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SUBJECT: Development of a Method for Predicting
Continuous Trickle-Type Column Dissolver
Behavior from Batch Data

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DATE APR 2 1957

For The Atomic Energy Commission

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1.0 SUMMARY

A method for determining dissolver solution concentration as a function of length of column traversed for trickle-type continuous dissolvers has been developed. An illustrative example is worked out for the mercury-catalyzed nitric acid dissolution of U-Al cast alloy slugs.

The method employs a graphical integration of simple functions of dissolution rates and acid concentrations. These rates and concentrations are easily obtained from batch experiments made over the important ranges of concentration.

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2.0 INTRODUCTION

The purpose of this report is to show how the solution composition in a column-type continuous dissolver may be calculated as a function of column height from batch experiments. Such calculations are of value because by means of them the behavior of a column dissolver can be predicted in a qualitative or semiquantitative way for a wide variety of conditions from comparatively inexpensive batch experiments, and the number of expensive column experiments which are necessary can be materially reduced.

3.0 DEVELOPMENT OF METHOD

The type of dissolver column which will be considered here is that in which the dissolver solution enters at the top of the column and runs down at less than flooding rates over the material to be dissolved. While the specific problem of dissolving U-Al alloy slugs with HNO_3 using a mercury catalyst prompted this work, it will become apparent that the method arrived at is applicable for any dissolver solution, and for any material being dissolved, e.g., caustic dissolution of U-Al alloy slugs, or HNO_3 dissolution of U slugs.

The following simplifying assumptions were made in the development:

- (1) The flow rate of dissolver solution is constant;
- (2) Material over the entire column is, on the average, covered equally well by the dissolver solution;
- (3) The area presented by the material being dissolved is the same per unit column length over the entire column (when this condition is not met, but the area distribution is known as a function of column length, a simple extension of the development is required to include the new variable);
- (4) The dissolver solution is neither concentrated by evaporation (or

other) losses, nor diluted by the introduction of liquid at any point in the column; and

- (5) The dissolver solution at one point in the column is not appreciably mixed with that at another point (this condition is approached by keeping solution flow below flooding).

To avoid using very general terms, which are likely to be vague and not easily understood, we will discuss the specific case of the mercury-catalyzed nitric acid dissolution of uranium-aluminum alloy slugs. The way in which the method may be extended to include other dissolutions of interest will be obvious from the specific case treated.

The batch data required by this method are most easily obtained by dissolving a small percentage ($< 10\%$) of an alloy slug wafer in each of a series of solutions each of whose volumes is sufficiently large that its action on the wafer does not change the solution's composition appreciably. From the initial weight of the wafer, its weight after dissolving a small fraction of it, and the average area it has during the dissolution, the rate of dissolution in mg/hr/cm^2 , or other appropriate units can be calculated for the solution employed. The solutions in which the wafers are partially dissolved should vary in acidity from the highest acidity one contemplates using as an acid feed in the column work, to the lowest acidity one expects in the product*. The solution should vary in aluminum concentration from 0

*The product solution may, of course, actually be an "acid deficient" solution. To facilitate the discussion, and the graphing of data, we will speak of acid deficient solutions as having "negative" acid concentrations, realizing all the while that such solutions are really acidic, having pH's of the order of 2. It is important to recognize that the analytical technique for determining acid concentrations in the aluminum-containing solutions has been mainly responsible for this choice of terminology. In the analytical determination, an excess of potassium oxalate, a powerful complexing agent for aluminum, is added to the solutions, thus displacing any hydroxyl ions which have bound themselves to aluminum in the process of hydrolysis. This release of titratable hydroxyl ions creates a basic solution, or one in which there is a "deficiency" of acid.

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to the highest aluminum concentration anticipated in the product. It is, manifestly, not worthwhile to make batch runs in solutions containing both the highest acid concentration expected for the feed dissolver solution, and also the highest aluminum concentration expected in the product, since the two conditions cannot co-exist. Similarly, many other runs of mutually exclusive acid and aluminum concentrations may be omitted, thereby materially reducing the batch work required.

When the batch data just described have been obtained, it is possible to calculate acid concentration as a function of the length of column the acid has traversed. We may show this by the following development.

