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CONSIDERATIONS OF PLANT DESIGN FOR SOLID -
LIQUID REACTIONS

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0.0 SUMMARY

The factors that influence the course of solid-liquid reactions have been reviewed. Conditions necessary to obtain chemical and dynamic similarity for solid-liquid reactions in agitated vessels have been considered and scaling-up rules have been given for different criteria of mixing.

The effect of the distribution of residence times on solid-liquid reactions in both chemical and diffusion regimes has been considered for simple and complex reactions, and the difference in performance between batch and continuous stirred tank reactor systems has been emphasised. Methods for translating batch reaction data to continuous operation have been given.

These considerations are of the greatest importance in relation to the production of phosphoric acid by the "wet" process and the acidulation stage of the production of complex fertilisers.

I N D E X

	<u>Page No.</u>	
0.0	SUMMARY	1
1.0	INTRODUCTION	2
2.0	REACTION RATE DETERMINING PROCESSES	-
2.1	Effect of temperature	3
2.2	Effect of agitation	3
2.3	Effect of speed of mixing	5
2.4	<u>Scale-up of rate-determining processes</u>	
2.41	Chemical similarity	5
2.42	Agitation similarity	5
2.421	Suspension of solids in liquids	5
2.422	Mass and heat transfer	6
2.423	Speeds of mixing	6
2.43	Power requirements for agitation	6
2.44	Compatibility of scale-up methods for agitation.	7
2.45	Recommended methods for design	8
3.0	DISTRIBUTION OF RESIDENCE TIMES	
3.1	Reactor flow systems	9
3.2	<u>Effect of flow system on chemical reactions</u>	
3.21	Simple reactions	9
3.22	Complex reactions	11
3.23	Diffusion - controlled reactions	13
3.3	Effect of flow system on physical changes	14
3.4	<u>Methods of scaling batch model data to full-scale continuous plant</u>	14
3.41	Algebraic method for reactions of known order	15
3.42	Graphical methods for reactions in the homogeneous phase	15
3.43	Graphical method for reactions in the dispersed phase	16
4.0	CONCLUSIONS	16
5.0	REFERENCES	17

CONSIDERATIONS OF PLANT DESIGN FOR SOLID-
LIQUID REACTIONS

1.0 INTRODUCTION

In considering plant design for solid-liquid reactions the problem has two aspects.

- a) Design of new plant starting with laboratory data.
- b) Assessment of existing plant or modification to existing plant.

For both of these cases, if accurate predictions are to be made of the performance of large-scale plants, it is necessary that the investigations should be carried out in a model of the full-scale plant.

There are two main considerations in designing plant in which chemical and physical changes take place, based on the performance of models.

- 1) Reaction-rate-determining processes; i.e. the variation of reaction rate with reactant concentration, temperature and conditions of mixing.
- 2) Competibility of "residence time distribution" in large and small plants with the chemical and physical changes occurring.

This paper is essentially concerned with model theory, and the chemical and physical aspects of plant design based on the considerations outlined above. As the chemical factors in solid-liquid reactions may sometimes be more important than the physical factors, the general case of solid-liquid reactions in a chemical regime has been included.

2.0 REACTION - RATE - DETERMINING PROCESSES

The general case of a reaction between a solid and a liquid or a gas may involve a number of primary stages.

- (a) Transport of the solute molecules to the interface.
- (b) Adsorption at the surface.
- (c) Reaction at the surface.
- (d) Desorption of the products.
- (e) Recession of the products from the interface.

Stages (b), (c) and (d) involve the interaction between liquids and solids, and may be termed the "chemical stages" whereas (a) and (e) may be termed "transport stages".

Heterogeneous reactions are often classified according to the rate-determining stage, as follows:-

- 1) Reactions in which the rate of reaction at the interface is faster than the rate of transport of reactants to or from the surface. These reactions are referred to as transport or diffusion-controlled.
- 2) Reactions in which the chemical reaction at the interface is slower than the rate of transport control. These reactions are known as chemically-controlled.
- 3) Reactions in which both chemical and diffusion control are significant.

The two main process variables, which affect the reaction control are temperature and agitation, and it is necessary to carry out experiments in the model at various levels of these variables in order to find the rate-determining factors.

2.1 Effect of Temperature

A rise in temperature will generally increase both chemical and transport rates, and the relationships on which these rates depend, approximate to an exponential form.

$$k = C_1 e^{\frac{-E}{RT}}$$

$$D = C_2 e^{\frac{-E_d}{RT}}$$

Where k is the chemical reaction velocity constant

D is diffusion coefficient

E is chemical activation energy

E_d is diffusion activation energy

C is a constant

The temperature coefficient of a reaction rate is commonly expressed as the relative increase in rate, which is caused by a temperature rise of 10°C . For 10°C rise a chemically-controlled reaction will give an increase in coefficient of 2 to 4 times. For mass transfer, D increases by 1.25 to 1.5 times. A few simple experiments at 10°C intervals may thus indicate the controlling factor.

2.2 Effect of agitation

Increase in agitation will not affect the reaction rate in a chemical regime, providing that the dispersed phase was adequately suspended originally. In a transport regime, the effect of agitation is to increase the degree of turbulence and reduce the thickness of streamline boundary films. The resistance to processes of heat and mass transfer by convection is thereby diminished and the overall reaction rate increases. If reaction rate varies as conditions of turbulence change, it is necessary to characterise the dynamics of the system.

The simplified general rate equation for transport control may be expressed as follows:

$$-\frac{dM}{dt} = Sk_d (c_s - c) = \frac{SD}{\delta} (c_s - c)$$

Where

- M = weight of solid reactant
- S = surface area of interface
- k_d = mass transfer coefficient
- c_s = concentration of solute in saturated solution
- c = concentration of solute in solvent
- D = diffusion coefficient
- δ = thickness of stagnant layer

For a diffusion-controlled reaction the effect on the reaction rate constant k_d may be expressed as:

$$\frac{k_d L}{D} = \frac{L}{\delta} = C_3 \left(\frac{\rho V L}{\nu} \right)^x \left(\frac{\nu}{\rho D} \right)^y$$

If the reaction is viscosity-controlled, so that heat transfer may have a significant effect on the reaction rate, the following relationship will be important.

$$\frac{hL}{R} = C_4 \left(\frac{\rho V L}{\nu} \right)^a \left(\frac{c_p \nu}{R} \right)^b$$

Where

- L = dimension characterizing system *
- ρ = density of homogeneous phase
- ν = viscosity of homogeneous phase
- R = thermal conductivity
- c_p = specific heat
- h = film heat transfer coefficient
- V = velocity of fluid or stirrer

The values of C_3 and C_4 , x, y, a and b, must be determined by experiment for the particular system being investigated. Experiments and a method of calculating these values are described in Ref. 1.

