Acid Corrosion Resistance of Boiler Steels.

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1 Summary

Four layer scales are noticed generally on corroded boiler tubes:

- a porous 'sponge' of oxide particles,
- a salt layer (e.g. , sulfates, silicates),
- a so-called top layer of more compact magnetite,
- a very laminated oxide crust

The salt and top layer create an occluded cell in which corrosive electrolytes can be concentrated. In case of condenser inleakages of sea water or acid forming river water, hydrochloric acid or ferrous chloride is present in the occluded cells. The acid corrosion resistance of about 60 steel samples of different chemical composition was tested in experiments with ferrous chloride solutions of various concentrations.

Boiler corrosion generally occurs under specific conditions such as: unfavorable thermohydraulic conditions, fouling of heater tubes, and condenser inleakages. Until now, little attention has been given to the quality of the tubes with regard to boiler corrosion resistance. In this paper, the acid corrosion resistance of different boiler steels will be dealt with. A functional relation between acid corrosion resistance and composition of the steel is given.

2 Initiation of Boiler Corrosion

In the heater of a natural circulation boiler the thermohydraulic conditions under normal circumstances are as follows: steam weight percent: 0-20; heat flux: maximum 300 kW/m^2 (94,100 $BTU/ft^2/h$); and mass flow: 1100 $kg/m^2.s$. Under these conditions, steam bubble flow and nucleate boiling will take place in the evaporator and no corrosion will be initiated in nonfouled tubes, even in case of rather high seawater condenser inleakages. This was the conclusion of corrosion studies in experimental boilers carried out by Combustion Engineering' and KEMA. Salts cannot be deposited on the tubes because of the low steam quality and high mass flow.

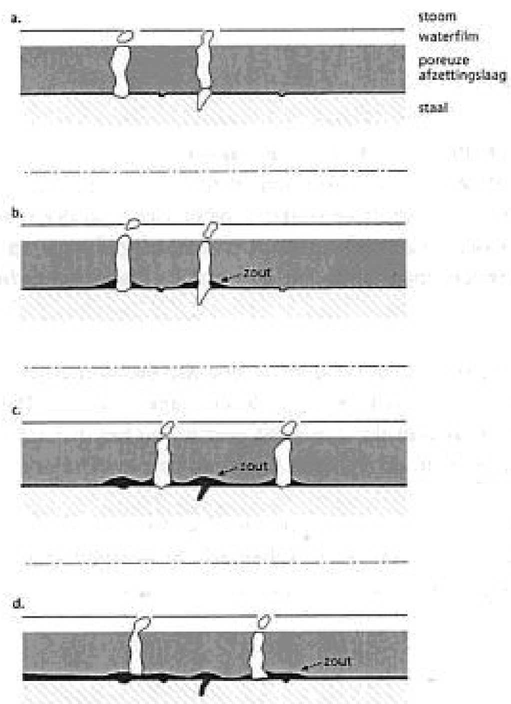

Figure 1: Model for salt formation in a porous deposited layer of oxide particles as a result of the wick boiling process.

However, during years of operation the heater tubes are fouled with loose oxide particles originating from the precipitation of dissolved iron, and from the flaking off of oxide on the preheater and evaporator tubes. On the heated sides of the tubes, oxide deposit layers of about 100 ,um thickness can be formed. In these deposits the water will be stagnant, so that the heat will be transferred by wick boiling. Steam bubbles will be formed on nucleates, where heat transfer is easiest, e.g., on scratches and small pits. Salts (silicates, phosphates, sulfates, etc.) will deposit in the wick boiling places as shown schematically in Figure 1. When the salts deposit locally, heat transfer will become difficult, so that wick boiling will begin in a more favorable place. In this way, the whole surface will ultimately be covered with a salt layer. On the steel tube a thin magnetite layer(1 to 2 micron), a salt layer, and a porous layer of deposited oxides may be noticed. Figure 2 shows two sectioned tube halves from a test tube from our experimental boiler facility. The upper half was heat charged, the other was not. On both halves, the layer of loose oxide particles could be removed by tap water rinsing. During exposure in the experimental boiler, sodium silicates were injected in the boiler water. This silicate appeared to be deposited in a network on the heat charged part of the tube as a result of the wick boiling process. In the SEM photograph (Figure 3), the boiling tunnels in the porous oxide layer can be seen clearly. The tube wall temperature will increase steadily because of the growing thickness of the, salt layer. At this high temperature, acid boiler water penetrating into cracks in the salt layer can be very corrosive. The initially protective thin magnetite layer is transformed into a more porous and irregular top layer of about 20 micron thickness and ultimately extensive corrosion will take place under this top layer. In the case of acid corrosion, the oxide scales are very laminated. Thus, 4 stages can be noticed in the acid on-load corrosion mechanism (Figure 4)

