Data evaluation of the corrosion resistance properties of selected stainless and alloy steels in dilute electrolytes

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Abstract. Comparison of the corrosion resistance of 304 austenitic stainless steel (304ST), Atlas F20S ferritic stainless steel (F20ST) and X77CrZn5 alloy steel (X77ST) was studied in 2 M H_2SO_4 solution at specific NaCl concentration. Corrosion resistance of 304ST varies with changes in NaCl concentration whereas the values observed for F20ST and X77ST were non-proportional. The alloys exhibit relative stability with respect to exposure time after few hours. Lower NaCl concentration results in higher corrosion rate for 304ST. The final corrosion rate values ranged from -0.029 mm/y at 0% NaCl to 0.261 mm/y at 3.25% NaCl. The values for F20ST andX77ST varied from -0.068 mm/y to 0.394 mm/y, and 2.406 mm/y to 0.348 mm/y. Without NaCl, 304ST exhibited the highest corrosion resistance at -0.029 mm/y compared to X77ST which exhibited the highest corrosion rate value of 2.406 mm/y. With NaCl 304ST has the highest average corrosion rate and X77ST has the lowest. Data from ANOVA analysis showed NaCl concentration is the dominant factor influencing the corrosion behaviour of the alloys at 99.74%, 99.08% and 97.05% compared to exposure time. The average corrosion rate values for 304ST varies slightly with respect to NaCl concentration compared to the values obtained for F20ST and X77ST signifying thermodynamic stability. The percentage of corrosion rate values for 304ST, F20ST and X77ST below 1 mm/y without and in the presence of NaCl concentration are 100%, 100% and 0%, and 76%,76% and 100%.

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1 Introduction

Stainless steels demonstrate significant resistance to corrosion in aqueous environments due to the formation of an instantaneous thin, and durable film. The passive film consists of an outer Fe-rich oxide, mainly Fe_2O_3 and $Fe(OH)_2$/$Fe(OH)_3$, and an inner Cr-rich oxide, often stated as Cr_2O_3 and $Cr(OH)_3$, with also some molybdenum as well as silicon species [1-4]. Cr_2O_3 is the chemical combination of Cr and O_2 on the steel surface although Cr is the major constituent responsible for passivation [5]. The minimum Cr content of 10.5% among other important alloying elements e.g. Ni, Ti etc. induces this property. The corrosion resistance of stainless steels allows for its versatile application across most industries where aqueous environments containing Cl^-, SO_4^{2-} anions etc. are present [6–8]. There are environmental and industrial conditions that results in breakage of the passive layer causing anionic penetration of the broken layers and subsequent corrosion of the steels [9-13]. Stainless steels undergo localized corrosion at requisite concentrations of corrosive species [14]. Pitting across the entire alloy surface leads to structural weakness and deterioration of the alloy [15]. Corrosion, is broadly defined as the surface deterioration of metallic alloys due to interaction of corrosive anions in aqueous environments with the alloy surface [16], is one of the major causes of structural collapse, breakdown of metallic components, industrial downtime, unpredictable accidents, harmful leakages etc. Significant corrosion damages occur oil rigs, refineries, desalination plants, mining sites, marine vessels, heat exchangers etc. [17]. Material selection and knowledge of the safe limit concentration of metallic alloys is of utmost importance in extending the useful lifespan of metallic structures in service. This invariably helps to alleviate the mitigating effect of corrosion damage, cost of repairs and maintenance [18, 19]. It is worthy of note that there are other corrosion prevention methods. However, appropriate material selection is the most cost effective [20-24]. 304 austenitic stainless steel is one of the most commonly used grades of stainless steels. It has good processability, weldability, corrosion resistance, heat resistance, low temperature strength and good hot workability. 304 steel is widely used in the industry, food processing, machinery parts, exhaust manifolds, medical industry, storage tanks, piping, surgical instruments, and implant materials etc. [25]. F20S stainless steel is widely regarded as ferritic alternative to grade 304 stainless steel [26]. It is a stabilized 20% chromium ferritic stainless steel, combining good corrosion resistance with high formability and weldability. This grade contains no nickel. It is commonly used in metal fabrication, gas flues, process equipment, tank cladding etc. This research .

studies and compares the corrosion resistance properties of 304 austenitic and Atlas F20S ferritic stainless steel in acid chloride solution.

