A Theorem Regarding the Poisoning of Fixed Catalyst Beds

Recently, Anderson and Whitehouse (*1*) considered the poisoning of fixed catalyst beds by an impurity in the feed and presented calculations based on simple hypothetical poisoning and poison distribution equations. In many of the examples in this paper (*1*) the relative activity of the bed decreased linearly with poison concentration of the bed at the start of the poisoning. The present note considers certain conditions under which this linear relationship is obtained. This work is a part of Bureau of Mines' research on the poisoning of catalysts used in converting coal to liquid and gaseous fuels.

The present development is limited to poisoning processes in which the concentration of poison on the inlet portion of the bed attains a constant value, S_0, at the beginning of the poisoning, and the concentration of poison at any distance, x, from the inlet is a given function of bx, where b is a constant at any given time. The value of b, however, decreases as the average poison concentration of the bed increases. Under these conditions increasing the poison concentration of a given bed or decreasing the length of the bed is equivalent.

The observed relative activity of the catalyst bed, $\bar{F}$,* is the average value of relative activity along the bed,

$$\bar{F}l = \int_0^l F_x dx,$$

and the poison concentration in the bed, $\bar{S}$, is a similar average

$$\bar{S}l = \int_0^l S_x dx.$$

* Relative activity is defined as activity of poisoned catalyst divided by activity of unpoisoned catalyst. Activity should be expressed in a proper form, such as the rate constant of the kinetic equation for a reaction in an isothermal bed of catalyst. The relative activity of an increment of the bed is a function only of the poison concentration in that increment.

In an increment of bed at a distance x from the inlet, the relative activity and poison concentration are F_x and S_x, respectively, and the bed length is l. We now differentiate the expressions for $\bar{F}$ and $\bar{S}$ with respect to l, and obtain

$$d\bar{F}/dl = (F_l - \bar{F})/l$$

$$d\bar{S}/dl = (S_l - \bar{S})/l$$

$$d\bar{F}/d\bar{S} = (F_l - \bar{F})/(S_l - \bar{S}) \qquad (1)$$

where subscript l denotes the values of F_x and S_x at the end of the bed. If none of the poison reaches the end of the bed, $S_l = 0$, and $F_l = 1$, and Eq. 1 becomes

$$d\bar{F}/d\bar{S} = -(1 - \bar{F})/\bar{S} \qquad (2)$$

which is the differential equation of a straight line,

$$\bar{F} = 1 - \alpha\bar{S} \qquad (3)$$

where α is a constant, $-\alpha = d\bar{F}/d\bar{S}$. Equation 3 is valid only when $S_l = 0$, except when the poisoning equation for an increment of the bed has the form $F_x = 1 - \alpha S_x$.

For all the poisoning processes in fixed beds for which S_x is a function of bx, as defined above, we may state as theorems:

1. The relative activity, $\bar{F}$, decreases linearly with poison concentration, $\bar{S}$, at least as long as the concentration of poison at the outlet end of the bed is zero.
2. The poison concentration, $\bar{S}$, at which this linear relationship fails, corresponds to the point where part of the poison begins to pass through the bed, except where $F_x = 1 - \alpha S_x$.
3. For $F_x = 1 - \alpha S_x$, the relative activity, $\bar{F}$, decreases linearly as poison concentration, $\bar{S}$, is increased, until $\bar{F} = 0$, irrespective of the distribution of poison as a function of bed length (*1*).

As an example, equations for α were obtained for the poisoning equation $F_x = (1 + aS_x)^{-1}$ and three poison distribution equations from the previous paper, (*1*) as shown in Table 1. For distribution equations A and B, S_l approaches 0 asymptotically, and α must be evaluated as

$$\underset{S_l \to 0}{\text{Limit}} \{(1 - \bar{F})/\bar{S}\}$$

For distribution equation A the linear equation is usually valid to values of $\bar{S}/S_0$ as large as 0.15. For equation B the linear relationship holds only at very low values of $\bar{S}/S_0$, as the poison is never completely adsorbed in the bed according to this distribution. For equation C the linear equation holds to $\bar{S}/S_0 = 0.5$. The effectiveness of the poison for different distribution equations increases in the order C, A, B.

The same arguments may be applied to adsorption processes. If the distribution of adsorbate is a function of bx as defined previously, the differential heat of adsorption is constant as long as the concentration of adsorbate at the outlet end of the bed is zero.

TABLE 1

Initial Slope of Poisoning-Concentration Curves for Poisoning Equation $F_x = (1 + aS_x)^{-1}$

	Poison distribution equation, S_x/S_0 =	Slope, α, of initial linear portion of poisoning equation: α =	Numerical value for $a = 1$, $S_0 = 10$
A	$\exp(-bx)$	$(1/S_0) \ln (1 + aS_0)$	0.24
B	$(1 + bx)^{-1}$	a	1.00
C	$(1 - bx)$	$(2/S_0)\{1 - (1/aS_0) \ln (1 + aS_0)\}$	0.15

Reference

1. Anderson, R. B., and Whitehouse, A. M., *Ind. Eng. Chem.* **53**, 1011 (1961).

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