1. Fouling of the tube surface by small oxide particles, giving a "sponge" layer,

2. formation of salts in the "sponge" layer,

3. attack of the initially protective thin magnetite layer and formation of the top layer,

4. accelerated corrosion, resulting in laminated oxide scales in acid environments.

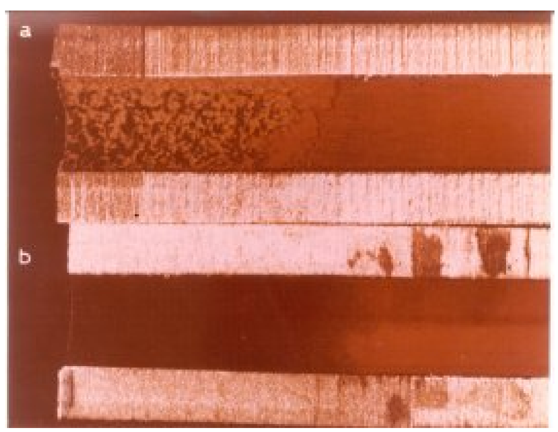

Figure 2: Two tube halves: (a) heat irradiated part, and (b) nonirradiated part. The loose oxide layer on both tube halves has been removed by water rinsing. On tube (a) a network of salts is noticed under the loose oxide layer.

Beneath the salts and the top layer, salt solutions (like $FeCl^2$) can be concentrated and become very corrosive. Autoclave tests in the cided salt solutions

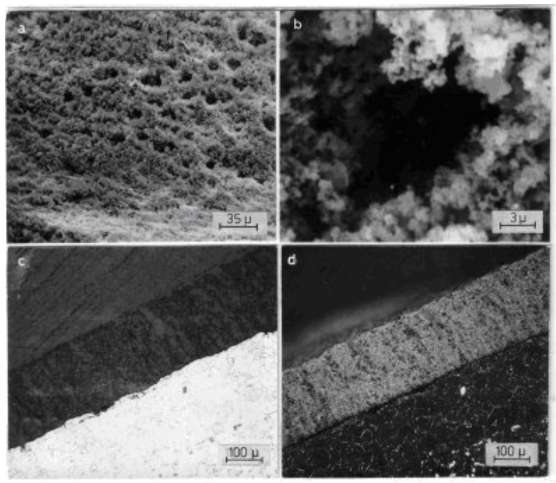

Figure 3: SEM picture of the porous oxide layer. Steam chimneys are present.

gave laminated oxide structures comparable with the heavily corroded evaporator tubes. So it seems useful to test the acid corrosion resistance of different boiler steel qualities with autoclave exposure experiments in ferrous chloride solutions.

