

Corrosion process assessment using a novel type of coupon installation

Daniel Musik¹, Krzysztof Wójcik¹, Małgorzata Sekuła-Wybańska¹, Rafał Rakoczy^{2,*}

¹ESC Global sp. z o.o.; daniel@escglobal.co.uk; krzysztof@escglobal.co.uk; biuro@gc2000.pl

²West Pomeranian University of Technology in Szczecin, Faculty of Chemical Technology and Engineering, 42 Piastów Avenue, 71-065 Szczecin, Poland; rrakoczy@zut.edu.pl

*Corresponding author: e-mail: rrakoczy@zut.edu.pl

The main aim of this experimental study is to test the novel type of coupon installation. This set-up was used to carry out the corrosion process under aggressive conditions. Moreover, the effect of corrosion inhibitors on the scale-forming tendency was evaluated. The corrosive conditions were defined by using the Langelier Saturation Index (this index is an approximate indicator of the degree of saturation of CaCO_3 in water) and the Ryznar stability index (this index is allowed to determine if the liquid sample is aggressive or not). Additionally, the inductively coupled plasma optical emission spectroscopy analysis was used to obtain the iron and calcium ions concentrations in the liquid samples from the tested coupon installation. The corrosion process for the established conditions was also described using the corrosion rate of the tested coupons. The obtained investigation contributes significantly by developing the novel coupon installation and demonstrating the procedure for testing the corrosion process with the application of coupons. This setup and method might be successfully applied for accelerated laboratory tests.

Keywords: coupon installation, corrosion, scaling, scale inhibitors.

INTRODUCTION

Recent years have seen renewed interest in the corrosion process¹. It should be noticed that the corrosion process is lead to high power consumption, maintenance costs and the loss of commercial income during downtime. The proper methods to measure and forecast the corrosion process would help in intervention in process production where corrosion is a common phenomenon. The prevention of the corrosion process allows economic and energy savings. The dynamic growth of the chemical industry is related not only to the demand for new apparatus or plants but also to the need for the control of the corrosion process. The main aim of corrosion protection is to reduce the corrosion rate to an acceptable level. Firstly, the right construction material should be selected to build a chemical installation. Secondly, the surrounding environment of the construction materials (mainly metals) should be analyzed. Moreover, the application of inhibitors, electrochemical protection, the application of coatings, and environmental modifications is recommended to protect the materials against corrosion².

From the practical point of view, the corrosion test is carried out in artificially created conditions which imitate natural conditions. The acceleration of the corrosion processes in comparison with the operating conditions might be established by the changed conditions in the specially designed chambers or apparatus³. The tests on the laboratory scale are realized using coupons which are placed in the liquids (the industrial liquids or the perpetrated solutions in the laboratory conditions). In the case of these accelerated tests one or more corrosive factors are strengthened, e.g. concentration of corrosive components, moisture condensation, relative humidity or temperature. To date, several studies have shown that the installation for testing the corrosion process is used to test the resistance of the material to corrosion^{4,5}.

It should be noticed that the Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI) might be used to infer the scale-forming potential of aqueous solutions from their composition⁶. The LSI is allowed to estimate the affinity of water to dissolve or precipitate CaCO_3

which is the main factor influencing water corrosivity⁷. This parameter might be treated as the measure of the stability of water for its degree of CaCO_3 saturation. The RSI used the LSI as a component in a formula to improve the accuracy in predicting the scaling or corrosion tendencies of water⁷. This index gives information about the scale thickness observed in water systems to the water chemistry⁶.

The main aim of this paper is to test the novel type of coupon installation which might be used to measure the corrosion process. The coupon installation is tested under controlled conditions (application of 1M NaOH or application of CaCl_2 and NaHCO_3). Moreover, the commercial product ESC R 26L (GLOBAL CONCEPTS 2000 Poland Ltd.) and the mixture of EPOC, HEDP, PAA, PCA, and TBCA ("mix") was applied for the prevention of the corrosion process. This experimental study attempts to improve the used methods of corrosion testing with the application of the novel type of coupon installation.

