

# Mixing Efficiency Determinations for Continuous Flow Systems<sup>1</sup>

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Models are defined for various mixing conditions, in continuous flow systems. Differential equations are derived which take into account an effective volume of mixing, possible short-circuiting, hold-up time of the system, partial displacement or piston flow.

The values of the different factors contained in the integrated equations can be determined experimentally by the particular response of a given system to a sudden change in composition of the feed.

A correlation of the effective volume of mixing and the agitator r.p.m. is presented.

A design procedure is suggested for tank flow reactors when partial mixing occurs.

MIXING, which has been referred to as one of the most intractable of all the unit operations of chemical engineering<sup>(1)</sup>, has been the object of more and more fundamental work over the past years, partly perhaps on account of the recognized complexity of the subject<sup>(2)</sup>. Many of the investigations in this field have dealt with batch systems and with the power requirements for mixing<sup>(3, 4, 5, 6)</sup>. The ever increasing conversion to continuous-flow processes in the industry has introduced various other aspects to the problem for others to explore. Among the numerous avenues of approach followed, a few can be found dealing with the efficiency of mixing. In spite of all the work done in this particular field, much more remains to be accomplished as indicated in recent chemical engineering works<sup>(1, 2, 7)</sup>.

The present investigation was undertaken with the purpose of providing a theoretical basis for evaluating the performance of mixers. The method developed for measuring mixing efficiencies applies to continuous-flow systems but it is intended to extend it to batch systems as well. After presenting a quantitative treatment of various factors likely to be encountered in actual mixing, an experimental study relating to part of the theoretical investigation is exposed.

## Previous work

MacMullin and Weber<sup>(8)</sup> were among the first to present an analytical study of the behavior of perfectly mixed systems, for continuous-flow mixing vessels in series. They, and others<sup>(9, 10)</sup>, used the term "short-circuit" or "mathematical by-passing" to denote conditions involving probability considerations, applicable to well agitated tanks in which the contents are substantially homo-

geneous, whereby some of the molecules in the feed stream appear almost immediately in the effluent as a result of good agitation. This may be confusing because, as pointed out by Colburn<sup>(11)</sup>, the term "short-circuit" should refer rather to the flow pattern in a tank where some of the feed is channeled to the outlet, reaching the latter without being mixed. It later occurred to MacMullin<sup>(12)</sup> that short-cut or channelized flow between inlet and outlet would indeed alter conditions in a tank. He suggested, rather qualitatively, that it could perhaps be possible to evaluate the efficiency of a stirrer by studying the conversion rate of a reacting system whose kinetics are known.

Statistical methods have been suggested to determine blending efficiencies<sup>(13)</sup> for batches of varying concentration fed into a stirred tank.

Danckwerts<sup>(14)</sup> has introduced the concepts of 'hold-back' and 'segregation' in order to compare actual to ideal mixing conditions in continuous flow systems. The concept of hold-back relates to the residence time of various elements in the system; the author cautions: "the whole F-diagram (and possibly other information) is needed if the actual performance of the reactor is to be calculated".

The notion of real 'short-circuit' is mentioned but none of the F diagrams shown take it into account. As to the concept of 'segregation', also obtained from F-diagrams, it is introduced to give an indication of the efficiency of mixing in a system. While it points to the degree of departure of a system from perfect mixing, it does not indicate fully how the system actually behaves. The H and S values thus defined involve rather tedious determinations besides being questionable as to their real advantage.

Les auteurs définissent des modèles pour différentes conditions d'agitation dans les systèmes à écoulement continu. Ils déduisent des équations différentielles qui tiennent compte d'un volume efficace d'agitation, de court-circuits possibles, du temps de rétention du système et de l'écoulement par déplacement ou "frontal".

Les valeurs des différents facteurs contenus dans les équations intégrées peuvent être obtenues à partir de la réponse particulière d'un système donné à un changement subit de la composition de l'alimentation.

Les auteurs présentent une corrélation entre le volume efficace d'agitation et la vitesse de l'agitateur. Ils proposent une méthode de calcul pour les réacteurs en régime continu lorsque l'agitation est partielle.

