



Trends in  
**Applied Sciences  
Research**

ISSN 1819-3579



Academic  
Journals Inc.

[www.academicjournals.com](http://www.academicjournals.com)

## **Comparative Studying of Marine Parameters' Effect, via Quantitative Method**

S. Atashin, M. Pakshir and A. Yazdani

Department of Materials Science and Engineering, Shiraz University, Shiraz, Iran

*Corresponding Author: S. Atashin, Department of Materials Science and Engineering, School of Engineering, No. 1, Shiraz University, Shiraz 7134851154, Iran Fax: +98 0711 6287294*

### **ABSTRACT**

The aim of present study was to investigate the contribution percentages of the most effective marine parameters in both individual and synergistic conditions. This analysis is known as a valuable statistical method in synergistic studies. The austenitic stainless steels, AISI 304 and AISI 316 have been exposed to the synthetic seawater for this application. The experimental data are obtained from potentiodynamic polarization scan. Fundamental parameters influencing corrosion in this environment, salinity, velocity, pH and temperature are identified. Quantitative analysis has been used to predict the value of variation applied to the corrosion rate via the full two-level factorial experimental design method. This analysis results to the valuable engineering data, which makes the comparison of parameters' effect possible. Quantitative analysis can assess the effects synergistically and considers all the possible contributions.

**Key words:** Environmental parameters, marine corrosion, synergistic effect, quantitative analysis

### **INTRODUCTION**

Marine corrosion is a costly worldwide problem. In addition to the huge cost in economic terms, corrosion is also blamed for devastating pollution to the environment (Bardal, 2004; Yang, 2008). Failure of operating equipment, like bridges and structures can have the disastrous results (Schweitzer, 2007; Duan *et al.*, 2008; Shifler, 2005; Melchers, 2005; Möller, 2006). AISI 304 and AISI 316 resist corrosion very well in seawater (Schumacher, 1979; Jones, 2001; Schweitzer, 2007). These alloys have been used in contact with seawater and many studies have investigated the corrosion resistance of them in marine atmosphere (Melchers, 2006; Mor and Beccaria, 2004; Schleich *et al.*, 2008; Al-Malahy and Hodgkiess, 2003; Sefaja and Malina, 1985). In spite of all these references, the effect of synergistic parameters has never been evaluated.

Temperature, flow velocity, pH and salinity are responsible for most of seawater corrosivity (Cristiani *et al.*, 2008; Al-Fozan and Malik, 2008; Ozturk and Grubb, 2005). Temperature and flow velocity alter the value of corrosion rate by affecting the value of dissolved oxygen and consequently the stability of the passive layer (Sasaki and Burstein, 2007; Bardal, 2004). The present chloride ion, in seawater accomplishes the breakdown of passive layer, formed on the metal surface (Schumacher, 1979). Salinity and pH affect and vary the corrosion rate by affecting the barrier properties of surface layers (Bardal, 2004). Corrosion generally, is a statistical effect governed by several variables such as environmental ones (Ekuma and Idenyi, 2007) and an alteration in one parameter can affect the relative effect of others (Schumacher, 1979). In all

previous studies, the effect of environmental parameters are studied just individually and the real synergistic condition is not considered. In this study, the synergistic effect of marine parameters has been evaluated via quantitative method. This analysis can describe the value of variation applied to corrosion rate. In this study, the quantity of mentioned environmental effects was survived individually and synergistically.

## **MATERIALS AND METHODS**

**Study area:** Experiments were conducted in the Corrosion Laboratory of Materials Engineering Department of Shiraz University (Iran) from November 2008 to October 2009.