MATERIAL AND METHODS

The investigations were carried out using the experimental set-up presented in Fig. 1. This novel type of coupon installation is detailed described in the patent application (P.440109; WIPO ST 10/C PL440109). The experimental set-up consists of a tank (1) for the corrosive liquid. This tank is equipped with protection against low liquid levels (3). The temperature control during the test is controlled by using the heater (6). The heater controller (2) is connected to the temperature sensor (5). The additional element of this system is protection against exceeding the maximum temperature of the liquid in the tank (4). This temperature-stabilizing system is used to maintain and control the assumed process temperature. The tank (1) is also equipped with a system of liquid circulating: the circulating pump (7), filter (8), three-way valve (9), a plate heat exchanger (10), and the vent valve for the circulating system (11). The system consists of the piping system for online corrosion monitoring ("zig-zag" system). This system (made of transparent polycarbonate pipes and elements) allowed us to observe the progress

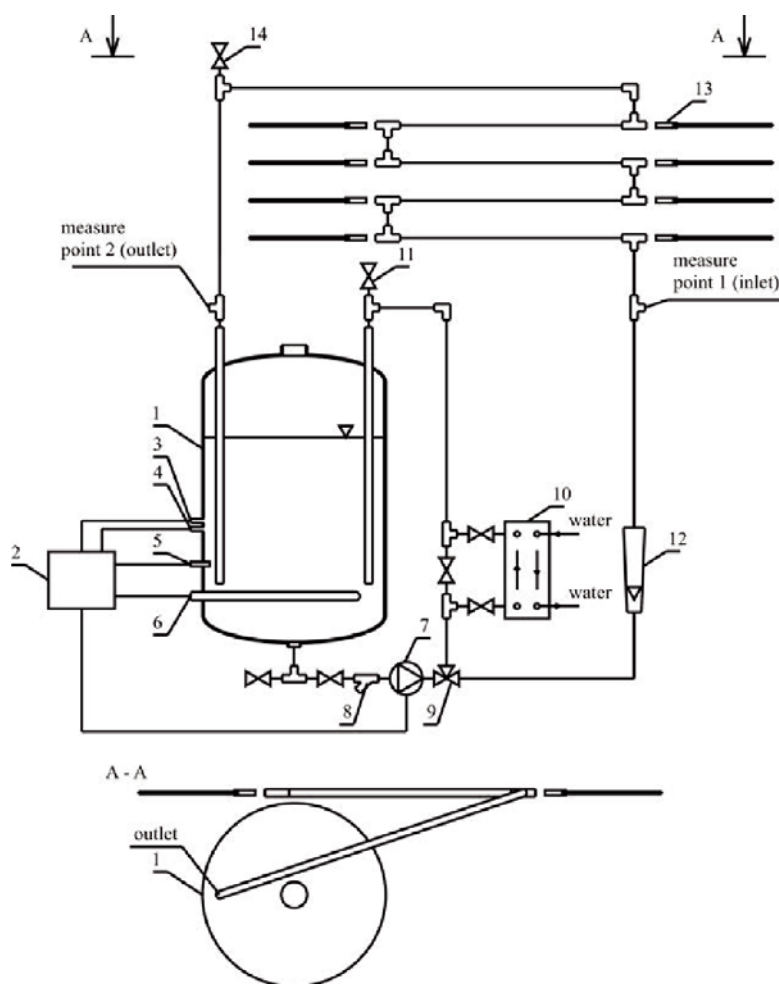


Figure 1. Schematic of the experimental setup: 1 – tank; 2 – heater controller; 3 – protection against low liquid level in tank; 4 – protection against exceeding the maximum temperature of the liquid in tank (maximum operating temperature is 60 °C); 5 – temperature sensor; 6 – heater; 7 – circulation pump; 8 – filter; 9 – three-way valve; 10 – plate heat exchanger (for cooling); 11 – vent valve for circulating system; 12 – rotameter; 13 – tested coupon sample, 14 – vent valve for circulating system with coupons (zig-zag system).

of the corrosion process on the tested coupon samples (13). The coupon installation comprises the rotameter (12) and the vent valve (14).

The tested coupon installation is equipped with adjustable coupon holders (see Figure 2). The application of these holders is allowed to adjust the position of the coupon in the experimental set-up. The coupons are inserted into the zig-zag system for a specified period. After this time, the coupons are removed from the coupon installation, checked and weighed. In the test were used mild steel coupons were produced by European Corrosion Supplies Limited, UK.

