Erosion-corrosion of carbon steel in wet steam

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Summary

The resistance against erosion-corrosion in wet steam was determined for 58 steels in a laboratory test. Minute quantities of chromium, copper, and molybdenum in-crease the resistance against erosion-corrosion. The erosion-corrosion resistance (R) can be calculated by the regression equation R = 0.61 + 2.43 Cr + 1.64 Cu + 0.3 Mo. Steels from in-service erosion-corrosion failures showed low resistance against erosion-corrosion in the laboratory test. No failures were found in steels with a calculated resistance value R of more than 1.0.

Introduction

Suspended iron oxides in steam-water circuits may cause trouble in both conventional and nuclear power stations. This happens rather often; e.g., corrosion in conventional boiler evaporators, corrosion in PWR steam generators and deposition of iron oxides on fuel elements in nuclear reac-tors.
In view of these problems, it is recommended that the iron content in steam water circuits be kept as low as possible. This iron comes from erosion-corrosion, the major sources of which are water separators, wet steam pipes, preheaters, and evaporators.
Erosion-corrosion depends on water chemistry, water velocity, and chemical composition of the steel. This report focuses on the relationship between the chemical composition of steel and erosion-corrosion resistance. This relation-ship has been neglected in the past because water chemistry and velocity were thought to be the dominant factors.

Experiment

Test apparatus

Discs of steel samples were exposed to wet steam. The samples were weighed before and after exposure. Weight loss after 100 hours of exposure was used to determine the resist-ance against erosion-corrosion.
The design of the test equipment is shown in Figure 1. Water (10 wt%) was injected into the steam before the opening of the jet tube. The sample was mounted in the test chamber at a distance of 5 cm and an angle of 45° below the jet tube opening. The test equipment consisted of 24 test chambers, and the steam and water came from the experimental test rig (Figure 2).

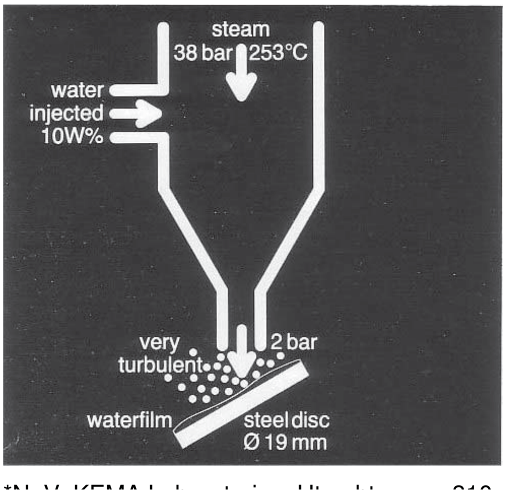

Figure 1 - Design of the erosion-corrosion loop.

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Figure 2 - Experimental boiler and erosion-corrosion test equipment.

The jet tube had a pressured drop of 36 bar, from 38 bar to 2 bar. The steam velocity at the exit tube was calculated to be 960 m/s (supersonic). The steam temperature was 253° C. The metal temperature (127° C) was measured during the test with a thermocouple in a steel test specimen. The water-steam mixture consisted of 25 wt% of water as it left the test chamber. Conductivity and oxygen content in the injected water and steam condensate were lower than $30\ 10^{-6}$ S/m and 210^{-9} kg/kg. The high water content in the test chamber must have caused a highly turbulent water film on the steel discs. Under these conditions. the corrosion rate depends considerably on the diffusion velocity of matter involved in the corrosion reactions.

Steel specimens

A number of steel samples were taken from various components of electric power stations. Some samples came from parts where severe erosion-corrosion had occurred. Many new materials were received from steel and boiler manufacturers. Discs were machined to a diameter of 19 mm and a thickness of 1 mm. The surfaces were fine ground. All the samples were exposed in duplicate. Because only 24 test chambers were available, the steel samples were tested in various batches. The steels listed in Table 1 have been grouped by increasing weight loss.
This research covered three types of steel: mild steel, 15Mo3 (0.3% Mo) and 14Mn4 (1 % Mn) steel. The reference steel used in the tests was carbon steel No. 7. The weight losses suffered after 100 hours of exposure were between 61 and 69 mg for the total of 6 test series for this reference steel.