* When geometrical similarity between solid particle and the vessel cannot be observed in scaling-up the group (L_s/L_v) may be introduced into the correlation, where L_s is dimension of particle and L_v is dimension of vessel or agitator.

2.3 Effect of speed of mixing

The speed of mixing or blending may be important in solid-liquid reactions, which are accompanied by precipitation and crystallization reactions. For example, it is well known that the rate and method of blending sulphuric acid into a "wet" phosphoric acid process is an important factor in determining the quality of gypsum produced in the process. Poor mixing with high local concentration of sulphate ions causes uncontrolled nucleation and crystallization.

In practice it is necessary to determine these effects under different conditions of mixing in the model. Methods for measuring the rate of mixing in stirred vessels are given in references 2 and 5.

2.40 Scale-up of rate-determining-process

2.41 Chemical similarity

If the experimental work has shown that the reaction is chemically-controlled, the conversion will depend on the reaction velocity, the equilibrium state and the reaction time:

$$\text{The equilibrium constant } K \propto e^{-\frac{\Delta F}{RT}}$$

$$\text{The reaction velocity constant } k \propto e^{-\frac{E}{RT}}$$

Where ΔF is the free energy change and E is the activation energy.

K and k are thus dependant on the absolute temperature of the system, and if the reaction time, or distribution of reaction times, are the same for large and small-scale plants, conversion is the same.

2.42 Agitation similarity

The three main criteria in scaling-up from model to full-scale plant are:

- (a) The solid particles should be completely suspended in the liquid.
- (b) The rate of mass and heat transfer should be the same.
- (c) The times for blending should be the same.

2.421 Suspension of Solids

The effect of agitation on both chemical and diffusion controlled reactions is to increase the rate, up to the point at which the particles are suspended, so that the surface area of the solid is freely exposed to the liquid, and fresh reactants are presented to the solid surface. Once these conditions have been realised in the model, the large-scale plant conditions can be found by the method recommended in Ref. 3. Assuming that the model and the full-scale plant are geometrically similar, and equal liquid and solid properties, for equal particle size, the stirrer speed can be calculated from the following formula:

$$NL^{0.85} \text{ is constant}$$

N is the stirrer speed and L is the stirrer diameter.

2.4.22 Mass and Heat transfer

When the fluid and solid properties are the same on both scales, the equations for mass and heat transfer given in section 2.2 are as follows:

$$\frac{k_d L}{D} = C_5 \left(\frac{\rho V L}{\mu} \right)^m = C_5 \left(\frac{\rho N L^2}{\mu} \right)^n$$

$$\frac{hL}{k} = C_6 \left(\frac{\rho V L}{\mu} \right)^m = C_6 \left(\frac{\rho N L^2}{\mu} \right)^n$$

Where m and n are the Reynolds indices for heat and mass transfer.

In the turbulent region, m and n vary from 0.6 to 0.8 depending on the geometry of the system. The value of m given in Ref. 1 is 0.62 for large Reynolds numbers and 1.4 for low Reynolds numbers.

For equality of k_d and h, $NL^{\frac{(2m-1)}{m}}$ and $NL^{\frac{(2n-1)}{n}}$ are constant.

When m and n = 0.8 $NL^{0.75}$ is constant

When m and n = 0.6 $NL^{0.33}$ is constant

2.4.23 Speeds of mixing

Scale-up rules for speeds of mixing are given in Ref. 5

For Re. $> 10^3 - 10^4$ for equal time of mixing,

$NL^{0.2}$ is constant.

For Re. < 250 , for equal time of mixing,

$NL^{1.4}$ is constant.

2.4.3 Power requirements for agitation

The power consumption in agitation can be expressed in the following form:

$$\frac{Pg}{\rho N^3 L^5} = C_7 \left(\frac{\rho N L^2}{\mu} \right)^r \left(\frac{N^2 L}{g} \right)^q$$

Where P is power consumption
g is gravitational acceleration

The value of r varies from 1.0 in the streamline region to zero for fully developed turbulence in baffled mixers. The value of q is zero in baffled mixers; in unbaffled mixers it is equal to

$$\frac{a_1 - \log \left(\frac{\rho N L^2}{\mu} \right)}{b_1}$$

Where the constants a_1 and b_1 depend upon the geometry of the system. For scaling-up baffled mixers operating under fully turbulent conditions.

$$\frac{Pg}{\rho N^3 L^5} \text{ is constant}$$

For equal power per unit volume $N^3 L^2$ is constant.

2.44 Compatibility of scale-up methods for agitation

The methods for fully turbulent conditions in baffled mixers are summarized below:

- | | | | | |
|-----|-----------------------------|------|---|-------------|
| (a) | Suspension of solids | | $NL^{0.85}$ | is constant |
| | | | 0.75 | |
| (b) | Mass and heat transfer | (i) | NL | is constant |
| | | (ii) | $NL^{0.33}$ | is constant |
| | | | (depending on the value of the Reynolds number index) | |
| (c) | Equal time of mixing | | $NL^{0.2}$ | is constant |
| (d) | Equal power per unit volume | | $N^3 L^2$ | is constant |

The method most commonly used for scaling-up agitation is equal power per unit volume so it is of interest to compare this with the other criteria (a), (b), (c), and (d).

Power per unit volume $P_v \propto N^3 L^2$

and if equations (a) (b) (c) and (d) are substituted into this

- | | |
|--------|-------------------------|
| (a) | $P_v \propto L^{-0.55}$ |
| (b)(i) | $P_v \propto L^{-0.25}$ |
| (ii) | $P_v \propto L^{1.0}$ |
| (c) | $P_v \propto L^{1.4}$ |

In cases (a) and (b), scale-up on the basis of equal power per unit volume, results in the provision of more power than is really necessary, so that in this sense the correlation can be looked on as a safe one for suspensions of solids in liquids and for mass and heat transfer when the Reynolds number index is more than 0.75.

When the index is less than 0.75, it is necessary to increase the power per unit volume as the scale is increased to obtain the same mass and heat transfer coefficients. Similarly, it is necessary to increase the power per unit volume for equal speeds of blending, although power requirements may be reduced by addition of reactants at a number of points in the vessel.

Recommendation for design

The recommended method for scaling-up is equal power per unit volume. In the case of mass and heat transfer, where it is necessary to increase the power per unit volume on scaling-up, it may be preferable to use equal power per unit volume and allow for the changes in heat and mass transfer coefficients rather than use very high stirrer speeds and excessive power consumption. For equal power per unit volume and geometrically similar systems, the ratio of coefficients in model and plant:

$$\frac{h_m}{h_p} = \left(\frac{L_m}{L_p} \right)^{(1.33n - 1)}$$

Where n is the Reynolds index and depends on the system.

Power requirements for agitated vessels may be obtained from the correlation described in Ref. 6 and shown in Fig. 1. The data are not entirely satisfactory in this form as both ordinate and abscissa contain N. It is more convenient to remove N from the abscissa as in Fig. 2.

