Corrosion analysis and studies on prediction model of 16Mn steel by grey system theory

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Abstract

The accident caused by the corrosion of steel in the production of alumina has become an important issue. The corrosion behaviour of 16Mn steel was investigated using weightlessness, scanning electron microscopy, energy-dispersive spectrometry and grey system theory in the sulfur-containing alkaline solutions. This paper proposes three methods to improve prediction accuracy of GM(1,1) model. Results indicated that corrosion time is the most important influence factor of the corrosion rate of 16Mn steel which satisfies the mathematical relationship of power function in the early stages of corrosion. The corrosion products is mainly composed of elements O, S, Fe, Al, Cr and C, and the particles with better crystallization are mainly oxides (Fe₃O₄), while the bulk particles are mainly sulfides (FeS). The accuracy of four GM(1,1) prediction models is better than that of the power function, among which metabolic GM(1,1) model is the best.

1. Introduction

Due to the lack of high-quality bauxite resources, High sulfur bauxite with high aluminum-silicon ratio, high quality and abundant reserves is an available resource [1]. However, due to various problems caused by its high sulfur content, such as corrosion [2], it has not been used on a large scale so far. So, it is impossible to carry out the corrosion experiment in the alkaline solution with high sulfur content. Pitting corrosion is considered to be an important corrosion form affecting the strength of materials (steel) [3]. 16Mn steel is often used as a material for pressure vessel equipment in Bayer alumina production, which inevitably suffer degradation due to the exposure to the corrosive environment (the alkaline solution containing sulfur) [4].

Current research on corrosion of 16Mn steel in the alumina production process mainly focus on corrosion kinetics [5] and corrosion mechanism [6]. However, traditional data analysis methods require a large number of samples, such as orthogonal experiment, and these highly nonlinear data are difficult to be analyzed by traditional methods. Grey system theory was originally proposed by Deng [7], which is an effective method to deal with incomplete data for system analysis, and includes grey relational analysis, GM(1,1) model, and so on. Grey relational analysis was used to classify the vibrational signals [8], obtain simultaneous optimum settings of input parameters [9] and estimate the weight of each sample that was required to avoid unreasonably treating each sample with equal importance in the traditional grey prediction [10]. Therefore, this paper analyzed the relationship between corrosion factors and corrosion rate of 16Mn by means of grey relational analysis in the sulfur-containing alkaline solutions.

GM(1,1) prediction model is characterized by the fact that it can conduct prediction with small sample of experimental data [11, 12]. GM(1,1) model has been applied widely for grey prediction. For example, Wang [13] used GM(1,1) model to predict the service life of anchor steel on four different working conditions, and Zhou et al [14] established GM(1,1) model to predict fiber diameter by a single-factor change. However, the prediction accuracy of traditional GM(1,1) model is sometimes not high. Therefore, many scholars studied the improvement of GM(1,1) model from different angles. Wang [15] improved the initial conditions and background values of grey model GM(1,1) based on the principles of sine transformation and error...
minimization, and Wang et al [16] used the Lagrange mean value theorem to construct the background value as a variable related to k. Cheng et al [17] improved the model’s parameter estimation without changing the model’s structure by using four methods. In addition, Zhu et al [18] predicted the corrosion data using the nonequidistant grey GM(1, 1) model, and the precision and dependability of model were evaluated. Kayacan E et al [19] established the modified GM(1, 1) model by using Fourier series to the time series, which has higher characteristics not only on model fitting, but also on forecasting. Li et al [20] applied GM(1, 1) model to predict the influencing factors on the service life of concrete structure. Zhao et al [21] presented the improved GM(1, 1) model to predict the reliability life data of wire rope, which not only optimizes the solution method and improves the prediction accuracy. In this work, the author will improved the smoothness of the initial sequence on the basis of not changing the model structure. GM (1, 1) model was used to build the mathematical models on corrosion time and conduct a further analysis of lifetime prediction of 16Mn steel.