Consider the alloy to be a rectangular parallelepiped. The acid dissolver solution is considered to pour over the top of the column and to run down over the faces, dissolving the alloy as it proceeds downward. We do not, however, consider the volume of the piece to be diminished, since it represents a column at a steady state condition, wherein alloy is being introduced at exactly the rate at which it is being dissolved away. If we designate by "m" the mass of the parallelepiped, then the specific rate of dissolution at a point x units of length down the column is defined as

$$(1) \quad \frac{dm}{dt} = R_x$$

If the dissolver solution flows at a constant feed rate, then the rate at which an element volume of acid feed proceeds down the column is constant, or

$$(2) \quad \frac{dx}{dt} = k_1$$

We may, therefore, rewrite equation 1 in terms of length of column traversed, x, so

$$(3) \quad \frac{dm}{dx} = k' R_x$$

It is apparent that the mass of alloy dissolved is directly proportional to the moles of acid consumed in the dissolution, $Vd(H)_x$, so

$$(4) \quad dm = k'' V d(H)_x,$$

where $(H)_x$ represents the acid concentration measured when the column is sampled at the point x , and analyzed for acid by the potassium oxalate method. It is also apparent that the total rate of dissolution, R , of the alloy is directly proportional to the surface available, S_x . Thus,

$$(5) \quad \frac{d(H)_x}{dx} = \frac{S_x k'}{k'' V} R_x.$$

In the general case S_x is a function of column length, x , and must be experimentally determined. While the inclusion of this new variable is accomplished rather simply, it is not advisable to introduce a complication of this nature before the basic features of the method have been developed. Therefore, for the purpose of simplification, the area distribution will be assumed constant. The term $\frac{S_x k'}{k'' V}$ is, therefore, a constant for the constant flow rate, steady state condition we have postulated, so we may write

$$(6) \quad \frac{d(H)_x}{dx} = k R_x, \text{ or, rearranging,}$$

$$(7) \quad \frac{d(H)_x}{R_x} = k dx.$$

Integration gives the expression which relates the acidity at any point, x , to the length of column traveled to reach that point. Thus,

$$(8) \quad \int_0^x \frac{d(H)_x}{R_x} = kx.$$

The integral on the left in equation 8 is measured by the area under the curve obtained when $\frac{1}{R_x}$ is plotted vs. $(H)_x$. Values of $\frac{1}{R_x}$ and the related

values of $(H)_x$ are obtained as follows: Data from the batch runs, made in the manner indicated above, are plotted as rates versus aluminum concentrations at fixed acidities, or fixed acid deficiencies (see Figures 1 and 2). A graph is then made of acidity versus aluminum concentration at constant rate for the range of rates of importance (see Fig. 3). (It is convenient to choose rates at increments of about 200 mg/hr/cm².) A line is then drawn from the point of feed acid concentration of interest (and zero aluminum concentration) to the point representing the product acid and salt concentrations. Go down this line to where it intercepts a line of constant R value. Plot the reciprocal of this value of R versus the corresponding acidity (see Fig. 4). Draw a smooth curve through sufficient points to include feed solution and product compositions. The area under the curve obtained is the value of the integral in equation 8. At equal increments along the $(H)_x$ axis construct perpendiculars up to the curve (see Fig. 4). The areas enclosed by the abscissa, two adjacent perpendiculars, and the curve are proportional to column length, x. The proportionality constant is easily evaluated by dividing the total area under the curve by the length of the column in centimeters, or other appropriate units. Since the curve in Fig. 4 extends from acid feed concentration (6 M) to the column product acid concentration (2 M), it is apparent from equation 8 that the ratio of any one of the enclosed areas to the total area under the curve is equal to the fraction of the length of column which is traversed in moving from the acid concentration at the perpendicular bounding the area on one side, $(H)_{x1}$, to the acid concentration at the perpendicular bounding the area on the other side, $(H)_{x2}$ (see Fig. 4). It should be observed that in graphs, such as in Figures 3 and 4, it is necessary to reckon areas from feed acid concentration to product acid concentration. Any time a new acid feed concentration is used, a new analysis must be made according to the method outlined above.

Finally, by plotting fraction of column length traversed versus acid concentration arrived at when that fraction of column has been covered, we have the desired form relating x and $(H)_x$ (Fig 5). It should be stressed again that such a plot is valid only for a given acid feed concentration and column length.

4.0 EXAMPLE USING DATA FROM HW-18414

The following example, calculated from batch dissolving data taken from HW-18414, illustrates the method. Since the Hanford batch data cover only the range from about 6 M HNO_3 to 2 M HNO_3 , we shall assume we have a column of such length, x , that 6 M nitric acid feed has been reduced in acid concentration to 2 M HNO_3 , and has an aluminum concentration of 1.07 M when it emerges as column product. The aluminum product concentration of 1.07 M follows from the fact that over the range of interest 3.75 moles of acid are consumed for each mole of Al dissolved (see ORNL-1208, p.70).

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Fig. 1

Fig. 2

Fig. 3

Fig. 4*

*Note that it is necessary to reckon areas from feed acid concentration to product acid concentration. Any time a new feed acid concentration is used, a new analysis must be made according to the method outlined above.

ILLUSTRATIVE FIGURES SHOWING THE STEPWISE PROCEDURE FOLLOWED
IN ARRIVING AT A FIGURE WHICH SHOWS ACID CONCENTRATION
AS A FUNCTION OF DISSOLVER COLUMN TRAVERSED

Fig. 5

ACID CONCENTRATION AS A FUNCTION OF
DISSOLVER COLUMN TRAVELLED