Results

Detailed chemical analyses were conducted for all steels. The analyses were all done in the same way by the same staff. Compositions and weight losses after exposure are given in Table 1. The table shows higher weight losses with a decrease in Cr, Cu, and Mo content. The frequency distribution of weight losses is given for the three steel categories in Figure 3: the in-service failures are shown in full black.
It was remarkable that steels from evident cases of erosion-corrosion damage also gave the highest weight losses after exposure.

Correlation between composition and weight losses

The absolute weight losses (G) of the steels to their chemical composition has been correlated [1,2]. The following regression equation was found for the steels listed in Table 1:

$$G=94-100Cr-120Cu-35Mo \qquad (1)$$

Significance level = 0.99:
Cr, Cu, and Mo wt% in the steel.
Ducreux[3] used a good method of calculating the regression equation for his erosion-corrosion test results. In each experiment, he included a reference steel; the ratio of weight loss of the reference to that of the steel sample served as a measure of erosion-corrosion resistance.

He found the following regression equation for his test conditions on unalloyed and low alloyed steels (up to 2.25% Cr):

$$R_{EdF} = - 5.2 + 28.9\, Cr + 51.9\, Cu + 11.5\, Mo \quad (2)$$

Significance level = 0.989.

The advantage of this method is that small variations in test conditions can be neglected. When applying the Ducreux method to the tests described here, the following regression equation is found for carbon steels:

$$R_{KEMA} = 0.61+2.43Cr+1.64Cu+0.3Mo \quad (3)$$

Significance level = 0.925.

TABLE 1 - Wet steam erosion-corrosion test results

Specimen No.	C	Mn	Si	P	S	Cr	Mo	Al	Cu	Ni	Average Weight loss
1	0.14	0.58	0.22	0.009	0.027	0.26	0.02	0.01	0.16	0.06	43
2	0.1	0.55	0.04	0.006	0.026	0.05	0.01	0.01	0.19	0.07	57
3	0.09	0.49	0.1	0.005	0.028	0.05	0.01	0.01	0.2	0.08	58
4	0.15	1.13	0.32	0.024	0.023	0.12	0.03	0.01	0.19	0 08	60
5	0.13	1.1	0.48	0.017	0.025	0.08	0.05	0.01	0.22	0.12	61
6	0.16	1.03	0.33	0.022	0.029	0.08	0.02	0.01	0.11	0.17	61
7	0.1	0.65	0.18	0.021	0.024	0.08	0.02	0.01	0.14	0.08	62
8	0.2	1.25	0.55	0.004	0.011	0.22	0.04	0.045	0.05	0.06	62
9	0.17	0.72	0.25	0.006	0.014	0.07	0.29	0.005	0.04	0.03	63
10	0.14	0.61	0.18	0.004	0.021	0.04	0.26	0.01	0.07	0.04	63
11	0.15	0.61	0.16	0.009	0.025	0.04	0.27	0.005	0.1	0.02	64
12	0.22	0.56	0.18	0.009	0.023	0.06	0.04	0.005	0.17	0.06	66
13	0.13	0.99	0.37	0.016	0.022	0.04	0.02	0.01	0.18	0.08	66
14	0.1	0.98	0.21	0.008	0.018	0.05	0.04	0.005	0.1	0.1	67
15	0.12	0.98	0.37	0.012	0.01	0.04	0.02	0.01	0.03	0.03	69
16	0.15	1.3	0.34	0.012	0.017	0.1	0.4	0.005	0.03	0.08	70
17	0.14	0.57	0.23	0.009	0.01	0.11	0.29	0.01	0.07	0.06	70
18	0.12	0.98	0.37	0.012	0.016	0.04	0.01	0.01	0.03	0.03	70
19	0.12	1.47	0.47	0.015	0.016	0.1	0.005	0.02	0.04	0.02	71
20	0.12	1.01	0.39	0.011	0.013	0.04	0.01	0.01	0.03	0.03	71
21	0.14	0.57	0.26	0.015	0.032	0.042	0.01	0.01	0.11	0.06	72
22	0.14	0.62	0.22	0.004	0.007	0.04	0.5	0.01	0.04	0.03	72
23	0.16	0.59	0.24	0.004	0.022	0.04	0.26	0.01	0.1	0.06	73
24	0.18	0.68	0.21	0.006	0.02	0.05	0.26	0.01	0.1	0.06	73
25	0.14	0.58	0.25	0.015	0.031	0.043	0.01	0.01	0.11	0.05	73
26	0.18	0.52	0.34	0.008	0.017	0.04	0.05	0.005	0.1	0.04	75
27	0.18	0.94	0.18	0.012	0.01	0.04	0.01	0.01	0.02	0.03	75
28	0.16	0.7	0.19	0.006	0.019	0.02	0.28	0.01	0.04	0.02	76
29	0.21	1.31	0.42	0.016	0.021	0.24	0.01	0.055	0.08	0.07	76
30	0.19	1.09	0.57	0.01	0.009	0.14	0.04	0.03	0.12	0.22	76