Corrections must be made for the particular shape of agitator, as Figs. 1 and 2 refer to simple paddle agitators.

For approximate power consumptions the following table may also be used.

<u>Degree of agitation</u>	<u>Estimated H.P. per 1000 gall. for thin liquids (s.g. ≈ 1)</u>
Very mild	0.10
Mild	0.25
Moderate	0.60
Vigorous	1.50
Intense	4.0 or more

3.0 DISTRIBUTION OF RESIDENCE TIMES

3.1 Reactor flow systems

The effect of flow system on overall reaction rate and yield, particularly for the case of complex reactions, may be very significant, and it is necessary that the flow system of the model and the full-scale plant should be adequately described.

If a stream of material is flowing steadily through a reactor system, the flow pattern will approximate to one of the following:-

(i) Elements of fluid which enter the vessel at the same moment move through it with constant and equal velocity, and leave it at the same moment. This type of behaviour is usually referred to as "piston" or "plug" flow. In a perfect piston-flow system all elements spend the same time in the reactor and conditions in the system are identical with those in a batch system, for the same nominal holding time. In practice perfect "piston flow" never occurs, and there is always some longitudinal mixing due to viscous effects and molecular or eddy diffusion.

(ii) The fluid in the vessel is completely mixed so that its properties are uniform and identical with those of the outgoing stream.

For a single vessel $y = e^{-\frac{t}{\theta}}$

Where y = fraction of material remaining in vessel for time longer than t

θ = nominal holding time in vessel

t = time.

y_n = fraction of material remaining in n vessels for time longer than t

When n vessels of equal size are operated in series

$$y_n = e^{-\frac{t}{\theta}} \left[1 + \left(\frac{t}{\theta}\right) + \frac{1}{2!} \left(\frac{t}{\theta}\right)^2 + \frac{1}{3!} \left(\frac{t}{\theta}\right)^3 + \dots + \frac{1}{(n-1)!} \left(\frac{t}{\theta}\right)^{n-1} \right]$$

A complete solution of these equations is given in Ref. 7. by plotting $t/n\theta$ v. y_n for a varying number of vessels in series.

(iii) The flow pattern is non-ideal and lies between (i) and (ii). For non-ideal flow systems relations must be obtained experimentally.

A method has been proposed by Danckwerts (Ref. 8.) for representing the residence time distribution function by 'C' or 'F' diagrams. The behaviour of fluid flowing continuously through a vessel is recorded graphically by injecting a quantity of some tracer material Q into the entering stream almost instantaneously and measuring the concentration of the injected material in the outlet stream after time t . A plot of VC/Q against t/θ is made, where V is the system volume and C is the concentration of tracer material in the outlet stream. This method of analysis is known as a "jump-signal". Examples of 'C' diagrams are shown in Fig. 3. Another method of analysis is by "step-signal". The concentration of the tracer in the in-going stream is raised suddenly from zero to some value C_0 and its value C at the outlet is measured at various times t . The 'F' diagram is the plot of C/C_0 against (t/θ) , and examples for various flow systems are shown in Fig. 3.

3.2 The effect of flow system on chemical reactions

3.21 Simple Reactions

Changes in the residence-time distribution in a continuous reactor may often bring about a significant change in the course of the reaction.

Sometimes it is possible to predict the changes that will occur from a knowledge of the reaction kinetics and the residence-time distribution.

Very often in the case of heterogeneous reaction, where the apparent order of reaction may change as the reaction proceeds, it is not possible to make these predictions. For chemically-controlled reactions, which are first order, or for transport-controlled reactions, which are pseudo - first order with respect to one of the reacting phases, the effect of flow system on the reaction can be easily shown.

Consider the first order reaction $A \xrightarrow{k} B$

then
$$-\frac{d(A)}{dt} = k(A)$$

Where (A) is the concentration of A at time t, k is the first order reaction velocity constant.

Then
$$\log \frac{(A)_0}{(A)} = kt$$

and
$$x = 1 - e^{-kt}$$

Where $(A)_0$ is the initial concentration of A, and x is the fractional degree of conversion that would be obtained in a batch system after time t or in an ideal piston flow system with a residence time t.

Assume now that the same reaction is carried out in a continuous flow reactor in which the distribution of residence times is $y = f(t/\theta)$, so that $y \cdot d(t/\theta)$ is equal to the fraction of material spending times between t/θ and $t/\theta + d(t/\theta)$ in the reactor. The function y is the same as VC/Q in Danckwerts "C" diagrams.

Then
$$1 - x = \int_0^{\infty} e^{-kt} f\left(\frac{t}{\theta}\right) d\left(\frac{t}{\theta}\right)$$

For a perfectly mixed vessel

$$y = f\left(\frac{t}{\theta}\right) = e^{-\frac{t}{\theta}}$$

and
$$1 - x = \int_0^{\infty} e^{-kt} e^{-\frac{t}{\theta}} d\left(\frac{t}{\theta}\right)$$

$$1 - x = \int_0^{\infty} e^{-\frac{t}{\theta}(k\theta + 1)} d\left(\frac{t}{\theta}\right)$$

$$1 - x = \frac{1}{1+k\theta}$$

For n equal vessels in series, it can be shown (Ref.7) that

$$1 - x = \frac{1}{(1+k\theta)^n}$$

The quantitative effect of flow pattern can be shown by evaluating these equations for differing degrees of conversion, and expressing the conversion times as a multiple of the time required to achieve the same degree of conversion in a batch or piston flow system.

Table 2.

Comparison of reaction times for batch and continuous stirred tank reactor system

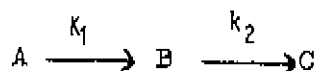
Conversion %	Batch time	Continuous stirred tank reactor system (n. ∞)			
		1 vessel	2 vessels	3 vessels	5 vessels
10	1	1.054	1.019	1.016	1.010
50	1	1.443	1.196	1.125	1.073
90	1	3.906	1.880	1.504	1.270
95	1	6.370	2.320	1.718	1.370
99	1	21.740	3.906	2.370	1.642

These results show that the volumetric efficiency of the batch or "piston" flow system is very much higher than the continuous stirred tank reactor system, and great care must be taken in translating results from a batch model to a full-scale continuous reactor.

3.22 Complex reactions

When a simple reaction is carried out in different flow systems the volumetric efficiencies of the systems may be different, but for the same degree of conversion of reactants the products of reaction are the same. When a complex reaction, such as a successive reaction is carried out in different flow systems it is likely that the products of reaction may be different for the same degree of conversion of initial reactants.

Consider the first order successive reaction carried out batchwise.