2 Material and methods

304 austenitic stainless steel (304ST) obtained from Vienna University of Technology, Vienna, Austria, Atlas F20S ferritic stainless steels (F20ST) obtained from the fuel line of an automobile and X77CrZn5 alloy steel (X77ST) were cut into dimensions of 10 mm by 10 mm respectively. The steel alloys were cut into 8 test specimens each. The surfaces of the steel samples were grinded with grit papers (80, 120, 220, 800 and 1000 grits) to partially smoothen the alloy surfaces. Their elemental compositions are shown in Table 1. Weighed specimens of the steels were immersed in 200 ml of 2 M H_2SO_4 (analar grade) at 0.25% NaCl, 0.75% NaCl, 1.25% NaCl, 1.75% NaCl, 2.25NaCl, 2.75% NaCl and 3.25% NaCl concentrations for 480 h. The specimens were weighed every 24 h with using Ohaus analytical weighing balance. Data obtained were used to determine the weight loss and corrosion rate the steel samples. Corrosion rate was calculated from the equation below;

$$C_R = \frac{87.6W}{DAT} \quad (1)$$

Where W represents weight loss in grams, D represents density in g/cm^2, A represents area in cm^2, and T represents time of exposure in hours. W was determined from the difference between the initial weight of the samples (maintained for 480 h) and every final weight gotten every 24 h interval for a total of 480 h.

Dual-factor analytical ANOVA test (F - test) was used to enumerate the statistical significance of CCM extract concentrations and measurement time on CCM protection efficiency results. The assessment was gotten at confidence level of 95% i.e. significance level of $\alpha = 0.05$ in respect of the numerical expressions below. The combination of squares for the columns (measurement time) was enumerated from equation 2 [27].

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \quad (2)$$

The combination of squares between the rows (CCM extract concentration) was gotten from equation 3 [27].

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \quad (3)$$

The total combination of squares is given in equation 4 [27].

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \quad (4)$$

Table 1 Elemental %Wt. composition of Al 4032, Mg-Ti, Al 4004 and Al-V

Elemental Composition (%)	Fe	Si	C	Cr	Mn	P	S	Ni	Al	N	Mo	Zn	Ca	Mg	Ti+Nb
X77ST	77.85	0.31	-	5	1.02	-	-	-	0.02	-	-	10.65	2.02	4.2	-
F20ST	79.34	0.1	0.02	20	0.2	0.03	0.003	-	-	0	-	-	-	-	0.3
304ST	70.75	1	0.08	18	2	0.045	0.03	8	-	0.1	0	-	-	-	-

3 Results and discussion

3.1 Corrosion rate studies

Corrosion resistance of 304ST, F20ST and X77ST alloys in 2 M H_2SO_4 solution at 0%, 0.25%, 0.75%, 1.25%, 1.75%, 2.25%, 2.75% and 3.25% NaCl concentration was studied. Table 2 shows the corrosion rate data for 304ST while Table 3 and 4 shows the corrosion rate data for F20ST and X77ST at specific NaCl concentration for 480 h of exposure. Comparison of Table 2 and 3 shows that corrosion resistance of 304ST varies proportionally with respect to NaCl concentration. Whereas the values observed for F20ST is non-proportional. However, both alloys exhibit relative stability of corrosion rate values with respect to exposure time. Table 2 shows that 304ST at 0% NaCl concentration exhibited the lowest corrosion rate values from 24 h to 480 h of exposure. The values initiated at -0.197 mm/y (24 h) compared to 304ST at other NaCl concentrations (0.25% - 3.25% NaCl) whose values ranged from 0.279 mm/y to 4.159 mm/y. Corrosion rate of 304ST at 0% NaCl concentration was generally stable till 480 h culminating at a value of -0.029 mm/y compared to other values which ranged from 0.261 mm/y to 3.543 mm/y. 304ST at 0.25% NaCl concentration generally exhibited the highest corrosion rate values. The values initiated at 4.159 mm/y (24 h), decreased to 3.123 mm/y at 48 h before remaining generally stable to 3.543 mm/y at 480 h of exposure. Observation of Table 2 shows that the lower the NaCl concentration, the higher the corrosion rate of 304ST at the NaCl concentrations studied throughout the exposure hours. This is proven from the final corrosion rate values at 480 h with values ranging from -0.029 mm/y at 0% NaCl to 3.543 mm/y, 1.129 mm/y, 0.702 mm/y, 0.569 mm/y, 0.476 mm/y, 0.350 mm/y and 0.261 mm/y at 3.25% NaCl concentration. Corrosion rate results in Table 3 and 4 appear well defined but follows a different defined trend. Similar to the observation in Table 2, corrosion rate of F20ST at 0% NaCl concentration is the lowest throughout despite attaining relative stability at 72 h of exposure. This was followed by the corrosion rate data for F20ST at 0.25% NaCl concentration. Beyond 0.25% NaCl, corrosion rate did not vary proportionately with NaCl concentration. Corrosion rate of X77ST at 0% NaCl concentration, exhibited the highest corrosion rate value of 1.196 mm/y at 24 h of exposure, while the corrosion rate of X77ST at 0.25% NaCl (-0.412 mm/y) was the lowest most especially among the X77ST samples with varying concentration of NaCl. Observation of the corrosion rate trend for X77ST in Table 4 shows relatively stable electrochemical behavior from 144 h of exposure to 480 h. At 480 h of exposure, corrosion rate of X77ST at 0% NaCl has increased to 2.406 mm/y retaining its value with the highest corrosion rate generally, while X77ST at 2.25% NaCl (0.757) exhibited the highest corrosion rate among the alloys with varying concentration of NaCl. X77ST at 3.25% NaCl concentration generally exhibited the lowest corrosion rate at 0.348 mm/y.5 Generally, corrosion rate results with respect to exposure time indicates stability of the metal surface in the presence of the reactive corrosive species in the electrolyte.

