Can the corrosion of components be simulated experimentally with coupons?

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Plate-shaped coupons offer a number of advantages for corrosion investigations, such as simple geometry and typically good manufacturability from components or material residues. Disadvantages are the limited volume and thus the limited chemical reservoir as well as the influence of corners and edges. In this paper, tests on coupons are compared with tests on pipes made of the same material and identical annealing conditions. The differences prove that the conclusions from coupons are not fully compatible with the observations on tubes.

Introduction

The data obtained from corrosion tests at various locations are always difficult to compare. This was generally observed regardless of the type of corrosion /1, 2, 3/repeated. These observations are also contrasted with examples from which it was concluded that parallelism is acceptable. Similar to the field test, the laboratory test on coupons may already show different corrosion conditions due to the location in the reactor, which lead to different corrosion rates or different characteristics of the corrosion layer. This applies in particular to experiments that are not performed under static conditions /4/. Other studies show that the principal mechanisms observed in laboratory experiments also work in real plants. S. Karlsson compared the effect of sulphur on chloride corrosion in laboratory tests and in a real waste incineration plant /5/. Also in the comparison between 2 experiments in the same laboratory the difference between the measured minimum and the measured maximum of the mass change of the samples can be clearly larger than the mean value of the mass change itself /6/. The comparison in this paper considers tubes for steam generators in power plants made of bainitic and martensitic materials with a mass fraction Cr between 0.024 and 0.12 and an austenite DMV310N with 0.245 Cr and 0.21 Ni. The VM12SHC is shown as a representative example.

Preliminary consideration

Coupons change the geometry of the corrosive interface in relation to the surface, which does not happen with pipes. This makes the oxidation kinetics laterally inhomogeneous. In particular, the area along the edges changes the transport routes, Figure 1. The original surface of the metal is rounded off by corrosion and the length of the boundary in cross-section relative to the length of the corresponding edge length becomes smaller. The limit line is only 0.64 of the corresponding length. Under the assumption that the surface of the oxide can absorb the same amount per unit area of reactive elements or

molecules and the concentration at the interface under the assumption of a reaction equilibrium identical at the interface, the chemical gradient in the edge region is determined by the ratio of the receiving surface to the metal oxide interface and the local layer thickness. If a uniform loss of material Δx is applied in all three spatial directions, then the actively corroding surface A´ of the coupon with the edge lengths a, b, c and, neglecting all terms, the square term $(\Delta x)^2$ is included,

$$A' \approx 2(ab+ac+bc-4(a+b+c)\Delta x)$$

If the active interface to the original surface falls below the ratio 0.95, the coupon is used and longer experiments would increase the influence of the change in chemical gradient. At the same time the metal will change its local composition by diffusion of mobile elements.

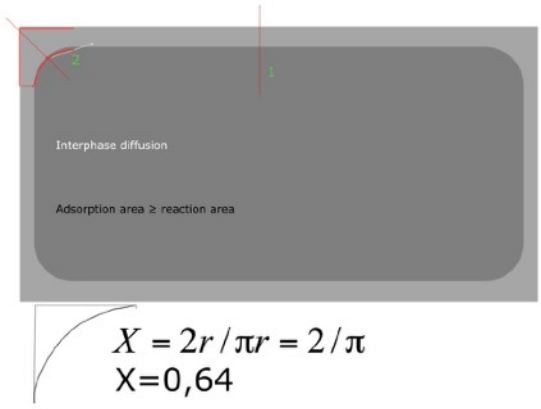


Figure 1: Changes in the geometry of the actively corroding interface.

This effect becomes essential when long oxidation times are desired. Coupons usually have less volume and the depletion of diffusing elements we faster will also be effective in the middle of the sample. Both described boundary conditions cause our team to use coupons only for a limited time depending on their size and the corrosion rate. For the purposes of this discussion, the test duration under consideration is 1000 h.