Four corrosion tests (see table 1) were performed in demi water (pH 5.5–7; conductivity < 0.1 $\mu\text{S} \cdot \text{cm}^{-1}$; heavy metals (pb) < 0.1 ppm; aluminium < 0.05 $\text{mg} \cdot \text{L}^{-1}$; barium < 0.01 $\text{mg} \cdot \text{L}^{-1}$; calcium < 0.01 $\text{mg} \cdot \text{L}^{-1}$; cadmium < 0.01 $\text{mg} \cdot \text{L}^{-1}$; chromium < 0.01 $\text{mg} \cdot \text{L}^{-1}$; copper < 0.01 $\text{mg} \cdot \text{L}^{-1}$; iron < 0.01 $\text{mg} \cdot \text{L}^{-1}$; potassium < 0.01 $\text{mg} \cdot \text{L}^{-1}$; magnesium < 0.01 $\text{mg} \cdot \text{L}^{-1}$; manganese

< 0.01 $\text{mg} \cdot \text{L}^{-1}$; molybdenum < 0.01 $\text{mg} \cdot \text{L}^{-1}$; sodium < 0.02 $\text{mg} \cdot \text{L}^{-1}$; nickel < 0.01 $\text{mg} \cdot \text{L}^{-1}$) at a controlled temperature (40 ± 1 °C).

The time duration of these tests was equal to 94 h. For the selected time points, the liquid in the coupon installation was checked. It should be noticed that the parameter pH was measured by means of the multimeter CX-601 (Elemetron, Poland). The Langelier Saturation Index (LSI) and the Ryznar stability index (RSI) were applied to assess the scaling and corrosion tendency of the used liquids⁸. The LSI assesses the corrosivity of a liquid sample and is used to estimate the affinity of water to dissolve or precipitate CaCO_3 . This substance is the main factor influencing water's corrosivity. The positive values of this index mean that water will deposit CaCO_3 on the metal surface indicating a super-saturated state leading to the marginal level of corrosion. The negative values of LSI show an under-saturated condition and corrosive surroundings. The RSI is the modification of LSI, and

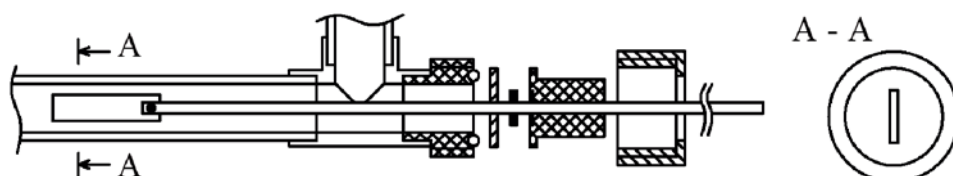


Figure 2. Schematic of the coupon holder used in the novel type of coupon installation

Table 1. Characteristic of the carried out experiments

Experiment	Description
1.	The coupon installation was tested by using aggressive corrosion conditions. This experiment was performed in demi water with an addition of 1M NaOH.
2.	The coupon installation was tested by using the controlled conditions. This experiment was performed in demi water with an addition of CaCl_2 and NaHCO_3 .
3.	This experiment was performed in demi water with an addition of CaCl_2 and NaHCO_3 (controlled conditions from experiment no. 2) and with the application of commercial product ESC R 26L ($20 \text{ mg} \cdot \text{L}^{-1}$). This product is a mixture of organic and inorganic corrosion inhibitors controlling the pH. This product is used in closed hot and cold water systems containing metal parts or elements.
4.	This experiment was performed in demi water with an addition of CaCl_2 and NaHCO_3 (controlled conditions from experiment no. 2) and with the application of the mixture of EPOC, HEDP, PAA, PCA, and TBCA ("mix"; $20 \text{ mg} \cdot \text{L}^{-1}$). This mixture was prepared by mixing equal volumes (equal volume of each component) of the inhibitors used in this experimental work (EPOC, HEDP, PAA, PCA, TBCA). The EPOC (enhanced phosphonocarboxylate) is an organic, halogen-stable, multi-functional corrosion and deposit control product. This substance reduces and eliminates reliance on metal and phosphate in corrosion control and disperses calcium phosphate and iron. The HEDP (1-hydroxy ethylidene-1,1-diphosphonic acid) is an organophosphonate acid corrosion inhibitor. This substance dissolves the oxidized materials on these metals' surfaces. The PAA (polyacrylic acid homopolymer) is soluble in water, it can be used in situations of alkaline and high concentration without scale sediment. This substance can disperse the microcrystals or microsand of calcium carbonate, calcium phosphate and calcium sulfate. The PCA (phosphinocarboxylic acid polymer) has dispersion properties for the scale of calcium carbonate and calcium phosphate. This substance is good to scale inhibition for barium sulfate, strontium sulfate and silica scale. The TBCA (2-Phosphonobutane-1,2,4-tricarboxylic Acid) has structural features of both phosphoric acid and carboxylic acid groups, which enable scale and corrosion inhibition properties. This organophosphonate is widely used in circulating cool water systems as a scale and corrosion inhibitor.

