# MODELING AND PREDICTION OF HIGH TEMPERATURE OXIDATION OF STEELS USED IN PETROLEUM REFINERY HEATERS

Naji Abdelwanis*, Abdelrahman S. Sultan**, Omar M Elmabrouk***, and Farag A. Maetouq****

**Abstract:** This paper implements Response Surface Methodology (RSM), with rotatable Central Composite Design (CCD), in modeling and prediction of high-temperature oxidation of steels used in petroleum refinery heaters. A mathematical quadratic model was developed for modeling and prediction of the relationship between the weights gained of the oxidized steel and condition parameters, namely chromium percentage, temperature and exposure time with a range of, 0-5wt%, 450-500°C, and 0-40hrs respectively. Also, the surface plots and response surface contour plots were constructed for investigating the simultaneous effect of the condition process parameters on the weights gained from the oxidized steel and determining the optimum values of the parameter conditions. The Mean Absolute Error (MAE) between the actual and predicted weights gained from the oxidized steel values was calculated to test the validity of the developed mathematical model. The value of the (MAE) was 0.42 which indicates that the developed mathematical model have good agreement with the actual. The statistical analysis of variance (ANOVA) was also utilized to analyze the effect of the investigated parameter condition, this analysis results demonstrated that chromium weight percent and temperature have the most significant effect on the weights gained oxidation of steels used in petroleum refinery heaters followed by exposed time.

**Keywords**: Modeling; Prediction, RSM, High temperature corrosion.

## INTRODUCTION

For oil refinery heaters (furnaces) are used to preheat feedstock to reaction or distillation temperatures. The fluid heaters are designed to increase the temperature to about 510°C (950°F) maximum. Based on economic assumptions, operating conditions, and emission requirements, the fuel burned may be remaining fuel oils, refinery gas, natural gas or combinations. The gaseous combustion products, which are mixtures of mainly; carbon dioxide, water, and nitrogen are surrounded by the steel pipes used in heaters. Additionally to other specifications, corrosion allowance the selection of heater tubes and their thicknesses are necessary (API standard 530, 2003). Due to the fact that the corrosion during operation leads to decrees the tube thicknesses. Also, for many industrial engineering and in many domains of material science e.g. high-temperature processes in petroleum industry or metal production and fabrication, the oxidation behavior of materials at elevated temperatures became of crucial importance. Moreover, to investigate and analyze the kinetics of the oxide film growth is very essential to control high-temperature oxidation (Knoll *et al*, 1999).

Thermogravimetric analysis (TGA) technique was used to investigate the oxidation behaviors of three different steel, C-5, P-11 and P-22, used in the construction of petroleum refinery heaters in two different environments namely air and $O_{22}H_20O_7$-52$N_2$. The temperature of the gas composition which simulates the combustion products of natural gas were 450 and 500°C (Sultan *et al*, 2012). The diffusional transport associated with high-temperature corrosion processes using numerical modeling was studied. The external scale formation and internal subscale formation during oxidation, coating degradation by oxidation

*Department of Mechanical Engineering-Omar Al-Mukhtar University. E-mail: nabdelw@g.clemson.edu.ly
**Department of Chemical and Petroleum Engineering-Elmergib University. E-mail: assultan@elmergib.edu.ly
***Department of Industrial &Manufacturing Systems Engineering-Benghazi University. E-mail: omar.elmabrouk@uob.edu.ly
****Department of Industrial &Manufacturing Systems Engineering-Benghazi University. E-mail: farag.maetouq@uob.edu.ly

and substrate inter diffusion, carburization, sulfidation and nitridation were included in the corrosion processes. The complexities such as concentration-dependent diffusivities, cross-term effects in ternary alloys, and internal precipitation where many compounds of the same element may form (e.g., carbides of Cr) or several compounds exist instantly (e.g., carbides containing varying amounts of Ni, Cr, Fe or Mo) were reviewed. Large number of boundary conditions that differ with time and temperature were also included. Either the solute or corrodant transport was modeled using finite- difference (F-D) techniques. High temperature corrosion modeling studies using F-D were also considered (James, 1995).