3 Acid Corrosion Tests

Three different steel qualities, simple carbon steel, 14Mn4 and 15Mo3 (for composition see Table 1 all used in evaporators of in Dutch power stations, were tested in autoclaves supplied with PTFE beakers. In each test about 20 samples (15 x 10 x 5 mm) were placed in a beaker (volume 190 ml) filled with 150 ml of $FeCl_2$. Solutions of 13 different concentrations were applied in those tests, namely: 0.0050, 0.0075, 0.010, 0.015, 0.020, 0.025, 0.035, 0.050, 0.075, 0.100, 0.175, 0.250, and 0.375 mol/L. The exposed surface area of each sample was about 5.5 cm^2. The steel samples were tested in solutions, beginning at low concentration and ending at the solution with the highest concentration in which the samples showed no corrosion resistance. For each test a new sample was used. The criterion for corrosion was the appearance of laminated oxide structures within 4 days of exposure at 310^oC and 10 MPa (1400 psi). Figure 5 shows the oxide layers on mild steels (numbers 2.17 and 2.19) formed in 3 different $FeCl_2$ concentrations. The layers became coarser with increasing concentrations. Table 2 gives the maximum $FeCl_2$ concentration (Yexp) in which the various steels did not corrode and also their service behavior. The steel samples originated from heater tubes of boilers in Dutch electrical power stations. The tubes were cut from the evaporators because of corrosion failures or because of inspection for fouling of the boiler. The nonheat charged sites of the tubes were used in this study. In addition, some new tubes from boilers under construction were tested.

Steel	C	Si	Mn	Mo	P(max)	S(max)
15Mo3	0.12-0.20	0.15-0.35	0.50-0.80	0.25-0.35	0.04	0.09
14Mn4	0.10-0.18	0.30-0.50	0.90-1.20		0.05	0.05

Table 1: Composition of Low Alloy Steels Tests

Note: The samples were not isolated from one another. As all rapidly developed an oxide layer with high electrical resistance, and galvanic corrosion between samples can be neglected. The results of some composative tests in which samples were placed in smaller separate autoclaves confirmed this assumption.

4 Relation of Test Results with In-Service Behavior

It is not simple to detect a good relation between the corrosion resistance of a steel as defined, and in-service failures in different boilers, because the thermohydraulic conditions, the amount of fouling, and the chemical quality of the boiler water (dependent on the cooling water and condenser inleakages) can differ greatly. In Table 2, the history of the tube samples is given, divided into 5 main groups. The samples of fouled boiler tubes and of mechanically damaged tubes are listed in the column headed NC. Tubes which were locally corroded as a result of unfavorable thermohydraulic conditions are identified in the column HSC. Heavy corrosion occurred in 4 evaporators that had to be renewed totally or partly. The samples (numbers 2.30, 2.3, and 2.5) originate from 3 different boilers, and the other samples mentioned in the column HC were taken from a very heavily corroded boiler. This boiler, a 15.5 MPa (2250 psi) natural circulation boiler built in 1964, showed many failures after 7 years of operation. The evaporator tubes showed corrosion accompanied by hydrogen cracking. The damage was so severe that the whole evaporator had to be rebuilt. After 2 years of operation, failures were observed again in this boiler. Two tubes were cracked. Besides these 2 tubes, 3 undamaged ones, lying near the corroded tubes, were removed for inspection. In these 3 evaporator tubes, fouling was noticed, but no corrosion. At that time, the corrosion tests in ferrous chloride solutions were started. Six tubes originating from the old evaporator and 5 tubes, (2 corroded and 3 uncorroded) from the rebuilt heater, were tested in autoclaves. In Table 2, the results of these boiler tube tests are summarized. All samples from the old evaporator had low corrosion resistance ($Y_{exp} = 0.021$. The 2 corroded tubes from the renewed heater also had poor corrosion resistance ($Y_{exp} = 0.02$), but the 3 undamaged tubes from the same part in the evaporator gave good results in the corrosion tests ($Y_{exp} = 0.035$). The composition of the 3 tubes differed considerably from that of the 2 failed tubes and of the old evaporator (Table 3).

Figure 4: Characteristic oxide scale on corroded boiler tubes. The 4 stages of the corrosion process can be recognized in the oxide crust. A: Porous layer of oxide deposits, B: Salt layer, C: Top-layer, D: Laminated oxide, E: Steel.