It is difficult to get the long-term corrosion data of 16Mn steel in the autoclave, so it will be a challenge for us to determine the main factors and build the prediction models for the corrosion rate. Grey theory has great advantages in dealing with small-sample and multiple factors [21]. In this paper, the established model based on grey theory under the small-sample condition can reflect the corrosion dynamic features of 16Mn steel. In this study, the corrosion factors, morphology and composition are analyzed and then a prediction model is established for corrosion rate of 16Mn steel. First, Grey Relational Analysis was used to determine the relationship between influence factors and the corrosion rate. Then, based on weightlessness method, scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) were used to characterize the morphology and composition of the surface corrosion layer of 16Mn steel. Finally, this study will establish grey theory under the small-sample condition can re

2. Materials and methods

2.1. Sample and test solutions

The substrate was 16Mn steel with composition (in wt.%): 0.178 C, 0.29 Si, 1.645 Mn, 0.041 Cr, 0.056 P, 0.017 S, and Fe balance. The steel coupons were made from 16Mn steel with the dimension of 20 mm × 10 mm × 1.0 mm. The steel coupons were mechanically ground from 600 grit to 1800 grit with SiC abrasive paper, degreased with acetone and rinsed with distilled water and dried, respectively.

Corrosive medium is the sulfur-containing alkaline solutions in the experiments. 255 g l⁻¹ NaOH solutions, which were prepared in a three-necked, round-bottomed flask at 80 ~ 90 °C by magnetic stirring. Science the alkaline solution is easy to be carbonized, and must be used promptly. The different concentrations of S²⁻ and S₂O3²⁻ of alkaline solutions can be got by dissolving analytical pure Na₂S·9H₂O and Na₂S₂O₃·5H₂O.

2.2. Corrosion experiment

The experiments were carried out at 383 K in the autoclave. There were five parallel samples for each set of experiments, of which three samples were used for corrosion rate measurement and two samples for morphology and composition observation respectively. The calculation formula of corrosion rate \( r \) \( (\text{mm} \cdot \text{a}^{-1}) \) is shown in equation (1) [22, 23].

\[
r = 8.76 \times 10^4 \times \frac{W_1 - W_2}{S \times t \times D}
\]

where, \( W_1 \) (g) is the sample quality before corrosion with an accuracy of ±0.0001 g, \( W_2 \) (g) is the sample quality after removing the surface corrosion products with an accuracy of ±0.0001 g, S (cm²) is the sample area with an accuracy of 0.01 cm², \( t \) (h) is corrosion time with an accuracy of 1 h, D (g/cm³) is the density of 16Mn steel.

2.3. Surface analysis

The morphology and composition of the surface corrosion products was observed by scanning electron microscopy (SEM) (SUPRA 40, German) and energy dispersive spectroscopy (EDS) (AZ tec.).

3. Theoretical background

3.1. Grey relational analysis

The analysis process of Deng’s grey relational degree is as follows [7, 11]:

Step 1. Determine the sequence of system characteristic behavior and the sequence of related factors.
It is assumed that the system characteristic behavior sequence is \( X_0 = [x_0(1), x_0(2), \ldots, x_0(n)] \), and related factors sequence is \( X_i = [x_i(1), x_i(2), \ldots, x_i(n)] \), \( i = 1, 2, \ldots, m \).

**Step 2.** The correlation coefficient \( \gamma(x_0(k), x_i(k)) \) between the system characteristic behavior sequence and correlation factor sequence \( k \) point was calculated.

The sequence data was normalized first, and then the correlation coefficient \( \gamma(x_0(k), x_i(k)) \) was calculated as follows:

\[
\gamma(x_0(k), x_i(k)) = \min_{k} \min_{k} \frac{|x_0(k) - x_i(k)| + \xi \max_{k} |x_0(k) - x_i(k)|}{|x_0(k) - x_i(k)| + \xi \max_{k} |x_0(k) - x_i(k)|}
\]

where \( \xi \) is the resolution coefficient, \( \xi \in (0, 1) \). \( \gamma(x_0(k), x_i(k)) \) can be abbreviated as \( \gamma_0(k) \).

**Step 3.** Calculate the grey relational degree \( \gamma(X_0, X_i) \). The calculation formula is shown in equation (3).

\[
\gamma(X_0, X_i) = \frac{1}{n} \sum_{k=1}^{n} \gamma(x_0(k), x_i(k))
\]

where \( \gamma(X_0, X_i) \) can be abbreviated as \( \gamma_0 \).