In the potential geological repository at Yucca Mountain, the chosen materials for the outer barrier of nuclear waste packages are wrought and cast low-carbon steel. The potential declination mode for these materials at the moderately high temperatures assumed at the container surface, e.g. 323-533K (50-260°C) is the dry oxidation. The prediction of the dry oxidation of iron and low-carbon steel was numerically predicted based on both the experimental data and the theory of parabolic oxidation. The Forward Euler approach was applied in the numerical method and applied to integrate the parabolic rate law for arbitrary and complex temperature histories. The assumption of the growth of a defect free, adherent oxide, the surface penetration of a low-carbon steel barrier following 5000 years of exposure to a severe, but repository-relevant, temperature history were predicted to be only about 0.127mm, less than 0.13% of the expected container thickness of 10cm.

The predicted metal penetration values were raised by permitting the oxide to spall when getting to a critical thickness, however degradation was still calculated to be negligible. According to the model calculations, dry oxidation was not expected to effectively degrade the performance of thick, corrosion tolerance barriers constructed of low-carbon steel (Henshall, 1996).

Very limited researches have been directed toward the modelling and prediction of the high temperature oxidation behavior of the steels used in petroleum refinery heaters using RSM. In this paper, the effect of the most significant oxidation process parameters namely, the temperature, time and chromium weight percent on the high temperature oxidation of the steels used in petroleum refinery heaters has been investigated and mathematically modeled using Response surface methodology (RSM) allowing with CCD. The model used to predict the oxidation behavior and validated using Mean Absolute Error (MAB).

## EXPERIMENTAL WORK

### Sample preparation

In this study, C-5, P-11, P-22 and P-5 steels have different chromium content as given in (Table 1) were used for air oxidation experiments. These steels are used in the construction of petroleum refineries pipes and equipments. Test specimens were cut and machined into 50mm x 25mm x 2mm steel pieces. The steel specimens were kept at 700°C for 1 hour and then let them to cool inside the furnace. The steel samples were prepared with 3mm diameter used to suspend them with quartz hook to the electro balance during the oxidation experiments.

Grinding without polishing was recommended to provide a surface that favored the nucleation of oxides and result in dense adherent scales. So, using SiC papers, the steel samples were ground sequentially starting from 120 grit and following 220, 320, 400 and 600 grits. The samples were ultrasonically cleaned and degreased by using alcohol to remove SiC and the steel particles left from the grinding. The surface areas of samples were calculated after measuring the dimensions of the samples with the aid of a micrometer. Table 1 shows the Chemical composition of the steel samples.

### Thermogravimetric analysis (TGA)

A CAHN C-1000 electro balance was used for the thermogravimetric analysis in this study. The sample weight change during oxidation was detected and converted to an electrical signals (voltage) output. These output signals were read and converted to weight change on a digital computer through a data obtaining unit. At the start of each experiment, the weight was zeroed by mechanical and electronic taring of the balance. The steel samples were hanged to the balance by a quartz hook in the middle of a Pyrex reaction tube in the hot zone of the furnace. The reaction tube had a diameter and a length of 5 and 80cm respectively and it was extended out of a vertical split furnace from both ends. The upper end of the reaction tube was connected the electro balance and the lower end was left open to the atmosphere.

Table 1. Chemical composition of the steel samples.

| Steel | ASTM | C% | n% | P% | S% | Si% | Cr% | Mo% | V% |
|---|---|---|---|---|---|---|---|---|---|
| C-5 | A 106 | 0.5 | 0.5 | 0.07 | 0.05 | 0.11 | -- | -- | -- |
| P-11 | A 335 | 0.5 | 0.5 | 0.03 | 0.03 | 0.77 | 1.25 | 0.57 | -- |
| P-22 | A 335 | 0.5 | 0.47 | 0.03 | 0.03 | 0.45 | 2.25 | 1.0 | -- |
| P-5 | A335 | 0.4 | 0.5 | 0.03 | 0.03 | 0.45 | 5.0 | 0.55 | -- |

### Air oxidation

The oxidation tests of four different steel samples were done in air at 450°C, 475°C and 500°C (temperature range depends on the designed by the program means it is optional). The durations changing between 35 to 96 hours were used. It was found that the nature of the oxides did not change for long and short oxidation periods, and 48 hours of oxidation period was selected for most of the tests in this study.

