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Evaluative Analysis of Silicon-Modified Gray Cast Iron Corrosion Rate in Hydrochloric Acid Solution

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Abstract: This paper presents an evaluative analysis of the impeded gray cast iron corrosion rate in hydrochloric acid solution due to silicon addition to the iron. The analysis was carried out within a range of process parameters such as 0.0462 – 0.218 (mm/yr), 12– 300 (hr) and 12-15.62 (%) for corrosion rates, exposure times and added silicon concentrations respectively. Critical assessment of results of the experiment shows that presence of silicon in the cast iron decreased its corrosion rate significantly from the corresponding control values. Experimental results evaluations also indicate that increase in silicon addition to the cast iron decreases the corrosion rate in line with derived model prediction. The empirical model which evaluated the silicon-modified gray cast iron corrosion rate from generated values of process parameters indicates that the corrosion rate is a sum two mathematical functions; power of silicon addition and natural logarithm of exposure time. The model; $\xi = 110003.5\vartheta^{-N} - 0.0273\ln\beta + 0.1779$ predicts the cast iron corrosion rate with maximum deviation < 8% (from actual results). This translated into over 92% operational confidence levels for the derived model. The validity of the model was rooted on the core model expression $\xi + S\ln\beta = \text{Ђ}\vartheta^{-N} + K$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the silicon - modified gray cast iron corrosion rate relative to values of the actual results is 0.0028%. The correlation coefficients between corrosion rate and exposure time and concentration silicon input were all > 0.97.

Key words: Evaluation - Corrosion rate - Gray cast iron - Silicon addition - Hydrochloric acid

INTRODUCTION

Cast iron is an engineering material that has found application in so many industrial processes such as in fabricating pipelines for water circulation. These pipes when buried during service deteriorate with time following the aggressiveness of the inherent environments surrounding the pipes. Reports [1, 2] has shown that these pipes deteriorate at different rates depending on a variety of factors which includes operation conditions, local geology and the type of cast iron materials. Studies [2-5] have shown that cast iron pipes basic deterioration mechanism is corrosion. This leads to pipe line reduction capacity and invariably the collapse of the pipes. Pit corrosion affects cast iron pipes negatively in that it is capable of acting as foci to stresses imposed to a pipe, leading to failure [3, 4].

Researches [6-10] have been carried out to determine the corrosion behavior of cast iron in aqueous environment of various degrees of corrosiveness. Most of these studies are successful investigations on cast iron corrosion, carried out within a space of hours, days, weeks and months. Not much work has been done on expounding the corrosion behavior of the metal within a long time frame such years.

Scientists [6, 7] have calculated the corrosion rates of cast iron in different test solutions at different exposure time considering the relevance of the corrosive medium and exposure time on the corrosion behavior of the iron. Electrochemical parameters of the cast iron specimens were also measured using DC polarization technique.

Polarization curves emanating from the results of investigation [11] on the corrosion of cast iron in

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concentrated sulphuric acid, under potentiostatic conditions show that gray cast iron corrodes in an active manner at the lower temperatures, but at temperatures higher than about 220°C, the cast iron will behave as a passive metal in the pure 96wt. - % acid. Dilution of the acid to about 93 wt.-% or the presence of reducing impurities results in an acid corrosion potential.

Researchers [12,13] have shown a number of factors which can combine and contribute significantly to the failure of gray cast iron pipes placed in service. These include; manufacturer`s flaws, corrosion damage, internal pressure and external loading. The failure of the cast iron due to its brittle nature stems on the tendency of the iron to corrode in aggressive environment. It has also been shown [14] that cast iron pipe failure is accelerated when the iron ages and eventually leaks.

Inorganic substances such as borates, arsenates, silicates, phosphates, chromates, dichromates, tung states and molybdates have all been found effective as inhibitors of metal corrosion. Introduction of these corrosion inhibitors have been widely considered a major breakthrough in protecting gray cast iron from excessive corrosion attack when deployed to serve in very aggressive environment. These inhibitors hinder corrosion reactions and thus reduce corrosion rate.

Research [15] has clearly shown that silicon exerts significant effects on gray cast iron when placed in aggressive media and during graphite formation depending on its added concentration. Silicon addition to gray cast iron at a concentration between 1.0 – 3.0% encourages graphitization, while 5.0-6.0% Si addition makes the iron a material for casting at temperatures up to 900°C. Furthermore, gray cast iron with silicon content between 14.0 – 17.0% inputs to the iron high corrosion resistance in aggressive media, as against the lower capability of gray cast iron without silicon addition. The high corrosion resistance of the silicon-modified gray cast iron was revealed [16] to be due to development of thin passive barrier film of hydrated oxide of silicon on the metal surface. Results of the investigation show that the film grows with time due to the dissolution of iron from the matrix, leaving behind silicon which hydrates due to presence of moisture.

