STUDY ON MATHEMATICAL MODELLING OF FLUIDIZED BED WITHOUT PERFORATED-PLATE FOR PRODUCING TiCl₄ AND ITS INDUSTRIAL APPLICATIONS

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ABSTRACT

The chlorination of titanium-bearing materials containing about 5 to 7 pct MgO+CaO in a fluidized bed is a difficult problem in the world. For this reason, the mathematical modeling of fluidized bed without perforated-plate, FBW, has been studied using the fluidized expression given by the author of this paper, \( R^* = \Delta p \times 10^c/[f^c + e] \times \rho_d \), as a criteria. A 0.75-m-ID clear plexiglass FBW was used for a simulating amplification. Based on the mathematical model, a 1.2-m-ID, 11.3-m-height commercial FBW chlorinator has been designed for chlorinating titanium-rich slag containing approximately 85 pct TiO₂ and 6.7 pct MgO+CaO impurities to produce TiCl₄. The chlorinator has run continuously for 55 days with a good fluidization and results.

Key words: fluidization, bed, model, titanium, slag, impurity, magnesium, calcium, chlorination

1. INTRODUCTION

There are abundant quantities of low grade ilmenite and other titaniferous minerals in massive rock deposits in the world. The Panzhihua Mine, China is the biggest rock deposit in the world. Unfortunately, these lower grade titanium raw materials contain MgO and CaO impurities. The troublesome impurities form high-boiling-point liquid chlorides, MgCl₂ and CaCl₂, produced during chlorination, which accumulate and stick to form solid masses with the coke and mineral particles in a conventional fluidized bed chlorinator with the perforated-plate. FBP. These solid masses can block the pores in the perforated-plate, eventually cause loss of fluidization in the chlorinator and force the termination of the chlorinator's operation within a few days. Therefore, the chlorination of titanium-bearing materials containing about 5 to 7 pct MgO+CaO in a fluidized bed is a difficult problem in the world. This problem prompted the scientists and engineers for years to devise new technology and fluidized bed for the continuous operation of chlorinator [1,2].

For this purpose, the mathematical modeling of fluidized bed without perforated-plate, FBW, has been studied using the fluidization indication expression \( R^* \) in a 0.75-m-ID clear plexiglass FBW. Based on the model, a 1.2-m-ID commercial FBW chlorinator has been designed for chlorinating titanium-rich slag with high content of MgO+CaO. The chlorinator had run smoothly and notable results were obtained.

2. ANALYSIS AND CHOICE OF DISTRIBUTOR TYPES

Fluidization is the operation by which fine solids are transformed into a fluidlike state through contact with a gas or liquid. Practically all the important industrial applications of fluidization are gas fluidized systems. At present, FBP is widely used in titanium production countries all over the world. But as was mentioned above, when chlorinating titanium-bearing materials with high content of MgO+CaO, the FBP chlorinator would be shut down within a few days due to the serious slugging and channelling etc. resulted from the sticky materials. Experiments by the researchers at home and abroad have shown that the quality of fluidized bed is strongly influenced by the type of gas distributor used. Distributor should be selected and designed with care, for this is the first step to the successful application of a fluidized bed process [3,4]. Scaling up and mathematical models of
fluidized bed have been described in the literature.[5,6]. The pattern of solids circulation in the FBP and FBW is shown in Fig. 1. Flow pattern simplified of gas through fluidized bed is shown in Fig. 2. The two patterns are very similar. It has been found that: for the normal fluidization state, the solid particles move towards down near inside-wall of the bed, which much like a wave, in the downcorner there is a region within the bed which forms a closed circulating loop of gas. When chlorinating non-bonding materials in FBP, such as titanium-rich slag obtained from beach sand ilmenite containing less than 1 pct MgO+CaO, because stagnant zones and semi-stagnant zones would keep dynamic equilibrium under certain condition, the fluidized bed runs very well (see Fig. 1a). But as was stated above, when chlorinating bonding materials in FBP, such as titanium-rich slag containing 5 to 7 pct MgO+CaO, solid agglomeration could be induced easily in stagnant zones and semi-stagnant zones near perforated-plate. These solid masses block pores in the perforated-plate, the solid agglomeration may grow, eventually force the termination of chlorination operation within a few days. Therefore, the selection of a good distributor may be of first importance for the success of the development as a whole. The streamline FBW is particularly suitable to the chlorination of bonding materials. The zones of stagnant or semi-stagnant solid in the vicinity of the distributor in FBW have been eliminated (see Fig. 1b). When the nozzles are occasionally blocked up, they can be immediately unblocked, ensuring the uniform distribution of gas flow. The sticky particles tend to clump and agglomerate, thus agitation of the bed is needed to maintain satisfactory fluidizing conditions. This can be done by using the kinetic energy of gas flow concentrated by the nozzles in FBW for agitating and dispersing the solids.