**Step 4.** Grey relational degree sort.

### 3.2. Establishment of GM(1, 1) model

**Step 1.** The original data sequence satisfies the criterion of quasi-smoothness.

The original data sequence is \( X^{(0)} = [x^0(1), x^0(2), \ldots, x^0(n)] \), \( x^0(k) \geq 0 \), \( k = 1, 2, \ldots, n \). If \( X^{(0)} \) satisfies the following conditions:

\[
\frac{x^0(k + 1) - \sum_{i=1}^{k} x^0(i)}{x^0(k) - \sum_{i=1}^{k-1} x^0(i)} < 1, \quad k = 2, 3, \ldots, n - 1
\]

\[
x^0(k) - \sum_{i=1}^{k-1} x^0(i) \in [0, \varepsilon], \quad k = 3, 4, \ldots, n - 1; \quad \varepsilon < 0.5
\]

Therefore, \( X^{(0)} \) is a quasi-smooth sequence. Whether the quasi-smooth sequence condition is met, which is an important criterion to test whether a grey system model can be established for a sequence [7, 11].

**Step 2.** Establishment of GM(1, 1) prediction model.

Through the accumulated generating operation (1-AGO) of the original date sequence \( X^{(0)} \), a new sequence \( X^{(1)} \) is obtained \([7, 11, 12]\).

\[
X^{(1)} = \{x^{(1)}(1), x^{(1)}(2), \ldots, x^{(1)}(n)\}
\]

where, \( x^{(1)}(k) = \sum_{i=1}^{k} x^{(i)}(i) \), \( k = 1, 2, \ldots, n \).

In order to establish the whitening differential equation of \( X^{(1)} \), an average generation of consecutive neighbours of \( X^{(1)} \) is generated.

\[
Z^{(1)} = [z^{(1)}(2), z^{(1)}(3), \ldots, z^{(1)}(n)]
\]

where, \( Z^{(1)}(k) = 0.5[x^{(1)}(k) + x^{(1)}(k - 1)] \), \( k = 2, 3, \ldots, n \).

According to the newly generated sequences \( X^{(1)} \) and \( Z^{(1)} \), the average difference equation and whitening differential equation of GM(1, 1) model can be established.

\[
x^{(0)}(k) + az^{(1)}(k) = b
\]

\[
\frac{dx^{(1)}}{dr} = ax^{(1)} + b
\]

where \( a \) and \( b \) are development coefficient and ash action, respectively. The parameter vector \( \hat{a} = [a, b]^T \) can be solved by least square method.

\[
\hat{a} = (B^T B)^{-1}B^T Y
\]
where $Y$ and $B$ are respectively:

$$
Y = \begin{bmatrix}
x(0) (2) \\
x(0) (3) \\
\vdots \\
x(0) (n)
\end{bmatrix}, \quad B = \begin{bmatrix}
-x^{(0)} (2) 1 \\
-x^{(0)} (3) 1 \\
\vdots \\
-x^{(0)} (n) 1
\end{bmatrix}
$$

(11)

To $x^{(1)} (1) = x^{(0)} (1) \ (t = 1)$ as the initial value, the solution (Time response function) of equation (9) can be obtained.

$$
\hat{x}^{(1)} (t) = \begin{bmatrix}
x(0) (1) - \frac{b}{a} \\
-x^{(1)} (1) \\
\vdots \\
-x^{(1)} (n)
\end{bmatrix} e^{-a(t-1)} + \frac{b}{a}
$$

(12)

Corresponding to equation (8), the time response sequence of GM(1, 1) model is:

$$
\hat{x}^{(1)} (k + 1) = x^{(0)} (1) - \frac{b}{a} e^{-ak} + \frac{b}{a}, \quad k = 1, 2, \ldots, n
$$

(13)

where $\hat{x}^{(1)} (k + 1)$ is the predicted value of $x^{(1)} (k + 1)$ at time $(k + 1)$.

