A universal alternating immersion simulator for accelerated cyclic corrosion tests

Dedicated to Professor Dr. Bernd Isecke on the occasion of his 60th birthday

A. W. Hassel*, S. Bonk, S. Tsuri and M. Stratmann

A new device for performing accelerated cyclic immersion tests is described. The main achievement is to realise a high cycling rate without a proportional increase in the test duration. The device is also capable of performing tests according to EU ISO 11130 specification. A minimal invasive drying system is used that neither heats air nor sample and the flow rate is still low as to prevent a mechanical delamination of paints or loose corrosion products. A multiple sample set-up is realised that provides individual reference electrodes. The random access through a multiplexer allows individual investigation of the samples even by electrochemical impedance spectroscopy under immersion conditions.

The device and its test principle are applicable in both industrial and laboratory scale applications. Two application examples are given to demonstrate the versatility of the alternating immersion tester. One addresses the corrosion protection performance of different zinc-coated steel sheets; the other quantifies the patina formation kinetics of low-alloyed steels with weathering properties.

1 Introduction

In order to compare the expected corrosion behaviour of materials under cyclic corrosion conditions standardized test procedures such as the European norm EN ISO 11130 are used [1]. The ever increasing performance of the materials themselves and their corrosion protection systems would increase the duration of tests accordingly. This conflicts the simultaneous trend to faster product cycles and thus a higher demand for advanced materials. Cyclic corrosion tests have become more popular in the past [2]. A side effect is that various sets of environmental conditions will be inherently realised in cyclic corrosion tests [3]. This can trigger various corrosion mechanisms and will in this way allow a more general evaluation of the corrosion performance of the material [4]. Some mechanisms of atmospheric corrosion have been studied in detail and the underlying mechanism for the acceleration has been identified. One example would be the rapid increase in the corrosion rate in thin electrolyte films on metals. The oxygen reduction rate as the cathodic reaction is the rate-determining step [5]. Since the corresponding electron transfer reaction is fast enough the diffusion of oxygen from the gas phase to the substrate surface is the rate-determining step; this rate will increase as the water film thickness decreases. The dry surface on the other hand cannot dissolve metal ions anymore and the corrosion will be kinetically hindered. The overall observed corrosion rate depends on the accumulated corrosion increments under the conditions used. A high share of conditions with a thin water film will therefore increase the share of aggressive conditions and eventually the overall corrosion attack. However, in some cases a proper drying of the sample is required to achieve a necessary reaction step. A pure prolongation of the humid phase alone cannot yield the maximum corrosion rate. In this case an increase in the number of cycles distributed over the same time span will increase the corrosion attack.

A limitation of this method is that the required conditions shall be achieved each on a proper level. Whereas a rigid wetting is relatively straightforward by dipping the sample of interest into the electrolyte solution, ensuring the dry conditions is not always that simple. For samples which are covered by paint in filiform corrosion testing [6,7] or those forming a thicker rust layer [5], the drying of the sample can be hindered. In the worst case the drying process would be incomplete which makes the entire corrosion testing questionable or even wrong. Efforts for an acceleration of the drying process can also lead to artefacts. Heating of the sample is usually prohibited as it can increase reactions such as the conversion of thin rust layers on weathering steels. A subsequent structural investigation is then obviously useless as another crystal phase was formed and the information on the performance of that scale is different from that obtained under natural conditions. Increasing the flow rate of the air to high values can also cause deteriorations, e.g. if a sharp air jet is blasting off a paint by applying a force to the paint that leads to its delamination.

This work reports on the development of a universal alternating immersion simulator for accelerated cyclic corrosion tests, which overcomes these limitations.

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2 Experimental

2.1 Technical set-up

A schematic of the set-up of the new alternating immersion simulator is shown in Fig. 1. For reasons of simplicity, only one basin with one sample is shown. The device is constructed in a modular way and can therefore be divided into different functional groups in order to realize various corrosion test periods, exposure electrolytes and in-situ electrochemical characterisation methods.

The central part of the test device is a set of three basins filled with the electrolyte of choice. The first phase of the wet–dry cycles is the immersion of the samples for its rigorous wetting. The basins are made of glass to avoid interferences with the corrosion process of the tested samples.