Then

$$- \frac{d(A)}{dt} = k_1 (A)$$

$$- \frac{d(B)}{dt} = k_2 (B) - k_1 (A)$$

$$\frac{d(C)}{dt} = k_2 (B)$$

Solving these equations gives,

$$(B) = \frac{(A_0)}{\left(\frac{k_2}{k_1} - 1\right)} \left(e^{-k_1 t} - e^{-k_2 t} \right) \quad \text{--- (a)}$$

Where (A_0) is the initial concentration of A.

The maximum value of B that can be obtained will be in time t_m and this can be found in the usual way by differentiating equation (a) and equating to zero.

$$t_m = \frac{1}{k_1 \left(\frac{k_2}{k_1} - 1 \right)} \text{Ln.} \frac{k_2}{k_1} \text{----- (b)}$$

When equation (b) is substituted into equation (a)

$$\begin{aligned} (B)_m &= \frac{(A)_0}{r-1} \left(\exp. \left(\frac{\text{Ln.} r}{1-r} \right) - \exp. \left(\frac{r \text{Ln.} r}{1-r} \right) \right) \\ &= \frac{(A)_0}{r-1} \exp. \left(\frac{r}{1-r} \text{Ln.} r \right) (\exp. \text{Ln.} r - 1) \\ &= (A)_0 \exp. \left(\frac{r}{1-r} \text{Ln.} r \right) \text{----- (c)} \end{aligned}$$

Where $r = \frac{k_2}{k_1}$

When the same reaction is carried out in a single stirred vessel with continuous overflow

$$\begin{aligned} (B) &= \int_0^{\infty} \frac{A_0}{\left(\frac{k_2}{k_1} - 1 \right)} (e^{-k_1 t} - e^{-k_2 t}) e^{-\frac{t}{\theta}} d\left(\frac{t}{\theta}\right) \\ (B) &= \frac{A_0 k_1}{k_2 - k_1} \left(\frac{1}{(k_1 \theta + 1)} - \frac{1}{(k_2 \theta + 1)} \right) \text{----- (d)} \end{aligned}$$

When (B) is a maximum

$$\begin{aligned} \frac{k_1}{(k_1 \theta + 1)^2} &= \frac{k_2}{(k_2 \theta + 1)^2} \\ \text{and } \theta_m &= (k_1 k_2)^{-\frac{1}{2}} \text{----- (e)} \end{aligned}$$

Where θ_m is the nominal holding time in the stirred vessel to give the maximum yield of B, $(B)_m$. Substituting equation (e) in equation (d) gives,

$$(B)_m = \frac{A_0 k_1}{k_2 - k_1} \left(\frac{1}{(k_1^{\frac{1}{2}} k_2^{-\frac{1}{2}} + 1)} - \frac{1}{(k_2^{\frac{1}{2}} k_1^{-\frac{1}{2}} + 1)} \right)$$

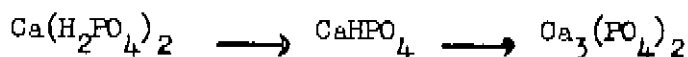
When $r = \frac{k_2}{k_1}$

$$\begin{aligned} (B)_m &= \frac{A_0}{r-1} \left(\frac{1}{(r^{-\frac{1}{2}} + 1)} - \frac{1}{(r^{\frac{1}{2}} + 1)} \right) \\ (B)_m &= A_0 (1 + 2r^{\frac{1}{2}} + r)^{-1} \text{----- (f)} \end{aligned}$$

When equations (o) and (f) are compared it can be seen that the maximum values of the intermediate product are different for the two different flow systems. The difference will depend on the values of k_1 and k_2 and the greatest difference will occur when $k_1 = k_2$. When this happens $(B)_m$ for the batch system is 47% greater than $(B)_m$ for the continuous system.

Although this example may appear to be of academic interest only it can be, in some ways, compared to the reactions occurring during ammoniation of superphosphate or nitrophosphates.

In these reactions the ammoniation process in the presence of calcium sulphate may be considered to be a successive reaction in which



The reaction is in fact much more complicated, due to the intermediate formation of ammonium phosphates and it is doubtful whether the reaction can be expressed in classical kinetic laws. However, consideration of the example for the ideal first order successive reaction, suggests that great care must be taken in translating data for this reaction from one scale to another, particularly in cases where flow systems are not identical. Both dicalcium phosphate and precipitated tricalcium phosphate are citrate soluble and the standard citrate-soluble test does not distinguish between them. The agronomic properties of dicalcium phosphate and precipitated tricalcium phosphate are known to be different, so the reproducibility of citrate-soluble fertilizer of the same agronomic properties depends on the identical distribution of phosphate compounds in the compound.

Generally, a batch process or a continuous stirred tank reactor system containing a large number of vessels will give a greater yield of an intermediate compound than a single or small number of stirred vessels in series.

3.23 Diffusion controlled reactions

In the case of some diffusion-controlled reactions, where the mass transfer coefficient is constant throughout the reaction, the treatment of the problem is similar to that of a first order chemically-controlled reaction, for comparable conditions of mixing.

In other cases, however, the mass transfer coefficient does not remain constant during the reaction and in these conditions it is almost impossible to predict the course of the reaction with different flow systems. The acidulation of phosphate rock with mixed acids is such a case, and the only useful method of studying this reaction is under the same steady-state conditions that are likely to be used in the full-scale plant.

When rock is attacked by mixed sulphuric and phosphoric acids in a batch system, an insoluble layer of calcium sulphate is formed on the surface of the rock. The thickness of the layer depends on the initial sulphuric acid concentration in the mixed acid. The partial inhibition of the later stages of the batch reaction depends on the history of the initial stages of the reaction, when a "protective layer" is built up on the surface of the rock due to the high initial sulphuric acid content. This history is lacking in the continuous reaction and thus inhibition does not occur to the same extent, as the mean sulphuric acid concentration in the system is lower. Comparison of the types of curves that are obtained by comparing batch and continuous systems are shown in Fig. 4.

3.3 Effect of flow system on physical changes

Very often the reactions between liquids and solids are accompanied by physical changes such as the dissolution of solids or the crystallisation of solids from the solution phase. In such cases it is virtually impossible to predict the performance of a full-scale plant from model work unless the distribution of residence times in the system is the same and conditions of mixing are truly comparable. It is surprising, therefore, to see that batch experiments are still commonly used to assess the reactivity of phosphate rock and the filtration characteristics of gypsum produced from the rock. The unreliability of batch experiments for assessing the reactivity of rock has been discussed above, and the unreliability of filtration data from batch experiments for assessing the performance of full-scale continuous plants can also be shown. In the "wet" phosphoric acid processes in which gypsum is being produced, a large recycle of slurry is used to maintain a relatively low degree of supersaturation of calcium sulphate in the liquid phase in the main reactor. Under these conditions nucleation is restrained, and large gypsum crystals which filter and wash easily are formed. When the same reaction is carried out batchwise the rapid initial attack on the rock results in a high degree of supersaturation of calcium sulphate and in uncontrolled nucleation. Gypsum is precipitated as small needle-like crystals which have normally poor filtration and washing characteristics. The results in Fig. 5 illustrate the differences in the characteristics of gypsum produced batchwise and under steady-state conditions in a single vessel, all other physical and chemical operating conditions being the same.