During the oxidation tests, the air flow rate was brought into the reaction chamber through the upper part by means of an air pump and controlled to be equivalent to 120 cm/min gas velocity in the reaction chamber. Figure 1 illustrates the schematic representation of setup for air oxidation (Khanna and Kofstad, 1990; Sultan *et al*, 2012).

To provide an inert atmosphere and to assure that the sample was not oxidized during heating, the reaction tube and the balance were flushed by a flow of nitrogen gas. Furthermore, the weight changes of the samples subjected to oxidation were recorded by using a PCLD 711 analog-to-digital (A/D) converter via a computer system. In this study, a 100 milligram recording range (with an accuracy of 0.1% of recording range) was used for 48 hours oxidation experiments with overall accuracy of ±0.2mg. A basic computer code was used to program the computer to get a reading from the data acquisition unit for every minute. After each experiment, the supply of the oxidizing gases was cut, but the continuous flow of the $N_2$ gas was conserved through the reaction tube until the system was cooled down. After cooling the furnace, the samples were taken out from the furnace and kept in desiccators for consecutive analysis of the oxidation products.

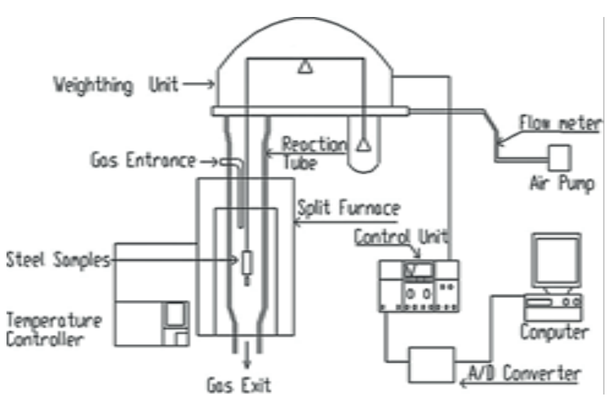


Fig. 1. Location map of the study area in NW Murzuq Basin, SW Libya.

## RESPONSE SURFACE METHODOLOGY

Modeling and prediction the effect of process parameters using response surface methodology involves five major steps, these steps are (1) statistically design the experiments, (2) performing experiments practically or using simulation technique, (3) determining the coefficients in a mathematical model, (4) predicting the response and (5) validate the model by calculating the difference between the actual or simulating response and the predicted response (Geoge *et al*, 2012).

Central composite design (CCD) has been employed in this paper to model and predict the effect of high temperature oxidation process parameter, namely the temperature, the exposed time and the weight percent chromium on the steel oxidation. CCD has been widely utilized for fitting a second-order model from experimental runs. The design consists of a 2n factorial or fraction (coded to the usual ±1 notation) augmented by 2n axial points ($\pm\alpha$, 0, 0,..., 0), (0, $\pm\alpha$, 0,..., 0),..., (0, 0,..., $\pm\alpha$), and center points (0, 0, 0,..., 0). In this case, the main effects and interactions may be obtained by fractional factorial designs running only a minimum experimental runs.

The responses and the corresponding parameters were modeled, analyzed and optimized using analysis of variance (ANOVA) approach to estimate the process parameters by means of response surface methodology (RSM).

RSM is statistical and mathematical techniques that widely used to develop, improve, optimize processes and evaluate the behavior of different influencing parameters (Raymond *et al*, 2009). RSM could also be defined as the most frequently used method of RSM is CDD, it is applicable for fitting a quadratic surface and helps to optimize the effective process parameters with a minimum number of experiments, as well as analyzing the interaction between these process parameters.