Many authors [17-27] have performed failure analysis of gray cast iron pipes in water and wastewater environments and assessed the corrosion behavior of the iron in acidic environments [11]. However, there is no evidence of any work on predictive or mathematical analysis of silicon-modified gray cast iron corrosion rate in hydrochloric acid on the basis of the consortium effect of exposure time and silicon input (as inhibitor) on the iron. Thus, the objective of the present study is to derive an empirical model for the purpose of the evaluative analysis. The results generated will be compared with gray cast iron corrosion rates in hydrochloric acid with and without of silicon addition to the iron.

MATERIALS AND METHODS

Materials Preparation: The gray cast iron was produced using gray cast iron scrap and foundry returns. The materials were charged into the Cupola furnace, melted before it was poured into a ladle. A control sample was cast into flat test coupons, before addition of silicon powder to the remaining molten metal inside the ladle. The silicon powder was added in percentages ranging from 12 –15.62% to 100kg of the molten gray cast iron. The mixture was vigorously stirred for homogenization and casting into an already prepare moulds. The cast were allowed to solidify and cooled for 24 hours before removal from the moulds. They were detached, cleaned, brushed and cut into sizes for corrosion tests [28].

Test Samples Preparation: The test samples after being cut to sizes were ground, polished and used for corrosion test. The test samples were immersed for a range of time; 12-300 hours, with the help of strings, in 200mL0.5M hydrochloric acid, contained in 300 mL glass beaker kept at 30 ± °C. The samples were retrieved after 12hour interval progressively from the acid. Each test was repeated in triplicates to confirm reproducibility of results and the average values recorded. Other experimental details and techniques for calculating the gray cast iron weight loss and corrosion rate are as stated in the previous work [28].

RESULTS AND DISCUSSION

Table 1: Variation of gray cast iron corrosion rate ξ with exposure time β and concentration of added silicon ϑ [28]

(β)	(ϑ)	(V)	(ξ)
12	12.00	0.2770	0.2180
120	13.00	0.1700	0.1130
240	15.00	0.0560	0.0510
260	15.21	0.0544	0.0494
290	15.52	0.0520	0.0470
300	15.62	0.0512	0.0462

Computational analysis of the actual results shown in Table 1, gave rise to Table 2 which indicate that;

$$\xi + S \ln\beta = ꜧ\vartheta^{-N} + K \qquad (1)$$

Introducing the values of K, ꜧ, S, and N into equation (1) reduces it to;

$$\xi + 0.0273\ln\beta = 110003.5\vartheta^{-N} + 0.1779 \qquad (2)$$

$\xi = 110003.5\vartheta^{-N} - 0.0273 \ln\beta + 0.1779$ (3)

where

K = 0.1779, Ђ = 110003.5, N = 5.635 and
S = 0.0273; equalizing constant (determined using C-NIKBRAN [29])
(ξ) = Corrosion rate of gray cast iron due to silicon addition (mm/yr)
(ϑ) = Concentration of silicon (%)
(β) = Exposure time (hr)
(V) = Corrosion rate of gray cast iron devoid of silicon addition (mm/yr)

Boundary and Initial Conditions: Consider short round shaped gray cast iron coupon submerged in 0.5M hydrochloric acid, interacting with some corrosion-induced agents. The solution is assumed to be affected by undesirable dissolved gases. The considered range of the corrosion rates, exposure times and added silicon concentrations are 0.0462 – 0.218 (mm/yr), 12– 300 (hr) and 12-15.62 (%) respectively.

Table 2:Variation of ξ + Slnβ with Ђϑ^{-N}+ K

ξ + Slnβ	Ђϑ^{-N} + K
0.2858	0.2691
0.2437	0.2360
0.2006	0.2038
0.2012	0.2019
0.2018	0.1993
0.2019	0.1986

Model Validity: The validity of the model is strongly rooted on the core model equation (1) where both sides of the equation are correspondingly almost equal. Table 2 also agrees with equation (1) following the values of ξ +S lnβ and Ђϑ^{-N} + K evaluated from the actual results in Table 1. Critical assessment of results of the experiment in Figs. 1-4 shows that presence of silicon in the cast iron decreased the iron corrosion rate significantly from the corresponding control values. Experimental results evaluations also indicate that increase in silicon addition to the cast iron decreases the corrosion rate in line with derived model prediction as shown in Figs. 1-4. The empirical model which evaluated the silicon-modified gray cast iron corrosion rate from generated values of process parameters indicates that the corrosion rate is a sum two mathematical functions; power of silicon addition and natural logarithm of exposure time.

