the saturated density data near the normal boiling point cited from International Critical Tables²⁾. The modified value of C_0 was determined by noting the fact that the fugacities for both phases become identical at the vapor-liquid equilibrium condition as shown in Fig. 1, and is presented in Table 1. By adopting the new constants for oxygen, vapor-liquid equilibria for the carbon dioxide-oxygen system were predicted. As shown in Fig. 2, a marked improvement for predicting bubble point lines was obtained. These new constants in the BWR equation for oxygen may be useful for other systems.

Nomenclature

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$: constants for the BWR equation

d^V	= molar density of vapor	[g-mol/l]
d^L	= molar density of liquid	[g-mol/l]
f^V	= fugacity of vapor	[atm]
f^L	= fugacity of liquid	[atm]
T	= temperature	[°K]
ω	= acentric factor	[—]

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SLIP-LINE ANALYSIS FOR POWDER COMPRESSION*

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From an analogy of the slip-line analysis of metal plastic working, the slip-lines in the stress field of a powder bed compressed by rough parallel plates were drawn and the normal stresses on the wall were calculated using Coulomb's equation. These calculated values were compared with the experimental data, and the following conclusions were drawn;

- (1) Under the critical stress state, the compressed powders reveal the same behavior of a continuum as far as it is possible to analyze neglecting the bed density.
- (2) The powder yield locus for the compressive stress field cannot be a Coulomb type straight line, but is a Farley-Valentin type curve convexing to the left.

In the analysis of stress conditions in a powder bed being compressed by a pair of parallel plates, it is possible to assume that the bulk density of the powder bed is zero when the ratio of bed length l to height h is large. This assumption⁴⁾ is also useful to the slip-line analysis in various cases and is adopted here for the two-dimensional stress field.

1 The equations of stresses along the slip-lines

If the internal stresses are high enough to neglect the bulk density of the powder and are in a state of plastic equilibrium obeying Coulomb's failure criterion, the slip-lines can be drawn with a protractor and a ruler. It is assumed that this condition applies here and the theory is limited to that case. Thus the equations of static equilibrium are

$$\frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau}{\partial y} = 0, \quad \frac{\partial \tau}{\partial x} + \frac{\partial \sigma_y}{\partial y} = 0 \quad (1)$$

The equations of characteristics of the hyperbolic diffe-

rential equations which are obtained substituting the yield conditions shown in Fig. 1 into Eq.(1), are

Fig. 1 Coulomb-Mohr diagram and the directions of stresses and slip-lines

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Fig. 2 Stress system in the compression

Fig. 3 Vertical stresses on the wall (Calculated values)

$$\frac{dy}{dx} = \frac{-\sin 2g \mp \cos \phi}{\cos 2g - \sin \phi} \quad (2)$$

Then the equations of equilibrium can now be replaced by the equations

$$\frac{\ln(p \tan \phi + c)}{\tan \phi} \mp 2g = \text{const} \quad (3)$$

along the first and second characteristics, respectively, where c is cohesion, ϕ is the angle of internal friction of the powder and the stress parameter p and the angle g are defined by the Coulomb-Mohr diagram of Fig. 1. Since the characteristics correspond to the slip-lines⁶, Eq.(3) gives the equations of stresses along the α and β slip-lines, respectively.

2 The assumed stress system and the vertical stresses on the wall

In this paper, the stress system as shown in Fig. 2 is adopted for a powder compressed by a pair of rough horizontal plates. Stresses in the plane of observation are assumed to be uninfluenced by stresses normal to the plane. This stress field, obtained from an analogy of the two-dimensional slip-line analysis²³ in metal plastic working, is divided into four parts (Fig. 2 shows a quarter of the whole).

Fig. 4 Experimental apparatus

Firstly, in the region AOG the stresses are free from the external force, i. e. the boundary AO (α slip-line) is a stress-free surface. Secondly, the region AOB₁ is a stress field that consists of straight lines (α slip-lines) and logarithmic spirals (β slip-lines). Thirdly, the region B₁OMB_n is a stress field in which the stresses in the whole field can be determined by generating α and β slip-lines from the boundary OB₁ and the axis of symmetry OM, where the envelope of α slip-lines is tangent to the wall because of the rough wall condition. Lastly, in the region B_nMC the slip-lines are determined by the boundary B_nM (α slip-line) and the axis of symmetry CM, so that the slip-lines are not tangent to the wall in this region.