it offers better corrosion resistance (this parameter can withstand increased Ca hardness and pH values)⁹.

The liquid from the coupon installation was characterized using the inductively coupled plasma optical emission spectroscopy analysis (Agilent 5100 ICP-OES). This analysis was carried out following the PN-EN ISO 11885, PN-EN ISO 5667-3, PN-EN ISO 15587-1, and PN-EN ISO 15587-2 standards. In the case of this experimental work, the iron and calcium ion concentrations are only analysed.

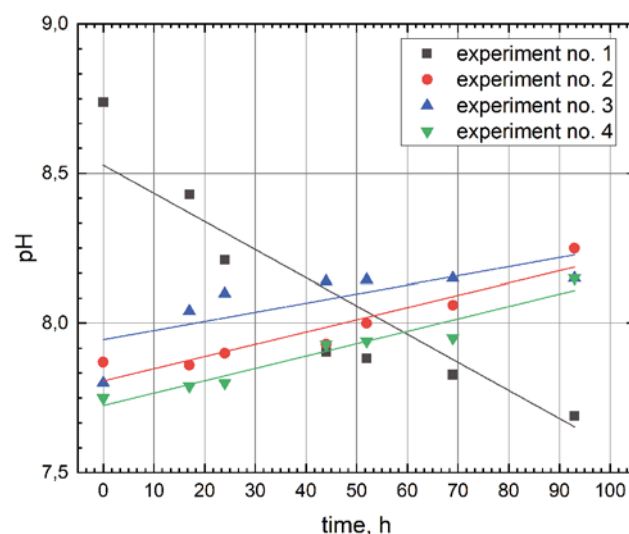
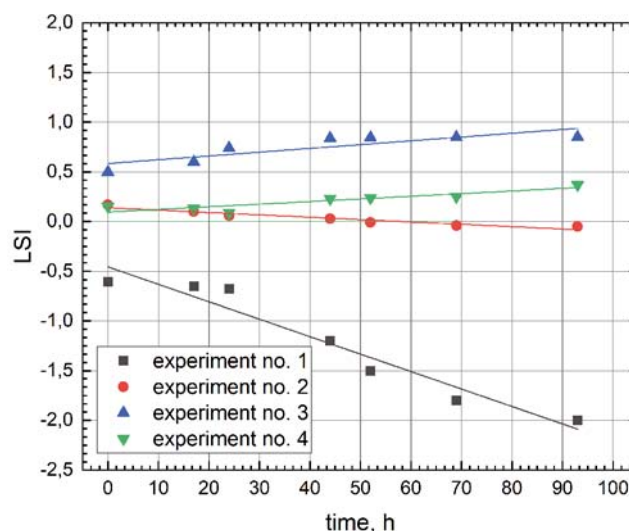
Moreover, the corrosion rate (CR) was measured using the corrosion coupon weight loss measurements¹⁰.