	<u>Gypsum from batch system.</u>	<u>Gypsum from continuous system</u>
Specific surface area by air permeability.	2500 sq.cm./gm.	1400 sq.cm./gm.

Another example of the importance of flow system on the physical changes that occur in the manufacture of phosphoric acid is the transformation of hemi-hydrate to gypsum. When calcium sulphate is precipitated from the system $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ the initial precipitation is as hemi-hydrate which then transforms to gypsum. Transformation rates for pure reactants are given in Ref. 9. Similar results can be obtained by reacting phosphate rock with mixed sulphuric and phosphoric acids. Under the conditions at which phosphoric acid is made in the "wet" gypsum process, i.e. about 75°C and 30% P_2O_5 , the transformation rate for about 95% of the hemi-hydrate to gypsum is several hours. If, however, the system is seeded with gypsum crystals the transformation rates are reduced considerably, as shown in Fig. 7. Factors such as degree of slurry recycle may thus influence the transformation rate of hemi-hydrate to gypsum and the final crystal form, emphasising again the importance of truly simulating the flow system in the model.

3.4 Methods of translating batch model data to full-scale continuous plant

Although the paper so far has emphasised the need to use similar flow systems in model and full-scale plant, particularly to assess the physical changes taking place, it is possible in certain cases to predict the chemical changes that will occur in a full-scale plant from a knowledge of small-scale batch data.

3.41 Algebraic Method for reactions of known order

If a reaction follows a first order law $x = 1 - e^{-kt}$

t is time

k is first order velocity constant

x is fractional conversion

The continuous plant be assessed from the equation

$$1 - x = \int_0^{\infty} e^{-kt} f\left(\frac{t}{\theta}\right) d\left(\frac{t}{\theta}\right)$$

where $f\left(\frac{t}{\theta}\right)$ is residence time distribution function

θ is nominal holding time in system.

In the case of a number of equal sized reactors in series

$$1 - x = \frac{1}{(1 + k\theta_1)^n}$$

Where θ_1 is nominal holding time in each vessel

n is number of vessels.

The algebraic solutions of second order reactions in stirred tank reactors are given in Ref. 7.

3.42 Graphical methods of assessment Homogeneous reaction

Usually for solid-liquid reactions it is not possible to express the reaction in classical reaction kinetics. However, in certain cases, when the reaction behaves as a homogeneous reaction in so far as the reaction rate depends entirely on the concentration of reactants in the homogeneous phase, a simple graphical technique can be used to predict the performance of the continuous stirred-reactor system using batch data.

There are several assumptions necessary before the method holds.

- (1) The composition in each vessel is uniform throughout.
- (2) The rate of change of reactant considered will be the same in a vessel in a continuous system as in a batch-wise system when the value of the reactant is the same in both vessels.
- (3) The reaction rate curve does not pass through a maximum or minimum during the course of the reaction.

The variation of concentration or degree of conversion x , with time t , in a batch system must be known. A graph of x versus t is drawn and from this dx/dt versus x . (Figs. 8 & 9).

Through the point $x = x_1, dx/dt = 0$, a straight line is drawn of slope θ_1 , where θ_1 is the nominal holding time in the first vessel. The point of intersection of this line with the plot dx/dt versus x gives x_1 , the concentration or degree of conversion in the first vessel. Next, through the point $x = x_1, dx/dt = 0$, a straight line of slope θ_2 is drawn, where θ_2 is the nominal holding time in the second vessel, and so on.

The method is described in detail in Refs. 10 and 11.

3.43 Reactions in the dispersed phase

The analysis of a solid-liquid reaction, in which the reaction rate is a function of the concentration of reactant in each phase, is more difficult than a homogeneous system, and until recently there have been no published methods by which the conversion in a continuous system can be calculated or predicted. A method has now been suggested (Ref.12) which will hold for heterogeneous systems in which the reaction occurs in the dispersed phase or in the boundary layer round this phase. It is assumed that the concentration in all continuous phase is the same throughout the vessel, but there is a spread in the degree of conversion in the dispersed phase corresponding with the spread of residence times of that phase.

Briefly, the method is as follows: differential rate data are obtained for differing initial concentrations C_0 , in the continuous phase, but for the same initial concentration D_0 in the dispersed phase, (Fig. 10.). From the batch experiments dD/dt , the rate of disappearance of the reactant in the dispersed phase, is determined at a constant level of C_1 , which is the required outlet concentration of the continuous phase (Fig.11). The value of dt/dD is plotted against D for the constant level of C_1 (Fig. 12) and the curve is integrated to give the concentration D in the dispersed phase as a function of its age, t .

The average concentration or degree of conversion \bar{D}_1 in the reactor outlet is found by integrating D over the spread of particle age which occurs in the stirred vessel.

$$\bar{D}_1 = \int_0^{\infty} D \left(\frac{t}{\theta} \right) d \left(\frac{t}{\theta} \right)$$

For a perfectly mixed vessel $\int_0^{\infty} \left(\frac{t}{\theta} \right) = e^{-\frac{t}{\theta}}$

and $\bar{D}_1 = \int_0^{\infty} D e^{-\frac{t}{\theta}} d \left(\frac{t}{\theta} \right)$

CONCLUSIONS

When considering the design of plants for solid-liquid reactions, factors such as agitation and flow system must be given full consideration if accurate predictions of full-scale plant is to be made from the experimental work carried out on models. Examples given in the text show that the manufacture of phosphoric acid, and ammoniation reactions, can only be studied accurately if the conditions of mixing and flow system are the same in the model as in the full-scale plant.

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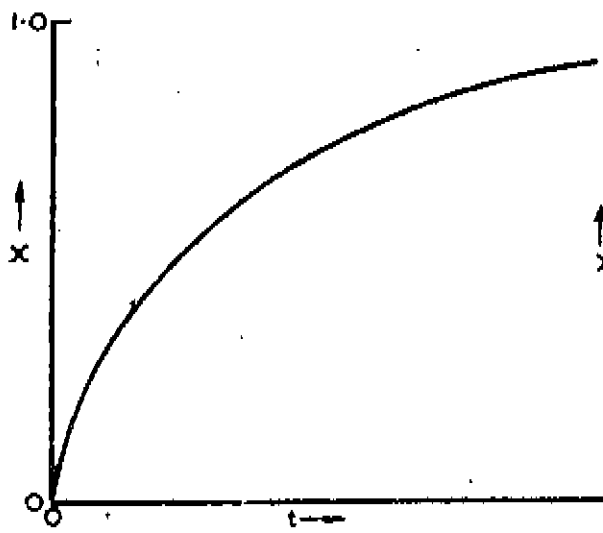


FIG. 8 BATCH REACTION CURVE.