1-AGO sequence represented by equation (13) can be going to an accumulation inverse operation to obtain the reduction value:

$$
\hat{x}^{(i)} (1) = x^{(0)} (1)
$$

$$
\hat{x}^{(i)} (k + 1) = \hat{x}^{(i)} (k + 1) - \hat{x}^{(i)} (k) = (1 - e^{a}) \left[ x^{(0)} (1) - \frac{b}{a} e^{-ak} \right]
$$

(14)

### 3.3. Modification of GM(1, 1) model

1. Logarithmic function method
   - The purpose of smoothness processing is to weaken the influence of abnormal data in the original data, strengthen the general trend of the original data, and transform the original data into exponential increasing sequence as far as possible.
   - Logarithmic function method is adopted for the original data, and the original sequence $X_2^{(0)}$ is:
   $$
   X_2^{(0)} = [x_2^{(0)} (1), x_2^{(0)} (2), \ldots, x_2^{(0)} (n)]
   $$
   (15)
   where, $x_2^{(0)} (k) = \ln (100000 * r (k)), \ k = 1, 2, \ldots, n. \ r (k)$ is the original data.

2. nth root method
   - nth root method is the real 8th root of the original data [24], then the original sequence $X_3^{(0)}$ is:
   $$
   X_3^{(0)} = [x_3^{(0)} (1), x_3^{(0)} (2), \ldots, x_3^{(0)} (n)]
   $$
   (16)
   where, $x_3^{(0)} (k) = r (k)^{1/8}, \ k = 1, 2, \ldots, n. \ r (k)$ is the original data.

3. Metabolic method
   - Metabolic method [25] used GM(1, 1) model to predicts a new data $x_4^{(0)} (n + 1)$, adds it to the original data, and removes the oldest data $x_4^{(0)} (1)$. Then, the sequence $X_4^{(0)} = [x_4^{(0)} (2), x_4^{(0)} (3), \ldots, x_4^{(0)} (n + 1)]$ is used as a new original date.

### 3.4. Evaluation of the accuracy of GM(1, 1) prediction model

In this paper, posteriori error ratio $C$ and small error probability $P$ are used to test the accuracy of GM(1, 1) prediction model.

$$
C = \frac{S_2}{S_1} = \frac{\frac{1}{n-1} \sum_{k=1}^{n} (e(k) - \bar{e})^2}{\frac{1}{n-1} \sum_{k=1}^{n} (x^{(0)} (k) - \bar{x}^{(0)})^2}
$$

(17)

$$
P = P \left[ |e(k) - \bar{e}| < 0.62745 S_1 \right]
$$

(18)

where, $e(k)$ is the residuals of $e$. $\bar{x}^{(0)}$ is the average value of $x^{(0)} (k)$. $\bar{e}$ is the average value of $e(k)$.

$$
e(k) = x^{(0)} (k) - \hat{x}^{(0)} (k)
$$

(19)
The accuracy of the model is evaluated jointly by $C$ and $P$, and is generally divided into four grades $[7, 11]$. The model accuracy classification is listed in table 1.

### Table 1. Accuracy classification of GM(1, 1) model.

| Accuracy grade | Grade 1 | Grade 2 | Grade 3 | Grade 4 |
|----------------|---------|---------|---------|---------|
| $P$            | $0.95 < P$ | $0.8 < P \leq 0.95$ | $0.7 < P \leq 0.8$ | $P \leq 0.7$ |
| $C$            | $C < 0.35$ | $0.35 \leq C < 0.5$ | $0.5 \leq C < 0.65$ | $0.65 \leq C$ |

4. Result and discussion

#### 4.1. Grey relational analysis of corrosion factors of 16Mn steel

In order to clarify the influence of corrosion factors (Corrosion temperature, Corrosion time, $S^{2-}$ concentration and $S_2O_3^{2-}$ concentration) on corrosion behavior of 16Mn steel, the correlation coefficient and correlation degree are calculated by using grey relational analysis. According to the results of weight loss method, the corrosion rate of 16Mn steel at each factor level is shown in table 2.