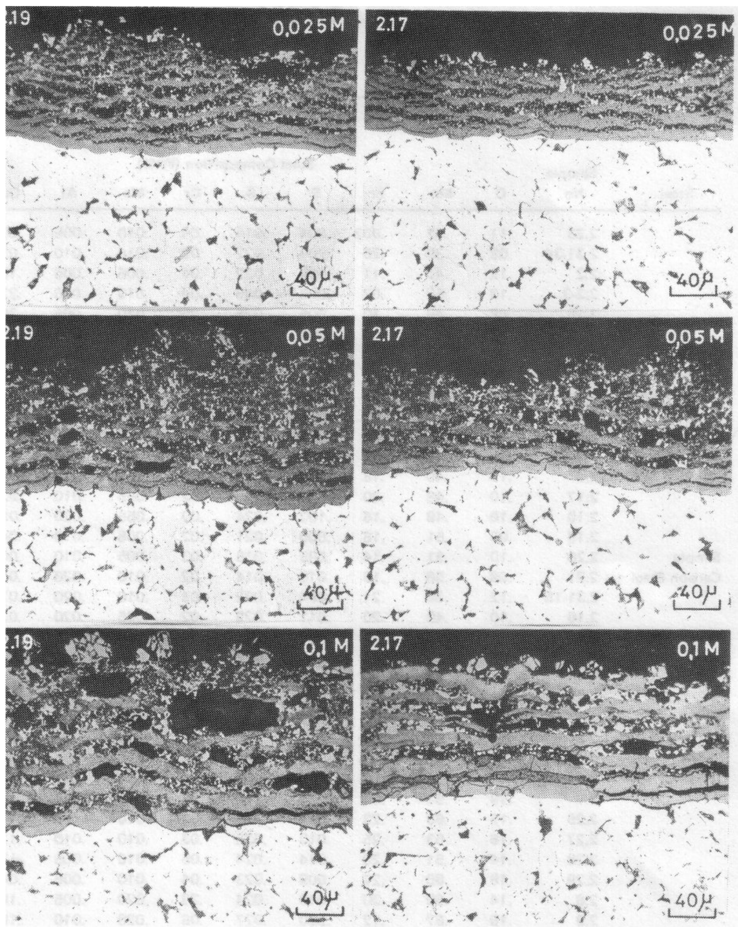

Figure 5: Samples steel corroded in ferrous chloride solutions of 3 various concentrations.

So a good correlation exists between the results from the autoclave tests and the in-service failures in the 4 boilers mentioned, and particularly in the boiler with the totally renewed evaporator. Regarding the other tested tube samples, there is not such a significant relation. A majority of the samples originated from boilers under construction and others from boilers in which failures occurred in the welds or at hot spots. Therefore, those samples are not so appropriate for comparing autoclave results with in-service failures. To establish a reliable correlation between the test and practical boiler failures, more samples of corroded and uncorroded boilers must be tested. Nevertheless, to avoid corrosion problems in the future, boiler tubes should have a yexp-value of at least 0.035, as based on practical experience with all the tubes tested.

Sample	Steel analysis wt%										$FeCl_2$ Concentration Mol/L
No.	C	Mn	Si	P	S	Cr	Mo	AI	Cu	Ni	Yexp
2.2.	0.12	0.	0.11	0.005	0.032	0.04	0.01	0.01	0.10	0.06	0.01
2.2./3	0.12	0.52	0.07	0.005	0.025	0.04	0.01	0.01	0.22	0.09	0.015
2.2./1	0.14	0.58	0.13	0.004	0.019	0.03	0.01	0.01	0.11	0.05	0.020
2.2./2	0.11	0.50	0.12	0.006	0.025	0.05	0.01	0.01	0.12	0.07	0.020
2.2.14	0.11	0.47	0.12	0.004	0.030	0.04	0.01	0.01	0.14	0.007	0.020
2.2./5	0.12	0.47	0.11	0.005	0.032	0.03	0.01	0.01	0.11	0.07	0.020
2.31/34	0.08	0.39	0.20	0.004	0.022	0.02	0.01	0.01	0.07	0.04	0.0075
2.31/18	0.12	0.38	0.21	0.004	0.022	0.03	0.01	0.02	0.07	0.03	0.020
2.31/28	0.11	0.44	0.23	0.007	0.029	0.06	0.02	0.01	0.08	0.04	0.035
2.31/32	0.10	0.43	0.23	0.007	0.030	0.06	0.02	0.01	0.08	0.04	0.035
2.31/40	0.10	0.44	0.20	0.006	0.030	0.06	0.02	0.01	0.08	0.04	0.035