The derived model was also validated by comparing the corrosion rate predicted by the model and that obtained from the experiment. This was done using various analytical techniques which includes statistical, graphical and deviational analyses.

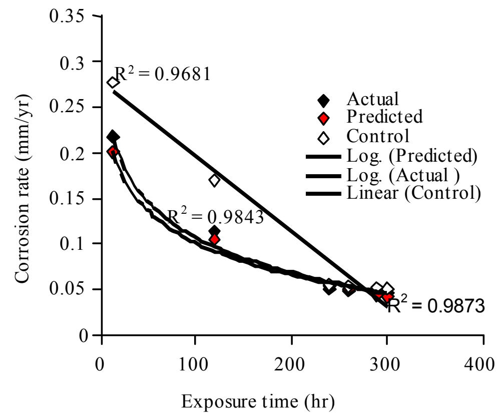

Fig. 1: Coefficient of determination between corrosion rate and exposure times obtained from actual, control and model-predicted results

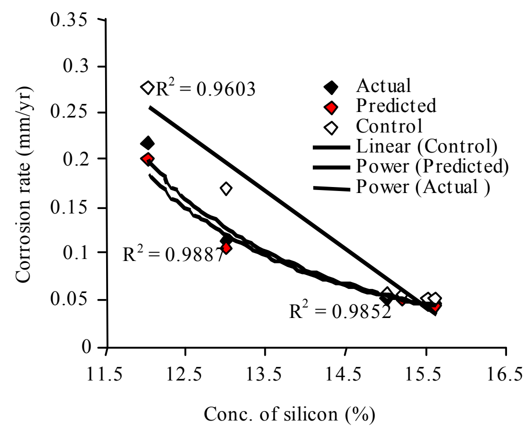

Fig. 2: Coefficient of determination between corrosion rate and concentration of silicon input as obtained from actual, control and model-predicted results

Statistical Analysis

Correlation: Evaluation of the correlation coefficient between corrosion rate and exposure time & concentration of silicon input was done using Microsoft Excel Version 2003. The results of the analysis as obtained from the actual, control and derived model are 0.9921, 0.9839 and 0.9936 & 0.9926, 0.9799 and 0.9943respectively. The evaluations were based on the coefficients of determination R^2 shown in Figs. 1 and 2, and then calculated using equation (4).

$$R = \sqrt{R^2} \quad (4)$$

Standard Error (STEYX): The standard error incurred in predicting the model-based corrosion rate relative to values of the actual results is 0.0028%. The standard error was evaluated using Microsoft Excel version 2003.

Graphical Analysis: The validity of the derived model was further verified by plotting (using Microsoft Excel (version 2003)) values of the predicted silicon-modified gray cast iron corrosion rates besides those of the gray cast iron produced with and without silicon addition. The essence of the plots was to evaluate the trend of results. Comparative analysis of Figs. 4 and 5 indicate very close alignment of curves which depicted significantly similar trend of data point's distribution for the actual, control and derived model-predicted corrosion rate. Actual and model-predicted results were in very proximate agreement.

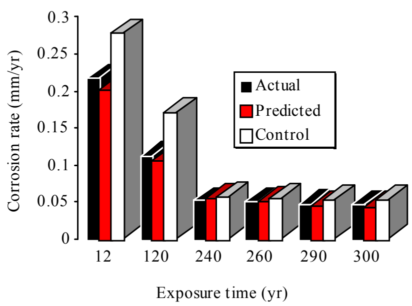

Fig.3: Variation of corrosion rates with exposure time as obtained from actual, control and model-predicted results

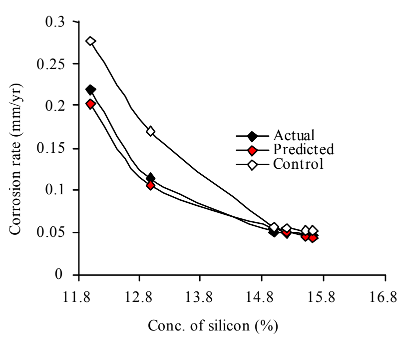

Fig.4: Variation of corrosion rate and concentration of silicon input as obtained from actual, control and model-predicted results

Deviational Analysis: Analysis of the corrosion rates obtained from the actual and model-predicted results shows little deviation on the part of model-predicted results. This was attributed to the fact that the effects of the surface properties of the gray cast iron which played vital roles during corrosion in hydrochloric acid were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted corrosion rate to those of the corresponding experimental values.