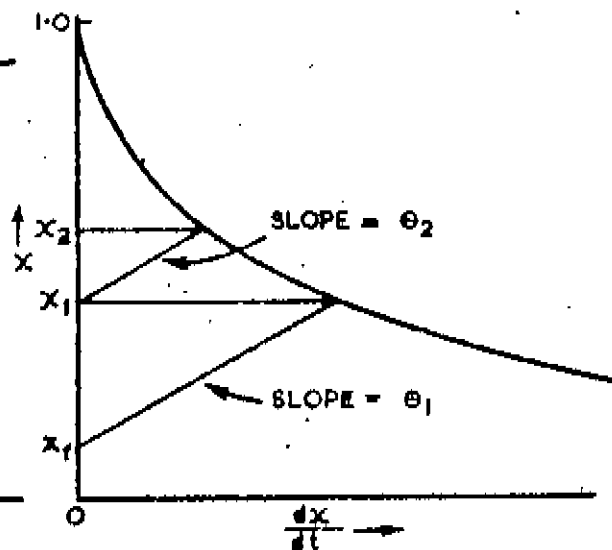
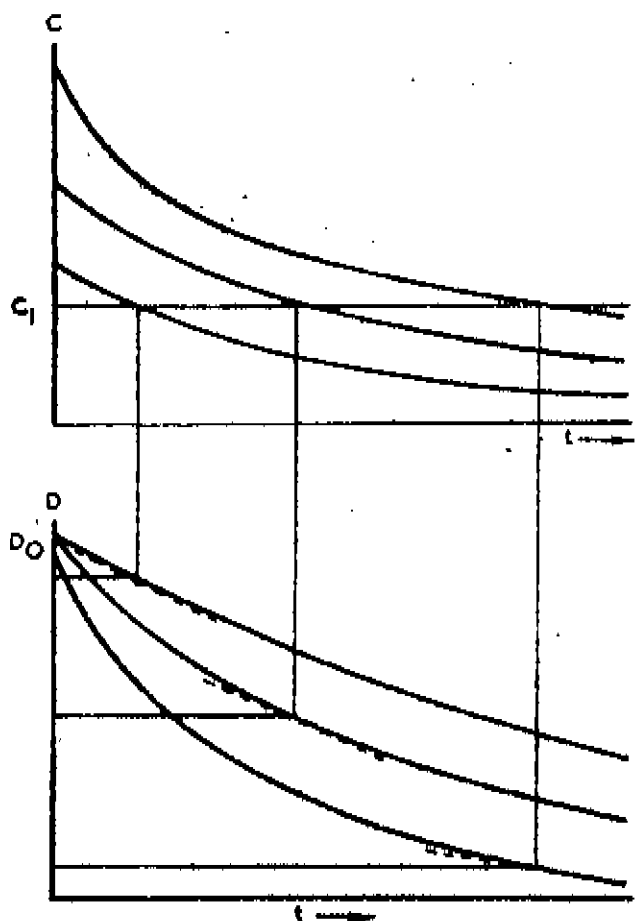


FIG. 9 REACTION RATE CURVE



1st BATCH EXPERIMENT
 2nd " " "
 3rd " " "

FIG. 10

1st BATCH EXPERIMENT
 2nd " " "
 3rd " " "

FIG. 11.

D = CONCENTRATION OF THE DISPERSED PHASE REACTANT
 C = CONCENTRATION OF THE CONTINUOUS PHASE REACTANT
 SUBSCRIPT O = INITIAL CONCENTRATION