Table 2: Results of Tests on Samples from a Severely Corroded Natural Circulation Boiler Before and After Rebuilding the Evaporator. Composition of Steel Samples in %. Remarks: **Tubes 2.2**: Removed from the boiler in 1970 before reconstruction of the evaporator; severe on-load corrosion, attended with hydrogen embrittlement. **Tubes 2.31**: Tubes removed in 1973, 3 years after reconstruction Tubes /34 and /18 corroded tubes; tubes /28, /32 and /40 noncorroded tubes

5 Correlation Between autoclave Test Results and Steel Analysis

From the results, it can be concluded that the steels 15Mo3 and 14Mn4 generally have better acid corrosion resistance than the simple carbon steels. The Mn-alloyed steel appeared to be of particularly good quality. Using a multiple regression analysis by means of a standard computer program of SPSS, developed by the National Opinion Research Center at the University of Chicago, a a correlation was established between the chemical composition and the acid corrosion resistance of all the steel samples. The regression analysis was performed in a stepwise fashion. The regression coefficient of each element was calculated, beginning with the element which explained the greatest part of the variance in the acid corrosion resistance (y) and ending with that contributing the least part of the variance in corrosion resistance. The coefficients of the

Sample nr.	C	Mn	Si	P	S	Cr	Mo	Cu	$Fe(Cl)_2$ Experi-mental	$Fe(Cl)_2$ Calcu-lated	HC	WC	HSC	NC	New tubes
2,23	0,11	0,47	0,003	0,004	0,014	0,04	0,01	0,07	0,005	0,0132					+
2,31-34	0,08	0,39	0,2	0,004	0,022	0,02	0,01	0,07	0,008	0,0008	+				
2,2	0,12	0,46	0,11	0,005	0,032	0,04	0,005	0,1	0,010	0,0140	+				
2.2-3	0,12	0,52	0,07	0,005	0,025	0,04	0,01	0,22	0,015	0,0204	+				
2,15	0,09	0,49	0,1	0,005	0,028	0,05	0,01	0,2	0,015	0,0193	+				
2,30	0,12	0,48	0,1	0,006	0,034	0,05	0,01	0,12	0,015	0,0203	+				
2,32	0,09	0,5	0,11	0,005	0,029	0,05	0,01	0,2	0,015	0,0204					+
2,1	0,14	0,49	0,12	0,005	0,026	0,05	0,01	0,18	0,020	0,0193					+
2,2-1	0,14	0,58	0,13	0,004	0,019	0,03	0,01	0,11	0,020	0,0225	+				
2,2-2	0,11	0,5	0,12	0,006	0,025	0,05	0,005	0,12	0,020	0,0222	+				
2,2-4	0,11	0,47	0,12	0,004	0,03	0,04	0,01	0,14	0,020	0,0132	+				
2,2-5	0,12	0,47	0,11	0,005	0,032	0,03	0,01	0,11	0,020	0,0132	+				
2,3	0,13	0,4	0,18	0,011	0,015	0,01	0,005	0,01	0,020	0,0139	+				
2.17	0,10	0,48	0,20	0,0072	0,0180	0,02	0,06	0,02	0,020	0,0179					+
2.18	0,11	0,53	0,23	0,0122	0,0270	0,02	0,01	0,03	0,020	0,0318					+
2.19	0,09	0,51	0,18	0,0092	0,0212	0,03	0,01	0,04	0,020	0,0246					+
2.20	0,10	0,51	0,14	0,0079	0,0200	0,03	0,01	0,04	0,020	0,0232					+
2.21	0,09	0,56	0,18	0,0100	0,0139	0,02	0,01	0,03	0,020	0,0316					+
2,31-18	0,12	0,38	0,21	0,004	0,022	0,03	0,01	0,07	0,020	0,0019	+				
2.16	0,10	0,49	0,20	0,0111	0,0222	0,02	0,01	0,04	0,025	0,0248					+
