Correlation between Electrochemical Corrosion Measurement and Short Time Weight Loss Tests for Efficiency Testing of Film Forming Corrosion Inhibitors

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Film forming inhibitors are widely used in refineries and petrochemical units. Evaluating their efficiency in the short term is a daily challenge for treatment companies. Well accepted in this particular industry is the so called wheel tester, which is based on small weight loss of steel coupons. Although it has the advantage of being easy to apply and to evaluate, it also has some significant drawbacks because of its lack of standardization and limited level of reproducibility. To verify the results from the wheel tester, classical polarization corrosion tests under similar experimental conditions have been performed. Various conditions such as inhibitor concentration and temperature were studied applying both methods, in particular using film forming corrosion inhibitors of different chemical compositions. The evaluation of the data shows a good correlation between both methods, as the rankings of the inhibitors regarding their efficiency were analogous.
The combination of both methods enables the reliable evaluation of inhibitors and formulations with good reproducibility in a relatively short time. This generates a flexible, reliable and fast method to develop and optimize organic based film forming corrosion inhibitors. This concept is described for the development of corrosion inhibitors intended to be used in refineries distillation units' overhead systems.

1. Background

Corrosion occurs in many refineries´ units. Even though these areas contain only very low concentrations of oxygen, topping units´ overhead systems are sensitive to corrosion since hydrochloric acid and hydrogen sulfide are present in high concentrations. Corrosion protection is therefore a challenge for unit managers and treatment companies. Widely used for this purpose are film forming inhibitors. Nevertheless, these chemicals are available in a wide variety. As a consequence, choosing the best chemical for the right application became a matter of reliability, time, and cost optimization.
In order to avoid long, dangerous, and expensive plant trials for each inhibitor, many methods for efficiency evaluation have been developed throughout the years. One of them is the so called wheel tester, a fast dynamic corrosion test described in [3]. The wheel tester is a fast and cheap test but its reliability has been questioned because of its lack of reproducibility and standardization. In order to maintain the advantages of this method while improving its reliability, we chose to combine it with a well known method in the water treatment industry. Electrochemical corrosion tests are often used to compare corrosion inhibitors´ protection performance in water based environments. Since this method is reproducible and fast [1] it ensures reliable results.

2. Experimental

2.1. Material, samples and chemicals

Standard low alloy steel test rods (metal coupons, l = 6.5 cm, d = 2 mm, material: St37, SAE 1010 or 1020) were used as test specimens. Generally, rods were treated with a pickling solution based on hydrochloric acid, rinsed with de-ionized water and acetone before using them in the test. Electrolytes were dilute hydrochloric acid, set to pH 1,5 for wheel tests and the 17 hours voltammetry precorrosion. Stock solutions were dilute raw materials in isobutanol (concentration: 1000 ppm). Na_2SO_4 (0,05M) was used as measurement medium for electrochemical corrosion tests.

2.2. Electrochemical tests

Voltammetric electrochemical corrosion tests have been performed with a computer controlled potentiostat (POS2 of company Wenking, Germany). For all experiments, a Duran glass cell was used in a standard three electrodes configuration. Test rods were first coated with a protective layer, leaving the tip free in order to set a defined surface to corrode, pickled and precorroded in an acidic medium containing the corresponding inhibitor. The scan was performed in 0,05M Na_2SO_4 in order to increase the conductivity at a scan speed of 50 mV/s. All samples were run in quintuple to increase precision and reliability.

Fig. 1: potentiostat and electrochemical test cell

2.3. Wheel tests

Test containers were 200mL beverage bottles. The inhibitor to be tested was injected into the bottle first. Test medium (hydrochloric acid of defined pH) was purged with nitrogen and then saturated with carbon dioxide in order to make it free of oxygen. The capped bottles were then placed on holders on the wheel and rotated for 72 hours at 20 rpm. Temperature was set to 40° in order to avoid any damage to the bottles. At the end of the test, samples were rinsed with an inhibited pickling solution to remove corrosion products and deionized water and dried with a soft cloth. The inhibition rate relative to blank samples was determined from the measured weight loss. All samples were run in quadruplicate to increase precision and reliability.

