COMPARISON OF DESIGN EXPERIMENT IN CARBON DIOXIDE (CO_2) CORROSION PREDICTION

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ABSTRACT

The excellent of mechanical properties and lower cost make carbon steel, low alloy steel, become the main structural material used in oil and gas industry. CO_2 corrosion is a common and serious problem. Every year, the CO_2 corrosion causes failure with a great loss. There are many factors influence CO_2 corrosion such as flow rate, CO_2 concentration, pH, temperature, pressure and material property. Base on the factors which affect in model calculation. Some of the models predict corrosion rates based on different parameters and assumptions. So, it can produce different results under the same cases. Consequently, data taken from the model can be over prediction or less prediction. The objective of the study is to compare the CO_2 predictive models calculated by several experimental design models (CRD, FFD, TM and RSM). Investigate the effects on carbon steel corrosion in CO_2 environment combination with pH, temperature, and flow. Application several designs of experiments are important to simplify CO_2 corrosion behavior.

ABSTRAK

Sifat-sifat mekanik yang terbail dan kos yang rendah untuk membuatkan lekuli karbon, telah menjadikan bahan struktur utama digunakan dalam industri minyak dan gas. CO_2 karat merupakan masalah yang biasa dan serius.Setiap tahun, hakisan CO_2 menyebabkan kegagalan dengan kerugian yang besar. Terdapat banyak faktor yang mempengaruhi hakisan CO_2 seperti kadar aliran, kepekatan CO2, pH, suhu, tekanan dan sifat bahan. Berdasarkan faktor-faktor yang memberi kesan dalam pengiraan model. Sesetengah model meramalkan kadar hakisan berdasarkan pelbagai parameter dan andaian. Jadi, ia boleh menghasilkan keputusan yang berbeza di bawah kes-kes yang sama. Oleh yang demikian, data yang diambil daripada model boleh diramalan atau kurang ramalan. Objektif kajian ini adalah untuk membandingkan model CO_2 ramalan dikira dengan beberapa model reka bentuk eksperimen (CRD, FFD, TM and RSM). Menyiasat kesan pada kakisan keluli karbon dalam gabungan persekitaran CO_2 dengan pH, suhu, dan aliran. Penggunaan beberapa reka bentuk eksperimen adalah penting untuk memudahkan kelakuan kakisan CO_2.

TABLE OF CONTENTS

Page

CHAPTER 4 RESULTS AND DISCUSSION

CHAPTER 5 CONCLUSIONS AND RECOMMENDATION

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Y	Corrosion rate
P	Pressure
T	Temperature
pH	Potential of hydrogen

LIST OF ABBREVIATIONS

CRD	Completely randomized designs
FFD	Full factorial designs
RSM	Response surface methods
TM	Taguchi methods
CO_2	Carbon dioxide
Fe	Ferrous ion
$FeCO_3$	Ferrous carbonate

CHAPTER 1

INTRODUCTION

1.1 Background

The excellent of mechanical properties and lower cost make carbon steel, low alloy steel, become the main structural material used in oil and gas industry. CO_2 corrosion is a common and serious problem. Every year, the CO_2 corrosion causes failure with a great loss. In 1995, the statistics show that, every year China loss of 10 million tons steel because corrosion, about half of the loss was the CO_2 corrosion's effect. In the United States, each person average loss $1000 just because corrosion. Most of them are caused by the CO_2 corrosion. Therefore, from the early 20th century, CO_2 corrosion has become an important research area (Wei S, 2006).

CO_2 corrosion is the gravest failure in the oil and gas industry. There are many factors, such as flow rate, CO_2 concentration, pH, temperature, pressure and material properties of CO_2 corrosion. The combined effect of these factors result in harsh environments will lead to increased corrosion rate. Since this is very important, many experiments and field studies conducted CO_2 corrosion behavior of the overall etching process to give a better understanding, and the scientists can predict CO_2 corrosion with better result.

Currently, there are many CO_2 corrosion prediction models developed by different oil companies and research institutions. Basing on the factors which are affected in the model calculation, each model has advantages and disadvantages. Some of the models predict corrosion rates based on different parameters and assumptions. So, it canproduce different results under the same cases. Consequently, data taken from the model can be over prediction or less prediction.

1.2 Problem statement

To reduce complexity of factors influence corrosion rate in the filed condition, it is important to develop design experiment. Using experimental design, key factors influencing corrosion rate can be screened. CO_2 corrosion is affected with complex factors in the experiment. By the experience-based approach we can predict the corrosion rate. Using empirical approach, modeling the interaction between species and working conditions at the same effect, not only requires a lot of experiments, but also the lack of statistical analysis and graphical data to support such a conclusion. Since majority the empirical relationship was obtained by applying a simple best fit regression, the existing empirical CO_2 corrosion models tend to be misinterpretation in predictions.