RESULTS

Figures 3, 4 and 5 show the changes in pH, LSI and RSI indicators for the four corrosion tests (see Table 1), respectively. The pH fluctuated from 8.7 (for the initial time of experiment no. 1) to 7.9 (after 93 h of the time duration of the process). It should be noticed that this parameter can hamper the process of scaling and corrosion¹¹. The pH is an essential factor influencing the formation of deposits such as CaCO_3 and this parameter is also used to calculate the LSI and RSI indicators. As follows from the obtained results (see Figure 3), the values of the pH parameter were changed sharply for experiments no. 2, no. 3, and no. 4. It should be emphasized that experiment no. 2 was carried out to check whether the pH parameters for the controlled conditions (with the addition of CaCl_2 and NaHCO_3) changed over time. For this experiment, they fluctuated from 7.9 (for the initial time) to 8.2 (after 93 h of time duration of the process). The introduction of ESC R 26L (experiment no. 3) and "mix" (experiment no. 4) into the liquid allowed us to maintain the pH value in the range of 7.8 to 8.1.

The LSI and RSI indicators were calculated based on pH values⁶. Figure 4 shows the variation of the LSI indicator for the tested conditions.

The LSI value below 0 shows the corrosive nature of the tested liquid (under-saturated water tendency, dissolves CaCO_3). The positive value of LSI indicates the

**Figure 3.** The variation of pH values for the tested conditions**Figure 4.** The variation of LSI values for the tested conditions

super-saturated water tendency (precipitates CaCO_3). In the case of these investigations (see experiment no. 1), the LSI varied in the range between -0.61 (for the initial time of process) to -2.0 (after 93 h of the time duration of the process). The controlled conditions (experiment no. 2) allowed us to obtain the LSI value approximately equal to 0. It means that the saturated conditions are obtained (CaCO_3 in equilibrium). The application of ESC R 26L (experiment no. 3) and "mix" (experiment no. 4) into the liquid allowed us to obtain the LSI values above 0 (the LSI value above 0.5 means the scaling process).

The RSI indicator is the modification of LSI, and it was developed to assess water-scaling tendencies. The variation of this indicator for the realized corrosion tests is graphically presented in Figure 5.

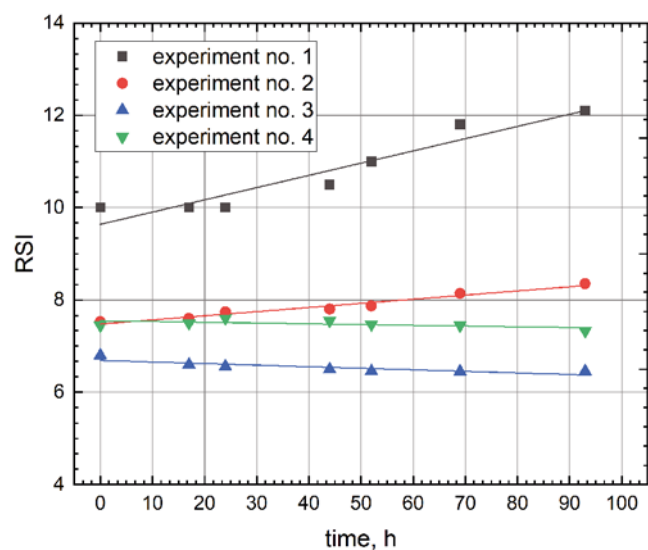


Figure 5. The variation of RSI values for the tested conditions

It should be noticed that the value of the RSI indicator above 8.5 means that the liquid is highly corrosive. According to the obtained results (see Fig. 5), the applied in this test of coupon installation water (experiment no. 1) is not scale-causing and highly aggressive. The controlled conditions (experiment no. 2) allowed us to obtain the RSI value varied between 7.5 (for the initial time) and 8.2 (after 93 h of the time duration of the process). The application of ESC R 26L (experiment no. 3) and "mix" (experiment no. 4) allowed for the reduction of the RSI values. The RSI value below 7.5 means that the water is not corrosive. According to the obtained results (see Fig. 4 and Fig. 5), the application of "mix" is allowed to generate the scale-causing and non-aggressive conditions.