These stress systems satisfy the condition of allowable stress field of the powder obeying Coulomb's failure criterion. Then from Eq.(3), the vertical stresses on the wall AB_n in Fig. 2 are

$$\sigma_{yw}(i) = \left[\left\{ \frac{1}{\tan \phi} + \frac{1}{\tan \left(\frac{\pi}{4} - \frac{\phi}{2} \right)} \right\} \exp \left\{ \frac{\pi}{2} + \phi + 4(i-1)\delta \right\} \tan \phi - \left(\tan \phi + \frac{1}{\tan \phi} \right) \right] c \cos^2 \phi \quad (4)$$

where i is the suffix of B in Fig. 2, δ is the angle also shown in Fig. 2 (see Appendix). The vertical stresses on the wall B_nC are calculated by the method of the literature²³.

The results of calculation are drawn in Fig. 3 to illustrate how the vertical stresses on the wall change with cohesion c and angle of internal friction ϕ .

3 Experiment

The experimental apparatus is illustrated in Fig. 4. Alumina of mean particle of 4μ (moisture content of 0.19 wt-%) was used as the powder. The powder was

Fig. 5 Vertical stresses on the wall (Experimental and Calculated values)

uniformly packed in the vessel, which was provided by a pair of horizontal walls with cloth files pasted inside them for roughness of wall⁵⁾ and the side walls. After removing the side walls the powder was compressed by the horizontal walls. Then the bed height of powder h , the stresses on the horizontal wall σ_{yw} and the bulk density of powder bed γ were measured. The vertical stresses were measured using wire resistance strain gages fixed on the lower wall (Fig. 2). The data for the experimental condition where the bed height h is 4.4cm, length l is 30cm and depth is 30 cm are shown in Fig. 5.

4 Results

The experimental values of stresses on the wall, which are increasing toward the center of wall C, don't agree with one of the calculation curves but agree with such combination of curves as is shown in Fig. 5; that is, these data tend to agree with a part of the curve where c is larger and ϕ is smaller, as the internal stresses are larger.

From the above results, it appears that the yield locus for the compressed powder is not linear as in Coulomb's equation but is curved as shown by Farley and Valentin¹⁾, and that the slip-line analysis neglecting the bulk density is available for the compression of fine powders.

Appendix

From the equations of stresses along the α and β slip-lines in Fig. 2, the following equations are obtained.

$$\left. \begin{aligned} \ln(p_1 \tan \phi + c) &= \ln(p_0 \tan \phi + c) + 2(g_0 - g_1) \tan \phi \\ \ln(p_a \tan \phi + c) &= \ln(p_1 \tan \phi + c) - 2(g_1 - g_a) \tan \phi \\ \ln(p_2 \tan \phi + c) &= \ln(p_a \tan \phi + c) + 2(g_a - g_2) \tan \phi \\ &\dots \dots \dots \end{aligned} \right\} \quad (A 1)$$

Fig. 6 Mohr's circles in the region AOG and at the wall $\overline{AB}_n$ in Fig. 2

Referring to Fig. 6

$$p_0 = c / \tan\left(\frac{\pi}{4} - \frac{\phi}{2}\right) \quad (A 2)$$

$$g_0 - g_1 = \frac{\pi}{4} + \frac{\phi}{2}, \quad g_1 - g_a = -\delta, \quad g_a - g_2 = \delta, \quad \dots \dots \quad (A 3)$$

Suffixes o, a, b, 1 and 2 represent the positions O, B_a, B_b, B₁ and B₂ in Fig. 2, respectively. Combining the above equations gives the stress parameter on the generalized position B_i in Fig. 2:

$$p_i = \left[\left(\frac{1}{\tan \phi} + \frac{1}{\tan\left(\frac{\pi}{4} - \frac{\phi}{2}\right)} \right) \exp\left\{\left(\frac{\pi}{2} + \phi\right) + 4(i-1)\delta\right\} \tan \phi - \frac{1}{\tan \phi} \right] c \quad (A 4)$$

As σ_y is less than σ_x at the wall (Fig. 6),

$$\sigma_{yw} = p_w - (p_w + c \cot \phi) \sin^2 \phi \quad (A 5)$$

From Eqs. (A 4) and (A 5), Eq. (4) can be derived.