Humid conditions are realized by positioning the samples above the electrolyte within the basin. By doing so, a well-defined relative humidity value is achieved depending on the selected height and the humidity gradient between the electrolyte surface and the opening of the basin.

During the dry period the samples are moved completely out of the basin to expose them to the ambient climate. For tests with rapid cycling an optional rapid drying system was used. It blows cleaned and physically dried pressure air with a relative humidity of nominally 2% over the sample surfaces. This method is used to avoid any thermal and mechanical stress as it occurs in other drying techniques, e.g. heating. Cleaning and drying of the air was done by a three-step filter system from BEKO (Drypoint M DPP2015, Clearpoint S050). A sketch of the filter system is shown in Fig. 2. The first unit removes oil and dirt particles by segregation, by an activated carbon filter, followed in a second step by a boron silicate fine filter for removal of
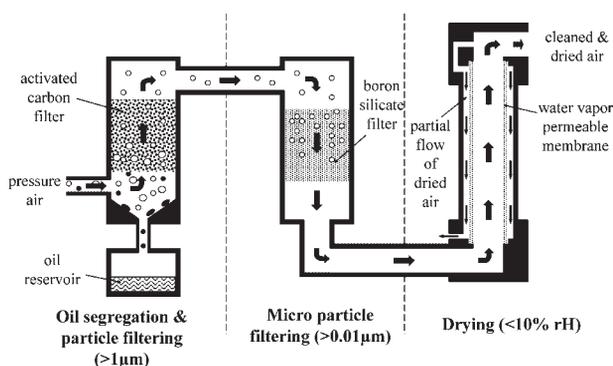
Fig. 2. Sketch of the cleaning and drying system for the pressure air. It is a three step filtering and drying process. In a first step particles with a diameter bigger than 1 μm and oil are segregated from the air flow using an activated carbon filter. In the second step particles less than 1 μm are filtered with the help of a boron silicate fine filter. Finally, in the third and last step the air is dried using an osmosis process of a water permeable membrane and a partial flow of dried air

micro-particles. In the third and final step the cleaned air is led through a membrane filter unit in which the humidity is reduced by an osmosis process. The remaining humidity can be controlled by the ratio between the airflow rates. Eventually, the air is blown from a special nozzle that allows a laminar stream over the specimen surfaces. The airflow is individually controlled for each basin by an electrical shut-off valve and a throttle valve.

The movement of the samples between the different test positions is realised using standard industrial linear drive units (ISEL, Germany) each actuated by a step motor with a movement reproducibility of 5 μm. This high precision guarantees an exact positioning of the samples relative to the individual reference electrode, at a precise height in the vertical humidity gradient and in the centre of the air stream. All three motors are controlled by one controller (ISEL motion control C10C) that is connected to the central control PC through a USB link.

Changes of corrosion relevant parameters such as the open circuit potential under immersion conditions can be monitored by means of electrochemical measurements. For this purpose each sample is equipped with its own reference electrode as indicated in Fig. 3. This reference electrode was either based on a silver wire for a Ag/AgCl electrode [8] or from an amalgamated gold wire for chloride free electrolytes such as Na_2SO_4 or CH_3COONa [9]. In both cases an agar solidified electrolyte was used in the reference electrode that simplifies handling, increases stability and slows or prevents drying and contamination by an in-diffusion of corrosion products. All details of the preparation steps of these robust and versatile electrodes are described in References [8,9].

