



## ENVIRONMENTALLY SOUND CORROSION INHIBITORS FOR COOLING WATER

Bernd Mayer, Wolfgang Hater and Matthias Schweinsberg  
Henkel KGaA  
Henkelstrasse 67  
40191 Dusseldorf (Germany)

### ABSTRACT

Standard corrosion inhibitors for cooling water are based either on heavy metals, phosphates or phosphonates and therefore contribute to the contamination of surface water with noxious substances. Evaluations in pilot plants suggest that phosphorous-free organic carboxylic acids might be promising alternatives to the well-established phosphonic acids. The carboxylic compounds are biodegradable and therefore environmentally favorable. Moreover, in order to accelerate the evaluation of new inhibitors, an electrochemical test has been implemented which operates under conditions close to industrial practice. Results show that a combination of the electrochemical method with various corrosion tests from the laboratory up to pilot-plant scale yields a comprehensive characterization of the corrosion inhibiting properties. Consequently, the development of tailored inhibitor systems focused on specific applications is accelerated.

Keywords: corrosion inhibitor, environmentally favorable, biodegradable, carboxylic acid, cooling water, electrochemistry, corrosion testing

### INTRODUCTION

Metal corrosion in water-conveying systems such as cooling water circuits is of major concern in industrial applications [1]. In order to decrease corrosion of pipes, heat exchangers etc. corrosion inhibitors are widely applied. In this regard, aspects like cost of treatment versus cost of corrosion damages as well as process safety and the impact of corrosion and corrosion treatment on the environment have to be taken into account.

Excessive corrosion does not only lead to serious damage of installations, it also causes considerable environmental pollution with heavy metals. State-of-the-art corrosion inhibiting products provide satisfying performance using zinc salts, molybdates, phosphate and phosphonates. Frequently, such inhibitors are discharged to the envi-

ronment without further treatment. Zinc and molybdenum represent heavy metals; phosphate and phosphonates (which are eventually converted into phosphates) contribute to the nitrification of surface water [2]. Furthermore, most of the common phosphonates are classified as poorly biodegradable.

Consequently, an objective is to develop low-toxic, heavy metal and phosphorus free corrosion inhibitors with good biodegradability [3, 4].

Accordingly, new inhibitor systems are searched for with regard to the following criteria:

- Optimum corrosion protection
- Acceptable cost of raw materials
- Low aquatic and human toxicity
- Excellent ecological compatibility :
  - biodegradable
  - phosphorous-, nitrogen-, and heavy-metal-free
- Cost reduction to the user due to reduced waste water charges

Unfortunately, the evaluation of corrosion inhibitors is time-consuming even under lab conditions, i.e. standard weight loss analysis takes several weeks if a quantitatively sound evaluation of inhibitors is desired. Therefore, an electrochemical short time test based on polarization resistance measurements has been implemented to accelerate the development of new products with improved environmental behavior.

## EXPERIMENTAL

### *Materials and sample preparation*

Panels of low-carbon steel (AISI 1010) were used as test specimen. Generally, the panels were treated with a pickling solution based on hydrochloric acid and nitric acid, rinsed with water and acetone and then dried at 70 °C. Aerated tap water with a conductivity of 0.45 mS/cm was used as for the corrosion tests; the ion content of the water is summarized in table 1.

TABLE 1  
DIFFERENT WATER QUALITIES USED FOR CORROSION TESTING

water quality	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	TAC	conductivity	pH
<b>hard</b>	1.15 mol/m <sup>3</sup>	1.15 mol/m <sup>3</sup>	1.15 mol/m <sup>3</sup>	1.15 mol/m <sup>3</sup>	K <sub>S4.3</sub> = 3.0-3.5 mol/m <sup>3</sup>	1.1-1.3 mS/cm	7.8
	115 ppm CaCO <sub>3</sub>	40 ppm CaCO <sub>3</sub>	41 ppm Cl <sup>-</sup>	110 ppm SO <sub>4</sub> <sup>2-</sup>	K <sub>S4.3</sub> = 150-175 ppm CaCO <sub>3</sub>	1.1-1.3 mS/cm	7.8
<b>medium hard</b>	1.0 mol/m <sup>3</sup>	0.4 mol/m <sup>3</sup>	0.55 mol/m <sup>3</sup>	0.6 mol/m <sup>3</sup>	K <sub>S4.3</sub> = 2.0-2.5 mol/m <sup>3</sup>	0.3-0.5 mS/cm	8.3
	100 ppm CaCO <sub>3</sub>	25 ppm CaCO <sub>3</sub>	20 ppm Cl <sup>-</sup>	58 ppm SO <sub>4</sub> <sup>2-</sup>	K <sub>S4.3</sub> = 100-125 ppm CaCO <sub>3</sub>	0.3-0.5 mS/cm	8.3
<b>soft</b>	0.2 mol/m <sup>3</sup>	0.25 mol/m <sup>3</sup>	7.3 mol/m <sup>3</sup>	0.36 mol/m <sup>3</sup>	K <sub>S4.3</sub> = 0.5-0.8 mol/m <sup>3</sup>	1.6-1.7 mS/cm	7.8
	20 ppm CaCO <sub>3</sub>	25 ppm CaCO <sub>3</sub>	260 ppm Cl <sup>-</sup>	35 ppm SO <sub>4</sub> <sup>2-</sup>	K <sub>S4.3</sub> = 25-40 ppm CaCO <sub>3</sub>	1.6-1.7 mS/cm	7.8