2,22	0,11	0,53	0,1	0,03	0,028	0,04	0,01	0,05	0,025	0,0723			+		
2,11	0,08	0,5	0,18	0,012	0,012	0,06	0,01	0,04	0,025	0,0367					+
2,10	0,11	0,49	0,23	0,006	0,024	0,03	0,02	0,1	0,035	0,0177					+
2,24	0,11	0,49	0,17	0,016	0,022	0,03	0,01	0,03	0,035	0,0376					+
2,31-28	0,11	0,44	0,23	0,007	0,029	0,06	0,02	0,005	0,040	0,0207				+	
2,31-32	0,1	0,43	0,23	0,007	0,03	0,06	0,02	0,08	0,035	0,0197				+	
2,31-40	0,1	0,44	0,2	0,006	0,03	0,06	0,02	0,08	0,035	0,0187				+	
2,5	0,11	0,53	0,15	0,009	0,028	0,09	0,03	0,02	0,035	0,0406	+				
2,7	0,19	0,57	0,23	0,012	0,019	0,03	0,01	0,12	0,050	0,0377			+		
2,25	0,15	0,63	0,23	0,011	0,028	0,03	0,01	0,1	0,050	0,0419					+
2,27	0,16	0,63	0,25	0,01	0,033	0,03	0,01	0,11	0,050	0,0398					+
2,28	0,14	0,51	0,2	0,014	0,024	0,05	0,01	0,17	0,050	0,0397					+
2,29	0,16	0,6	0,27	0,009	0,023	0,04	0,01	0,04	0,050	0,0368					+
2,6	0,14	0,6	0,2	0,01	0,024	0,33	0,02	0,15	0,075	0,0987				+	
2,9	0,19	0,67	0,12	0,02	0,027	0,06	0,02	0,15	0,075	0,0709			+		
2,26	0,15	0,63	0,23	0,011	0,028	0,03	0,01	0,1	0,075	0,0419					+
1,3	0,14	0,7	0,24	0,014	0,021	0,05	0,32	0,12	0,035	0,0723			+		
1,5	0,16	0,59	0,24	0,0040	0,0220	0,04	0,26	0,10	0,035	0,0360					+
1,6	0,18	0,68	0,21	0,0060	0,0200	0,05	0,26	0,10	0,035	0,0514					+
1,9	0,14	0,61	0,18	0,0040	0,0210	0,04	0,26	0,07	0,035	0,0381					+
1.10	0,16	0,70	0,20	0,0058	0,0152	0,02	0,28	0,04	0,050	0,0479					+
1.11	0,16	0,70	0,19	0,0065	0,0150	0,02	0,28	0,04	0,050	0,0494					+
1.12	0,16	0,69	0,18	0,0070	0,0200	0,02	0,28	0,04	0,050	0,0491					+
1.13	0,16	0,73	0,18	0,0064	0,0184	0,02	0,27	0,04	0,050	0,0518					+
1.14	0,16	0,72	0,20	0,0063	0,0204	0,01	0,27	0,04	0,050	0,0492					+
1.15	0,14	0,57	0,23	0,0093	0,0100	0,11	0,29	0,07	0,050	0,0605			+		
1.16	0,14	0,62	0,22	0,0042	0,0070	0,04	0,50	0,04	0,050	0,0488			+		
1,4	0,15	0,68	0,17	0,0060	0,0240	0,06	0,55	0,12	0,075	0,0657					+
1,8	0,15	0,67	0,17	0,0060	0,0240	0,06	0,60	0,12	0,075	0,0667			+		
1,1	0,15	0,76	0,25	0,0110	0,0340	0,07	0,34	0,20	0,100	0,0773				+	
3.3	0,15	1,18	0,33	0,0102	0,0202	0,05	0,02	0,18	0,075	0,1010		+			
3,6	0,16	1,11	0,42	0,0070	0,0220	0,08	0,02	0,10	0,075	0,0938					+
3.7	0,16	1,09	0,26	0,0200	0,0320	0,03	0,01	0,12	0,075	0,1071					+
3.10	0,12	0,98	0,37	0,0120	0,0100	0,04	0,02	0,03	0,075	0,0828					+
3.11	0,12	1,01	0,39	0,0114	0,0132	0,04	0,01	0,03	0,075	0,0840					+
3,1	0,16	1,17	0,43	0,0130	0,0090	0,05	0,01	0,03	0,100	0,1055				+	
3,4	0,16	0,95	0,34	0,0180	0,0100	0,07	0,01	0,06	0,100	0,0973				+	
3,5	0,14	1,19	0,45	0,0140	0,0260	0,06	0,03	0,21	0,100	0,1126			+		
3,8	0,15	1,04	0,36	0,0200	0,0280	0,08	0,02	0,12	0,100	0,1131		+	+		
3.9	0,13	0,99	0,37	0,0162	0,0220	0,04	0,02	0,18	0,100	0,0915		+			
3.12	0,12	0,90	0,37	0,0119	0,0158	0,04	0,01	0,03	0,100	0,0734					+
3.13	0,15	0,11	0,32	0,0240	0,0230	0,12	0,03	0,19	0,100	0,0344					+