Since all samples and all reference electrodes within one basin are immersed into the same electrolyte, a proper electrical separation is required. This was realised by three daisy chain eight channels multiplexer with two contact mechanical relays. It allows selecting exactly one sample and its corresponding reference electrode while all other electrodes are electrically disconnected. Mechanical relays were used rather than the more common solid-state relays since their inner resistance is much higher. Especially for impedance characterisations and electrochemical noise measurements the leakage currents of the solid-state relays could lead to artefacts [10].
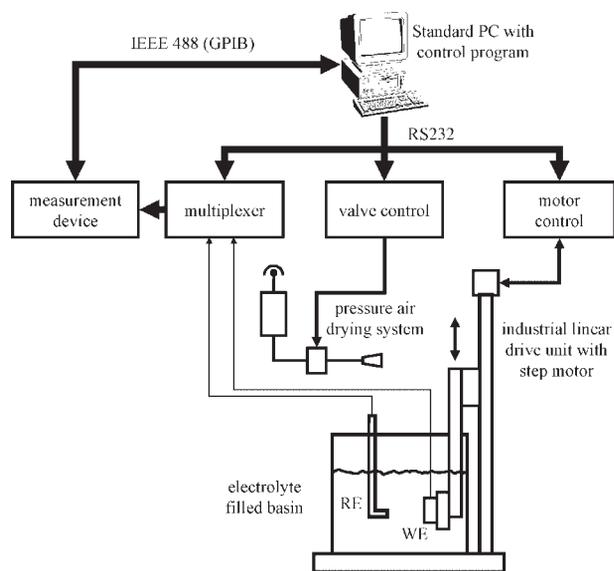
Fig. 1. Sketch of the new cyclic immersion test device. It is divided into three functional groups: (1) the mechanical part for the sample movement with the step motor control, (2) the part for the realisation of different corrosion exposure conditions consisting of the electrolyte filled basins and the minimally invasive drying system and (3) the electrochemical measurement system consisting of the measurement device, the multiplexer, reference electrodes and the samples in the sample holders. All parts are controlled by a software
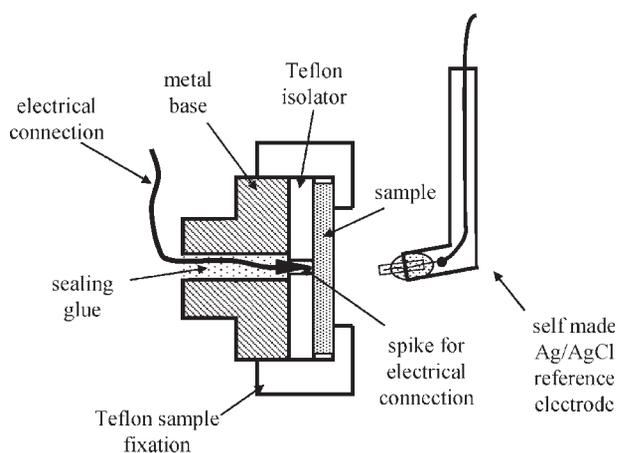
Fig. 3. Cross-sectional views of the sample holder and the reference electrode showing the electrical connection of the sample. The sample is fixed in the holder by two Teflon parts sealing the cut edges of the sample from the electrolyte. In addition, the sample is isolated electrically from the metal base of the holder. The connection with the multiplexer system is realized by a little spike at the backside of the sample. The reference electrode is placed in front of the opening of the outer Teflon fixation

Experiments that require a polarisation of the sample of interest, of course require an additional electrode as a counter electrode. A Teflon rod supported Pt band electrode, a gold wire coiled Plexiglas electrode and a rigid stainless steel electrode have been successfully employed.

Figure 3 shows details of one possible realisation of the working electrode. It consists of a metal base made from stainless steel with an outer thread. An electrically isolated wire with a sharp spike goes through the inner channel of the metal base and ends in front of the Teflon isolator. The wire is fixed into the channel by means of a silicon sealant. Finally, the holder is assembled by means of a sample fixation that is screwed onto the metal holder pressing the sample onto the metal spike for electrical connection and against the Teflon isolator simultaneously. This construction was water tight as confirmed by the unchanged colour of a piece of silica gel with water indicator that was placed in the small cavity beside the spike during the entire test cycle.

For a simple ocp measurement the multiplexer was connected to a voltmeter. For potentiodynamic measurements and electrochemical impedance spectroscopy a potentiostat and a frequency response analyser were used in addition.

In Fig. 4 the electrical circuitry of one of the 1 to 8 multiplexers is shown. For addressing one of the channels a control command is send to the corresponding multiplexer. To ensure that never more than one sample is connected at the same time a security loop has been realised. It reads back the status of the relays from the multiplexer boxes before it records the ocp or even, more important, polarises a sample to the desired potential.