Nomenclature

c	= cohesion	[G/cm ²]
g	= angle between y direction and major principal stress direction	[rad]
h	= bed height of the compressed powder	[cm]
l	= bed length	[cm]
p	= stress parameter defined by Fig. 1	[G/cm ²]

Greek letters

α, β	= families of slip-lines shown in Fig. 1	
γ	= bulk density	[G/cm ³]
δ	= angle shown in Fig. 2	[rad]
θ	= angle between x direction and slip-line direction	[rad]
σ	= normal compressive stress	[G/cm ²]
τ	= shearing stress	[G/cm ²]
ϕ	= angle of internal friction	[rad]

Subscripts

1, 2, i, n;	a, b	= positions shown in Fig. 2
w		= wall
x, y		= component x and y

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LETTER TO THE EDITOR

REMARKS ON APPROXIMATE ESTIMATION OF CATALYST EFFECTIVENESS FACTOR*

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It is illustratively shown that the approximate method of estimating the catalyst effectiveness factor, previously presented by the authors, is widely applicable in general cases and also that the nonisothermal effect within the catalyst on the effectiveness factor is minor.

The authors⁴⁾ have proposed an approximate method of estimating the catalyst effectiveness factor using the effective diffusivity, which was defined as a conventional constant for the multicomponent gaseous reaction system. In that work, the rate of reaction was linearly approximated with concentration and temperature under the conditions at the catalyst surface. Here, the authors will add some remarks to criticize this approximate method.

The Asymptotic Solution There have been some approximate methods to evaluate the catalyst effectiveness factor for reactions where rate expressions are other than first-order, but one is not able to estimate a priori the errors resulting from the approximations made.

Petersen^{5,6)} proposed the method of giving an asymptotic solution under isothermal conditions within the catalyst particle, that is

$$E_f = \frac{\sqrt{2}}{h} \left[- \int_0^1 r_A(C) dC \right]^{1/2} \quad (1)$$

$$\text{where } h = \frac{R}{3} \sqrt{\frac{r_A(C_{As})}{D_{Ai} C_{As}}}, \quad C = \frac{C_A}{C_{As}} \quad (2)$$

The value of E_f obtained from Eq.(1) is asymptotically correct, and therefore it is close to the exact value at small values of E_f but may be different when approaching unity.

Bischoff²⁾ modified Petersen's concept to apply to general rate forms, but the use of their method is limited to certain cases such as simple n -th order reac-

tions.

The Authors' Approximate Method On the contrary, the approximate method proposed by one of the authors¹⁾ is very simple but can be applied to the general rate forms.

The reaction rate is expanded in Taylor series about the condition at the catalyst surface, and neglecting the terms more than the second order,

$$r_A = r_A(C_{As}, t_s) + r'_{cs}(C_A - C_{As}) + r'_{ts}(t - t_s) \quad (3)$$

$$\text{where } r'_{cs} = \left(\frac{\partial r_A}{\partial C_A} \right)_{C_A=C_{As}}, \quad r'_{ts} = \left(\frac{\partial r_A}{\partial t} \right)_{t=t_s} \quad (4)$$

Thus the analytical solution of the diffusion equation for a spherical porous catalyst can be easily obtained, and then

$$E_f = \frac{3}{h} \left[\frac{1}{\tanh h} - \frac{1}{h} \right] \quad (5)$$

$$\text{where } h = R \sqrt{- \left(\frac{r'_{cs}}{D_{Ai}} + \frac{r'_{ts} Q_A}{\lambda} \right)} \quad (6)$$

Illustrative Calculations for n -th Order Reactions Consider the reaction $lA + mR = 0$, which proceeds at rate $r_A = -kC_A^n$. Assuming that no inert component is included, the effective diffusivity is expressed as follows by accounting for the effect of volume change⁴⁾.

$$D_{Ai} = D_{AR} / (1 - \alpha z_{As}) \quad (7)$$

where

$$\alpha = 1 + m/l$$

The modulus h in Eq.(6) can be expressed under isothermal conditions by

$$h = h_0 \sqrt{n z_{As}^{n-1} (1 - \alpha z_{As})} \quad (8)$$

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