Experiments

The tests on coupons were carried out in flowing flue gas. The smoke composition in mol/100 mol was 67 CO_2 - 30 H_2O - 2 O_2 - 1 SO_2 and in few experiments with 0.5 mol SO_2/100 mol. With a reduced SO_2 content, the CO_2 content was increased. The test temperatures included in the comparison were 575 °C for the samples containing 0.024 Cr by mass and 600 °C for the materials with higher Cr content. Samples with a test time of 1000 h were selected for comparison. The flue gas velocity was set at 0.01 m/s in both test arrangements. The coupons are isothermally stored, since the thermal gradient over the length of the sample is less than 1 K. The coupons are isothermally stored. The pipes build up a thermal gradient along the pipe axis, which can amount to about 100 K/m. The thermal gradient of the pipes is determined by the thermal gradient of the pipe axis. During the test, preheated steam with a pressure of 270 bar was conducted through the inside of the pipe, which significantly influenced the thermal gradient. The temperature

control along the pipe axis is carried out with at least 5 maximum 7 thermocouples, which are attached to the pipe with NiCr brackets. The used corrosion equipment for coupons fig.2 and tubes fig. 3 is used simultaneously in our laboratory.

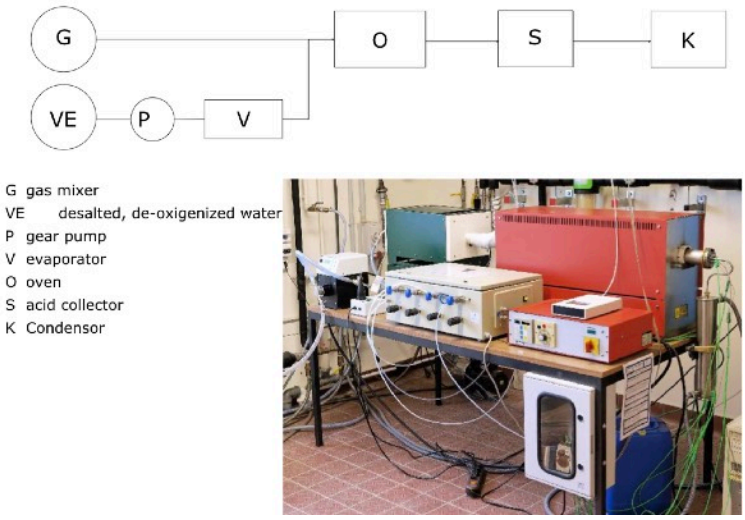


Figure 2: Experimental setup for coupon experiments

surface are fixed. A bracket fixes the tip of the thermocouple to the tube surface. The brackets are spot welded electrically. A good heat transfer is ensured by the welded joint.

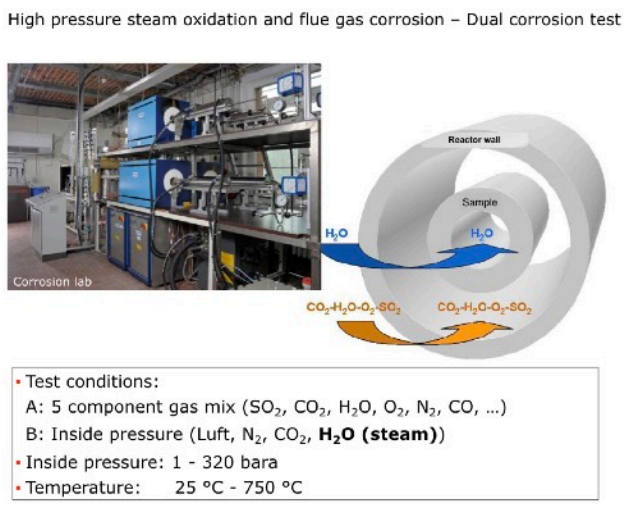


Figure 3: Device for testing steam generator tubes

Materials and sample preparation

Table 1: Materials in comparative test.