Table 3: Composition of the steel samples, the test results and the origin of the samples. **HC**: Heavy Corrosion, **WC**: Corrosion on the Welds, **HSC**: Hot Spot Corrosion, **NC**: No Corrosion.

Element	Composition (Wt%) Average	Standard Deviation	All elements B	Standard Deviation	Insignificance	Restricted to B	Standard Deviation	Insignificance
Mn	0.653	0.226	0.073	0.024	0.003	0.103	0.013	0.000
P	0.0098	0.0058	2.364	0.565	0.000	2.037	0.513	0.000
Cr	0.049	0.042	0.172	0.068	0.014	0.205	0.062	0.002
Mo	0.087	0.148	0.045	0.021	0.037	0.042	0.018	0.026
AI	0.0086	0.006	0.674	0.481	0.167			
Si	0.214	0.093	0.077	0.051	0.134			
Cu	0.096	0.058	0.089	0.080	0.270			
Ni	0.053	0.027	0.150	0.155	0.34			
C	0.132	0.028	0.044	0.121	0.71			
S	0.022	0.0067	0.063	0.528	0.91			
Constant			0.053	0.018	0.0005	0.052	0.008	0.000

Table 4: Results of the Multiple Regression Analysis

preceding elements were corrected when the coefficient of the last element was adjusted. The results of the computer analysis for all the elements are given in Table 4. Except for the elements Mn, P, Cr, and Mo, the insignificance is rather high, so that we cannot predict the influence on corrosion resistance of all the alloying elements. For that reason, the regression equation of the correlation between chemical composition and the results of our autoclave tests has to be restricted to the elements Mn, P, Cr, and Mo. So, the stepwise regression was continued until the insignificance level of an element exceeded 5% (Table 3), and the regression equation can be written as follows:

y = 0.103 Mn + 2.037 P + 0.205 Cr + 0.042 Mo-0.052.

The calculated y values are summarized in Table 2. The regression equation can only be applied for the steel qualities of composition within the range as mentioned in Table 4. Presently, the performance of a factorial experiment is being considered to establish the exact influence of all the alloying elements on the corrosion resistance and more specifically the influence of each single alloying element and its possible interaction with any other alloying element. In this case, special steel melts will be used. In addition, the influence of the steel structures is being studied, e.g., the effect of perlite, bainite, grain width, decarburized surface, etc.

6 Conclusions

1. The acid corrosion resistance of boiler steels can be determined by means of a ferrous chloride autoclave test.

2. A correlation exists between autoclave test results and the acid on-load corrosion in boilers of the power stations in the Netherlands.

3. From experience obtained so far, a yexp value of at least 0.035 for evaporator steel tubes of boilers under construction is advisable to avoid serious corrosion problems within a few years of operation.

4. A correlation exists between steel composition and the autoclave test results. A regression equation has been established.

5. More research has to be done on special molten steel samples to get exact information about the influence of each single element on the corrosion resistance.

7 References

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