Table 2. Corrosion rate of 16Mn steel under different corrosion factors.

| Number | Corrosion temperature/°C | Corrosion time/day | $S^{2-}$ concentration/g·l$^{-1}$ | $S_2O_3^{2-}$ concentration/g·l$^{-1}$ | Corrosion rate/mm·a$^{-1}$ |
|--------|--------------------------|--------------------|-----------------------------------|--------------------------------------|---------------------------|
| 1      | 110                      | 5                  | 3                                 | 1                                    | 0.147                     |
| 2      | 110                      | 5                  | 3                                 | 2                                    | 0.185                     |
| 3      | 110                      | 5                  | 3                                 | 4                                    | 0.135                     |
| 4      | 110                      | 5                  | 3                                 | 5                                    | 0.069                     |
| 5      | 110                      | 5                  | 1                                 | 3                                    | 0.044                     |
| 6      | 110                      | 5                  | 2                                 | 3                                    | 0.099                     |
| 7      | 110                      | 5                  | 3                                 | 3                                    | 0.233                     |
| 8      | 110                      | 5                  | 5                                 | 3                                    | 0.126                     |
| 9      | 65                       | 1                  | 4                                 | 2                                    | 0.012                     |
| 10     | 65                       | 2                  | 2                                 | 5                                    | 0.013                     |
| 11     | 65                       | 3                  | 0.5                               | 1                                    | 0.007                     |
| 12     | 110                      | 4                  | 5                                 | 4                                    | 0.039                     |
| 13     | 110                      | 5                  | 3                                 | 0.5                                  | 0.133                     |
| 14     | 110                      | 6                  | 1                                 | 3                                    | 0.047                     |

Table 3. Gray correlation degree of 16Mn steel.

| Corrosion factor | Corrosion temperature $\gamma_{\theta_1}$ | Corrosion time $\gamma_{\theta_2}$ | $S^{2-}$ concentration $\gamma_{\theta_3}$ | $S_2O_3^{2-}$ concentration $\gamma_{\theta_4}$ | Grey relational degree |
|------------------|------------------------------------------|-----------------------------------|-----------------------------------------|-------------------------------------------------|------------------------|
| $\bar{e}$        | $\frac{1}{n} \sum_{k=1}^{n} e(k)$        |                                   |                                         |                                                 | 0.8644                |
| $\varepsilon_k$  | $\frac{|e(k)|}{x_{\theta_1}(k)} \times 100\%$ |                                   |                                         |                                                 | 0.8776                |
| $\bar{\varepsilon}$ | $\frac{1}{n} \sum_{k=1}^{n} \varepsilon_k$ |                                   |                                         |                                                 | 0.8755                |

(20) \(\bar{e} = \frac{1}{n} \sum_{k=1}^{n} e(k)\)

(21) \(\varepsilon_k = \frac{|e(k)|}{x_{\theta_1}(k)} \times 100\%\)

(22) \(\bar{\varepsilon} = \frac{1}{n} \sum_{k=1}^{n} \varepsilon_k\)

The accuracy of the model is evaluated jointly by $C$ and $P$, and is generally divided into four grades $[7, 11]$. The model accuracy classification is listed in table 1.

As can be seen from table 3 and figure 1, $\gamma_{\theta_1}$ of corrosion time $> \gamma_{\theta_3}$ of $S^{2-}$ concentration $> \gamma_{\theta_4}$ of corrosion temperature $> \gamma_{\theta_2}$ of $S_2O_3^{2-}$ concentration. That is, corrosion time is the most important factor of the corrosion rate of 16Mn steel. Since the grey correlation between corrosion time, $S^{2-}$ concentration and corrosion temperature is similar, it can be considered that corrosion time, $S^{2-}$ concentration and corrosion temperature are the main factors determining the corrosion rate of 16Mn steel, while $S_2O_3^{2-}$ concentration is the secondary factor.
4.2. Corrosion rate

The corrosion rate of 16Mn steel is shown in figure 2 based on weightlessness method with different corrosion time in the 255 g l$^{-1}$ NaOH solution containing 5 g l$^{-1}$ S$^{2-}$ and 3 g l$^{-1}$ S$_2$O$_3^{2-}$. The corrosion rate of steels varies greatly with corrosion time. The corrosion rate decreases obviously with corrosion time in the initial stage of corrosion, and changes gently in the later stage, because the corrosion product layer formed on the steel surface with corrosion, which hinders the corrosion to some extent. LI et al [26] found that the precipitate phases become coarse with prolonging the ageing time, which can effectively block the corrosion of the alloy. In order to determine the mathematical relationship between corrosion rate and corrosion time, it is found that the corrosion rate has a better power function relation with corrosion time by mathematical fitting. The power function can be expressed as shown in equation (23) which is consistent with the conclusion in literature [27].

