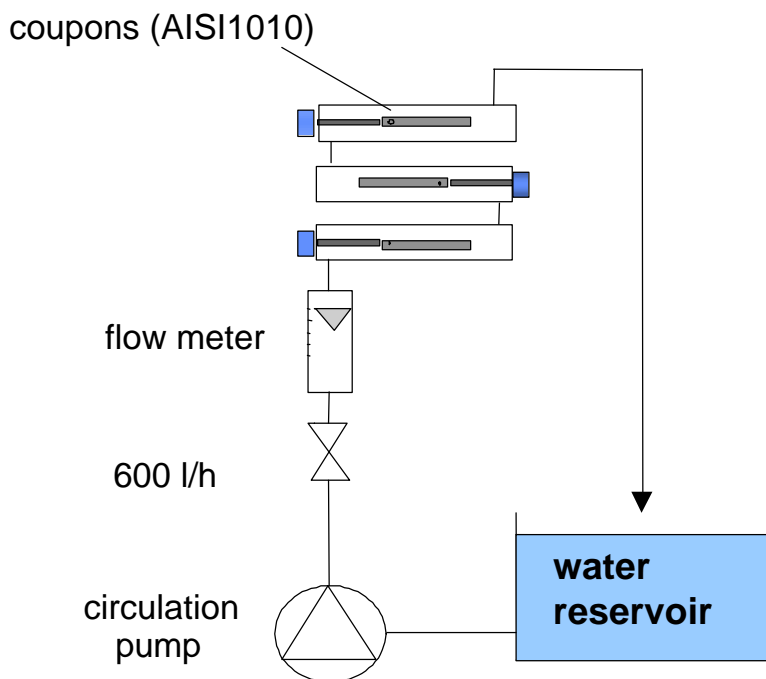
## Methods and Results

**1. Corrosion Tests.** Three different types of corrosion tests are routinely employed corresponding to different stages of development :

**a) Screening beaker experiments.** In the first screening phase, potential inhibitors are assessed by stirring mild steel test coupons in cooling water containing 20 ppm of the substance to be tested. After stirring for 24 h, the corrosion inhibition is measured by the iron content of the solution compared to the blind value as measured by Atomic Absorption Spectroscopy.

**b) Laboratory-scale circulation experiments.** Promising substances are subjected to additional tests in a laboratory-scale circulation device resembling the flow conditions encountered in actual cooling circuits. The nominal testing time for weight loss evaluation is 6 days. If electrochemical polarisation resistance measurements (cf. below) are used instead, testing times of 24 h are usually sufficient. A schematic view of the circulation devices is shown in Fig. 1.

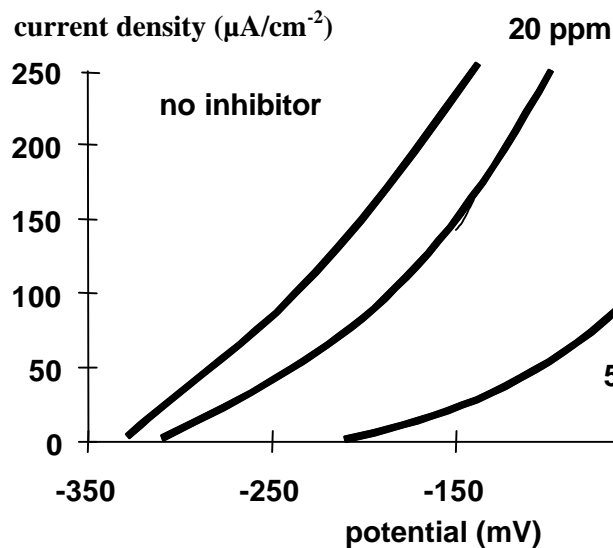
**c) Pilot plant experiments.** Pre-optimized formulations from the circulation experiments are finally tested in a pilot plant which is a complete model of an industrial cooling circuit including heat exchangers and process control. Corrosion tests are typically carried out for 14 days with evaluation by both weight loss and electrochemical corrosion rate measurement (CORRATER system).



**Fig. 1 :** Laboratory-scale circulation device

**2. Electrochemistry.** Most physical parameters with direct relevance to inhibitor performance are readily available from standard electrochemical measurements.