Table 2 Corrosion rate data for 304ST in 2 M H_2SO_4 solution at 0% to 3.25% NaCl concentration

NaCl Conc. (%) / Exp. Time (h)	0% NaCl	0.25% NaCl	0.75% NaCl	1.25% NaCl	1.75% NaCl	2.25% NaCl	2.75% NaCl	3.25% NaCl
24	-0.197	4.159	1.792	1.742	1.660	0.641	0.575	0.279
48	-0.222	3.123	1.496	0.855	0.847	0.526	0.304	0.477
72	-0.159	2.970	1.195	0.751	0.532	0.433	0.411	0.345
96	-0.123	3.193	1.027	0.727	0.432	0.296	0.386	0.308
120	0.007	3.209	1.147	0.575	0.395	0.283	0.289	0.164
144	-0.074	3.216	1.055	0.559	0.359	0.359	0.321	0.216
168	-0.075	3.391	1.064	0.578	0.371	0.322	0.319	0.242
192	-0.072	3.319	0.988	0.530	0.386	0.327	0.372	0.150
216	-0.086	3.432	0.988	0.508	0.290	0.278	0.216	0.132
240	-0.207	3.539	0.888	0.524	0.133	0.159	0.182	0.156
264	-0.064	3.501	0.970	0.463	0.398	0.272	0.269	0.190
288	-0.099	3.427	0.912	0.538	0.358	0.266	0.274	0.296
312	-0.046	3.487	0.945	0.579	0.336	0.295	0.301	0.236
336	-0.013	3.520	0.966	0.605	0.309	0.302	0.291	0.263
360	-0.058	3.458	0.944	0.601	0.384	0.315	0.294	0.163
384	-0.055	3.494	0.978	0.637	0.470	0.331	0.268	0.222
408	-0.039	3.559	0.961	0.591	0.490	0.245	0.278	0.252
432	-0.005	3.598	1.042	0.642	0.465	0.251	0.225	0.237
456	-0.064	3.498	1.001	0.528	0.545	0.387	0.301	0.236
480	-0.029	3.543	1.129	0.702	0.569	0.476	0.350	0.261

Table 3 Corrosion rate data for F20ST in 2 M H_2SO_4 solution at 0% to 3.25% NaCl concentration