$$r = 0.066 \times t^{-0.935}$$

(23)

4.3. SEM morphology analysis

SEM morphology and composition of 16Mn steel surface corrosion products with different corrosion time are shown in figure 3 and table 4. It can be seen from figure 3 that the corrosion degree of steel surface becomes more and more serious with corrosion time. Table 4 shows the element distribution of surface corrosive were obtained by energy spectrum analysis with different corrosion times. The surface corrosive is mainly composed of elements O, S, Fe, Al, Cr and C.

A large number of crystal particles of uniform size are evenly distributed on 16Mn steel surface for 1 day, but the thickness of the corrosion layer is not uniform, table 4 shows that the content of element O in the surface
The corrosion layer is relatively high, while the content of element S is relatively low. When the corrosion lasted for 2 days, the surface was covered by a layer of larger crystal particles, and the corrosion layer thickness was more uniform, the elemental composition of the corrosion layer is the same as that of 1 day. The local corrosion particles have obvious agglomeration phenomenon and larger agglomeration particles are formed for 3 days. As can be seen from Table 4, the element composition of the corrosion layer changed greatly, and the content of

![Figure 3. Morphology of surface corrosion products with different corrosion time.](image)

**Table 4.** Element composition of surface corrosion products with different corrosion time (At. %).

| Corrosion time/day | C   | O    | Na  | Al  | Si  | P   | S   | Cr  | Mn | Fe   |
|------------------|-----|------|-----|-----|-----|-----|-----|-----|----|------|
| 1                | 7.22| 49.39| 0.14| 1.09| 0.18| 0.00| 0.50| 0.20| 1.14| 38.33|
| 2                | 12.86| 46.70| 0.10| 1.72| 0.12| 0.02| 0.42| 3.81| 0.41| 33.84|
| 3                | 32.17| 33.25| 1.98| 1.89| 0.58| 0.06| 7.76| 1.32| 0.31| 20.67|
| 4                | 0.00| 58.60| 1.99| 2.31| 0.19| 0.00| 0.70| 4.62| 0.34| 31.27|
| 5                | 7.72| 49.41| 0.24| 1.86| 0.04| 0.00| 0.92| 3.57| 0.50| 35.73|
element O decreased while that of element S increased greatly. As the surface corrosive continues to react with the ions in the solution, the steel surface is very uneven, and the corrosion particles were refined and the corrosion layer thickness increased for 4 days. When the corrosion time reaches 5 days, the crystallized refined particles were completely formed into octahedral particles with good crystal morphology which were evenly deposited on the steel surface. The uniform crystal particles formed a dense corrosion layer on the surface, which hinders the diffusion of ions and slows down the corrosion. When corroded for 4 to 5 days, its elemental composition is basically the same as that of 1 day.

The content of element O in table 4 is far greater than that of element S, indicating that the surface corrosion is mainly composed of oxides. Combined with the molecular percentage of elements O, S and Fe in table 4, it can be seen that S: Fe = 1:1, Fe: O = 0.75, so, it was also found presumably that the crystalline particles with better crystallization were mainly oxides (Fe₃O₄), while the bulk particles were mainly sulfides (FeS).

4.4. Establishment of corrosion rate prediction model based on GM (1, 1) model

4.4.1. Corrosion rate prediction model based on four GM (1, 1) models

(1) Traditional GM(1, 1) model

**Step 1.** \(X_i^{(0)} = [0.06720, 0.02090, 0.01280, 0.0131, 0.00901]\), which satisfies the condition of quasi-smooth sequence.

**Step 2.** Based on traditional GM(1, 1) model, the corrosion rate model of 16Mn steel is obtained according to equations (6)–(14).

\[
\begin{align*}
\hat{x}_1^{(0)}(1) &= x_0^{(0)}(1) \\
\hat{x}_1^{(0)}(t) &= -0.21067[x_0^{(0)}(1) - 0.17518]e^{-0.19117(t-1)} \quad t = 2, 3, \ldots, n
\end{align*}
\]  

(24)

where, \(t\) is the corrosion time (day), \(\hat{x}_1^{(0)}(t)\) is the corrosion rate of 16Mn steel for \((2t-1)\)th day.