### Corrosion Testing

Samples were treated for at least 24 hours in all corrosion tests. Three different experimental setups were chosen reflecting three different stages of product development.

*Beaker-scale screening experiments.* As a first step to evaluate the inhibition potential of a new substance, a simple experiment was carried out in which the specimens are mounted on a stirring bar and moved in a defined amount of the corrosive medium at constant speed (100 rpm). For a schematic representation of the setup, see fig. 1. The iron content in the water is evaluated after the corrosion test (24 h) and serves as a measure of corrosion protection if compared to simultaneously recorded reference values without the addition of inhibitor.

*Laboratory-scale circulation experiments.* If prospective substances have shown some inhibiting properties in the beaker tests, a second set of experiments was run on the laboratory scale in a circulation device designed to closely match application conditions in cooling water circuits. For this, the steel coupons were mounted in a miniaturized cooling circuit with a test rack according to ASTM 2688 [4]. Water was then circulated from a reservoir at 600 l/h for the predefined exposure time (usually between 1 and 3 days). Fig. 2 shows a schematic representation of the apparatus. Visual inspection, polarization resistance measurement and weight loss evaluation (after pickling, rinsing

and drying) were then used to evaluate inhibitor performance. The optical appearance of the coupons was graded from -- (severe corrosion) to ++ (no visual corrosion damage), taking into account both planiform and localized corrosion attack. Corrosion protection factors were calculated from the weight loss measurements with untreated water as the reference system.

*Pilot plant experiments.* Inhibitor systems which have shown good performance in the laboratory-scale experiments were subsequently tested in an upscaled pilot plant experiment. The pilot plant used is a fully-equipped simulation facility operating under field conditions. A closed primary cooling circuit and an open secondary circuit are combined to form the basic framework. Heat transfer between the circuits is achieved via combination of tube-bundle heat exchanger (HE) and a single tube HE. Back-cooling of the circulation water is effected by a spiral condenser. Application of treatment chemicals and water exchange in the circuit are implemented such as to closely resemble field conditions. A scheme of the facility is shown in fig. 3. Corrosion rates can be measured both by test coupon analysis (visual inspection & weight loss evaluation) and electrochemical corrosion rates (Corrater<sup>®</sup> system). A typical testing time in the pilot plant is 14 days.

### *Electrochemistry*

All electrochemical experiments were performed with commercially available equipment (Zahner IM5d potentiostat) using a standard three-electrode configuration. The steel samples from the circulation device were used as the working electrode. Water from the device was used as the electrolyte, thereby ensuring measurement parameters within parameters relevant to field conditions. The measurement of polarization conductance [5] was selected to characterize the degree of corrosion of the steel samples. Due to the high sensitivity of the method, 1 day of testing in the circulation apparatus is usually sufficient to obtain a clear evaluation of product performance.

## RESULTS AND DISCUSSION

### *Correlation Between Weight Loss Data and Electrochemical Tests*

In a first set of experiments, correlation between the results from standard weight loss tests and electrochemical measurements have been evaluated. According to [6], the formation of dense barrier layers from corrosion inhibitors should be completed within days. Therefore, the time-scale of the corrosion tests was varied from 24 h to 14 days.

Three different products a, b and c, all being commercially available formulations based on different phosphonic and polycarboxylic acids have been tested. Products b and c exhibit a distinctively superior performance than a. This is easily understood due to the fact that product a is a typical scale inhibitor whereas b and c are specific corrosion inhibiting agents.