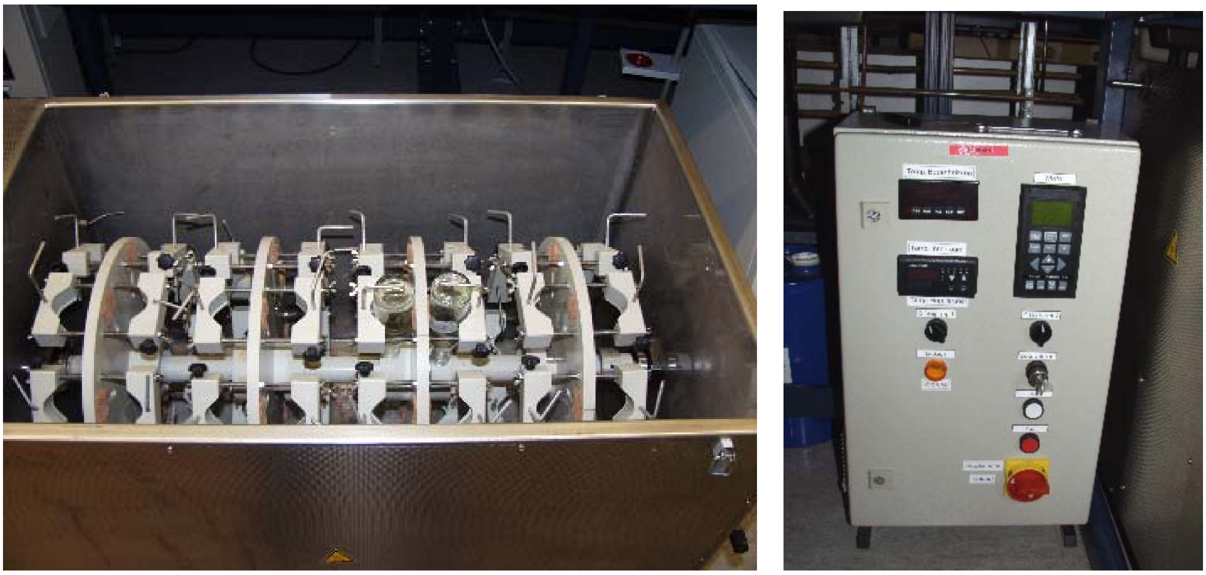

Fig. 2 : Pictures of wheel tester control unit and container

3. Results and discussion

3.1. Voltammetry Measurements

Physical parameters with direct relevance to inhibitor performance are readily available from standard electrochemical measurements. In voltammetry, the change of corrosion potential and the anodic / cathodic current densities upon application of an inhibitor indicates its principles of action (anodic vs. cathodic) while serving as a fast measure of its effectiveness. Figure 3 shows the variation of corrosion potential and current density of a steel electrode immersed into a sodium sulfate conductive solution after 17 hours precorrosion in a pH 1,5 bath containing the respective amounts of inhibitor. Exactly as in softer conditions [2], a clear differentiation can be achieved between uninhibited samples and different concentrations of inhibitors.

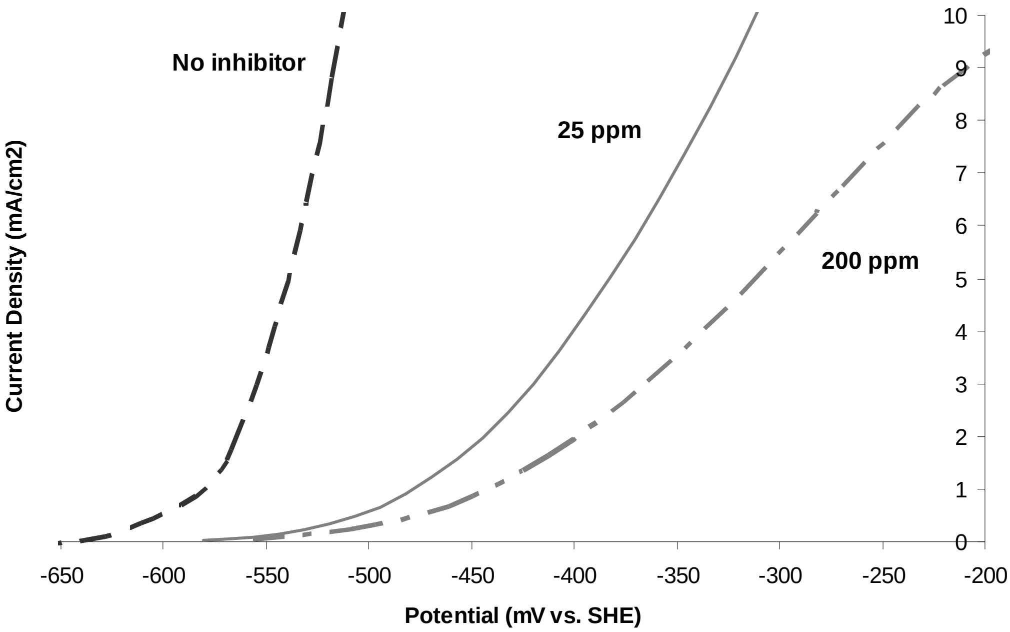

Fig. 3: Anodic polarization curves of a steel electrode treated with different concentrations of a corrosion inhibitor with known efficiency