The application of RSM is achieved with measurable input parameters, the response surface can be expressed, in Equation 1, as follows (George *et al*, 2012):

$$Y = f(X_1, X_2, X_3, X_4, \ldots, X_n) \quad (1)$$

Where Y is the output or response of the process, Xi is the input process parameters and n is the number of parameters. The aim of the RSM is to mathematically model and predict the response variable (Y) and search for a suitable approximation of the functional relationship between the input measurable parameters and the output or response surface. Second degree quadratic model as given by Equation 2 was utilized for creating the model formation.

The maximum and minimum values of the independent measurable parameters values are given in (Table 2), α is 2n/4, n= number of variables (Hussein, 2015).

(In this study; α is 23/4 = 1.68).

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

Where Y is the predicted response calculated values using the mathematical model, xi and xj are the input variables, β0 is the constant coefficient, βi , βii and βij are the inter-action coefficients of linear, quadratic, and the second order terms, respectively, and k is the number of studied factors. For statistical analysis, Xi are the actual experimental variables (Hussein, 2015).

The analysis of variance (ANOVA) was utilized to determine the lack of fit and the effect of linear, quadratic and interaction terms on response variables y. MINITAB (version 16) statistical analysis software was used to design the experiment, to analyze the experimental data and to plot the response surface and contour plots and to obtain the mathematical model. Table 2 shows the different variables used in the experiment and their levels, and Table 3 shows the planning matrix of the experiment with the experimental weight gained.

It is observed from the adequacy test by ANOVA that linear terms %Cr, interaction term %Cr with Temp. and Time with %Cr and Temp. with Time and square terms Time2 are significant. The levels of significant are illustrated in the Table 4. The fit summary recommended that the quadratic model is statistically significant for analysis of wt. gain. For the relevant fitting of

Table 2. Different variables used in the experiment and their levels.

| Variable | Coding | Level | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| Cr (%wt) | A | 0 | 2.5 | 5 |
| Time (hr) | B | 0 | 24 | 48 |
| Temperature (°C) | C | 450 | 475 | 500 |

Table 3. The planning matrix of the experiment with the experimental weight gained.

| wt.gain (g) | Temp. (Co) | Cr (%wt) | Time (hr) |
|---|---|---|---|
| 0 | 450 | 5 | 0 |
| 0.254087 | 475 | 2.5 | 24 |
| 0.254087 | 475 | 2.5 | 24 |
| 0.254087 | 475 | 2.5 | 24 |
| 0 | 450 | 0 | 0 |
| 0.254087 | 475 | 2.5 | 24 |
| 0.15242 | 450 | 5 | 48 |
| 0.117983 | 475 | 5 | 24 |
| 0.375659 | 475 | 0 | 24 |
| 0.177854 | 500 | 5 | 48 |
| 0.254087 | 475 | 2.5 | 24 |
| 0.311769 | 450 | 0 | 48 |
| 0.350096 | 500 | 2.5 | 24 |
| 0.158262 | 450 | 2.5 | 24 |
| 0.644323 | 500 | 0 | 48 |
| 0 | 500 | 5 | 0 |
| 0 | 500 | 0 | 0 |
| 0.254087 | 475 | 2.5 | 24 |
| 0 | 475 | 2.5 | 0 |
| 0.359333 | 475 | 2.5 | 48 |

wt. gain. the non-significant terms (p-value is greater than 0.05) are eliminated by backward the elimination process.

The ANOVA Table for the curtailed quadratic model for wt. gain is illustrated in (Table 4), the reduced model results demonstrate that the model is significant (R2 and adjusted R2 are 95.99% and 92.37%, respectively), and lack of fit is non-significant (p-value is less than 0.05). After eliminating the non-significant terms (Table 5), the final response equation for weights gained is given as follows.

wt. gain = -2.41496 + 0.29693% Cr - 0.00014 Time2- 0.00061 Temp.*%Cr + 0.00007 Temp.*Time - 0.00130% Cr*Time

The last model tested for variance analysis (F-test) found that the adequacy of the test is established. The computed values of response parameters, model graphs are generated for the further analysis in the next section. Table 6 shows the analysis values for weight gained mathematical model.