**Solution preparation:** Experimental solution of seawater was prepared according to (ASTM D1141, 1999). The pH of solution, fixed by 5 molar sodium hydroxide solution (Zamanzade *et al.*, 2007). In order to prevent variations in species' concentrations during the formation of deposits, a large volume glass electrochemical cell (1000 mL) was used (Zamanzade *et al.*, 2007). The temperature of was set by the hot plate HP-840 and the fluid velocity was fixed by the mechanical stirrer, Heidolph RZR 2021. Salinity (the total weight in grams of solid matter dissolved in 1000 L of water) determined by measurement of chlorinity in the seawater (Schumacher, 1979; Roberge, 2000).

To achieve the desired salinity, the chloride-ion content was adjusted by changing the quantity of sodium chloride as the main part of seawater composition, while the value of other spices was fixed according to standard.

**Sample preparation:** This study examined the corrosion rate of commercially supplied austenitic stainless steels, AISI 304 and AISI 316 specimens. These alloys were obtained in rod form (12 mm diameter). The samples were first embedded in epoxy resin then, they polished successively with metallographic emery paper for increasing fineness of up to 1200 grits. Then, they were washed by distilled water, degreased by ethanol and dried by cool air.

**Electrochemical method:** A Standard Calomel Electrode (SCE) was used as the reference electrode and Pt gauze as the auxiliary. The samples were tested exactly after being immersed for 5 h in the solution of controlled cell. Electrochemical experiments were performed using a  $\mu$  Autolab type III/FRA2 electrochemical interface potentiostat-galvanostats. For potentiodynamic polarization experiments the potential was scanned from about -0.3 V to +0.3 V across the corrosion potential to achieve the linear range and the scan rate was  $0.005 \text{ mV sec}^{-1}$  to maintain a stable corrosion potential and a steady-state behavior (Perez, 2004). The instruments were controlled by the GPES version 4.9 software program. The corrosion rates, in  $\text{mm year}^{-1}$  were determined using Tafel extarpolarisation method (Yang, 2008).

**Analysis method:** Four parameters were chosen as mentioned earlier: salinity, pH, temperature and velocity. Each parameter was set at two levels, so there were  $2 \times 2 \times 2 \times 2 = 16$  trials (Meng *et al.*, 2007). The salinity was set at 30 and 40; pH trials were at 7.5 and 10.5, velocities were adjusted at 0 and 1000 rpm and temperature was fixed at 23 and  $65^\circ\text{C}$ . These ranges were defined according to variation limit of environmental parameters in the most natural seas. For each condition, at least three tests were carried to make sure about the reproducibility of the results. According to the full two-level factorial experimental analysis, each parameter should be applied in both high and low intense conditions. All the possible trials, which satisfy this phenomenon, are shown in Table 2. In

Table 2, each parameter is considered in both low and high levels shown by 1 or 2 signs and all the possible trials resulted from the combined action of parameters in each of the low or high levels are also gathered. For example, trial 4 represents the condition in which velocity and temperature are applied in high levels, while pH and salinity are in their low levels.

**RESULTS**

**Corrosion rate results:** In all conditions, the corrosion rates of AISI 304 and AISI 316 calculated by Tafel Extrapolation Method and gathered in the Table 2. The  $C_n$  relates to the corrosion rate of trial condition n, as in Table 1.

**Quantitative analysis results:** Quantitative analysis is capable of providing statistical data, which is very valuable in engineering designs. Quantitative effects of environmental parameters and their interactions on varying the value of corrosion rate were calculated by the analysis of variance via factorial experiment. Factorial experiment is consisted of two or more factors, each with discrete possible values or levels and takes on all possible combinations of these levels across all such factors. Using four factors each taking two levels, a factorial experiment with sixteen treatment combinations in total was defined, which resulted to a  $2 \times 2 \times 2 \times 2$  factorial design. As a first step, the average effects of the factors for each level were calculated. The pH factor is at the low level for trial conditions 1, 2, 3, 4, 5, 6,7 and 8 in Table 2. Hence, the calculation for the average effect of pH at the low level is shown:

Table 1: Design matrix for a four-parameter, sixteen-run experiment

Trial	pH	Salinity	Velocity	Temperature	Corresponding corrosion rate
1	1 <sup>a</sup>	1	1	1	C <sub>1</sub>
2	1	1	1	2	C <sub>2</sub>
3	1	1	2	1	C <sub>3</sub>
4	1	1	2	2	C <sub>4</sub>
5	1	2	1	1	C <sub>5</sub>
6	1	2	1	2	C <sub>6</sub>
7	1	2	2	1	C <sub>7</sub>
8	1	2	2	2	C <sub>8</sub>
9	2 <sup>a</sup>	1	1	1	C <sub>9</sub>
10	2	1	1	2	C <sub>10</sub>
11	2	1	2	1	C <sub>11</sub>
12	2	1	2	2	C <sub>12</sub>
13	2	2	1	1	C <sub>13</sub>
14	2	2	1	2	C <sub>14</sub>
15	2	2	2	1	C <sub>15</sub>
16	2	2	2	2	C <sub>16</sub>

<sup>a</sup>The No. 2 in this matrix represents high level of all parameters, while 1 represents low level

Table 2: Corrosion rate results gathered in trial conditions

Corrosion rate (mm year <sup>-1</sup> )	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>
AISI 304	1.048E-3	3.762E-3	5.121E-4	4.303E-3	4.676E-4	3.311E-3	1.029E-3	1.480E-3
AISI 316	6.472E-4	1.122E-2	3.392E-4	3.112E-3	8.474E-4	2.650E-3	7.862E-4	5.568E-2
Corrosion rate (mm year <sup>-1</sup> )	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>
AISI 304	2.371E-4	7.060E-2	2.511E-2	4.736E-3	1.325E-5	1.761E-3	1.944E-3	6.119E-2
AISI 316	2.969E-4	2.424E-2	1.027E-3	7.908E-2	3.805E-4	1.184E-3	3.638E-3	1.637E-2

$$C_{ip} = 1/8(C_1+C_2+C_3+C_4+C_5+C_6+C_7+C_8) \tag{1}$$

where,  $C_1, C_2, C_3, C_4, C_5, C_6, C_7$  and  $C_8$  are the corrosion rates in Table 2. The others including all interactions computed in the same manner as  $C_{iT}$ . The values of average effects of the factors for each level and are shown in Table 3. Where,  $C_{l/h,n}$  refers to average effects of the factor n and l or h refers to the low and high range respectively.  $C_{1,2,...,16}$  relates to corrosion rate of trial conditions 1, 2, ..., 16 as tabulated in Table 2. S, T, V, P refers to salinity, temperature, velocity and pH. The next step in this analysis was defining the Sum of Squares (SS).

For example, the sum of squares due to pH factor is calculated using the following formula:

$$SS_p = 2(C_{ip}-C_g)^2 + 2(C_{hp}-C_g)^2 \tag{2}$$

where,  $C_{ip}$  and  $C_{hp}$  refer to the average effects corresponding to the pH low and high levels and  $C_g$  is the average corrosion rate for 16 trial conditions. The sums of squares for other factors including possible interactions were computed in the same way and are tabulated in Table 4. The  $SS_n$  refers to sum of squares related to parameter n. S, T, V, P refers to salinity, temperature, velocity, pH as before and the combined form of them corresponds to the synergistic action of mentioned parameters.

Table 3: Average effects of the factors for each level

Parameter	Calculated value for AISI 304	Calculated value for AISI 316
$C_{iV}$	1.015E-02	5.183E-03
$C_{hV}$	1.254E-02	2.000E-02
$C_{iS}$	1.379E-02	1.500E-02
$C_{hS}$	8.899E-03	1.019E-02
$C_{iP}$	1.989E-03	9.410E-03
$C_{hP}$	2.070E-02	1.578E-02
$C_{iT}$	3.795E-03	9.953E-04
$C_{hT}$	1.889E-02	2.419E-02