The ICP-OES analysis allowed us to define the amount of iron and calcium leached into the medium during the analysed processes. Table 2 shows the iron content for the selected liquid samples from the coupon installation. In the present study, the iron ion concentration for

Table 2. The iron contents (ppm) for the four corrosion tests

Time [h]	Experiment no. 1	Experiment no. 2	Experiment no. 3	Experiment no. 4
24	0.2875	0.0000	0.3625	0.1655
52	0.3753	0.0000	0.4850	0.2981
69	0.3967	0.0000	0.5079	0.3739
93	0.4312	0.0000	0.5880	0.4559

experiments no. 2, no. 3, and no. 4 increased by increasing the time duration of the process. The exception is experiment no. 2 during which no iron ion concentration was observed in the collected liquid samples.

Table 3 presents the variation of calcium ion concentration over time for the four corrosion tests. It should be noticed that when calcium ions concentration increases, water corrosivity decreases since calcium forms scales of CaCO_3 , forming a protective coat on the coupon surface to regulate corrosion¹². The obtained results give a clearer picture that the water corrosivity decreases (calcium ions concentration increases during the process) for experiment no. 3 (the application of ESC R 26L) and experiment no. 4 (the application of "mix").

The corrosion rate (CR) calculation for the corrosion tests is collected in Table 4. The obtained mean values of CR are changed from 0.5164 to $2.0563 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. It should be noticed that the highest CR value is obtained for experiment no. 1 (the aggressive corrosion conditions). The application of ESC R 26L (experiment no. 3) and "mix" (experiment no. 4) allowed for to reduction of the corrosion process (lower CR values were obtained).

Table 4. The calculated values of CR for the corrosion tests

Time [h]	Coupon Serial Number	CR [g·m ⁻² ·h ⁻¹]	Mean value of CR [g·m ⁻² ·h ⁻¹]
Experiment no. 1	919	2.0401	2.0563
	920	2.0297	
	921	2.0762	
	922	2.0793	
Experiment no. 2	651	1.6889	1.6210
	652	1.6151	
	653	1.6183	
	924	1.5617	
Experiment no. 3	31	0.5105	0.5164
	32	0.5094	
	33	0.4696	
	34	0.5759	
Experiment no. 4	42	0.5895	0.5636
	43	0.5906	
	44	0.5497	
	45	0.5246	
Remarks:			
1) The corrosion rate (CR) was measured using the corrosion coupon weight loss measurements ¹³ .			
2) The CR is calculated as follows ¹⁴ : $CR = (W_b - W_a)/(A \cdot t)$ (where W_b is coupon weight measured before immersion in the liquid samples, g; W_a is coupon weight measured after immersion in the liquid samples, g; A – the exposed area of coupon, m ² ; t exposure time, h;			
3) In the case of this experimental work the parameter A is equal to 0.002032 m ² (dimensions of coupon 3 × 1/2 × 1/16”) and the exposure time is equal to 94 h.			

Table 3. The calcium contents (ppm) for the four corrosion tests

Time [h]	Experiment no. 1	Experiment no. 2	Experiment no. 3	Experiment no. 4
24	0.8859	35.0731	49.9036	55.7446
52	0.5900	26.3182	49.4201	55.7132
69	0.6467	17.7989	58.5561	56.3799
93	0.5432	11.3102	59.1473	57.7949

CONCLUSIONS

From the results of the present study, the novel type of coupon installation might be successfully used in testing corrosion phenomena. The tests of this installation were carried out with the application of the controlled conditions (demi water with the addition of NaOH and demi water with the addition of CaCl_2 and NaHCO_3). Moreover, the application of various scale inhibitors (ESC R 26L and "mix") was tested to evaluate its influence on the scale formation tendency. The primary factors influencing corrosion in water systems are water temperature, pH (the impact of this parameter on corrosion indices is the most), Ca hardness, total dissolved solids (TDS), and alkalinity. The order of sensitivity in which water parameters affect corrosion indices is as follows: $\text{pH} > \text{alkalinity} > \text{Ca hardness} > \text{temperature} > \text{TDS}$ ¹⁵. The obtained results were allowed to monitor the corrosion process and observe the progress of corrosion using the pH parameter or the LSI and RSI indicators. It should be noticed that the measurement of these parameters might provide an indirect measure of the extent of scale formation with industrial systems. Finally, due to the successful corrosion tests, it can be suggested that the proposed coupon installation can be used in experimental works using aggressive environments and for testing new compounds with the potential of inhibitors.

ACKNOWLEDGEMENTS

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