3. THE SIMULATING AMPLIFICATION TEST

3.1. APPARATUS

The 0.75-m-ID FBW was fabricated from clear plexiglass and consisted of two main sections. There were 5 sets of different bottoms and nozzles for replacement parts. The bottom of FBW had the general shape of an inverted frustocone. Horizontal inlet nozzles being connected to a gas supply system were disposed in 2 rows around the tapering walls of the bottom. A synthetic rutile was used as fluidizing material. A compressed air was used as fluidizing agent.

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Fig. 1. Normal pattern of solids circulation in FBP and FBW
a. FBP  b. FBW

Fig. 2. Flow pattern simplified of gas through fluidized beds
A. Core of center zone  A+B  C. Outer circulation zone
3.2. DISTINGUISHING THE QUALITY OF FLUIDIZATION.

Three are three different states of fluidization, i.e. good fluidization, channelling and slugging in the fluidized bed. A well fluidization is characterized by a smooth fluidization and good gas-solid contacting, the small pressure fluctuation and large frequency, while both the channelling and slugging are unusual phenomena. Based on our experiments and derivation, a fluidization indication expression, with $R$ as a criteria, is given by the author of this paper for distinguishing a quality of fluidization as the following:

$$R = \frac{\Delta p}{f \times p_0} \times 10^4 \tag{1}$$

Where $\Delta p$ is the average pressure drop in fluidized bed (Pa), $f$ is the frequency of pressure fluctuations within 10 sec., $p_0$ is the average pressure drop at minimum fluidization (Pa).

The way to distinguish a quality of fluidization by Eq. (1) is: the smaller the $R$, the better the quality of fluidization; and vice versa. When the included angle at the apex of the cone, $\alpha$, is 75° and 90°, there are obvious stagnant zones in most of tests, in this case, the expression can be modified as the following:

$$R^* = \frac{\Delta p}{(f^* + \epsilon) \times p_0} \times 10^4 \tag{2}$$

Where $f^*$ is the frequency to be modified, $\epsilon$ is the fit modified factor, $\epsilon = 0.169$. The Eq. (2) is satisfactory in the tests.

3.3. EXPERIMENTAL SIMULATION METHOD.

First of all, the factors, i.e. parameters, and the range of parameters employed have been determined based on our investigation and experiments. They are shown in table 1. The manometer, computer, microprocessor, differential pressure transducer and signal processor etc. were connected to the FBW for processing data (100 times/sec) in a real-time on-line operation. Six technological parameters were investigated in about 200 tests arranged by orthogonal designing method.

<table>
<thead>
<tr>
<th>Table 1 6 Factors, 30 levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (°)</td>
</tr>
<tr>
<td>D (mm)</td>
</tr>
<tr>
<td>h (mm)</td>
</tr>
<tr>
<td>v (m³/h)</td>
</tr>
<tr>
<td>L (mm)</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>7.5</td>
</tr>
<tr>
<td>5.4</td>
</tr>
</tbody>
</table>

Note: $a$: the included angle at the apex of the cone; $D$: nozzle inside diameter; $h$: vertical height between nozzle and horizontal flange plane of the cone bottom; $v$: volumetric flow rate of gas; $L$: height of fixed bed; $K$: $K = n/n_1$, where $n_1$ is the number of upper nozzles, $n$ is the number of lower nozzles

3.4. DATA PROCESSING AND RESULTS ANALYSIS

3.4.1. Orthogonal Designing Test
Table 1. with 6 factors and 30 levels was arranged as first group for orthogonal tests. Three sheets of orthogonal table, $3 \times L_{50}(10^1 \times 5^{10})$, were selected for investigating 150 tests.

The variances analysis of $R^*$ values of the tests indicate that (see Table 2): (1) The effect of $\alpha$ and $L$ on $R^*$ is specially obvious, when $\alpha = 45^\circ - 60^\circ$, $R^*$ is very small, i.e., the quality of fluidization is good; the reduction in $R^*$ with increase in $L$. (2) The effect of factor $K$ on $R^*$ value is not obvious. (3) The slightly reduction in $R^*$ with the reduction in $D$. (4) The effects of $v$ and $h$ on $R^*$ are not obvious.