31	0.15	0.73	0.25	0.013	0.014	0.02	0.29	0.01	0.03	0.03	76
32	0.11	0.54	0.07	0.009	0.017	0.03	0.01	0.04	0.05	0.04	76
33	0.16	0.69	0.18	0.007	0.02	0.02	0.28	0.01	0.04	0.02	77
34	0.15	1.22	0.38	0.017	0.013	0.02	0.01	0.01	0.03	0.04	78
35	0.08	0.5	0.18	0.012	0.012	0.06	0.01	0.02	0.04	0.04	79
36	0.09	0.56	0.18	0.01	0.014	0.02	0.01	0.02	0.03	0.02	79
37	0.16	0.73	0.18	0.006	0.018	0.02	0.27	0.01	0.04	0.02	79
38	0.16	0.7	0.2	0.006	0.015	0.02	0.28	0.01	0.04	0.02	79
39	0.1	0.48	0.25	0.009	0.026	0.03	0.01	0.005	0.1	0.04	80
40	0.16	0.72	0.2	0.006	0.02	0.02	0.27	0.01	0.04	0.02	81
41	0.15	1.18	0.33	0.008	0.018	0.05	0.02	0.01	0.18	0.07	83
42	0.1	0.51	0.14	0.008	0.016	0.03	0.01	0.01	0.04	0.02	83
43	0.09	0.51	0.18	0.009	0.021	0.02	0.01	0.01	0.04	0.02	85
44	0.16	1.09	0.26	0.02	0.032	0.03	0.01	0.01	0.12	0.06	88
45	0.14	1.05	0.005	0.014	0.019	0.017	0.003	0.003	0.05	0.02	89
46	0.16	1.11	0.42	0.007	0.022	0.08	0.02	0.03	0.1	0.06	89
47	0.1	0.49	0.2	0.011	0.022	0.02	0.01	0.02	0.03	0.02	90
48	0.18	0.99	0.28	0.011	0.009	0.02	0.005	0.03	0.01	0.02	90
49	0.1	0.48	0.2	0.007	0.018	0.02	0.01	0.01	0.02	0.02	90
50	0.37	0.63	0.32	0.004	0.026	0.02	0.01	0.01	0.07	0.04	91
51	0.1	0.49	0.16	0.012	0.024	0.02	0.01	0.02	0.03	0.02	93
52	0.15	1.15	0.005	0.027	0.034	0.01	0.003	0.003	0.04	0.02	95
53	0.09	0.55	0.1	0.028	0.018	0.01	0.005	0.02	0.03	0.05	97
54	0.18	1.09	0.005	0.011	0.025	0.018	0.003	0.003	0.06	0.02	98
55	0.17	0.64	0.26	0.015	0.014	0.01	0.005	0.02	0.02	0.01	98
56	0.17	0.64	0.28	0.017	0.016	0.005	0.003	0.02	0.02	0.02	103
57	0.18	1.11	0.32	0.014	0.024	0.014	0.003	0.05	0.02	0.02	107
58	0.09	0.97	0.23	0.009	0.014	0.01	0.005	0.003	0.01	0.01	116