## RESULTS AND DISSCUSION

The effect of the high temperature oxidation process parameters (chromium weight percentage, temperature and exposed time) on the response variables high temperature oxidation (weight gain per unit surface area) have been investigated by conducting experiments as described previously in the experimental work section.

Minitab software 16 was used for further analyze the results. The second-order mathematical model was proposed in find the correlation between the weight gain per unit surface area and the oxidation process parameters taken into account.

The analysis of variance (ANOVA) was utilized to evaluate the sufficiency of the second-order mathematical model. The results obtained from the experiments were compared with the predicted values calculated from the model as shown in (Table 7).

Table 4. Anova table for wt.gain (before elimination) Estimated Regression Coefficients for MRR.

| Term | Coef | SE Coef | T | P | |
|---|---|---|---|---|---|
| Constant | -2.41496 | 9.89535 | -0.244 | 0.812 | non significant |
| Temp. | 0.00827 | 0.04172 | 0.198 | 0.847 | non significant |
| %Cr | 0.29693 | 0.12453 | 2.384 | 0.038 | Significant |
| Time | -0.01875 | 0.01297 | -1.446 | 0.179 | non significant |
| Temp.*Temp. | -0.00001 | 0.00004 | -0.152 | 0.882 | non significant |
| %Cr*%Cr | -0.00184 | 0.00439 | -0.42 | 0.684 | non significant |
| Time*Time | -0.00014 | 0.00005 | -2.867 | 0.017 | Significant |
| Temp.*%Cr | -0.00061 | 0.00026 | -2.386 | 0.038 | Significant |
| Temp.*Time | 0.00007 | 0.00003 | 2.781 | 0.019 | Significant |
| %Cr*Time | -0.0013 | 0.00027 | -4.862 | 0.001 | Significant |
| S = 0.0455052 R-Sq = 95.99% R-Sq(adj) = 92.37% | | | | | |

Table 5. ANOVA table for MRR (after backward elimination.

| Term | Coef | SE Coef | T | P | Remark |
|---|---|---|---|---|---|
| Constant | 31.162 | 1.1599 | 26.867 | 0.00 | (most significant) |
| Ip | 11.012 | 0.9115 | 12.08 | 0.00 | (most significant) |
| Ton | 14.405 | 0.9115 | 15.803 | 0.00 | (most significant) |
| Toff | -5.21 | 0.9115 | -5.715 | 0.00 | (most significant) |
| Ip×Ip | -3.553 | 0.9136 | -3.889 | 0.002 | (significant) |
| Ton×To n | -2.205 | 0.9136 | -2.414 | 0.033 | (significant) |
| Ip×Ton | 6.959 | 1.1768 | 5.913 | 0.000 | (most significant) |
| Ton×Tof f | -2.959 | 1.1768 | -2.514 | 0.027 | (significant) |
| S = 3.328 R-Sq = 97.6% R-Sq(adj) = 96.2% | | | | | |

Table 6. Analysis of Variance for wt. gain mathematical model.

| Source | DF | Seq SS | Adj SS | Adj MS | F | P |
|---|---|---|---|---|---|---|
| Regression | 9 | 0.495272 | 0.495272 | 0.05503 | 26.58 | 0 |
| Linear | 3 | 0.379119 | 0.016101 | 0.005367 | 2.59 | 0.111 |
| Square | 3 | 0.039388 | 0.039388 | 0.013129 | 6.34 | 0.011 |
| Interaction | 3 | 0.076766 | 0.076766 | 0.025589 | 12.36 | 0.001 |
| ResidualErorr | 10 | 0.020707 | 0.020707 | 0.002071 | | |
| Lack-of-Fit | 5 | 0.020707 | 0.020707 | 0.004141 | * | * |
| Pure Error | 5 | 0 | 0 | 0 | | |
| Total | 19 | 0.51598 | | | | |

Table 7. The predicted weight gained, the actual weight percent, the absolute error and the mean absolute error.