Steel	alloy.		C	Si	Mn	Cr	Ni	Mo	W	Co
T24	7CrMoVTiB10-10	1.7378	0.05 -0.1	0.15-0.45	0.3 – 0.7	2.2 - 2.6		0.9 – 1.1		
P92	X10CrWMoVNb9-2	1.4901	0.07-0.13	< 0.5	0.3-0.6	8.5 – 9.5	< 0.4	0.3-0.6	1.5 - 2	
VM12SHC	X12CrCoWMoVNb12-2-2	1.4915	0.155	0.49	0.35	11.5	0.29	0.29	1.5	1.6
DMV310N	X6CrNiNbN25-20	1.4952	0.05 - 0.07	0.3 – 0.5	1.0 - 1.4	24.5 -25	20.8-21.5			

Table 1 shows the standard composition of the materials under consideration. All samples were examined with regard to their composition. The material composition was always within the specification.

The evaporator tubes were cleaned from impurities inside and outside with ethanol. Rust film and loose corrosion layers resulting from storage were brushed off before wet cleaning. The pipes were not mechanically machined and thus incorporated into the corrosion test as they were produced. Some power plant operators pickling the inner surface of the pipes to remove the oxide layer from the production process. This was not done before these experiments.

The coupons were made from the pipes and had different sizes depending on the pipe wall thickness. Typical dimensions are 20 x (10 - 15) x (3 - 6) mm, with the long side parallel to the pipe axis. The surface is ground and polished. The final polishing was carried out with 3 µm diamond paste, which results in surface roughness R_a below 0.01 µm.

Measurement techniques

The layer thicknesses were determined by measuring the layer on optical microscopic images. Element distributions were recorded with a microprobe JEOL JXA-8900 RL or

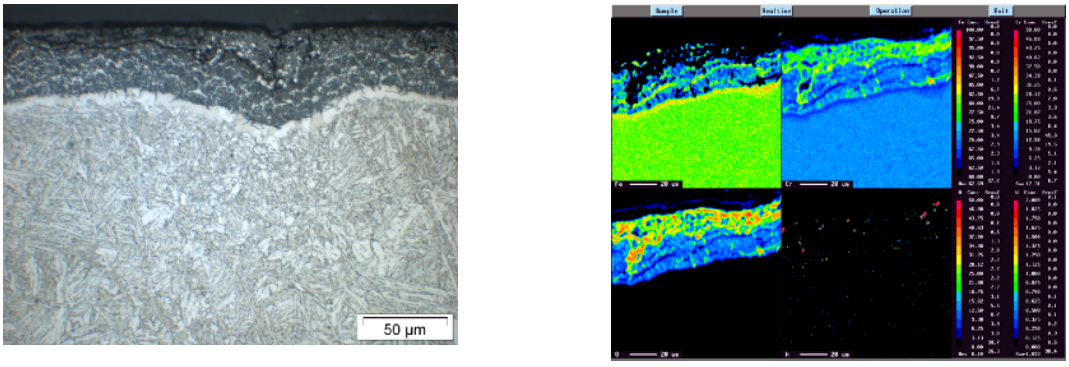
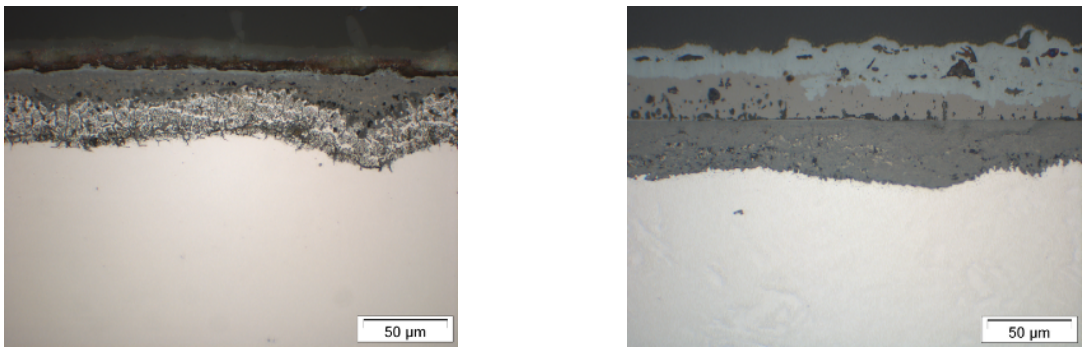


Figure 4: right the structure of the VM12 SHC and the layer produced on the pipe surface by the production, left the element distribution within the surface layer. The element



distribution diagram shows Fe at top left, Cr at top right, O at bottom left and W at bottom right.