Considering these limitations, it is important to choose the CO_2 corrosion model which either supported the basic theory or strong statistical background that can express the relationship between the operating conditions (temperature, pH and pressure).

1.3 Research objectives

The objective of the study is to compare the CO_2 predictive models calculated by several experimental design models.

- Investigate the effects on carbon steel corrosion in CO_2 environment combination with pH, temperature, and flow.

- Apply several designs of experiments such as: CRD, FFD and RSM to simplify CO_2 corrosion behavior.

1.4 Scope of study

This study will investigate the corrosion rate in CO_2 artificial environment in several pH, temperature and pressure. Various parameters in the model related to the discussion of the corrosion mechanism are based on the available experimental data and industrial corrosion software.

In this research, completely randomized designs (CRD), full factorial designs (FFD), taguchi methods (TM) technique will proposed to construct an empirical model that relates effects of temperature and flow on CO_2 corrosion rate simultaneously. Using FFD, TM, CRD lead to investigate effects of the variables tested analytically. Furthermore, observation regarding individual and combination effects of variables tested can be obtained.

1.5 Organization of the theses

This dissertation consists of five chapters. Chapter 1 describes the research background related to CO_2 corrosion of carbon steel. Chapter 1 gives overview of oil field environments, corrosion predictions models, problem statement, research objectives, and scope of study.

Chapter 2 contains extensive of review on CO_2 corrosion. The literature review regarding design experiment is also presented in this chapter. In addition to, this Chapter 2 discussed predictive models developed by researchers and their comparison with published papers for justification.

In Chapter 3, detail of material specification, material preparation, corrosion testing methodology, and experimental design methodologies are explained.

The next, Chapter 4, analyses of the results obtained are presented. In this study, published papers, corrosion experimental data from researchers and from experiments were compared and discussed to verify the models. The models are analyzed to observe trends that can provide parametric relationships for variables tested.

Finally, Chapter 5 contains of conclusion. The conclusion summarizes the results and compares the models to determine the most appropriate model for the CO_2 corrosion pattern.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon dioxide (CO_2) Corrosion

The corrosion mechanism of mild steel in the presence of CO_2 in various conditions has been a widely reviewed by researchers, especially corrosion that occurs in oil and gas industry (Nesic, 2007). In order to identify the key mechanism influencing CO_2 corrosion, the effects of main parameters such as pH, temperature and flow conditions are still under investigation. It is due to large variety of corrosion rates and mechanisms may effect to the corrosion rate. In order to predict corrosion rate, a large number of theoretical backgrounds such as chemical reaction, electrochemical, mass transport processes and various possibilities reactions should be considered. Now days, the researchers have investigated the various variables that relate to the corrosion rate to developed a prediction models accurately. But, the model of CO_2 corrosion is still disputable and sometimes contradicts. Thus, further discussions regarding models of CO_2 and its effects on main factors such as temperature, pH and flow conditions are still open to explore.

In CO_2 corrosion of carbon steel, there are two basically main types of reaction. They are cathodic reaction and anodic reaction. At the cathodic site, CO_2 dissolves into the water phase and becomes to hydrated form carbonic acid. At the anodic site, oxidation reaction occur to form ferrous (Fe^{2+}) ions.

2.2 Factors affecting Carbon dioxide (CO_2) corrosion

2.2.1 pH

In the chemical field, pH value is a measure of hydrogen ion activity solvent. p[H], the determination of hydrogen ion concentration is closely related to, generally denoted pH value. At 25 ℃, the pH of pure water is very close to 7. In the corrosion process, pH value is an important parameter. Typically, the corrosion rate will be lower when the pH is higher.

2.2.2 Temperature

Temperature is a physical property to quantify a common concept. Temperature in the natural sciences in various fields, including physics, geology, chemistry, atmospheric science and biology plays an important role.

Under the different conditions of temperature carbonic acid protective layer formation has different property. At a temperature below 60℃ and high solubility of Ferrous carbonate ($FeCO_3$), the ratio of precipitation is slow, and the protection film cannot be formed until the pH is increased by more than the solubility product (Gulbrandsen, 2006).