Table 4: Sum of squares of factors and their interactions

Parameter	Calculated value for AISI 304	Calculated value for AISI 316
$SS_V$	5.703E-06	2.197E-04
$SS_S$	2.390E-05	2.307E-05
$SS_p$	3.501E-04	4.054E-05
$SS_T$	2.279E-04	5.381E-04
$SS_{VS}$	2.961E-05	2.427E-04
$SS_{Vp}$	3.558E-04	2.602E-04
$SS_{pS}$	3.740E-04	6.361E-05
$SS_{ST}$	2.518E-04	5.612E-04
$SS_{pT}$	5.780E-04	5.786E-04
$SS_{VT}$	2.336E-04	7.577E-04
$SS_{SVT}$	2.575E-04	7.808E-04
$SS_{VpT}$	8.837E-04	7.983E-04
$SS_{pST}$	6.019E-04	6.017E-04
$SS_{VSp}$	3.797E-04	2.833E-04
$SS_{VpST}$	6.076E-04	8.214E-04

Table 5: Contribution percentage of each factor

Parameters	Percentage							
	V	S	P	T	VS	VP	PS	ST
AISI 304	0.117	0.4917	7.202	4.689	0.609	7.319	7.693	5.181
AISI 316	3.343	0.3510	0.617	8.189	3.694	3.960	0.968	8.540

  

Parameters	Percentage							
	PT	VT	SVT	VPT	PST	VSP	VPST	
AISI 304	11.890	4.807	5.298	12.010	12.380	7.811	12.500	
AISI 316	8.806	11.532	11.883	12.149	9.157	4.311	12.500	

The final part of the analysis was obtaining the percentage contribution with the Eq. 3:

$$K (\%) = \frac{SS_K}{(SS_V + SS_S + SS_P + SS_T + SS_{VS} + SS_{VP} + SS_{PS} + SS_{ST} + SS_{PT} + SS_{VT} + SS_{SVT} + SS_{VPT} + SS_{PST} + SS_{VSP} + SS_{VPST})} \times 100\% \quad (3)$$

where, K is the factor that its effect should be calculated. For example, ST% is the percentage contribution of combining action of salinity and temperature. Table 5 contains the final results about the percentage contribution, which illustrates the quantitative effect of parameters on varying the value of average corrosion rate, while acting alone or synergistically.

## DISCUSSION

### Quantitative discussion

**Stainless steel 304:** Temperature has a remarkable contribution percentage. This result is expected according to previous studies (Sasaki and Burstein, 2007; Bardal, 2004; Möller, 2006; Melchers, 2005; Jones, 2001; Al-Malahy and Hodgkiess, 2003). The obtained results support the previous outcomes obtained by qualitative method too (Atashin *et al.*, 2010). According to the theoretical bases, high temperature reduces the amount of dissolved oxygen and prevents the formation of passive layer.

The contribution percentages of combined action of parameters are higher in the presence of temperature. This result satisfies the predicted outcome, given by qualitative method (Atashin *et al.*, 2010). Qualitative method results show that the temperature is such a dominant factor that neutralizes the other factor's effect, to some extent. The previous qualitative results support the quantitative data obtained by this method, which consider the temperature as a factor that increases the value of contribution factor of the other factors, while acting synergistically with them. These kinds of results have not been considered in previous researches that considered individually actions, not the synergistically ones.

Most of the contribution percentages are less than 10%. On the other hand, the contribution percentages of synergistically acting parameters are higher than single-acting ones. So, the remarkable role of interaction is obvious and the effect of synergistic action is observable. It shows the great value of considering the effects in synergistic manner in comparison to previous studies, which considered the individual effects (Sasaki and Burstein, 2007; Bardal, 2004; Möller, 2006; Melchers, 2005; Jones, 2001; Al-Malahy and Hodgkiess, 2003).

The pH has a high contribution percentage, while the contribution percentage of velocity is low. It shows that pH, by affecting the barrier properties (Bardal, 2004) has a larger effect than velocity by affecting the oxygen transport to the metal surface (Sasaki and Burstein, 2007; Bardal, 2004).