TABLE 2  
COMPARISON OF WEIGHT LOSS AND POLARIZATION CONDUCTANCE (HARD WATER)

		<i>no inhibitor</i>	<i>product a</i>	<i>product b</i>	<i>product c</i>
concentration		-	50 ppm	50 ppm	50 ppm
weight loss [mg]	1 day	80	40	40	30
	3 days	140	110	70	30
	14 days	590	400	100	110

		<i>no inhibitor</i>	<i>product a</i>	<i>product b</i>	<i>product c</i>
% corrosion inhibition	1 day	0	48	52	67
	3 day	0	21	49	78
	14 days	0	35	83	81
polarization conductance [ $\mu\text{S}/\text{cm}^2$ ]	1 day	1400	650	400	250
	3 days	1300	850	700	200

The data summarized in table 2 indicate that the barrier properties of such layers are qualitatively identical after one day and after two weeks. The figures also show that the ranking of corrosion inhibiting efficiency is identical for the electrochemical data obtained after one day and the weight loss data after 14 days. Therefore, the differentiation of various products in the electrochemical procedure seems to be superior compared to the standard test. Further experiments (cf. below) indicate that the correlation is also valid for different water qualities.

### *Environmentally Sound Corrosion Inhibitors*

During the evaluation of new prospective ecologically compatible inhibitor systems, several classes of organic compounds have been investigated. The most promising results were obtained using selected carboxylic acids and derivatives thereof.

Typical examples of experimental results obtained after 24 h of testing are given in tables 3-5 and figs. 4-6.

TABLE 3  
CORROSION INHIBITION BASED ON SCREENING BEAKER EXPERIMENTS  
(20 ppm INHIBITOR, HARD WATER)

Inhibitor	Corrosion Inhibition [%]
citric acid	78
propanetricarboxylic acid	69
butanetetracarboxylic acid	62
polyaspartic acid	50
lactic acid	31
4-hydroxybenzoic acid	6
hydroxyethane-diphosphonic acid	80

TABLE 4  
CORROSION INHIBITION OF DIFFERENT INHIBITORS, LAB CIRCULATION DEVICE  
(20 ppm INHIBITOR, HARD WATER)

Inhibitor	Corrosion Inhibition [%]	Polarization Conductance [ $\mu\text{S}/\text{cm}^2$ ]	Visual Inspection
propanetricarboxylic acid	82	550	+
butanetetracarboxylic acid	85	350	++
hydroxyethane-diphosphonic acid	79	340	+
polyaspartic acid	63	285	+
hydroxyphosphonoacetic acid	68	340	+

The results clearly show that the inhibition performance of the carboxylic acids is comparable to that of conventional phosphonate based inhibitor systems. The concentration

dependence of inhibitor efficiency as measured by the polarization conductance after 24 h corrosion testing also shows similar performance levels of the two substance classes. As expected, barrier properties and inhibitor efficiency increase with raised concentration levels as the equilibrium surface coverage is increased (table 5, figure 6).

TABLE 5  
CORROSION INHIBITION AS FUNCTION OF CONCENTRATION (HARD WATER)

concentration [ppm]		0	5	10	20	35	50
<b>Butanetetra-carboxylic acid</b>	polarization conductance [ $\mu\text{S}/\text{cm}^2$ ]	1400	800	600	300	250	300
	visual inspection	--	-	o	+	++	++
<b>Hydroxy-phosphono-acetic acid</b>	polarization conductance [ $\mu\text{S}/\text{cm}^2$ ]	1400	1600	650	250	280	150
	visual inspection	--	--	o	+	++	++

These results clearly indicate that the high performance level of phosphonate-based systems can also be achieved by using environmentally more acceptable carboxylic acids. An integrated experimental approach employing both electrochemical methods and traditional weight loss evaluation significantly benefits the development time of new formulations as the influence of process parameter variation (i.e. concentration, water quality) can be assessed on considerably accelerated time scales.

TABLE 6  
CORROSION INHIBITION OF DIFFERENT CORROSION INHIBITORS (HARD WATER)

	<b>citric acid</b>			
concentration [ppm]	0	5	10	20
visual inspection	--	+	+	++
polarization conductance [ $\mu\text{S}/\text{cm}^2$ ]	700	280	150	50
corrosion inhibition [%]	0	73	75	79

	<b>tartaric acid</b>			
concentration [ppm]	0	5	10	20
visual inspection	--	+	+	++
polarization conductance [ $\mu\text{S}/\text{cm}^2$ ]	700	125	50	50
corrosion inhibition [%]	0	60	71	74

	<b>polyaspartic acid</b>			
concentration [ppm]	0	5	10	20
visual inspection	--	-	+	+
polarization conductance [ $\mu\text{S}/\text{cm}^2$ ]	700	-	93	86
corrosion inhibition [%]	0	-	50	63

	<b>butanetetracarboxylic acid</b>			
concentration [ppm]	0	5	10	20
visual inspection	--	-	+	+
polarization conductance [ $\mu\text{S}/\text{cm}^2$ ]	1400	800	600	300
corrosion inhibition [%]	0	50	71	85

Additional inhibitor systems with excellent biodegradability are citric, tartaric and polyaspartic acid, respectively. As summarized in table 6 and fig. 7, all of these substances effect a pronounced corrosion inhibition which increases with increasing concentration and is reflected in both weight loss and polarization conductance characteristics. Moreover, the corrosion inhibition of these carboxylic inhibitors can be further enhanced by employing inhibitor systems comprised of more than one compound, i.e. mixtures of citric or tartaric acid and polyaspartic acid.