The deviation Dv, of model-predicted corrosion rate from the corresponding actual result was given by;

$$Dv = \left(\frac{\xi_P - \xi_E}{\xi_E}\right) \times 100 \qquad (5)$$

where,

ξ_E and ξ_P are corrosion rates evaluated from actual and model-predicted respectively/

Fig. 5 shows that the model; $\xi = 110003.5\vartheta^{-N} - 0.0273 \ln\beta + 0.1779$ predicts the silicon-modified gray cast iron corrosion rate with maximum deviation < 8% (from actual results).This translates into over 92% model operational confidence. The figure shows that the least and highest deviations of model-predicted results (from actual results) are 1.42 and -7.71 %.

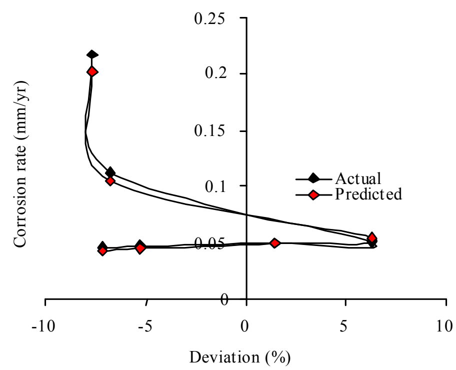

Fig. 5: Deviation of model–predicted results from actual values

These deviations correspond to model-predicted corrosion rates: 0.0501 and 0.2012 (mm/yr); exposure times: 260 and 12(hr) and concentration of silicon inputs: 15.21 and 12 (%) respectively.

Correction factor, Cf to the model-predicted results was given by;

$$Cf = -\left(\frac{\xi_P - \xi_E}{\xi_E}\right) \times 100 \qquad (6)$$

Critical analysis of Fig. 5 and Fig. 6 show that the evaluated correction factors are negative of the deviation as shown in equations (5) and (6).

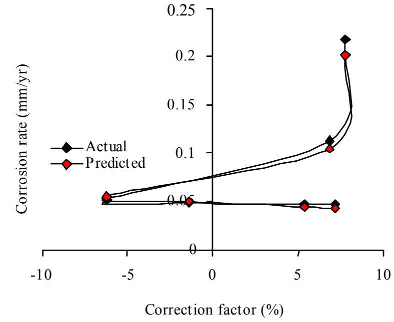

Fig. 6: Correction factor to model–predicted results

The correction factor took care of the negligence of operational contributions of the effects of surface properties of the gray cast iron which actually affected the corrosion process. Introduction of the corresponding values of Cf from equation (6) into the model gives exactly the corresponding actual corrosion rate. Fig. 6 indicates that the maximum correction factor to the model - predicted corrosion rate was less than 8%. The table shows that the least and highest correction factors to the model-predicted results (from actual results) are – 1.42 and 7.71 %. These correction factors also correspond to model-predicted corrosion rates: 0.0501 and 0.2012 (mm/yr); exposure times: 260 and 12 (hr) and concentration of silicon inputs: 15.21 and 12 (%) respectively.

The deviation of model predicted results from that of the actual is just the magnitude of the value. The associated sign preceding the value signifies deviation deficit (negative sign) or surplus (positive sign).

CONCLUSION

Following the evaluative analysis of silicon-modified gray cast iron corrosion rate in hydrochloric acid, presence of silicon in the cast iron decreased its corrosion rate significantly from the corresponding control values. Increase in silicon addition to the cast iron decreases its corrosion rate in line with derived model prediction. The empirical model which evaluated the silicon-modified gray cast iron corrosion rate from generated values of process parameters indicates that the corrosion rate is a sum two mathematical functions; power of silicon addition and natural logarithm of exposure time. The model; $\xi = 110003.5\vartheta^{-N} - 0.0273\ln\beta + 0.1779$ predicts the cast iron corrosion rate with maximum deviation < 8% (from actual results). This translated into over 92% operational confidence levels for the derived model. The validity of the model was rooted on the core model expression $\xi + S\ln\beta = Ђ\vartheta^{-N} + K$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the silicon-modified gray cast iron corrosion rate relative to values of the actual results is 0.0028%. The correlation coefficients between corrosion rate and exposure time and concentration silicon input were all > 0.97.

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