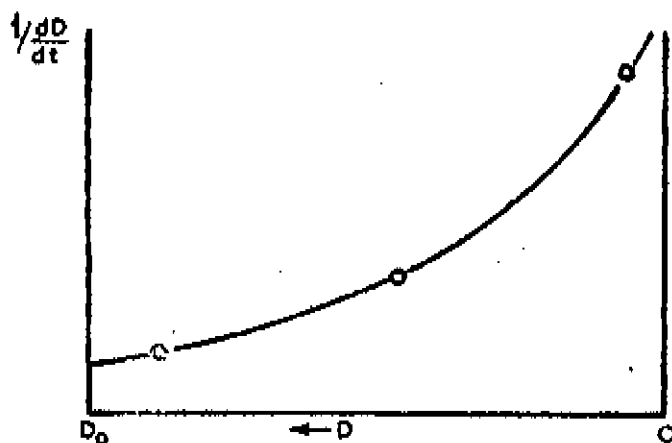


FIG. 12

REACTION RATE CURVE FOR A CONSTANT LEVEL OF CONCENTRATION OF C IN THE CONTINUOUS PHASE

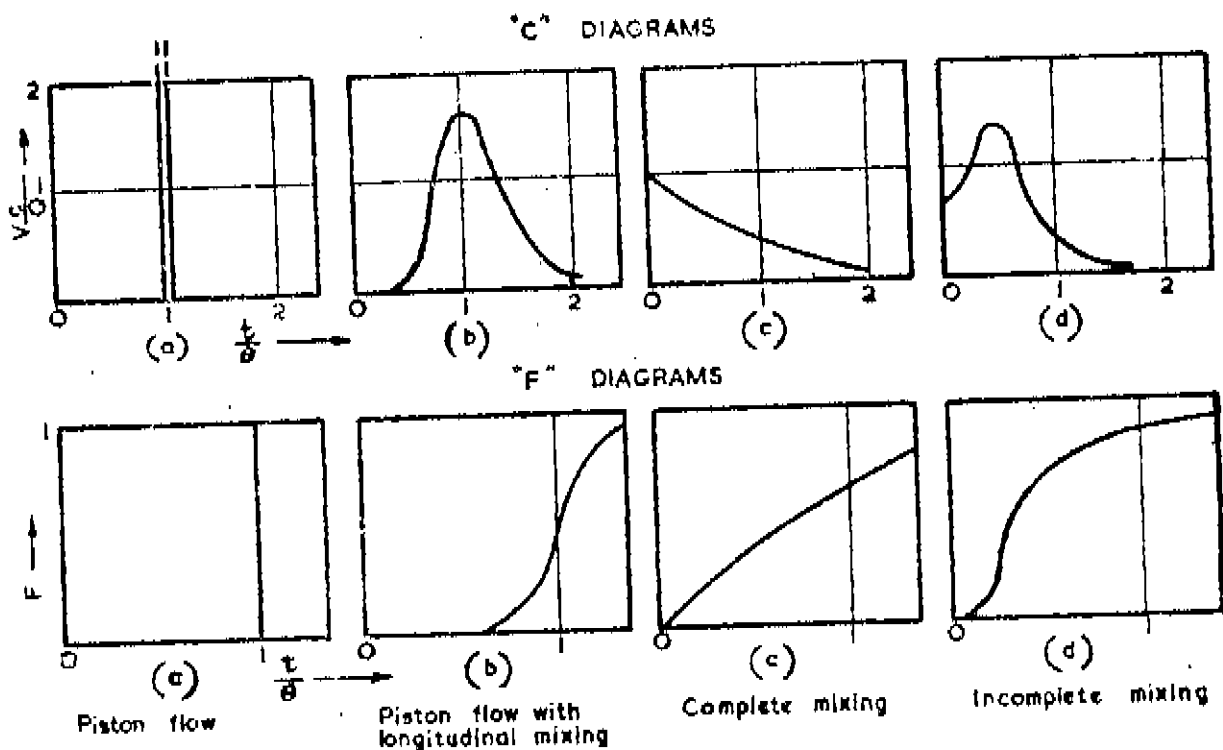


FIG. 3. FLOW DISTRIBUTION DIAGRAMS

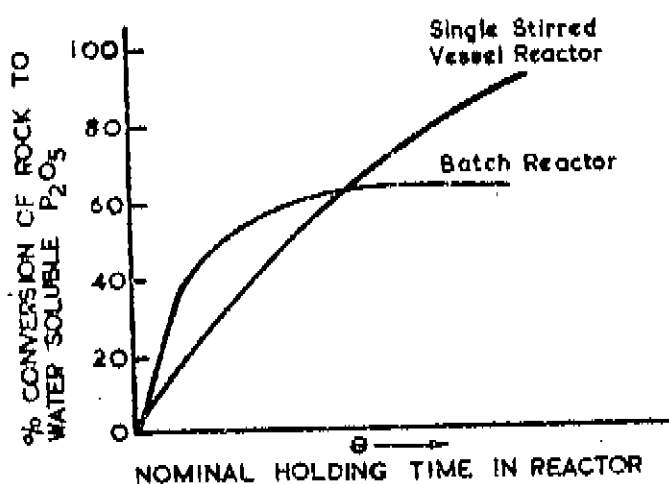


FIG. 4. COMPARISON OF BATCH AND CONTINUOUS RESULTS FOR PHOSPHATE ROCK ACIDULATION.

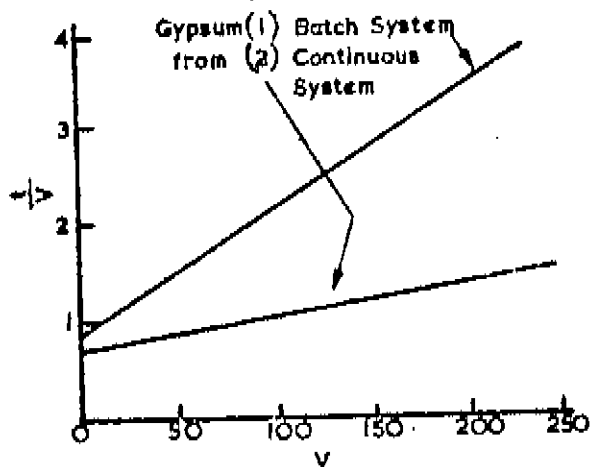


FIG. 5. STANDARD FILTRATION CURVE.