The most influential parameter is VpST, which shows the synergistic action's effect of all 4 parameters. After that, pST and VpT play the relatively important roles in varying the value of corrosion rate.

**Stainless steel 316:** By considering the data of Table 5, it is obvious that temperature has an important role in varying the corrosion rate of AISI 316. These results are expected and similar to which is reported in previous researches (Sasaki and Burstein, 2007; Bardal, 2004; Möller, 2006; Melchers, 2005; Jones, 2001; Al-Malahy and Hodgkiess, 2003). As the temperature gets higher, the amount of dissolved oxygen reduces. This prevents the formation of passive layer, so the corrosion rate increases in higher temperature and this factor can cause to the marked effect on the corrosion rate of active-passive alloys, like AISI 316. This result supports the obtained data of qualitative analysis (Atashin *et al.*, 2010).

Temperature increases the value of contribution percentages significantly, while being added to the other parameters. It is a surprising result which has not been considered in individually researches (Sasaki and Burstein, 2007; Bardal, 2004; Möller, 2006; Melchers, 2005; Jones, 2001; Al-Malahy and Hodgkiess, 2003).

In this kind of stainless steel, like AISI 304, most of the contribution percentages are less than 10% and the contribution percentages of synergistically acting parameters are higher. It really proves the importance of synergistically researches that considers the real condition. As can be seen here, in individual researches, the most contributing parameters are ignored. In previous qualitative analysis (Atashin *et al.*, 2010), the effect of one parameter can be influenced by the others and its variation direction may be reversed and the great role of combining action is obvious too. Both these analysis, showed undeniable role of synergistic action.

The pH has a low contribution value in AISI 316, while the contribution percentage of velocity is high. It shows that in contrarily to AISI 304, velocity, by affecting the oxygen transport to the metal surface (Sasaki and Burstein, 2007; Bardal, 2004) has more functional effect than pH, by affecting the barrier properties (Bardal, 2004).

The most influential parameter is VpST. VpT and SVT are the next two effective parameters for AISI 316 that affect the variations of the value of corrosion rate.

## CONCLUSIONS

The following conclusions can be drawn from this quantitative study:

- Quantitative analysis is incapable in predicting the variation direction of corrosion rate, but its specific importance in providing the quantitative data makes it really valuable. This makes the pre estimates possible, in engineering designs and result to comparative studying of effective parameters
- Synergistic action of parameters always increases the contribution value of parameters in variation of average corrosion; it is really valuable in engineering designs, in which the acceptable safety factor is vital
- In both AISI 304 and AISI 316 samples, temperature has a remarkable effect on varying the value of corrosion rate

- The pH has a high contribution percentage on varying the corrosion rate, in AISI 304 and low contribution value in AISI 316
- The contribution percentage of velocity on varying the corrosion rate is high in AISI 316 and low in AISI 304
- According to the obtained contribution percentages of parameters on varying the corrosion rate, the corrosion rate is not largely affected by each of the factors separately and the sharp role of interaction is obvious