In red: specimens obtained from real erosion-corrosion failures

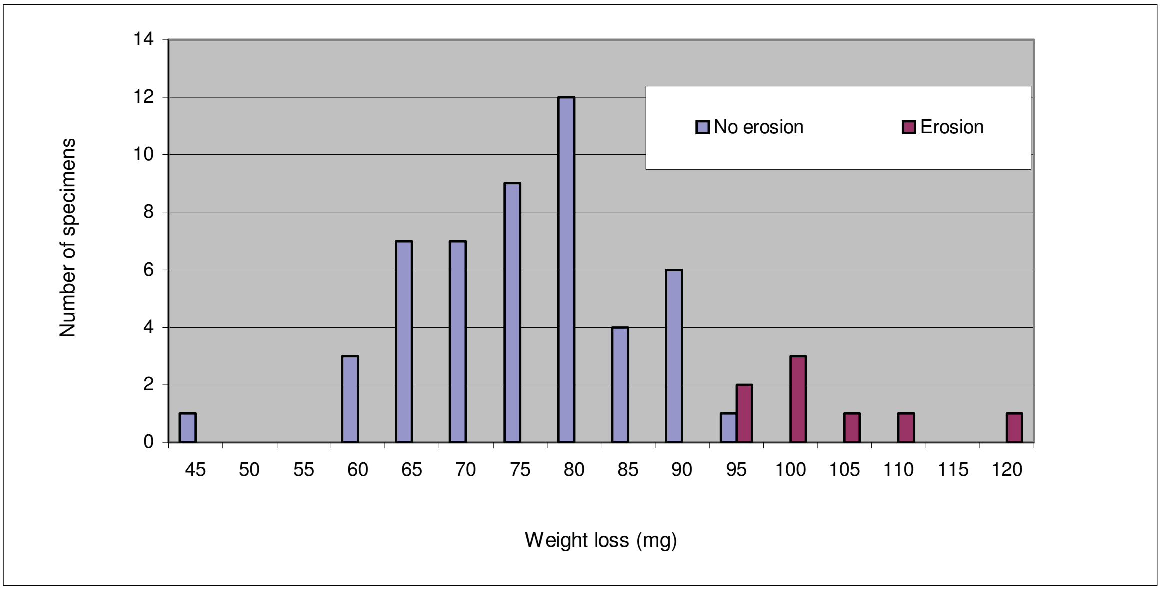

Figure 3 - Frequency distribution of measured weight losses after exposure- Full black indicates that the specimens were obtained from in-service failures because of erosion-corrosion.

In-service failures

After finishing the experiments in 1982, several erosion-corrosion cases were offered for further research. Because good fitting correlation equations had been established, the new samples were not tested in the erosion-corrosion loop. They were only analyzed chemically as to Cr, Cu and Mo content, and the erosion-corrosion resistances were calculated.

Table 2 gives a survey of the cases, and Figure 4 shows the frequency distribution diagram.

The failures occurred in the steam-water circuit of power stations, i.e.. In water separators, wet steam pipes, economizers, preheaters, and evaporators. Hydraulic conditions and chemical water treatment can differ greatly for these components.