The control of the equipment as well as the storage of the data are realised by in-house developed software. It was realised in the visual engineering environment Agilent VEE.

A standard PC can be used which might be extended by additional interface ports such as serial ports or through an IEEE 488 expansion card. The control program analyses the status of the machine, switches the drying system on or off and controls the positions of the samples by sending the required control codes to the step motor control. Data
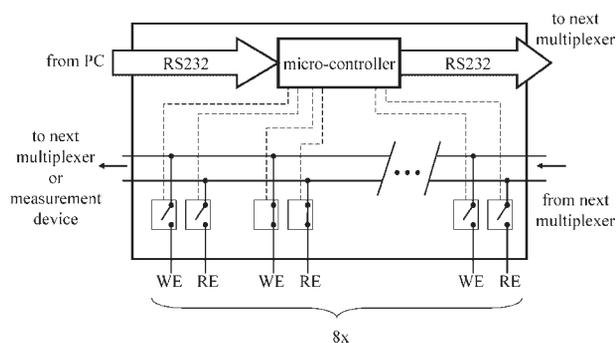

Fig. 4. Sketch of the electrical wiring for the multiplexer device used in the set-up. Up to 255 multiplexers could be connected and addressed in a cascade to the computer over the serial RS232 bus. Each of the multiplexers has a maximum of eight input pairs for measuring sample signals. During operation only one sample at a time is connected to the measurement device
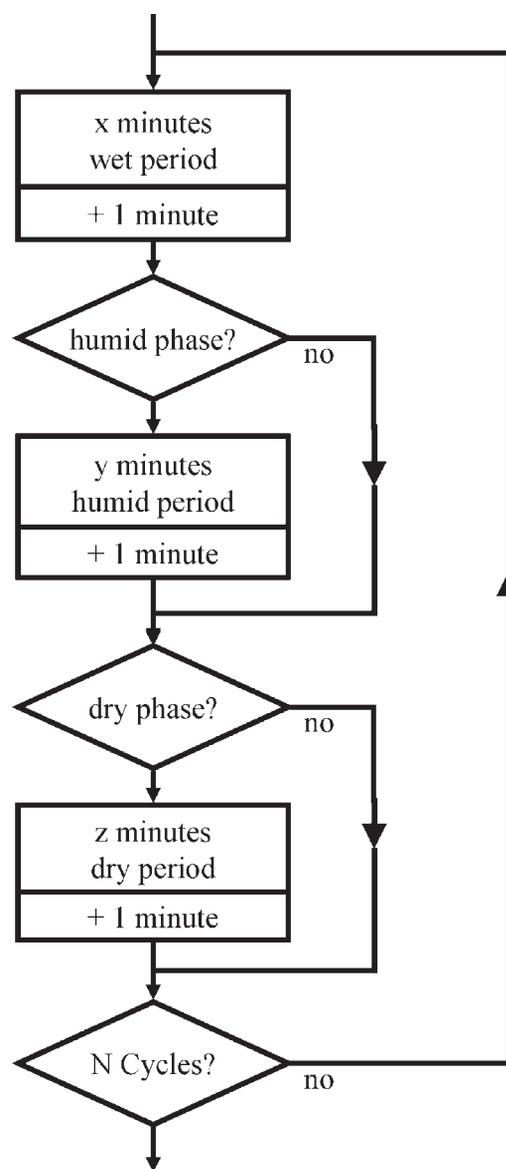

Fig. 5. Flowchart of the cyclic testing that can be performed. Humid and dry phase are optional

Table 1. Composition of the low-alloyed steel types studied in the accelerated corrosion tests

Steel type	Element (wt%)							
	C	Si	Mn	P	S	Cr	Cu	Ni
Mild steel	0.13	0.23	1.45	0.013	0.003	–	–	–
Weathering steel	0.11	0.41	1	0.011	0.006	0.5	0.33	0.16
3Ni steel	0.1	0.29	1	0.019	0.002	0.006	0.37	3.04

The amounts of the listed elements are given in weight-percent.

acquisition and storage to a hard disc and to a flash storage is realised in concurrent backup. An unexpected power break will be automatically handled by an interrupt routine to ensure that the data acquired so far are stored in a protected data storage area depending on where the last valid data set was available.