#### *Effect of Water Quality on Inhibitor Performance*

Table 8 shows the results for the corrosion inhibition efficiency of tartaric acid and citric acid after 24 h of corrosion testing in the circulation device employing two different water qualities. Medium A is a synthetically prepared water quality based on

deionized water; medium B is a soft water quality prepared as a simple 1:1 mixture between standard tap water and deionized water (cf. table 1).

TABLE 8  
INHIBITOR PERFORMANCE OF CARBOXYLIC ACIDS IN DIFFERENT MEDIA

concentration		0	5	10	20
<b>citric acid</b>	% inhibition, soft water	0	21	52	75
	% inhibition, medium hard water	0	73	75	79
<b>tartaric acid</b>	% inhibition, soft water	0	29	64	73
	% inhibition, medium hard water	0	60	71	74
<b>Polyaspartic acid</b>	% inhibition, soft water	0	-	51	62
	% inhibition, medium hard water	0	-	63	71

While the concentration dependence follows the expected behavior of decreasing corrosion rate with increasing inhibitor concentration in all cases, significant differences are observed between the two testing media. Upon the transition from medium B to medium A, inhibitor performance drops sharply. This is a clear indication of the strong interaction between the carboxylic acids and the hydrated ions. While the addition of certain ionic species might in some cases work to the benefit of inhibitor performance due to synergistic co-adsorption effects (such as observed i.e. with benzylchinolinium-chloride in Cl-containing media [6], this might also deteriorate inhibitor performance as observed in this case. This effect is probably caused by the increased corrosiveness of medium A along with complexation and co-adsorption effects of the ions with the inhibitor molecules (i.e. coulombic repulsion between carboxylic groups and strongly adsorbed chlorine ions). This emphasizes the need for extended investigation of various different process parameters in the course of development projects, also pointing out the importance of integrated experimental approaches employing both standard corrosion tests and accelerated electrochemical testing methods.

### *Pilot Plant Testing*

Promising results from the laboratory-scale corrosion tests must subsequently be verified under field-conditions in the pilot plant facility. Here, such an extended test will be briefly discussed using a) butanetetracarboxylic acid and b) polyaspartic acid as inhibitor. A 14-day circulation test was carried out in order to evaluate the field performance of the two systems having shown excellent results in the lab-scale experiments. The results summarized in table 9 clearly indicate that the excellent performance in the

screening tests is validated in the pilot plant test. Thus, the feasibility of the three-stage experimental approach to the development of new inhibitor systems has been demonstrated.

TABLE 9  
CORROSION INHIBITION OF BUTANETETRACARBOXYLIC ACID AND POLYASPARTIC ACID  
PILOT PLANT RESULTS (30 ppm INHIBITOR)

	corrosion rate	mm/a	mpy
<b>untreated</b>	medium hard water	0.06	2.4
	soft water	0.56	22.4
<b>butanetetracarboxylic acid</b>	medium hard water	0.04	1.6
	soft water	0.12	4.8
<b>polyaspartic acid</b>	medium hard water	0.03	1.2
	soft water	0.14	5.6

## CONCLUSIONS

Corrosion inhibiting systems based on different carboxylic acids have been developed which achieve an inhibition efficiency comparable to state-of-the art phosphonic acid based systems while additionally providing enhanced environmental compatibility and biodegradability. An integrated approach featuring a combination of classical corrosion testing and electrochemical methods was employed for this development. A major advantage of the experimental design is manifested in the subsequent considerable acceleration of testing procedures from several days down to 24 hours. Electrochemical testing procedures provide a full characterization of inhibitor properties as a function of practically relevant process parameters (i.e. water quality, pH, concentration) in very short periods of time. Thus, the fast development of corrosion protection systems tailored for specific customer demands is facilitated, focusing on corrosion inhibition, process cost and environmental compatibility.