Figure 5: on the right the surface of the annealed pipe and on the left the corroded surface of the coupon.

with the scanning electron microscope LEO 1530 VP. The exterior of the pipes exposed to the flue gas was examined and compared with the coupons stored in the flue gas.

Results

Differences between the prepared and adapted surfaces of the coupons and the surfaces of the tubes can be determined for all samples. The tubes also have different surfaces as a result of the manufacturing process. The coupons have a smooth surface due to the polish, while the surface of the tubes is uneven parallel to the tube axis, Figure 4. In this paper the VM12SHC is shown as a representative example. The structure of the coupons corresponds in each case to the structure of the pipes, since they were prepared from these. The drawn tubes have a mixed structure of remaining alloy and oxide on their surface. This layer adheres exceptionally well to the pipes and is dense. Figure 4 shows a comparison between the microstructure and the element distribution of a VM12 SHC tube. It can be seen that the surface already has a Cr-enriched zone after manufacture, which effectively reduces high-temperature corrosion in the test. As a result, the corrosion rate measured on the coupon is always higher than the corrosion rate measured on the industrially manufactured pipe. After removal from storage, the original mixed structure of the pipes is still preserved, as is their protective effect. The tube shows no zone of internal oxidation. The outer hematite layer, recognizable by its light grey hue, is neglected thin. Additional oxide is externally grown and forms a dense layer. Sulphur is only stored in the outer oxide layer. The coupon shows a pronounced inner oxidation zone and a comparatively thick layer of hematite. Sulphur is also stored in the inner oxidation zone. Both samples show oxidizing internal interfaces. Already from the thickness of the oxide layer it becomes clear that the oxidation rate of the tube is significantly lower than the oxidation rate of the coupon, Fig. 5. Similar observations apply to all materials. A summary of the outer surface of industrial pipes is shown in Figure 6.

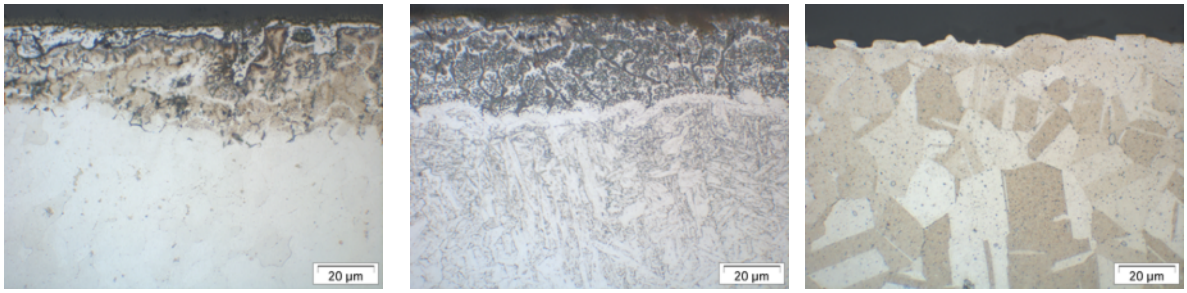


Figure 6: From left to right the surface of drawn tubes made of T24, P92 and DMV310N is shown.

Discussion and Conclusion

Depending on the manufacturing method, the surface of industrially manufactured pipes already has a modified surface with a mixed structure of metallic material and oxide. In all cases an enrichment of Cr in the oxidic material of this layer could be detected. The exception is the DMV 310 N, which had no such layer.

This process-related difference between the technical components and prepared coupons makes it very unlikely that the initial oxidation in the first thousands of hours is comparable. In addition, during this time the driving force for diffusion in the pipe remains almost identical, while the metallic part of the coupon changes geometrically, whereby the gradient of the chemical potential varies locally in the area of the edges and corners. As a result, local corrosion attacks on pipes were observed far less frequently. "Hot corrosion" was not possible under the experimental conditions.

Under all test conditions applied in thus study, the corrosion rate of the industrial was lower than that of the coupons. A lifetime estimate based on the corrosion kinetics of the coupons would have underestimated the lifetime of the tubes.

Literature

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