<table>
<thead>
<tr>
<th>Source of variance</th>
<th>Quadratic sum</th>
<th>Degree of freedom</th>
<th>Meansquare</th>
<th>$F$</th>
<th>Obviousness</th>
<th>Checking critical value of $F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>$4.707 \times 10^3$</td>
<td>29</td>
<td>$1.623 \times 10^4$</td>
<td>1.857</td>
<td>*</td>
<td>$F 0.01(4100)=3.51$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$8.111 \times 10^4$</td>
<td>4</td>
<td>$2.028 \times 10^4$</td>
<td>23.20</td>
<td>**</td>
<td>$F 0.05(28100)=1.59$</td>
</tr>
<tr>
<td>$L$</td>
<td>$3.532 \times 10^4$</td>
<td>4</td>
<td>$8.830 \times 10^4$</td>
<td>10.10</td>
<td>**</td>
<td>$F 0.10(4010)=2.00$</td>
</tr>
<tr>
<td>$D$</td>
<td>$7.676 \times 10^4$</td>
<td>4</td>
<td>$1.919 \times 10^4$</td>
<td>2.195</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>576.9</td>
<td>1</td>
<td>576.9</td>
<td>0.0660</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v$</td>
<td>$1.340 \times 10^4$</td>
<td>4</td>
<td>3350</td>
<td>0.3833</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error $E$</td>
<td>$9.004 \times 10^4$</td>
<td>103</td>
<td>8741</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sum $\Sigma$</td>
<td>$2.626 \times 10^4$</td>
<td>149</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to the analysis of data obtained from first group of 150 tests, we found second group of 18 tests arranged by orthogonal table, $L_{18}(6^1 \times 3^6)$. The orthogonal table, $L_4(2^3)$, was selected for third group of 4 tests.

3.4.2. Mathematical Statistic Model

The monadic multinomical regression analysis of data recorded in a real-time on-line operation was finished for first group of 150 tests (see Table 3).

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$35^\circ$</th>
<th>$45^\circ$</th>
<th>$60^\circ$</th>
<th>$75^\circ$</th>
<th>$90^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>58.80</td>
<td>45.59</td>
<td>51.12</td>
<td>103.6</td>
<td>241.3</td>
</tr>
</tbody>
</table>

The special equation for $\alpha - R$ was obtained:

$$R = 43.39 + 4.033 \alpha - 0.1556 \alpha^2 + 1.502 \times 10^{-3} \alpha^3\quad \alpha \in [35^\circ, 90^\circ]$$ (3)

With Eq. (3) find the minimum of $R$, gives the optimum value $\alpha = 52^\circ$.

The special equation for $L - R$ was obtained:

$$R = 20.64 + 0.1808L - 6.635 \times 10^{-4}L^2 + 5.802 \times 10^{-7}L^3$$ (4)

With Eq. (4) find the minimum of $R$, gives the optimum value $L = 585\text{mm}$. Using $v - R$ data and the relevant calculation, a better value $v = 520\text{m}^3/\text{h}$ was obtained.

3.4.3. A Typical Experiment for the Optimum Parameters

A typical experiment has been done under the optimum conditions, i.e., $\alpha = 60^\circ$; $K = 9.6$; $D = 20\text{mm}$; $L = 585\text{mm}$; $v = 520\text{m}^3/\text{h}$. The experimental data were show in Fig.3. The value of fluidization index $R$ was better.
than those above mentioned.

Fig. 3. Changing pressure drop with time (1000 data)

4. COMMERCIAL TEST

Based on our research work and the mathematical model, a 1.2-m-ID, 11.3-m-length commercial FBW chlorinator has been designed for chlorinating titanium-rich slag obtained from electric arc smelting of Panzhihua ilmenite to produce TiCl₄. The main parameters of the FBW were: $\alpha=52^\circ$, $D=25\text{mm}$, $n=25$. The chemical composition of titanium-rich slag is given in Table 4.

Table 4. Composition of titanium-rich slag

<table>
<thead>
<tr>
<th>Constituent</th>
<th>TiO$_2$</th>
<th>$\Sigma$Fe</th>
<th>MgO</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>84.86</td>
<td>3.19</td>
<td>5.38</td>
<td>1.33</td>
<td>2.33</td>
<td>1.54</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The slag containing approximately 85 pct TiO$_2$ and 6.7 pct MgO+CaO impurities is reacted with chlorine and petroleum coke under reducing condition in the FBW chlorinator operating at 950 to 1100°C to produce TiCl₄. The chlorinator had run continuously for 55 days with a good fluidization and complete reaction. Discharge of residue runs smooth and notable results were obtained: titanium chlorinated was more than 97 pct., the daily output was 25 tons of TiCl₄. It has been shown by commercial production that such a FBW reactor is particularly suitable to the chlorination of titanium-bearing raw material with high content of MgO and CaO. In addition it has been applied to chlorinate titanium-rich slag made from beach sand ilmenite to produce TiCl₄, and to dry minerals etc..

CONCLUSIONS

1. The fluidization indication expression, $R' = \Delta p \times 10^4 / [ (f^' + e) p_o ]$ as a criteria, for distinguishing a quality of fluidization is given by the author of this paper. A 0.75-m-ID clear plexiglass FBW was used for a simulating amplification, and the mathematical model was obtained.
2. According to the mathematical model, a 1.2-m-ID FBW chlorinator has been designed for chlorinating titanium-rich slag containing approximately 85 pct TiO$_2$ and 6.7 pct MgO+CaO for producing TiCl₄. The chlorinator has run continuously for 55 days with good fluidization and notable results.
3. It has been proven by the commercial-scale experiment and production that such a FBW reactor is particularly suitable to the chlorination of titanium-bearing raw material with high content of MgO and CaO.

LITERATURE