| Predicted Wt. gained | Actual Wt. gained | Absolute error |
|---|---|---|
| 0.015 | 0 | 0.015 |
| 0.256 | 0.254 | 0.001 |
| 0.256 | 0.254 | 0.001 |
| 0.256 | 0.254 | 0.001 |
| 0 | 0 | 0 |
| 0.256 | 0.254 | 0.001 |
| 0.098 | 0.152 | 0.054 |
| 0.156 | 0.117 | 0.038 |
| 0.333 | 0.375 | 0.042 |
| 0.221 | 0.177 | 0.0431 |
| 0.256 | 0.254 | 0.0019 |
| 0.354 | 0.311 | 0.0422 |
| 0.307 | 0.350 | 0.0430 |
| 0.197 | 0.158 | 0.0387 |
| 0.631 | 0.644 | 0.013 |
| 0 | 0 | 0 |
| 0.056 | 0 | 0.056 |
| 0.256 | 0.254 | 0.001 |
| 0.013 | 0 | 0.013 |
| 0.342 | 0.359 | 0.017 |
| MAE | | 0.42 |

It is clear that the regression the values of mathematical model is reasonably well fitted with the observed values. The mean absolute error is calculated as the mean absolute difference between the predicted and observed values as 0.42.

Figure 2. shows the estimated response surface for weight gain per unit surface area in relation to high temperature oxidation process parameters of chromium weight percentage and temperature. It is clear from the figure that, the weight gain per unit surface area tends to increase, significantly with increase in temperature and lower value of chromium weight percentage. Hence, maximum weight gain per unit surface area is obtained at high peak temperature (500°C) and chromium weight percentage, as shown by the arrow in (Fig. 2), this is due to lost effect of the chromium, in other words, in high temperature working condition, the lower content of chromium steel should not be selected.

Figure 3 represents the weight gain per unit surface area as a function of chromium weight percentage and exposed time, whereas the temperature remains constant in its higher level of 475°C. The results show that the highest weight gain per unit surface area values occurred at the higher time and lower chromium weight percentage.

The direction of further improvement is illustrated in the counter plots presented as arrow. This is the direction taken in further experimentation. From this observation, it can be concluded that exposed time is directly and chromium weight percentage is inversely proportional to the weight gain per unit surface area for the studied range of the conducted experiments

Additionally, The effect of the temperature and the exposed time is on the estimated response surface of weight gain per unit surface area is shown in (Fig. 4), the chromium weight percentage is hold constant in its average value of 2.5%. The results show that the weight gain per unit surface area increases when the temperature

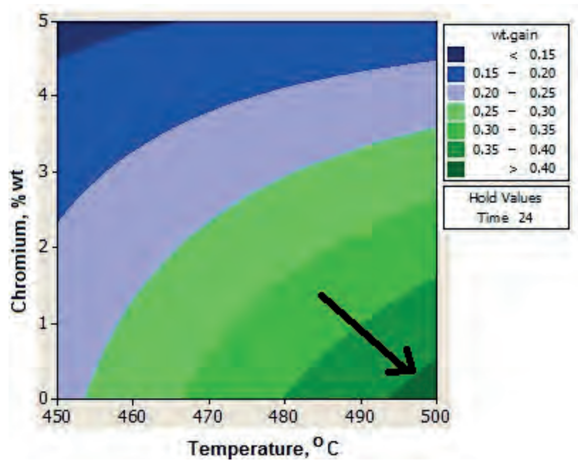


Fig.2. The estimated response surface for weight gain per unit surface area in relation of chromium weight percentage and temperature.

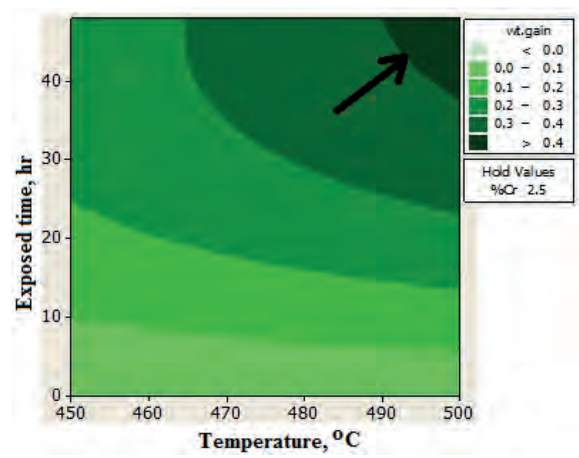


Fig.4. The estimated response surface for weight gain per unit surface area in relation of temperature and exposed time.