NaCl Conc. (%) / Exp. Time (h)	0% NaCl	0.25% NaCl	0.75% NaCl	1.25% NaCl	1.75% NaCl	2.25% NaCl	2.75% NaCl	3.25% NaCl
24	-1.362	-0.034	2.540	0.740	6.324	2.103	3.717	0.454
48	-0.555	-0.185	1.640	0.614	4.626	1.245	2.515	0.151
72	-0.224	-0.056	1.189	0.813	3.885	0.886	2.024	0.409
96	-0.235	-0.029	1.051	0.753	3.482	0.803	1.657	0.353
120	-0.249	-0.034	1.137	0.659	2.775	0.676	1.413	0.151
144	-0.163	-0.031	0.976	0.606	2.529	0.659	1.205	0.238
168	-0.269	-0.036	1.129	0.646	2.139	0.608	1.314	0.296
192	-0.135	-0.025	1.203	0.488	1.873	0.517	1.148	0.273
216	-0.179	-0.036	0.989	0.549	1.779	0.493	1.093	0.344
240	-0.264	-0.059	0.949	0.395	1.573	0.442	1.060	0.183
264	-0.211	-0.002	0.933	0.517	1.596	0.564	1.066	0.304
288	-0.170	-0.017	0.973	0.426	1.553	0.555	1.037	0.308
312	-0.022	-0.022	0.950	0.432	1.497	0.543	1.100	0.301
336	-0.124	-0.005	0.924	0.455	1.432	0.481	0.992	0.203
360	-0.160	-0.006	0.940	0.452	1.374	0.598	1.005	0.250
384	-0.150	-0.015	0.924	0.487	1.392	0.597	1.017	0.362
408	-0.118	-0.009	0.969	0.489	1.429	0.636	0.981	0.347
432	-0.120	-0.025	0.934	0.516	1.446	0.662	1.007	0.250
456	-0.073	-0.038	0.984	0.459	1.355	0.651	0.947	0.287
480	-0.068	-0.007	0.975	0.506	1.410	0.722	1.024	0.394

Table 4 Corrosion rate data for X77ST in 2 M H_2SO_4 solution at 0% to 3.25% NaCl concentration

NaCl Conc. (%) / Exp. Time (h)	0% NaCl	0.25% NaCl	0.75% NaCl	1.25% NaCl	1.75% NaCl	2.25% NaCl	2.75% NaCl	3.25% NaCl
24	1.196	-0.412	0.706	0.118	0.137	0.823	-0.372	-0.219
48	0.725	-0.804	0.284	0.196	-0.255	0.559	-0.304	-0.631
72	1.085	-0.242	0.477	0.268	0.007	0.660	-0.163	-0.376
96	1.255	-0.025	0.466	0.338	0.181	0.725	0.230	-0.265
120	1.266	-0.008	0.435	0.227	0.122	0.623	0.235	-0.192
144	1.467	0.013	0.578	0.317	0.248	0.582	0.219	-0.070
168	1.392	0.036	0.448	0.176	0.202	0.535	0.269	0.058
192	1.478	0.064	0.419	0.218	0.221	0.534	0.194	0.145
216	1.636	0.102	0.399	0.261	0.261	0.597	0.301	0.092
240	1.617	0.108	0.431	0.274	0.339	0.490	0.271	0.096
264	1.778	0.114	0.351	0.351	0.233	0.602	0.249	0.092
288	1.946	0.225	0.377	0.284	0.286	0.595	0.337	0.132
312	2.191	0.172	0.483	0.449	0.463	0.584	0.502	0.050
336	2.257	0.211	0.403	0.382	0.375	0.561	0.399	0.109
360	2.307	0.303	0.387	0.366	0.417	0.665	0.429	0.239
384	2.371	0.355	0.379	0.369	0.468	0.712	0.480	0.253
408	2.392	0.356	0.319	0.337	0.465	0.670	0.446	0.278
432	2.436	0.399	0.355	0.337	0.467	0.687	0.451	0.290
456	2.413	0.443	0.396	0.402	0.512	0.757	0.547	0.327
480	2.406	0.503	0.428	0.414	0.562	0.757	0.567	0.348

3.2 Statistical analysis

ANOVA analysis was employed to assess the statistical relevance of NaCl concentration and exposure time on the corrosion resistance behaviour of 304ST and F20ST alloys throughout the exposure period. Table 5 shows the ANOVA data for both alloys. On Table 5, the statistical significance factor depicts the mathematical implication of NaCl concentration and exposure time on the vulnerability of the alloys to deterioration. The theoretical significance factor indicates the mathematical importance such that the mean square ratio is to be greater than, for the statistical significance factor to be important for the analysis. On Table 5, the mean square ratios for NaCl concentration with respect to the three alloys are greater than the theoretical significance factor. As a result, NaCl concentration is statistically relevant with respect to its impact on the resistance of the alloys to corrosion. The corresponding statistical relevance factor for the alloys are 99.74%, 99.08% and 97.05%. However, exposure time is statistically irrelevant for the alloys. This is proven from the statistical relevance factor values of -10.81%, -26.47% and -18.59. The ANOVA results shows that NaCl concentration substantially alters the corrosion resistance of the 304ST, F20ST and X77ST alloys in comparison to the influence of exposure time.