The immersion simulator introduced here allows the simulation of any wet/humid/dry cycle with completely free decision of duration of each test period ranging from minutes to days or even weeks, if necessary. This is important especially when the required time of wetting is investigated [11]. Additionally, the inclusion of the humid and dry period into the test is selectable by setting these periods' duration either to zero or to a value different from zero.

Figure 5 shows the flow chart of a feasible test cycle. Due to technical restrictions, an additional time gap of 1 min is used between phase changes in which the samples are moved to their new position.

2.2 Accelerated corrosion testing of low-alloyed steels

The new test equipment was applied to low-alloyed steels with different compositions especially with respect to the alloying elements nickel and chromium (see Table 1). The aim of this testing was directed toward an evaluation of the application of these steels under weathering conditions near the coast if the chloride content of the atmosphere is not negligible. The accelerated cyclic immersion tests were therefore performed simulating the natural day and night changes using different exposure times. In addition, the

influence of electrolyte solutions with different chloride concentrations was used. An overview of the test conditions and cycles is given in Table 2. Due to the type of these investigations the fast drying system was not used in the experiments. During immersion potential and impedance measurements were performed using an EG&G potentiostat and a SOLARTRON frequency response analyser.

2.3 Accelerated corrosion testing of zinc-coated steel sheets

In a second case the machine was used for the accelerated testing of zinc-coated steel sheets. The goal was to get information about their corrosion behaviour under accelerated cyclic testing and to monitor the influence of various pre-treatments. Also, the role of exposure time was of interest. These experiments are part of investigations dealing with the behaviour of zinc-coated steel sheets with different zinc alloys, for use in the automotive industry, and the understanding of the corrosion processes going on under protecting paint coatings. They are also relevant for the investigation of the environmental embrittlement of automobile spring steels [12]. The sample specifications are given in Table 3. For these tests the pressure air drying system was used to accelerate the test cycles. The experimental details are summarized in Table 4.

2.4 Accelerated corrosion tests on other systems

Several other corrosion tests have been performed with this set-up. The investigation of biomedical materials such as titanium [13] or shape memory alloys like NiTi [14] can be performed in artificial saliva, simulating the conditions of wet–dry cycles if a material is used for orthodontic arch wires. With these tests a quick screening of the performance of a process becomes possible [15]. Other materials or sample geometries such as copper [16], copper-based alloys like brass or bronze [17] and zinc alloys [18], have been tested as well. In this case the CO_2 content of the air can be of importance which can be simply realised under the tests conditions when a CO_2 enriched test gas is blown against the sample.

Table 2. Different test cycles for the accelerated testing concerning the corrosion behaviour in chloride containing environments. Accelerated drying was not used in this test

Test type	Test periods and conditions		
	Wet period (immersion in x mM NaCl)	Humid period ($\approx$95% rH, $\approx$20°C)	Dry period ($\approx$55% rH, $\approx$20°C)
10 mM, 3 h	3 h, 10 mM NaCl	2 h	7 h
40 mM, 3 h	3 h, 40 mM NaCl	2 h	7 h
40 mM, 9 h	9 h, 40 mM NaCl	2 h	7 h

Table 3. Nomenclature for the surface treated hot-dip galvanized steel sheets undergoing accelerated screening tests

Sample identifier	Sample layout		
	Substrate	Protective coating	Surface treatment
ZN	Standard steel type DX 56	Hot-dip galvanized (zinc $\approx$99,5%)	Untreated
ZP	Standard steel type DX 56	Hot-dip galvanized (zinc $\approx$99,5%)	Trication-phosphatisation (Granodine 5855)
ZG	Standard steel type DX 56	Hot-dip galvanized (zinc $\approx$99,5%)	Chrome-free pre-treatment (Granodine 1455)

Table 4. Test cycles for the accelerated screening test of the hot-dip galvanized steel sheets

Test identifier	Test periods and conditions		
	Wet period (Immersion in 5 wt% NaCl)	Humid period (≈95% rH, ≈20 °C)	Dry period (<10% rH, ≈20 °C)
1 min/30 min	1 min	–	30 min
15 min/30 min	15 min	–	30 min
Continuously	Whole runtime	–	–