**Step 3.** According to equations (17) and (18), posteriori error ratio (C) and small error probability (P) were calculated respectively, \(C = 0.0928, P = 1.05\). It can be seen from table 1 that the accuracy grade of the traditional GM(1, 1) model is grade 1.

(1) Logarithmic GM(1, 1) model

**Step 1.** According to equation (15), \(X_i^{(0)} = [8.81284, 7.64492, 7.15462, 7.00307, 7.17778, 6.80351]\), which satisfies the condition of quasi-smooth sequence.

**Step 2.** Based on logarithmic GM(1, 1) model, the corrosion rate model of 16Mn steel is obtained according to equations (6)–(14).

\[
\begin{align*}
\hat{x}_2^{(0)}(1) &= x_0^{(0)}(1) \\
\hat{x}_2^{(0)}(t) &= -0.02365[x_0^{(0)}(1) - 333.2743]e^{-0.02337(t-1)} \quad t = 2, 3, \ldots, n
\end{align*}
\]  

(25)

The logarithmic inversion is performed on equation (25).

\[
\begin{align*}
\hat{x}_2^{(0)}(t) &= 1 \times 10^{-5}e^{0.02365[\ln(100000x_0^{(0)}(1)) - 333.2743]} \quad t = 2, 3, \ldots, n
\end{align*}
\]  

(26)

Where, \(t\) is the corrosion time (day), \(\hat{x}_2^{(0)}(t)\) is the corrosion rate of 16Mn steel for \((2t-1)\)th day.

**Step 3.** According to equations (17) and (18), \(C = 0.0941, P = 1.05\). It can be seen from table 1 that the accuracy grade of logarithmic GM(1, 1) model is grade 1.

(1) nth root GM(1, 1) model

**Step 1.** According to equation (16), \(X_i^{(0)} = [0.71354, 0.61662, 0.57996, 0.56908, 0.58165, 0.55506]\), which satisfies the condition of quasi-smooth sequence.

**Step 2.** Based on nth root GM(1, 1) model, the corrosion rate model of 16Mn steel is obtained according to equations (6)–(14).
The $n$th root inversion is performed on equation (27).

\[
\begin{align*}
\hat{x}_3^{(0)}(1) &= x_3^{(0)}(1) = 0.71354 \\
\hat{x}_3^{(0)}(t) &= -0.0213[x_3^{(0)}(1) - 29.72533]e^{-0.02108(t-1)} \\
&= 2, 3, \ldots, n
\end{align*}
\]  

The $n$th root inversion is performed on equation (27).

\[
\begin{align*}
\hat{x}_3^{(0)}(1) &= x_3^{(0)}(1) = 0.71354 \\
\hat{x}_3^{(0)}(t) &= 4.23679 \times 10^{-14}[x_3^{(0)}(1)]^{1/2} - 29.72533 \times 0.16864(t-1) \\
&= 2, 3, \ldots, n
\end{align*}
\]  

Where, $t$ is the corrosion time (day), $\hat{x}_3^{(0)}(t)$ is the corrosion rate of 16Mn steel for $(2t-1)$th day.

**Step 3.** According to equations (17) and (18), $C = 0.0952, P = 1$. It can be seen from table 1 that the accuracy grade of $n$th root GM(1, 1) model is grade 1.

1. **Metabolic GM(1, 1) model**

**Step 1.** Based on metabolic method, the new sequence is $X_4^{(0)} = [0.02090, 0.01280, 0.01100, 0.01310, 0.00901, 0.00723]$, which satisfies the condition of quasi-smooth sequence.

**Step 2.** Based on metabolic GM(1, 1) model, the corrosion rate model of 16Mn steel is obtained according to equations (6)–(14).

\[
\begin{align*}
\hat{x}_4^{(0)}(1) &= x_4^{(0)}(1) \\
\hat{x}_4^{(0)}(2) &= x_4^{(0)}(2) \\
\hat{x}_4^{(0)}(t) &= -0.12309(x_4^{(0)}(2) - 0.14161)e^{-0.16864(t-3)} \\
&= 3, 4, \ldots, n
\end{align*}
\]  

Where, $t$ is corrosion time (day), $\hat{x}_4^{(0)}(t)$ is the corrosion rate of 16Mn steel for $(2t-1)$th day.