Table 2 - In-service failures

Case No.	Erosion corrosion	Origin of samples	Calculated resistance to erosion corrosion (R)
1	Yes	Plate in steam expansion vessel of experimental boiler	0.9
2	Yes	Steam sieves	0.74
	Yes		0.68
	Yes		0.72
3	Yes	Spindle	0.75
4	Yes	Switch levers	0.65
	Yes		0 73
5	Yes	Control valve housing	0.67
6	Yes	Wet steam pipe of welded plates in BWR	0.67
	No		0.89
	N o		0.89
7	Yes	Wet steam tubes in BWR	0.69
	Yes		0.69
8	Yes	Water separator of BWR	0.76
	Yes		0.7
9	Yes	Water separator of PWR	0.65
	Yes		0.65
	No		1.2
10	No	Preheater of back pressure unit	1.03
	Yes		0.74
11	Yes	High pressure preheater tubes with butt welds (downstream)	0.81
	Yes		0.84
	No		1.01
12	Yes	Low pressure preheater: Slight erosion-corrosion in 3 tubes.	0.97
	Yes		0.84
	Yes		0.96
13	Yes	Low pressure preneater	0.93
14	Yes	Low pressure Preheater	0.74
	Yes		0.88
15	vies	Connection tubes trom low pressure evaporator to outlet header	0.66
16	Yes	Bent tube of low pressure evaporator	0.8
	No		1.17
17	Yes	Bent tube of steaming economiser	0.68
18		Removed tubes of Fessenheim heat steam generators	
	No	Cat 1. straight A	1.29
	No	Cat 1. bend D	0.74
	Yes	Gat. 2. straight B	0 74
	Yes	Cat 2. straight C	0.74
	vies	Cat.2. bend D	0.74
	Yes	Cat 3. siraight B	0.74
	No	Cat 3. bend F	0.85
	No	Gat 3. bend E	0 86

Case	R value range	0.6-0.7	0.7-0.8	0.8-0.9	0.9-1.0	1.0-1.1	1.1-1,2	1.2-1,3
1	Protecting plate			1				
2	Steam sieves	1	2					
3	Spindle		1					
4	Switch levers	1	1					
5	Valve housing	1						
6	Wet steam pipe	1		2 (green)				
7	Wet steam tubes	2						
8	Water separator	1	1					
9	Water separator	2					1 (green)	
10	Pregeater		1			1 (green)		
11	Preheater			2		1 (green)		
12	Preheater			1	2			
13	Preheater				1			
14	Preheater		1	1				
15	Evaporator	1						
16	Evaporator		1				1 (green)	
17	Economiser	1						
18	Steamgenerator, Cat 1		1 (green)					1 (green)
18	Steamgenerator, Cat 2		3					
18	Steamgenerator, Cat 3		1	2 (green)				

Green: no erosion corrosion

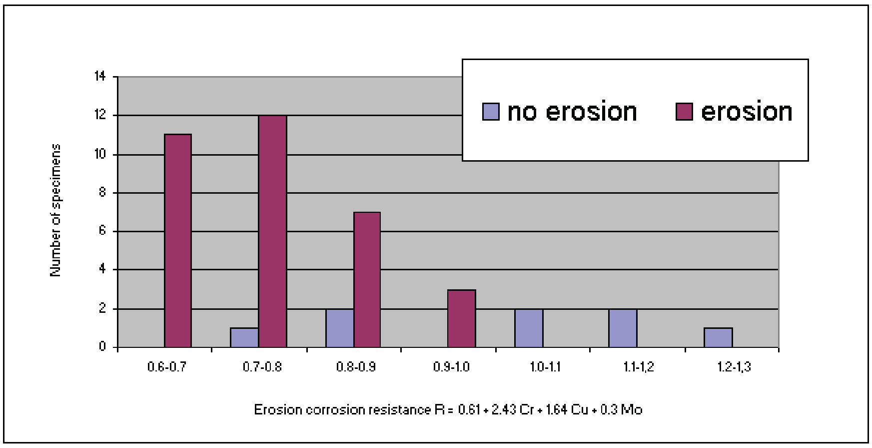

Figure 4 Frequency distribution of the calculated erosion-corrosion resistance R for the steels from the in-service failures. • R erosion-corrosion resistance R 0.61+243Cr+1.64Cu+0.3Mo

Erosion-corrosion was observed on steels having low Cr, Cu, and Mo content: steel parts having higher Cr, Cu, and Mo content did not show erosion-corrosion. Special attention was therefore paid to the cases in which certain parts of the component were corroded but, other parts did not have damage, even though they had been operated under the same conditions.