## REFERENCES

- Al-Fozan, S.A. and A.U. Malik, 2008. Effect of seawater level on corrosion behavior of different alloys. *Desalination*, 228: 61-67.
- Al-Malahy, K.S.E. and T. Hodgkiess, 2003. Comparative studies of the seawater corrosion behavior of a range of materials. *Desalination*, 158: 35-42.
- Atashin, S., M. Pakshir and A. Yazdani, 2010. Comparative studying of marine parameters effect via qualitative method. *Trends Applied Sci. Res.*, 5: 120-128.
- ASTM D1141, 1999. Standard practice for the preparation of substitute ocean water. ASTM International, West Conshohocken, PA.
- Bardal, E., 2004. *Corrosion and Protection*. 11th Edn., Springer-Verlag, London, pp: 199-201.
- Cristiani, P., G. Perboni and A. Debenedetti, 2008. Effect of chlorination on the corrosion of Cu/Ni 70/30 condenser tubing. *Electrochim. Acta*, 54: 100-107.
- Duan, J., S. Wu, X. Zhang, G. Huang, M. Du and B. Hou, 2008. Corrosion of carbon steel influenced by anaerobic biofilm in natural seawater. *Electrochim. Acta.*, 54: 22-28.
- Ekuma, C.E. and N.E. Idenyi, 2007. Statistical analysis of the influence of environment on prediction of corrosion from its parameters. *Res. J. Phys.*, 1: 27-34.
- Jones, R.H., 2001. *Environmental Effects on Engineered Materials*. Marcel Dekker Inc., New York, pp: 39.
- Melchers, R.E., 2005. The effect of corrosion on the structural reliability of steel offshore. *Corrosion Sci.*, 47: 2391-2410.
- Melchers, R.E., 2006. Modelling immersion corrosion of structural steels in natural fresh and brackish waters. *Corr. Sci.*, 48: 4174-4201.
- Meng, H., X. Hu and A. Neville, 2007. A systematic erosion–corrosion study of two stainless steels in marine conditions via experimental design. *Wear*, 263: 355-362.
- Mor, E.D. and A.M. Beccaria, 2004. Effects of temperature on the corrosion of copper in sea water at different hydrostatic pressures. *Mater. Corros*, 30: 554-558.
- Möller, H., 2006. The corrosion behavior of steel in seawater. *Proceedings of the 8th International Corrosion Conference*, Nov. 14-15, The Southern African Institute of Mining and Metallurgy, pp: 1-9.
- Ozturk, B. and J.F. Grubb, 2005. Review of N08367 seawater service experience. Houston, TX, Paper 05239. <http://www.allegHENyludlum.com/ludlum/Documents/Seawater.pdf>
- Perez, N., 2004. *Electrochemistry and Corrosion Science*. Kluwer Academic Publishers, New York, pp: 173.
- Roberge, P.R., 2000. *Handbook of Corrosion Engineering*. McGraw-Hill Companies Inc., New York, pp: 129-131.
- Sasaki, K. and G.T. Burstein, 2007. Erosion–corrosion of stainless steel under impingement by a fluid jet. *Corr. Sci.*, 49: 92-102.



- Schleich, W., R. Feser, G. Schmitt, S. Haarmann and K. Schnier, 2008. Effect of seawater chlorination on the erosion corrosion behavior of CuNi90/10. Houston, TX, Paper 08231. <http://www.copper.org/Applications/cuni/pdf/1182.pdf>
- Schumacher, M.M., 1979. Seawater Corrosion Handbook, Corrosion of Metals in Marine Environments-an Overview. Noyes Publications, Berkshire, ISBN: 0-8155-0736-4, pp: 5-7.
- Schweitzer, P.A., 2007. Fundamentals of Metallic Corrosion: Atmospheric and Media Corrosion of Metals, Corrosion Engineering Handbook. 2nd Edn., Taylor and Francis Group, Florida, ISBN: 978-0-8493-8243-7, pp: 109-111.
- Sefaja, J. and J. Malina, 1985. Electrochemical aspects of steel corrosion in sea water. Surf. Technol., 26: 369-380.
- Shifler, D.A., 2005. Understanding material interactions in marine environments to promote extended structural life. Corr. Sci., 47: 2335-2352.
- Yang, L., 2008. Techniques for Corrosion Monitoring. 11th Edn., Woodhead Publishing Ltd., Cambridge, ISBN: 978-1-84569-187-5, pp: 63-65.
- Zamanzade, M., T. Shahrabi and A. Yazdian, 2007. Improvement of corrosion protection properties of calcareous deposits on carbon steel by pulse cathodic protection in artificial sea water. Anti-Corros. Meth., 54: 74-81.