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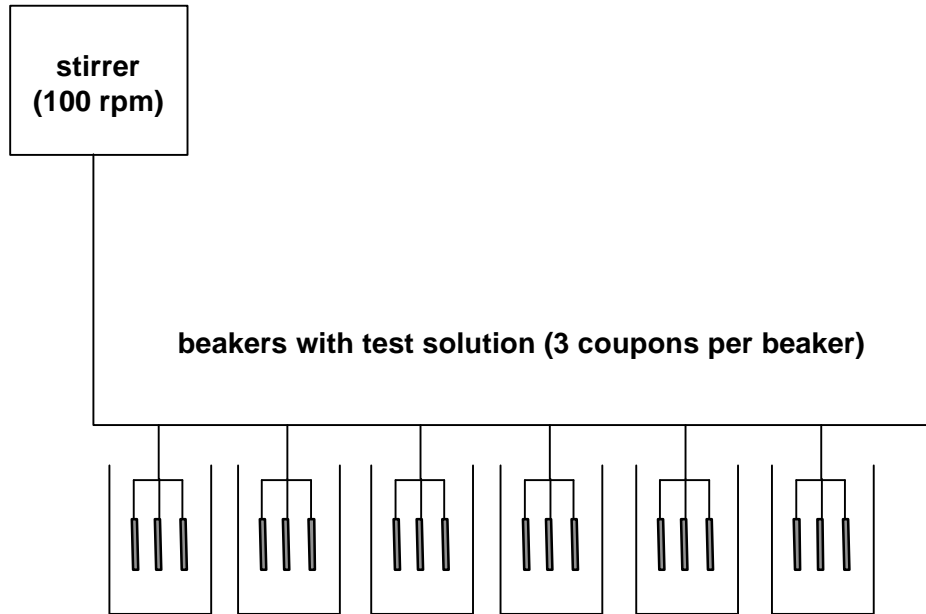


FIGURE 1 - Screening beaker experiments

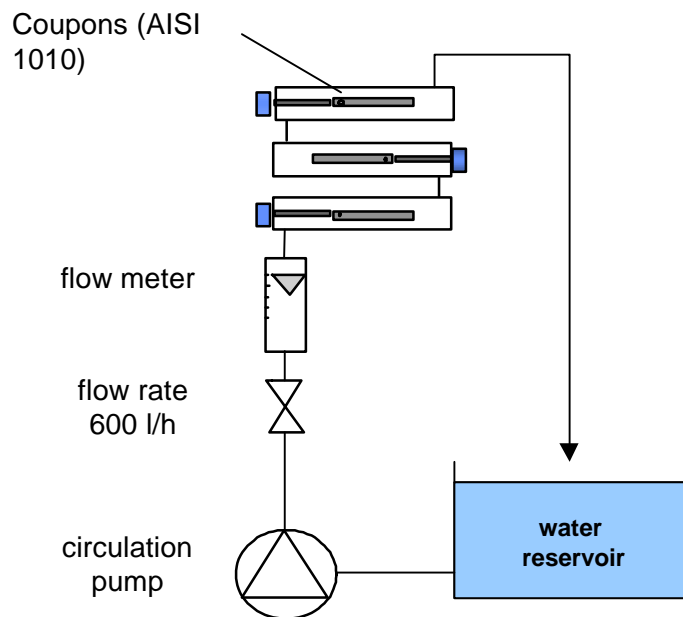
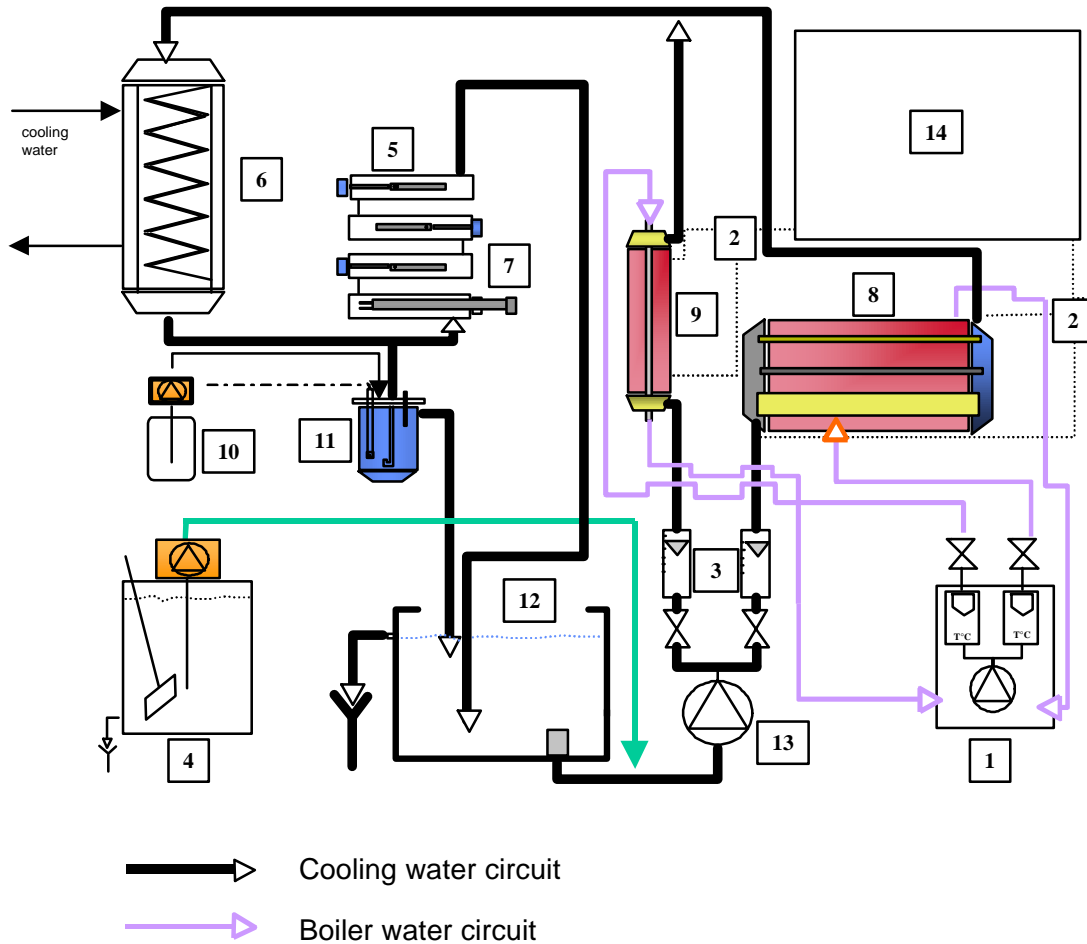