Various appendages

Power companies provided various erosion-corroded specimens. They came from steam sieves, a spindle, switch levers in feed water pumps, and a control valve housing. All the corroded steels had low Cr, Cu, and Mo content.

Case 1. In the experimental boiler, erosion-corrosion occurred in a steam pressure drop vessel in which steam expands and a water steam jet hits the vessel wall. After 10 years of operation, there was a leakage. The vessel wall had a protecting steel plate opposite the steam inlet tube. The steel plate (10 mm thick) and the vessel wall (5 mm thick) were corroded and leakage occurred.
The resistance R calculated for the steel plate was 0.90.

Case 2. A number of steam sieves suffered erosion-corrosion. Chemical analyses showed that three different steel heats were applied. The calculated resistances were rather low (0.70).

Case 3. A spindle from a condensate effluent valve of a low pressure preheater was coated only partly with a 9% chromium steel. On top of the spindle. this coating was lacking. Erosion-corrosion was observed there. Again low Cr. Cu, and Mo values were found, and the resistance value R amounted to 0.75.

Case 4. The switch lever of a supply water pump had been attacked severely by erosion-corrosion. Steel No. 58 appeared to have suffered a high weight loss in the laboratory test, i.e..
number of specimens 116 mg. The operation time of this lever was 10,000 hours. Another lever from an identical pump at the same station after 40,000 hours showed less corrosion. The Cr, Cu, and Mo content of this steel is slightly higher. The calculated R values of the two levers amounted to 0.65 and 0.73, respectively.

Case 5. There was heavy erosion-corrosion in a control valve housing, resulting in leakage. This steel No. 57 suffered a high weight loss in the erosion-corrosion test, 107 mg. Cr, Cu, and Mo content was low, and the resistance value R was 0.67.

Wet steam pipes and water separators

Erosion-corrosion had occurred in wet steam pipes and ir the low and high pressure water separators of a BWR and a PWR. These components were made of a simple carbon steel.

Cases 6, 7, and 8. A pipe behind the BWR water separator was constructed by welding bent steel plates (Figure 5).

Figure 5 - Case 6: The wet steam pipe after the pre-water separator. The pipe was welded of bent steel plates. One plate had been corroded severely (R = 0.67). The adjacent noncorroded plates had higher resist-ances (R = 0.89).

One of those plates had been attacked severely (specimen 56). The other plates, both upstream and downstream, had not been attacked (specimens 21 and 25). The corroded plate showed a different chemical composition. The resistance of this steel was 0.67, whereas the values of the non corroded plates were much higher, 0.89.
Other, smaller diameter wet steam tubes also showed erosion-corrosion, and the R value of the two different heats amounted to 0.69.
The water separator of the BWR also suffered heavy erosion-corrosion. Low Cr, Cu, and Mo content was measured in the steels (R = 0.76 and 0.70).
The low and high pressure water separators, the prewater separator and the wet steam tubes in the BWR were replaced by stainless steel components in the last few years, bef ore the erosion-corrosion tests were finished.

Case 9. Some specimens of an erosion-corroded water separator of a PWR were received. Figure 6 shows one of the specimens from the water separator. Two plates had been received. In one of them there was a weld. The three steels were analyzed. The uncorroded steel had a much higher resistance value R (1.20 against 0.65 of both corroded steels).