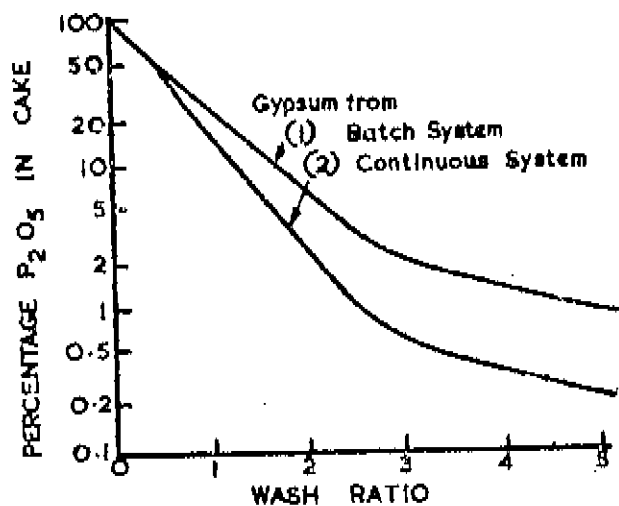


FIG. 6. WASHING CURVE

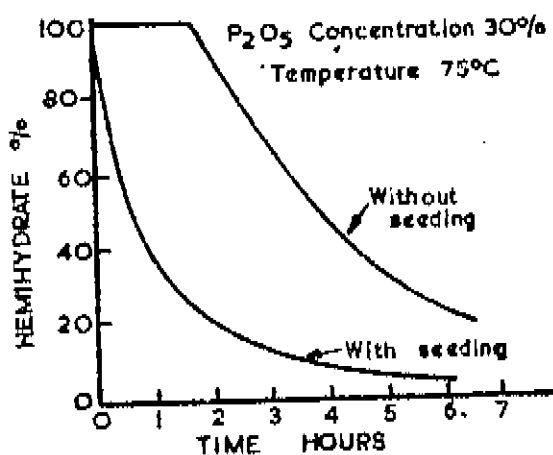


FIG 7 EFFECT OF SEEDING ON HEMI-HYDRATE TRANSFORMATION TO GYPSUM

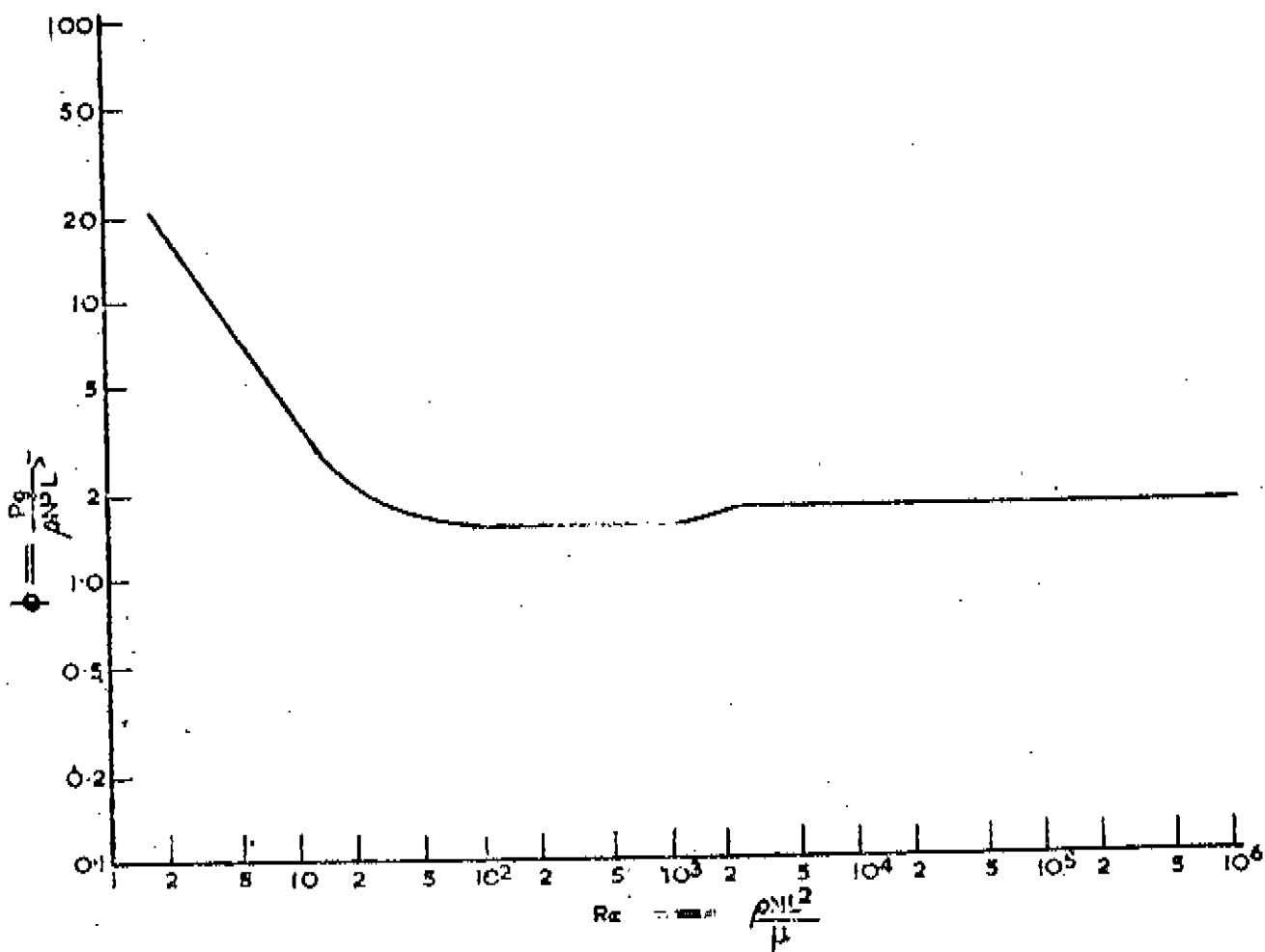


FIG. 1. POWER INPUT TO STANDARD FLAT PADDLE AGITATOR IN CYLINDRICAL VESSEL, FULLY BAFFLED.

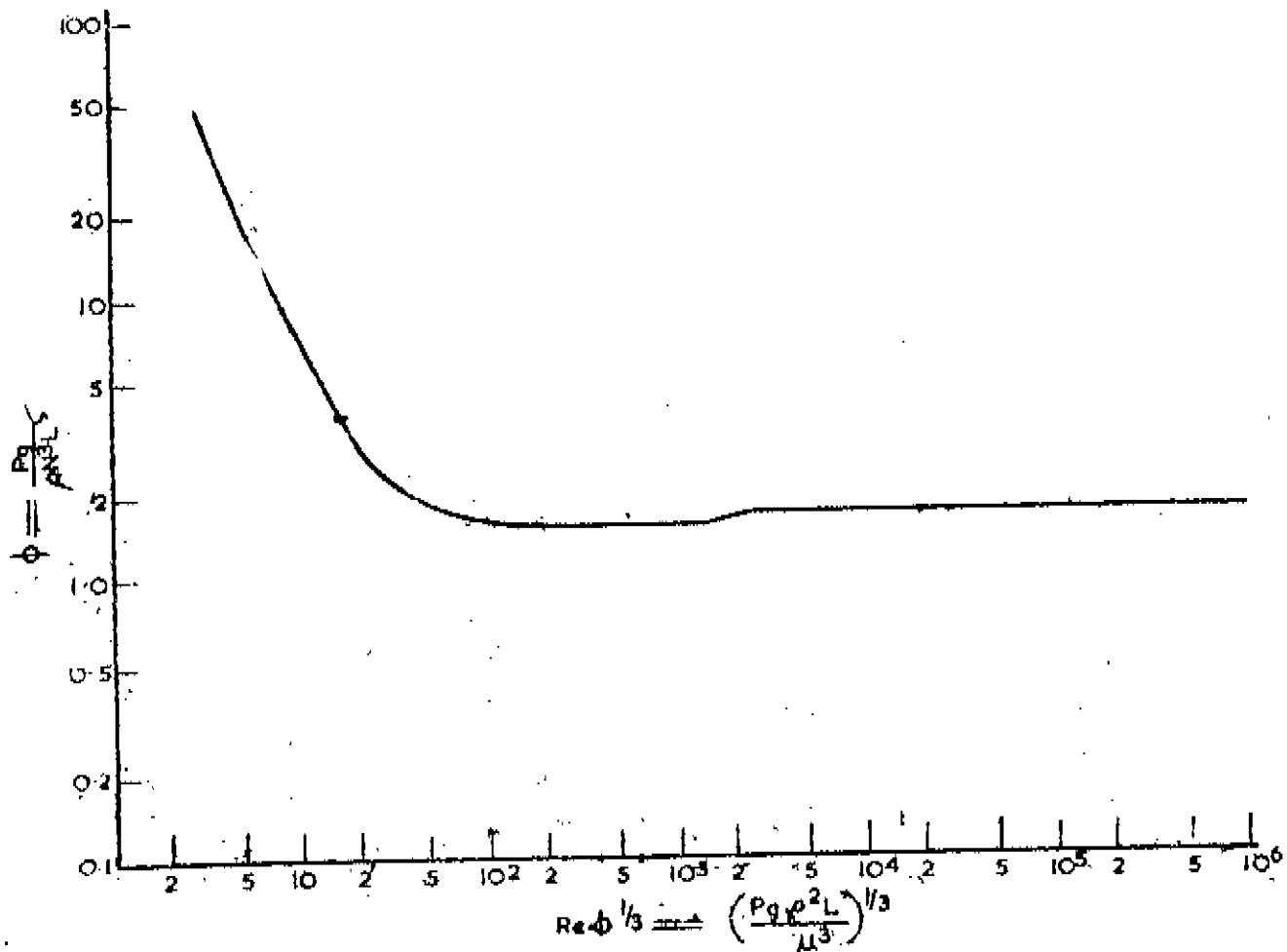


FIG. 2. PLOT OF $Re\phi^{1/3}$ vs ϕ FOR STANDARD FLAT PADDLE AGITATORS IN VERTICAL CYLINDRICAL VESSELS, FULLY BAFFLED.