Table 5 ANOVA data for corrosion resistance of 304ST alloy from 2 M H_2SO_4 solution at 0.25% to 3.25% NaCl concentration

304ST			
Source of Variation	**Mean Square Ratio (F)**	**Theoretical Significance Factor**	**Statistical Relevance Factor, F (%)**
NaCl Concentration	81.06	2.16	99.74
Exposure Time	-6.83	2.03	-10.81
F20ST			
Source of Variation	**Mean Square Ratio (F)**	**Theoretical Significance Factor**	**Statistical Relevance Factor, F (%)**
NaCl Concentration	32.55	2.16	99.08
Exposure Time	-6.76	2.03	-26.47
X77ST			
Source of Variation	**Mean Square Ratio (F)**	**Theoretical Significance Factor**	**Statistical Relevance Factor, F (%)**
NaCl Concentration	40.57	2.16	97.05
Exposure Time	-6.04	2.03	-18.59

3.3 Standard deviation, mean and margin of error

Table 6 shows the standard deviation, average data values and margin of error for 304ST and F20ST corrosion rate data at all concentrations studied. The average data values for the alloys are comparable. However, the values for 304ST and X77ST tends to be more consistent or varies minimally with respect to NaCl concentration compared to the values obtained for F20S. The shows 304ST and X77ST are thermodynamically and electrochemically stable in the presence of Cl^- anions in H_2SO_4 solution. Although it must be noted that the average data values for 304ST at 0.25% NaCl concentration, and X77ST at 0% NaCl concentration are relatively and significantly high compared to other NaCl concentration and values. The SD values for 304ST, F20ST and X77ST are comparable with respect to NaCl concentration. Comparing these values, it shows generally the extent of corrosion rate results obtained throughout the exposure hours vary minimally with exposure time, hence marginal thermodynamic instability and variation in the electrochemical properties of the alloy surface in the acid chloride.

Table 6 Data for standard deviation, mean and margin of error for 304ST and F20ST alloys in H_2SO_4 solution at specific NaCl concentration

304ST								
Conc. (%)	**0% NaCl**	**0.25% NaCl**	**0.75% NaCl**	**1.25% NaCl**	**1.75% NaCl**	**2.25% NaCl**	**2.75% NaCl**	**3.25% NaCl**
SD	0.027	0.049	0.062	0.067	0.089	0.071	0.032	0.038
Mean	-0.047	3.509	0.985	0.589	0.432	0.314	0.285	0.236
Margin of Error	0.12%			**Total Data below 1 mm/y**	12.16%			
F20ST								
Conc. (%)	**0% NaCl**	**0.25% NaCl**	**0.75% NaCl**	**1.25% NaCl**	**1.75% NaCl**	**2.25% NaCl**	**2.75% NaCl**	**3.25% NaCl**
SD	0.056	0.011	0.023	0.034	0.078	0.069	0.043	0.057
Mean	-0.122	-0.015	0.951	0.474	1.448	0.601	1.018	0.301
Margin of Error	8.96%			**Total Data below 1 mm/y**	79%			
X77ST								
Conc. (%)	**0% NaCl**	**0.25% NaCl**	**0.75% NaCl**	**1.25% NaCl**	**1.75% NaCl**	**2.25% NaCl**	**2.75% NaCl**	**3.25% NaCl**
SD	0.222	0.125	0.045	0.046	0.176	0.071	0.095	0.107

Mean	2.250	0.308	0.388	0.369	0.425	0.659	0.441	0.212
Margin of Error	7.25%			**Total Data below 1 mm/y**	88%			

Conclusion

304 austenitic stainless steel exhibited linear variation in corrosion rate with respect to NaCl concentration in H_2SO_4 solution. This corrosion behavior significantly contrasts the observation for Atlas F20S ferritic stainless steel and X77CrZn5 alloy steel where the corrosion rate variation was not and marginally proportional to changes in NaCl concentration. Experimental outcome shows the alloys exhibited thermodynamic stability throughout the exposure hours. Statistical data showed NaCl concentration is the dominant influencing factor responsible for the corrosion behavior of the alloys. Data from corrosion rates of the alloys generally varied minimally from mean values. The standard deviation for Atlas F20S ferritic stainless steel are generally the lowest and X77CrZn5 alloy steel were the highest with respect to NaCl concentration.

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