2.2.3 Effects of CO_2 partial pressure

In the case where no protection film, the corrosion rate increases when the partial pressure of carbon dioxide increases. At higher partial pressure of CO_2, CO_3^{2-} ions concentration will have higher super saturation (at the high pH) which leads to increasing the corrosion rate.

The total gas pressure increase will lead to increase the corrosion rate. However, with the increasing pressure the non-ideal gas will play an increasingly larger role.

2.2.4 Effect of Fe^{2+} concentration

The effects of Fe^{2+} ions on corrosion rate are influenced by its ability to form iron carbonate. It has been generally accepted solid iron carbonate scale deposited on the steel surface when CO_2 aqueous solution of Fe^{2+} and CO_3^{2-} ions concentration exceeds the solubility limit. The Fe^{2+} results in higher saturation will accelerate sedimentation rate, and leads to higher fouling tendency of increased (Parakala, 2005). Protective scale will not form when the scaling tendency is very low although Fe^{2+} has achieved a saturation value. In this condition, the iron carbonate film that forms is very porous and is not protective, which will not be effective in reducing corrosion rate (Hunnik & Hendriksen, 1996).

2.3 Design of experiments

In general, the design of experiments (DOE) or experiments design is designed to gather any of the information collection process, whether or not in full control of the experimenter. However, in statistics, these terms are commonly used to control the experiment. Formal planning experiments are often used to evaluate the physical object, chemical formulas, structures, components and materials.

There are several types of response surface design provided by researchers (Box, 1987). Generally, each model was developed based on the number of experiments and the number of design variations that can be constructed.

2.3.1 Randomization

Randomized, it means the experimental operation of the unit is randomly determined order. Completely randomized design is probably the simplest experimental design, no matter data analysis or convenience. With this design, subjects were randomly assigned to treatment.

2.3.2 Response Surface

Response Surface method goal is to enable us to estimate interaction and even quadratic effect, so let us know what we are investigating and response surface shape. For this reason, they are called a response surface methodology (RSM) designs. RSM is designed for:

a. Improve or optimize the process settings.
b. Resolving the problems and weaknesses of process.
c. Make a product or process more robust against external and non-controllable influences. "Robust" means relatively insensitive to these influences.

2.3.3 Full factorial designs in two levels

Every setting of each factor appears with all other factors is a full factorial design. A common design of experiments is each on two levels with all input factors. These levels are called 'high' and 'low' or '+1' and' -1 ', respectively. All possible high / low combinations of all input factors are called a design full factorial design at two levels.

If there are k factors, each at the two levels, 2^K run will in full factorial design. As shown by the below table 2.1, when the factor number is equal to or greater than 5 full factorial designs requires a lot of running, is not very effective. Recommended Design

Guidelines Table, fractional factorial designs or using Plackett-Burman design is a better choice for 5 or more factors.

Table 2.1: The concentration of reactant v.s. the amount of the catalyst

Factor		Treatment	Replicate			
A	*B*	Combination	I	II	III	Total
−	−	*A* low, *B* low	28	25	27	80
+	−	*A* high, *B* low	36	32	32	100
−	+	*A* low, *B* high	18	19	23	60
+	+	*A* high, *B* high	31	30	29	90

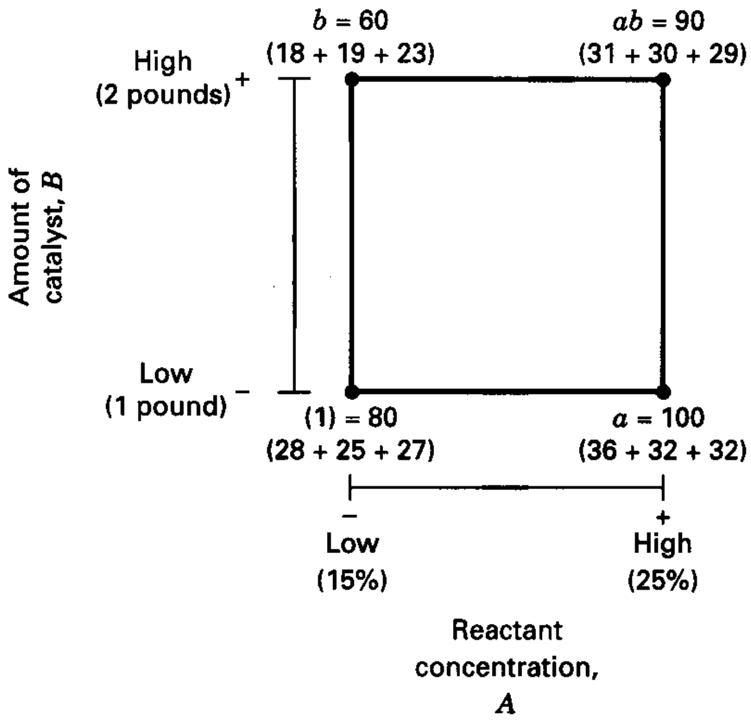

Figure 2.1: Treatment combination in the 2^k design

- Screening designs to identify which factors/effects are important.
- When it consists of 2 - 4 factors and can perform a full factorial.
- When it has more than 3 factors and want to begin with as small a design as possible.
- When it has some qualitative factors, or you have some quantitative factors that are known to have a non-monotonic effect.