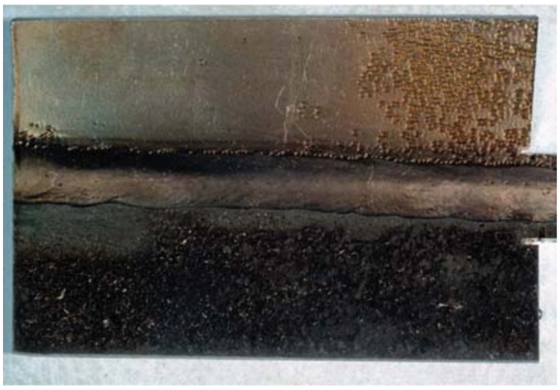

Figure 6 - Case 9: Steel part from the PWR water separator. One steel plate had suffered erosion-corrosion, and much oxide was deposited on the other. The resistance value of the erosion-corroded steel was much lower than that of the noncorroded steel (0.65 to 1.20).

Preheaters.

Case 10. Two tubes of a back-pressure unit were received: one had suffered erosion-corrosion, and the other had only some corrosion spots. The erosion-corrosion resistance calculated for the uncorroded tube was much higher than that of the corroded tube (1.03 vs 0.74).

Case 11. In a high pressure preheater, erosion-corrosion was found downstream behind severat butt weids (Figure 7). The inner diameter of the 15Mo3 steels amounted to 20 mm, and the weid heights for the three tubes were 1.8. 1.55, and 1.7 mm. The removed tube parts, upstream of the butt weids, had good erosion-corrosion resistance, while the downstream parts had lower values. Two tubes were corroded severely, one having had a leakage. One downstream tube, however, did not show corrosion visually, and this steel contained more Cr, Cu, and Mo.

Case 12. Slight erosion-corrosion was observed on thin tubes in a low pressure preheater of a power station, particularly at the bends of the tubes. The resistance values were 0.97, 0.84, and 0.96.

Figure 7 - Case 11: Tubes from the high pressure pre-heater. Erosion-corrosion downstream from the butt welds: (a) leakage (R = 0.81), (b) erosion-corrosion (R = 0.84), and (c) no erosíon-corrosion (R = 1.01).

Case 13. The preheater of a power station suffered local corrosion near the support plates (Figure 8). Coarse magnetite crystals were found adjacent to the corroded area. Scanning electron microscope photographs of these crystals are shown in Figure 9. Precipitation of such coarse iron oxide crystals is often observed with erosion-corrosion.

Figure 8 - Case 13: Erosion corrosion of preheater tubes near support plates. Coarse crystalline magnetite was found (R = 0.93) next to the erosion-corrosion place.

Figure 9 - Case 13: Scanning electron microscopic photograph of magnetite crystals on preheater tube from Figure 8.

Case 14. The preheater of a PWR had to be renewed because of severe erosion-corrosion (Figure 10). Twenty-four tubes from it were analyzed. For that, the preheater had to be dismantled row by row. The 24 tubes had been made from 2 different heats. It could be seen that in one row some tubes were corroded more severely than other tubes adjacent to them. The most severely attacked tubes were found to have the lower resistance values (0.74 vs 0.80).

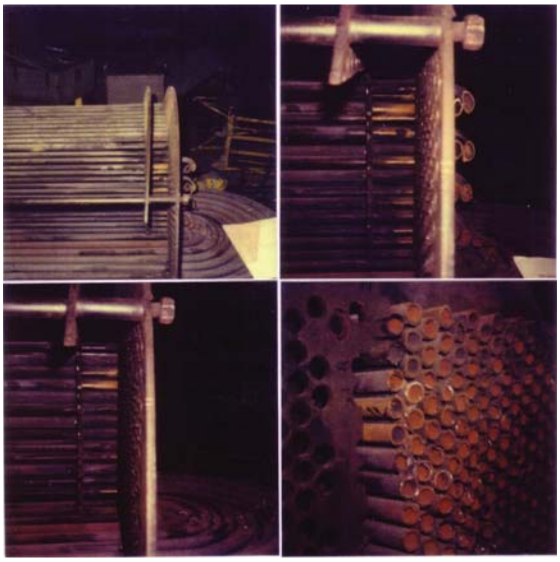

Figure 10 - Case 14: Low pressure preheater of PWR. During dismantling of the preheater, some tubes in one row appeared to have been attacked more than their neighbors. Some difference in R value was found. Most corroded tubes had R = 0.74. Less corroded tubes had R = 0.88.