**Step 3.** According to equations (17) and (18), $C = 0.3026, P = 1$. It can be seen from table 1 that the accuracy grade of metabolic GM(1, 1) model is grade 1 (Good).

**4.4.2. Corrosion rate prediction of 16Mn steel based on GM(1, 1) models**

The prediction results of traditional GM(1, 1) model, logarithmic GM(1, 1) model, $n$th root GM(1, 1) model and metabolic GM(1, 1) model and power function for corrosion rate of 16Mn steel are shown in figure 4 and table 5. Mean of relative error (MRE) can be obtained according to equations (21)–(22). It can be seen that the accuracy grades of GM(1, 1) model and power function equation are all grade 1 (Good). Combined with MRE, metabolic GM(1, 1) model is superior to the others. So, metabolic GM(1, 1) model will be selected to predict the corrosion rate of 16Mn steel in the sulfur-containing alkaline solutions.
Table 5. Comparison of five prediction models of 16Mn steel.

| No | Measured/mm·a<sup>-1</sup> | Traditional model [13, 14] | Logarithmic model | nth root model | Metabolic model [25] | Power function [27, 28] |
|----|-----------------------------|-----------------------------|-------------------|-----------------|---------------------|------------------------|
|    |                             | Predicted       | Error     | Predicted       | Error     | Predicted       | Error     | Predicted       | Error     |
| 1  | 0.0672                      | 0.0672         | 0         | 0.0672         | 0         | 0.0672         | 0         | 0.0672         | 0         | 0.0660        | 0.0179     |
| 2  | 0.0209                      | 0.0188         | 0.1010    | 0.0180         | 0.1395    | 0.0180         | 0.1397    | 0.0209         | 0         | 0.0236        | 0.1292     |
| 3  | 0.0128                      | 0.0155         | 0.2125    | 0.0151         | 0.1818    | 0.0152         | 0.1867    | 0.0132         | 0.0336    | 0.0147        | 0.1484     |
| 4  | 0.0110                      | 0.0128         | 0.1655    | 0.0128         | 0.1612    | 0.0128         | 0.1673    | 0.0118         | 0.0709    | 0.0107        | 0.0273     |
| 5  | 0.0131                      | 0.0106         | 0.1916    | 0.0108         | 0.1735    | 0.0108         | 0.1725    | 0.0105         | 0.1992    | 0.0085        | 0.3511     |
| 6  | 0.0090                      | 0.0088         | 0.0289    | 0.0092         | 0.0227    | 0.0091         | 0.0100    | 0.0093         | 0.0366    | 0.0070        | 0.2231     |
| MRE| 0.1166                      | 0.1131         | 0.0248    | 0.1127         | 0.0681    | 0.1519         |           |                |           |                |            |
| C  | C = 0.0928                  | C = 0.0941     | C = 0.0952| C = 0.3026     | C = 0.1215|                |           |                |           |                |            |
| P  | P = 1                       | P = 1          | P = 1     | P = 1          | P = 1     |                |           |                |           |                |            |
| Grade|                         | 1              | 1         | 1              | 1(Good)★  | 1              |           |                |           |                |            |
5. Conclusions

In the present paper, results from weight loss measurement (weight loss versus corrosion time) for 16Mn steel in the sulfur-containing alkaline solutions are reported and analyzed for the corrosion and passivation of steel used in the alumina production. The following main conclusions can be obtained.

(i) Corrosion time is the most important factor of corrosion rate of 16Mn steel by Grey relational analysis, followed by $S_2^{\text{de}}$ concentration and corrosion temperature. This will provide the basis for the anticorrosion of alumina production equipment in the future.

(ii) The corrosion rate of 16Mn steel decreases obviously in the early stages of corrosion and the corrosion rate has a better power function relation with corrosion time. The particles with better crystallization were mainly oxides (Fe₃O₄), while the bulk particles were mainly sulfides (FeS) by EDS analysis.

(iii) The accuracy of four GM(1, 1) prediction models is better than that of the power function, among which metabolic GM(1, 1) model is the best.

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