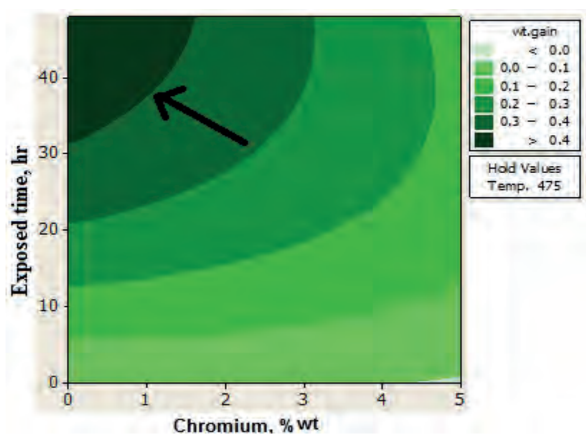


Fig.3. Estimated response surface for weight gain per unit surface area in relation of chromium weight percentage and exposed time.

and the exposed time increase, as indicated by the arrow shown in (Fig. 4). The reason is the same as explained previously, however with the increase in temperature, weight gain per unit surface area increases, this is highly expected because the oxidation processes is highly controlled by the diffusion processes of the oxygen ions. The higher the temperature, the higher the diffusion rate.

## CONCLUSIONS

In this study, the mathematical models for three input parameters namely temperature, exposed time and chromium weight percent for the high temperature oxidation process of steel using response surface method was developed and introduced. The second-order response models have been validated using analysis of variance and evaluated using the mean absolute error. It is found that all the three input parameters and some of their interactions have significant effect on weight gained per unit area investigated in the present study. This is also concluded the response surface method is a powerful tool to model and predict the high temperature oxidation processes.

## REFERENCES


API Standard 530, (2003). Calculation of Heater Tube Thickness in Petroleum Refineries. *5th Edn., American Petroleum Institute*, Washington DC.

George, E.; Dieter, L. and Schmidt, C. (2012). Engineering Design, *5th edition*, New York, McGrawHill.

Henshall, G. A., (1996). Numerical Predictions of Dry Oxidation of Iron and Low Carbon Steel at Moderately Elevated Temperatures. In: *MRS Symposium Proceedings*, Boston, MA, December 1996.

Hussein. A. K. (2015). Application of Response Surface Methodology for Modelling and Optimization of Hot Corrosion Rate of Nimonic 75 Coated by Ce-doped Aluminizing-Titanizing. Al-Nahrain University, *College of Engineering Journal (NUCEJ)*, ***18***: 240-249.

James, A. (1995). Numerical Modeling of High-Temperature Corrosion Processes, Oxidation of Metals, ***44 (1&2)***: 309–338

Khanna, A. S. and Kofstad, P. (1990). Microscopy of Oxidation. Presented at *International: Conference on Microscopy of Oxidation*, London, England: 113-118.

Knoll, A.; Smigiel, E.;Broll, N and Cornet, A. (1999). JCPDS-International Centre for Diffraction Data 1999 ISSN 1097-0002, Advances in X-ray Analysis, ***4***.

Raymond, H.; Montgomery, D. C. Christine, M. and Anderson, C. (2009). Response Surface Methodology: Process and Product Optimization Using Designed Experiment. A Wiley Interscience Publication. *3rd Eddition:* 282p.

Sultan, A.; Karakaya, A. I. and Erdogan, M. (2012). Influence of Water Vapour on High Temperature Oxidation of Steels used in Petroleum Refinary Haeters. *Materials and Corrosion*, ***63 (2)***: 119-126.