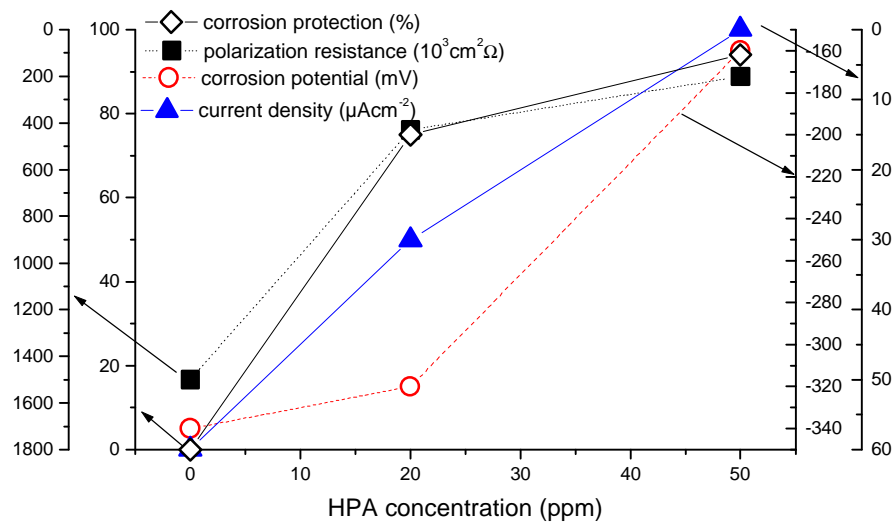
**a ) Voltammetry.** The change of corrosion potential and the anodic/ cathodic current densities in Cyclic Voltammetry upon application of an inhibitor indicates its principles of action (anodic vs. cathodic) while serving as a good qualitative measure of its effectiveness. This is illustrated in Fig. 2, which shows the variation of corrosion potential and anodic current density of a mild steel electrode immersed into a neutral aqueous solution containing different amounts of the classical inhibitor hydroxyphosphonoacetic acid (HPA).



\*HPA = hydroxyphosphonoacetic acid

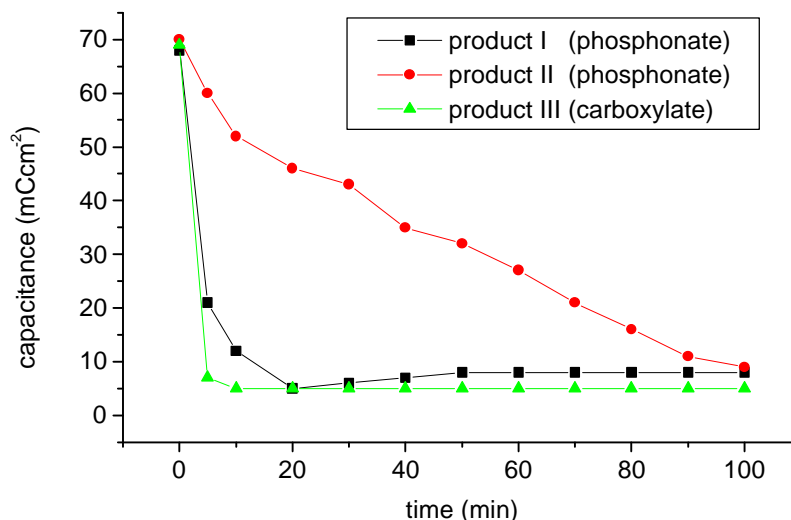
**Fig. 2 :** Anodic polarization curves of a mild steel electrode treated with different concentrations of a phosphonate inhibitor in 0.1 M  $\text{Na}_2\text{SO}_4$ .

The correlation of voltammetry data with the results of corrosion tests is very good (Fig. 3). A simple, semi-quantitative evaluation of voltammetry data such as in Fig. 3 is usually sufficient to obtain the desired qualitative ranking scheme for different experiments without the need for a complete, time-consuming analysis (e.g. from Tafel slopes).