Evaporators

Cases 15 and 16. In the waste-heat boilers of two power stations, the connection tubes from the low pressure evaporators to the header suffered severe erosion-corrosion. The leakages occurred behind a bend of 30°. The steels contained little Cr, Cu, and Mo. A tube from one evaporator was checked for chemical composition. This tube was not corroded at all, though it had sharp 90° bends. The resistance value of this steel was higher than those of the erosion-corroded connection tubes (1.17 vs 0.66 and 0.80).

Case 17. There was heavy erosion-corrosion in the economizer tube bends of a waste-heat boiler (Figure 11). Steaming occurred in the economizer. This could also be concluded from some damaged tube surfaces where erosion-corrosion occurred on the outer radius and steam blanketing occurred on the inside. The water film had come loose from the inner radius surface where coarse magnetite crystals had formed. Sample composition shows the erosion-corrosion resistance of this steel to be low, this being one of the causes of the leakage (R = 0.68).

Figure 11 - Case 17: Erosion-corroded tube from a steaming economizer (R = 0.68).

Case 18. Trottier [4] discussed the erosion-corrosion problems at Fessenheim power station, describing corrosion observed in three steam generators. Thirteen tubes were removed for further examination. Three categories of corrosion could be distinguished on the straight and bent tube parts: (1) tubes were not free of corrosion in the straight and bent parts (3 tubes), (2) tubes were corroded severely in both the straight and bent parts (6 tubes). and (3) tubes had severe corrosion in the straight parts but were free of it in the bends (4 tubes). Trot-tier also mentioned the chemical composition of the steels. At least six different heats had been applied in the steam generators. Though the figures for Cr. Cu, and Mo were identical for some heats, the figure for the other elements (e.g.. Ni and Mn) showed that the six heats were different.

Combrade. et al. .4 suggest an effect of Mn and Ni on erosion-corrosion resistance. Such influence, however, was not found in either Ducreux's or the author's erosion-corrosion experiments.

The category 3 corroded straight tubes had lower calculated resistance values than the non corroded bends. That there was no corrosion in low resistance bends of category 1 may be because of the local hydraulic circumstances in those steam generators.

Conclusions

The laboratory erosion-corrosion tests indicate that low (approximately 0.1 %) Cr, Cu, and Mo content can produce a remarkable increase in erosion-corrosion resistance. The resistance of steel can be calculated using this equation:

$$R_{KEMA} = 0.61 + 2.43\,Cr + 1.64\,Cu + 0.3\,Mo \qquad (4)$$

No erosion-corrosion was found in preheaters, evaporators, wet steam pipes, and other components sensitive to erosion-corrosion with calculated resistance values R of more than 1.0. Designers can minimize the erosion-corrosion risk by selecting steels with erosion-corrosion resistance values of at least R = 1.0. This criterion is based on current knowledge of in-service failures.

There appears to be a remarkable similarity between laboratory test results and practical experience. Steels involved in in-service failures because of erosion-corrosion also showed the highest weight losses in the wet steam test.

In modern high pressure plants (conventional and nuclear), the iron content in the water steam circuit should be kept as low as possible. Erosion-corrosion can result in leakages, requiring replacement of large components. The continuous delivery of iron to the water, as a result of erosion-corrosion, is rather harmful and can be decreased not only by proper chemical water treatment and hydraulic construction, but also by choosing an unalloyed steel of more than minimum Cr, Cu, and Mo content.