3 Results

Figure 6 shows potential transients recorded on different steel types. A 40 mM NaCl solution was used in a test cycle of 3 h wetting, 2 h humid (≈90–95% rH) and 7 h drying at ambient conditions. The transients show the potential during the immersion period of the corresponding immersion cycle. It is seen that the potential is similar for all three materials. After about 20 cycles, differences become visible especially between the weathering steel, which shows a slower increase in the corrosion potential as compared to the 3Ni steel and the mild steel. During the initial 20 cycles the weathering steel showed the steepest increase in corrosion potential. Afterwards the increase per cycle slows down significantly and a more or less linear increase with about 1 mV/cycle is observed. The phase of steeper increase is longer for the mild steel and in particular for the 3Ni steel. This behaviour of the 3Ni steel is not surprising and it results from the enrichment of Ni in the rust layer forming. The corrosion potential of the 3Ni steel remains the highest even after 180 cycles.

The advantage of this approach is the formation of a rust layer or patina, as it would be called in the case of weathering steels, in a short time. Further studies on the oxide layers are possible, e.g. by means of an oxygen consumption Kelvin probe [19]. The test presented here is in this way useful for performing a screening of various alloys which can be subsequently investigated by a confirmatory test.
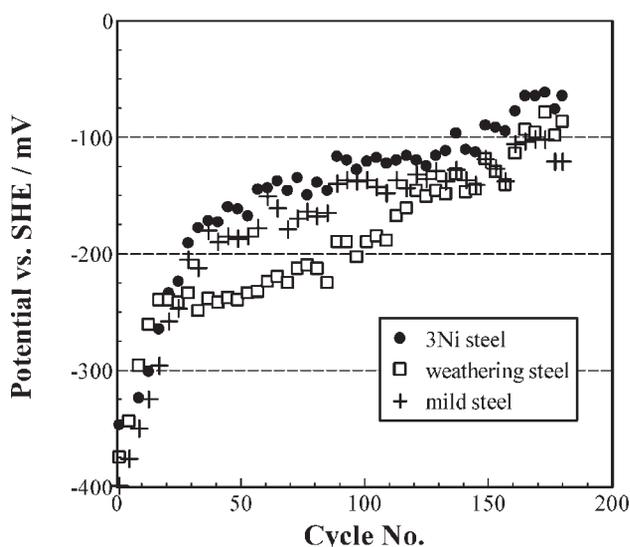
This versatile corrosion simulator allows completely different investigations one of which should be exemplified here. In Fig. 7 a typical potential transient of a hot-dip galvanized sample without additional surface treatment (type ZN) is shown. A heavily accelerated cycling procedure was employed here. The sample was immersed for only 1 min into a 5 wt% NaCl solution and subsequently dried for 30 min with cleaned and dried pressure air at room temperature. After 2 days an initial change of the potential is seen but a strong increase after 3 days for about 350–400 mV indicates the breakdown of the corrosion protection. A plateau is reached on the fourth day that coincides with the complete coverage of the sample by red rust. This red rust is formed from the bulk of the steel. A simple optical inspection would not give these results with this accuracy.