FIGURE 2 - Laboratory scale circulation device



**Captions**

1. Thermostat
2. Temperature Sensors
3. Flow meters
4. Make-up water storage tank with pump
5. Coupon test rack (circulation cell according to ASTM 2688)
6. Intensive chiller
7. Electrochemical corrosion rate measurement
8. Tube-bundle heat exchanger
9. Single tube heat exchanger
10. pH-control with acid storage tank
11. pH-measurement
12. Cooling water tanks
13. Circulation pump
14. Temperature measurement box (8 measuring points)

FIGURE 3 - Pilot plant device

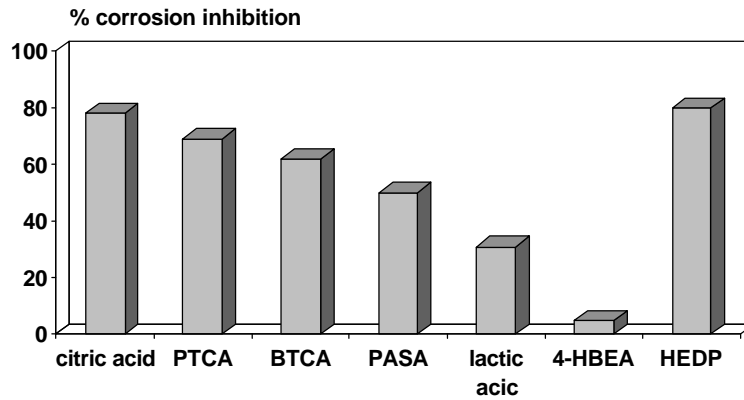


FIGURE 4: Results based on beaker experiments

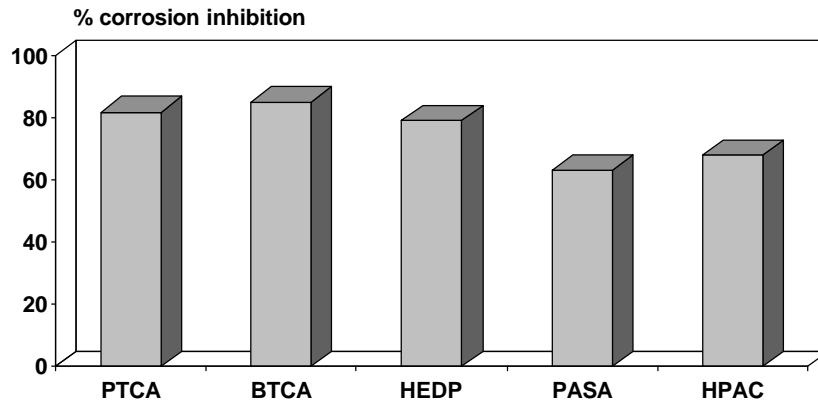


FIGURE 5a: Results after 24 h in the lab circulation device

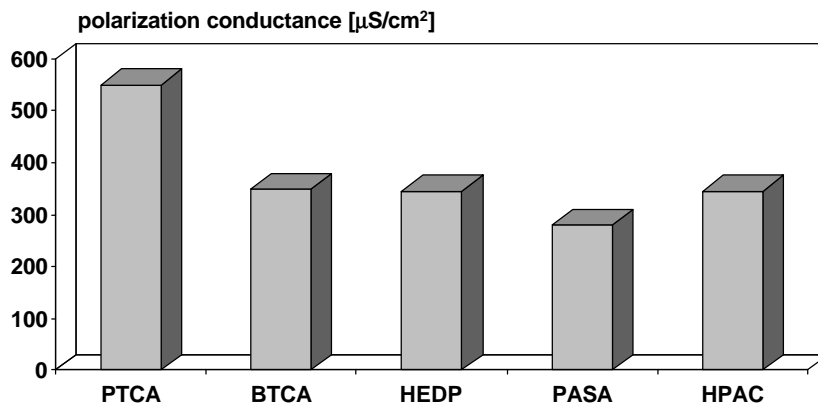


FIGURE 5b: Electrochemical results after 24 h circulation testing

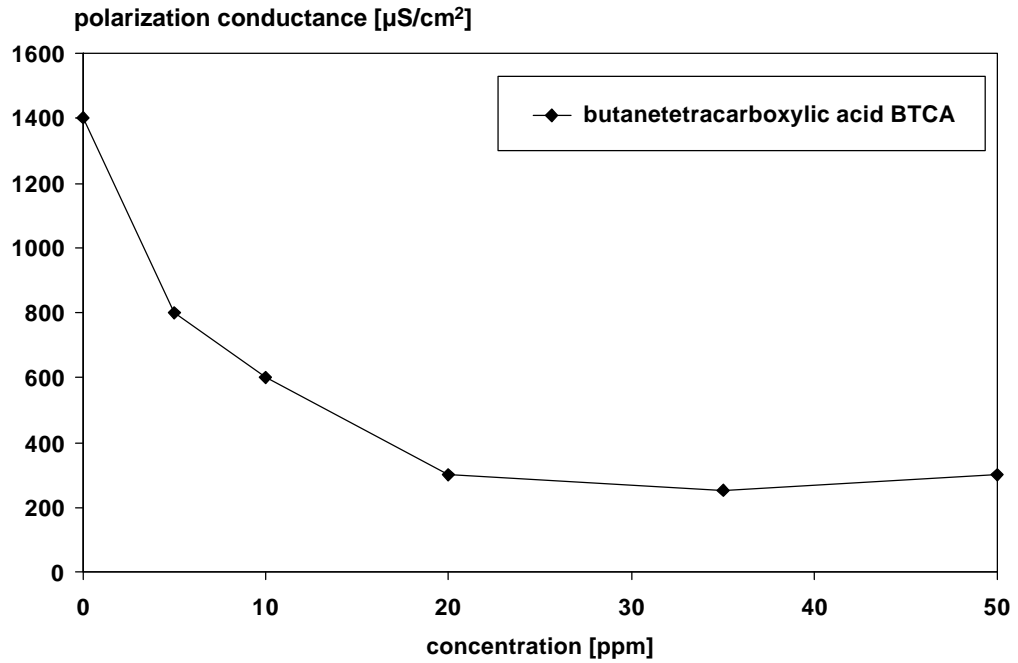