The quality of the measurements, as demonstrated in Figure 4 is strongly influenced by the precorrosion time applied to the electrode. During the first 5 hours, the inhibitor's layer is building on the surface to be protected. As a consequence, the sensitivity to corrosion is higher during this time than after 5 hours when the protective layer is well settled. For practical purposes, we selected the current density at a potential of 0,2V versus Standard Hydrogen Electrode as the measurement value on which to base the evaluation.

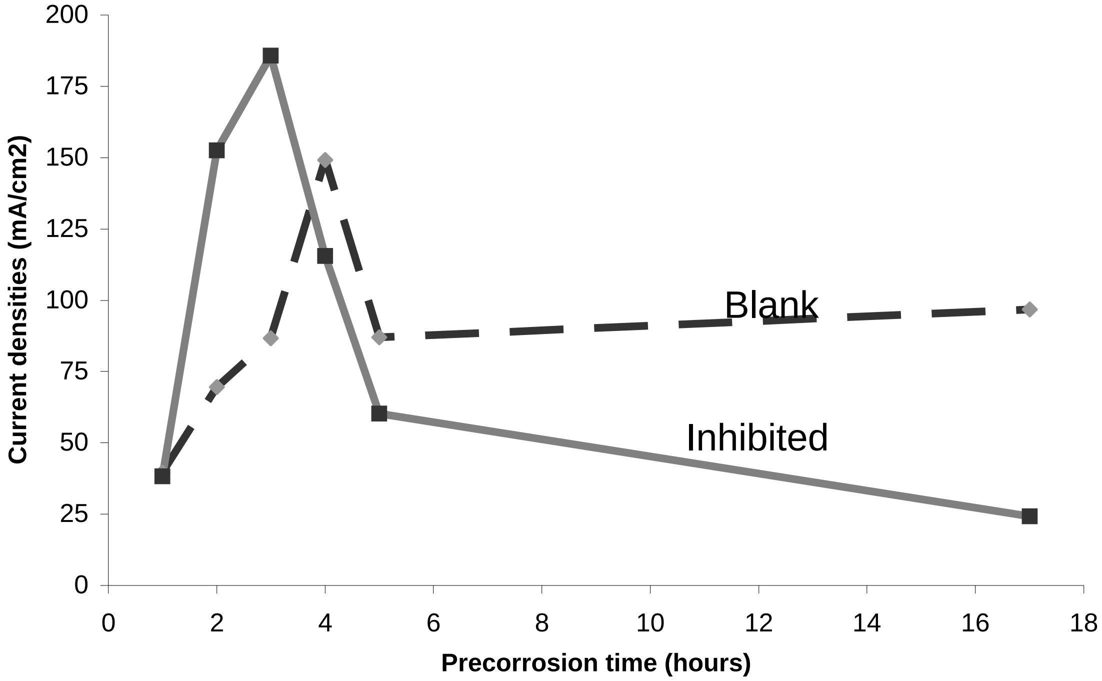

Fig. 4 : influence of precorrosion time on the current densities

The optimal precorrosion time chosen is 17 hours, allowing a more accurate experimental planning while preserving the quality of the results.

3.2. Wheel Tests

Weight loss is the primary data obtained from the wheel test runs. The corrosion time is once again a decisive parameter for the quality of the results. The weight loss must reach a maximum while preserving the equipment. The optimum time chosen is 48 hours.

More than a simple efficiency test, wheel tests differentiates the inhibitors not only by their maximum efficiency but also by the concentration needed to protect a surface. In figure 5, we observe that at high dosages the protection is similar. But for lower dosages, inhibitor A performs a lot better, allowing a lower dosage of the product in the plant, thus saving money and reducing environmental effects.