Response Surface modeling to achieve one or more of the following objectives:

- Hit a target.
- Maximize or minimize a response.
- Reduce variation by locating a region where the process is easier to manage.
- Make a process robust.

2.3.4 Regression modelling

To estimate an accurate model to quantify the dependence response process input variables (s). The test starts with a comprehensive model that includes all conceivable to test the impact of the phenomenon under investigation. Then test the initial components integrated model to determine a more comprehensive sub-model that fully accounting for the phenomenon under investigation. Finally from these candidate sub-models, single out the simplest sub model, which by the principle of parsimony the test take to be the "best" explanation for the phenomena under investigation.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Corrosion rate calculation

Corrosion data calculated by commercial corrosion model is used to predict corrosion rate in several parameters conditions. The corrosion prediction software is Cassandra, Norsok and Minitab. Then, the available data is used to build mathematical model regression. Mathematical model regression equation was calculated using several design experiment method. The last, comparing the prediction corrosion data from each design experiment.

3.2 Model accuracy measurement

To check how accurately the model describes the data and predicts a response, there are common parameters that can be used to observe the data. To check model performance, the following valuation test will be conducted:

Residual

The residual sum of squares is the variation attributed to the error. The larger this value is, the better the relationship explaining data.

Residual (r) is defined by:

$$r = Y - \hat{Y} \quad (1)$$

Coefficient determination

Coefficient determination (r^2) is defined as:

$$r^2 = \frac{ss_{regression}}{ss_{total}} = \frac{\sum\left(\hat{y} - \bar{y}_i\right)}{\sum\left(y_i - \bar{y}_i\right)} \tag{2}$$

Where $\bar{y}_i =$ i[th] observed response value, $\hat{y}_i =$ mean response and SS = sum of square.

In matrix form, scalars SS_r, SS_e, are calculated and used to obtain the coefficient of determination r^2 (goodness-of-fit) and F statistic (statistical significance) as follows:

$$SS_r = b^T X^T Y - (1/n)(Y^T U U^T Y) \tag{3}$$

$$SS_e = Y^T Y - b^T X^T Y \tag{4}$$

$$SS_{total} = Y^T Y^T - (1/n)(Y^T U U^T Y) \tag{5}$$

$$r^2 = SS_r/SS_{total} \tag{6}$$

$$F = (SS_r/k)/(SS_e/(n-k-1)) \tag{7}$$

F-test

It is a hypothesis test that examines the ratio of two variances to determine their equality. An F-test evaluates whether the observed statistic exceeds a critical value from the distribution. If the observed F-statistic exceeds the critical value, the null hypothesis is rejected. That equation is more commonly shown in an equivalent form:

$$F = \frac{(SS_1 - SS_2)/(DF_1 - DF_2)}{SS_2 / DF_2} \tag{8}$$

Where, SS_i = Sum of square of variable I and DF_i = Degree of freedom of variable i.

Correlation

The correlation coefficient allows researchers to determine if there is a possible linear relationship between two variables measured on the same subject.

$$S_{xy} = \sum xy - \frac{(\sum x)(\sum y)}{n} \quad (9)$$

Standard error estimation

The standard error for the predicted response is calculated by:

$$S_{y(x)} = s\sqrt{x^{(m)'}(x'x)^{-1}x^{(m)}} \quad (10)$$

The variable s is standard deviation of the response while x is the orthogonal matrix and x^m is the particular location of response.

Variance Analysis

The variance analysis for the predicted response is calculated by:

$$\text{Un-similarity} = \frac{\text{average } \sqrt{(\mathrm{E}^2)}}{\text{average Prdc.}} *100\% \quad (11)$$

3.3 Common basis for comparison

In order to compare the results from each of the model described, it was necessary to put them on a common basis. The common basis was a set of physical and chemical conditions which could then be manipulated to be applied to each model.

Input Requirements

Each of the models described has a different set of input requirements which are summarized.