FIGURE 6a - Corrosion inhibition as function of concentration

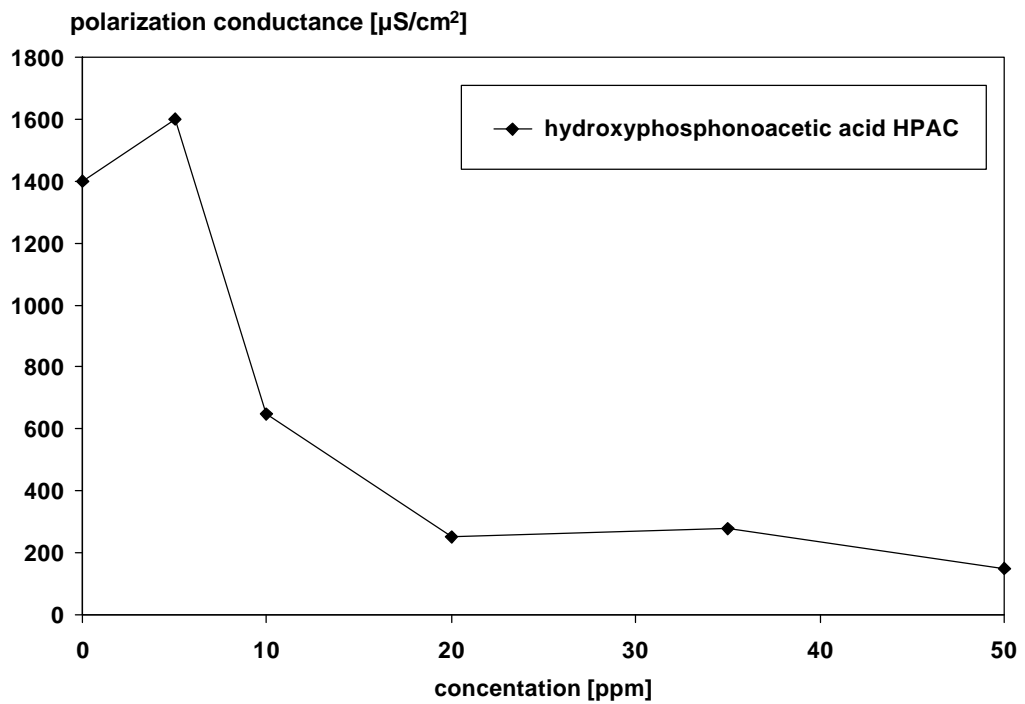


FIGURE 6b - Corrosion inhibition as function of concentration

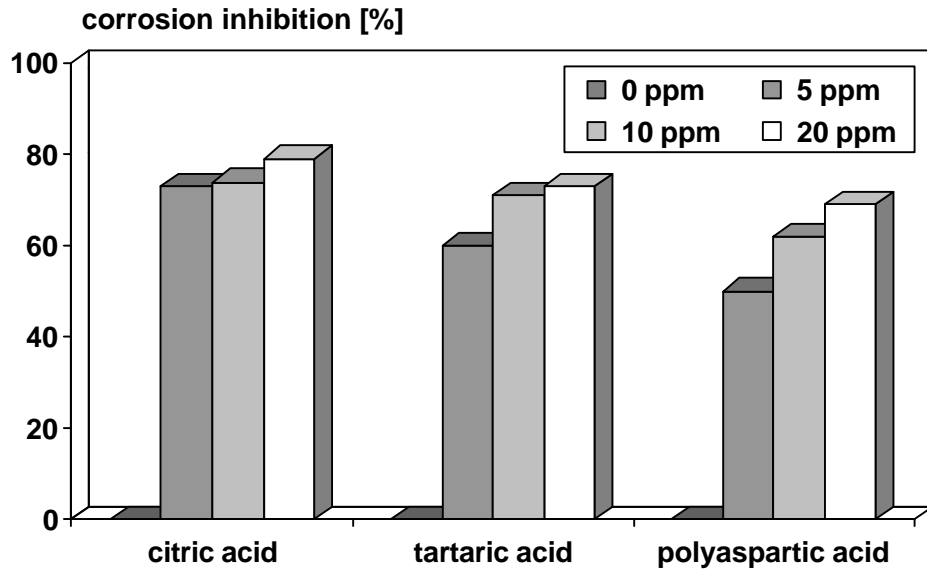


FIGURE 7a  
Corrosion inhibition of new inhibitor systems  
after 24 h of circulation testing

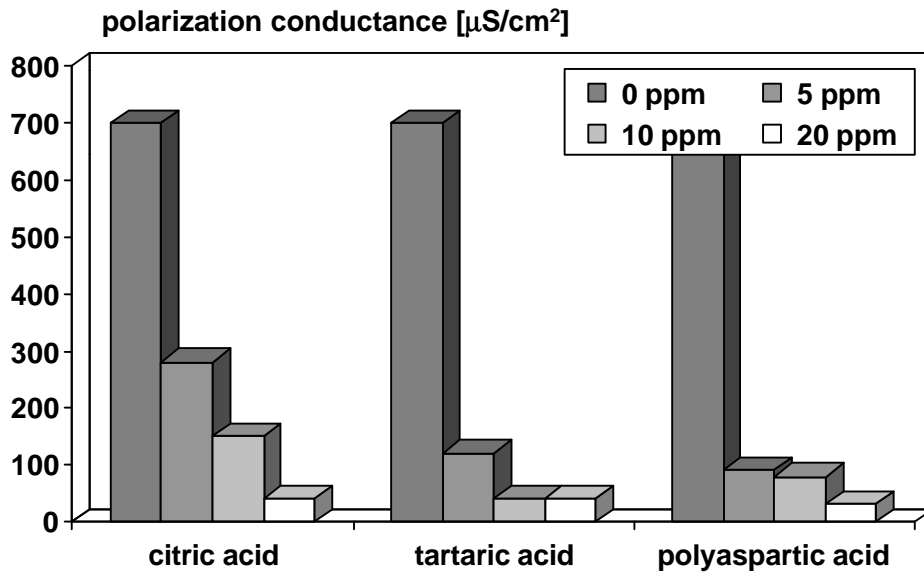


FIGURE 7b  
Polarization conductance of new inhibitor systems  
after 24 h of circulation testing