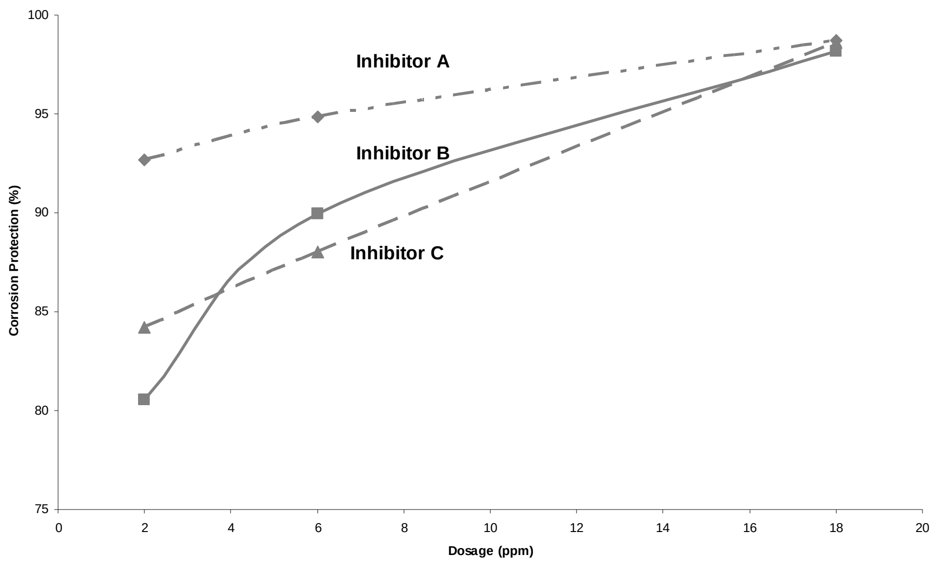

Fig. 5 : wheel test results by inhibitors and concentrations

3.3. Correlation between voltammetry and weight loss

Since wheel tester results are repeatable only to a certain extent, that is to say that a change in the preparation of the test (operator, schedule, etc) may modify the results, a comparison of both methods provides reliability that none of the methods alone can guarantee. As shown in Figure 6, a good ranking correlation of both methods proves the correct handling and the accuracy of the results. This also demonstrates the method´s reliability.

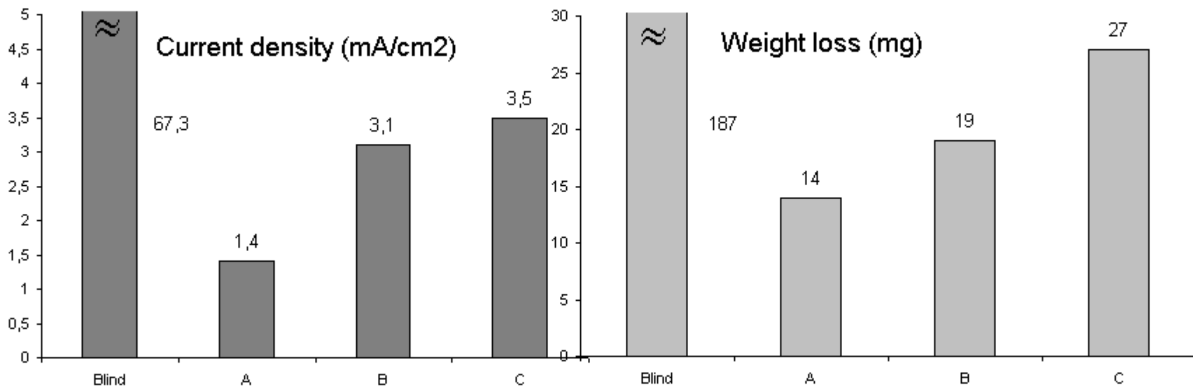

Fig. 6 : Correlation between wheel test experiment and voltammetry tests

4. Conclusion and outlook

The fast evaluation of the efficiency of film forming inhibitors while keeping reliable results is possible by combining two different approaches. Within 3 days, a ranking of several inhibitors can be supplied, allowing thus a fast, reliable, and relatively economical product development for refinery industry corrosion inhibitors. Plant trials are then carried out under safer conditions, creating a new set of possibilities for product line extension and tailored treatments.

Further testing of media composition, electrode composition and higher temperatures is planned for the future.

References

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[3] NACE international publication 1D182 "Wheel Test method used for evaluation of film-persistent corrosion inhibitors for oilfield applications"; item no. 24007

[4] NACE international publication 1D196 "Laboratory test methods for evaluating oilfield corrosion inhibitors"; item no. 24192