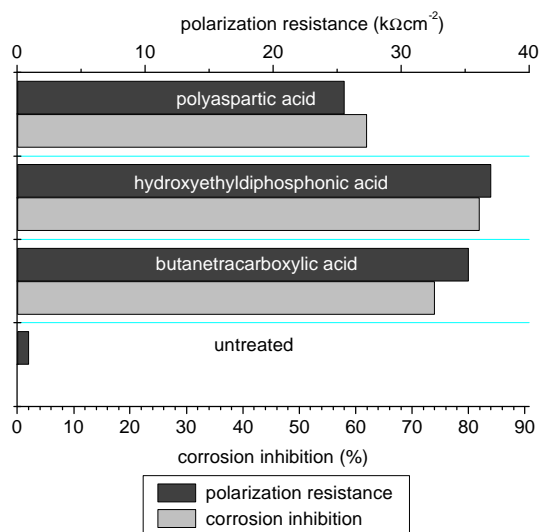
**Fig. 3 :** Correlation between electrochemical data and corrosion test results for mild steel specimens treated with different concentrations of HPA.

**b) Capacitance Measurements.** The adsorption characteristics of any prospective inhibitor on metal surfaces can be followed in real time by capacitance measurements. The resulting curves yield information on rates of adsorption, equilibrium surface coverages covering and the strength of molecule-surface interactions. These parameters are crucial for the optimisation of formulations for different environments (pH, flow rate, salt concentration, co-adsorption). Fig. 4 shows a typical example of two different inhibitor systems in a hard water solution under cooling circuit conditions at pH 8.2. Clearly, the phosphonate-based product I shows the strongest adsorption effects, while a different phosphonate (product II) exhibits only a weak interaction. The carboxylate-based (ecologically more compatible) product III also exhibits strong adsorption under the test conditions



**Fig. 4 :** Capacitance of Gold electrodes in aqueous solutions of different inhibitors (concentration: 20 ppm)

**c) Polarisation Resistance Measurements.** Measurement of the polarisation resistance is a very sensitive indicator of both barrier properties of adsorbates and the beginning of corrosion processes. Since the method does not have a high sensitivity to ohmic potential drops in low-conductivity media, it can conveniently be employed in the actual cooling water. Thus, this easy-to-use method can be applied under conditions close to industrial practice. Especially the evaluation of circulation experiments can be significantly accelerated, since a differentiation is already possible when there still is no visible corrosion damage on the test specimens. Fig. 5 illustrates this by comparing polarisation resistances measured after 1 day of exposure with corrosion inhibition percentages as obtained from weight loss evaluation after 14 days of circulation testing. Fig. 5 also shows the excellent performance of new ecologically favourable carboxylate-based corrosion inhibitors in comparison to classical phosphonates such as hydroxyethanediphosphonic acid (HEDP).



### Final Assessment : Pilot plant testing

Promising new substances and formulations are ultimately required to pass application tests in real cooling circuits before they are released for prospective customers. The last stage of development testing before that final step are systematic trials at a pilot plant facility. Especially new developments favoured for their ecological compatibility must be thoroughly tested on whether they can in fact replace conventional inhibitor systems based on phosphonic acids. The optimisation process has already been pursued to a highly sophisticated stage at this point due to the close interfacing between the electrochemical methods and the lab-scale corrosion tests. Consequently, more time is available for pilot plant trials accurately simulating many different effects encountered in industrial practice.

The final pilot plant results for several new carboxylate-based inhibitors are summarised in Table 1 along with the results from the previous laboratory testing phase. Clearly, the correlation between the different methods is excellent, thereby confirming the validity of this approach.

Substance (concentration: 20 ppm, soft water)	Beaker screening : corrosion protection (%)	Electrochemistry : adsorption characteristics	Electrochemistry : polarization resistance (k /cm <sup>2</sup> )	Circulation testing : corrosion protection (%)	Pilot Plant Testing : corrosion rate (mm/a)
Untreated	0	n/a	2	0	0.56
Hydroxyethylphosphonic acid	88	++	74	80	0.11
Butanetetracarboxylic acid	76	++	82	84	0.12
Polyaspartic acid	64	+	62	58	0.14

## Conclusions

An integrated approach to the development of new inhibitor systems was presented. Based on electrochemical measurements in addition to laboratory-scale corrosion tests, the optimisation of formulations can be significantly accelerated. Compared to standard corrosion tests running for 14 days, the performance of new substances can be assessed within a period of 24 hours. Consequently, time-consuming pilot plant trials commence only after extensive optimisation has already been performed. This greatly facilitates accelerated development of new products and a fast response to customer demands.

As an example, the performance of new carboxylates as raw materials for inhibitor formulations was tested. A highly consistent trend was found, indicating that selected carboxylic acids form an environmentally safe alternative to classical phosphonates while retaining a high corrosion protection at typical application concentrations.

### **Acknowledgement**

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