In Fig. 8 the time required for achieving a complete coverage with red rust is given. The missing bars indicate conditions under which a complete coverage with red rust could not be obtained during 12 days of testing. Obviously, there is a tremendous influence of the test conditions on the corrosion rate. For none of the three coatings a complete coverage was found for a continuous wetting. A combination of 15 min immersion with a period of 30 min drying lead to a complete coverage for the ZN and the ZG coating but not for the ZP coating. An accelerated cycle with a wetting time of only 1 min and the same drying time of 30 min yield complete red rust coverage for all three
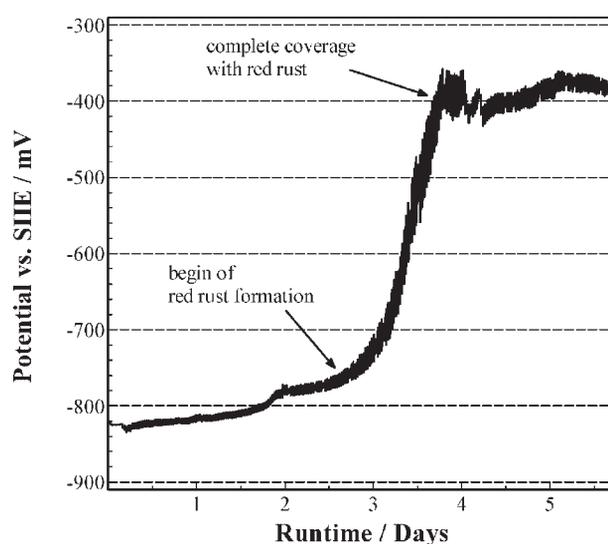
Fig. 6. Corrosion potential transients for three different types of low-alloyed steels undergoing a corrosion test concerning their passivation behaviour under chloride containing environments. The data shown is from a test with a 40 mM NaCl solution and a test cycle of 3 h wetting, 2 h humid (≈90–95% rH) and 7 h drying at room conditions

Fig. 7. Corrosion potential of a hot-dip galvanized steel sample without additional surface treatments. The sample underwent a test cycle including 1 min wetting and 30 min drying with use of the fast pressure air drying system. Complete coverage by red rust was observed after 4 days. This observation is confirmed by the potential change that reaches a plateau after 4 days
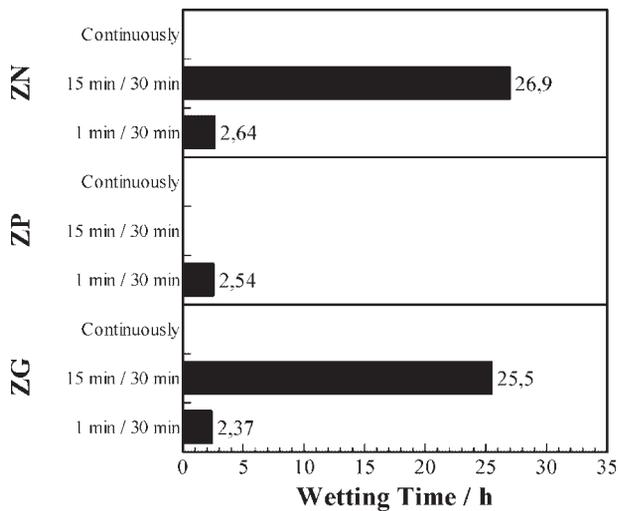
Fig. 8. Time required achieving complete rust coverage on samples with different surface treatment depending on the wetting time and type of performed cyclic testing. The missing values represent samples on which a complete red rust coverage was not observed within 12 days

coatings within less than 3 h of wetting time. These results demonstrate that acceleration by a factor of 10 with respect to the wetting is possible.

Testing of these samples was performed in a standard salt spray test but the same attack could not be reached within the entire test cycle of 4 weeks.

4 Discussion and conclusions

A universal alternating corrosion simulator was developed that is extremely versatile and useful for a large number of different corrosion tests. The modular set-up allows an efficient adaptation to the requirements of the user. The basic set-up consists of a basin and a step motor driven rail allowing a random positioning of the sample either in the electrolyte during immersion, above the electrolyte during the humid phase or outside the basin during the dry period. A set of reference electrodes, one for each sample is used for monitoring the ocp during immersion. Eight channels multiplexer are used to select either of the samples in one basin. Since the multiplexers are connected in a daisy chain, an extension of the set-up by more units is straightforward. Since both working and reference electrodes are disconnected by the relays one common counter electrode can be used for experiments in which further electrochemical measurements such as cyclic voltammetry or impedance spectroscopy are used. Rapid drying of the samples is achieved by a physical drying unit that uses a laminar flow of physically dried pressure air. This rapid drying allows an acceleration of the corrosion tests especially those in which

the wet–dry transition is the overall rate-determining step. The share of these conditions can be significantly increased, which might lead to an acceleration by a factor of 10 or more as compared to slower cycling or continuous immersion.

The system can be easily modified and allows for example the production of A4 size steel sheets of weathering steel as samples for cosmetic evaluation of samples.

5 References

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