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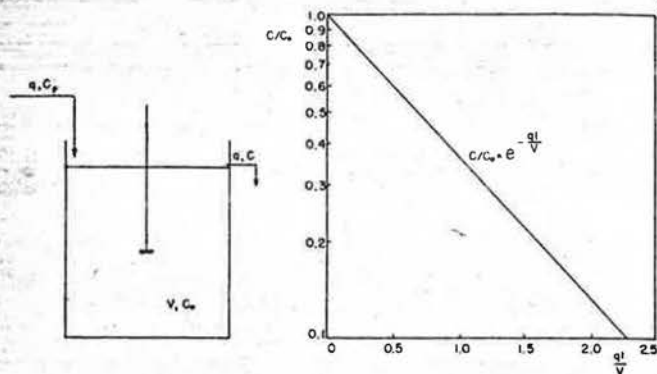


Figure 1—Perfect mixing: the feed is dispersed instantaneously. The composition of the outlet stream is the same as that of the tank contents.

### Factors involved

With two miscible liquids, in a batch process, a perfectly homogeneous mixture can be obtained when agitation, with the help of diffusion if necessary, is maintained for a long enough period of time. In a continuous flow system, however, it may be that perfect mixing can never be attained. There can be stagnant regions in the reservoir, part of the feed may go directly to the outlet, piston or plug flow may take place. In order to study the behavior of such a system and the efficiency of mixing, one can consider the tank or reservoir to act as a damper to variations in feed composition. The mathematical treatment of this problem thus becomes similar to one performed on a capacity in a servo-mechanism circuit, where a transfer function exists, from which can be obtained transient or permanent responses.

Three factors that may be met in actual mixing conditions are taken into account.

#### (a) Effective volume

For a given agitator, part only of the total tank contents may be well mixed the rest being taken up by stationary or stagnant zones. That part of the total volume where mixing is complete will be referred to as the 'Effective Volume of Mixing': it is the part which acts as a damper to any variation in feed composition and which is considered in determining the transfer function. A somewhat similar concept has been used by Germain<sup>(15)</sup> for evaluating contact time in a tubular reactor: the author replaces the reactor volume, in which the temperature is variable and passes through a maximum of  $T_m$ , by a smaller 'equivalent volume' in which the temperature is uniform, at  $T_m$ .

MacDonald and Piret<sup>(16)</sup> have observed qualitatively that dead volume can retain solution for indeterminate periods of time within a vessel. Danckwerts<sup>(14)</sup> also considered dead space in a mixing tank when introducing the concept of hold-back.

#### (b) Short-circuit

Depending on the relative position of the inlet with respect to the outlet, part of the feed may go directly to the latter without being mixed, causing channeling or a short-circuit. Only the remaining portion is thus available for mixing. This situation is unlike that arising from the definitions of short-circuit introduced by some authors as mentioned already.

MacDonald and Piret<sup>(16)</sup> report that they have observed channeling, in the course of experimental determinations, especially at low levels of agitation.

#### (c) Piston flow

In many systems, depending on conditions, part of the

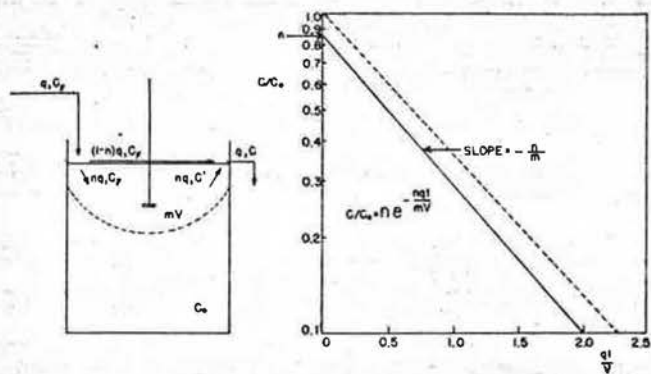


Figure 2—Partial mixing and short-circuit: a fraction of the total volume is perfectly mixed; part of the feed goes directly to the outlet.

feed, or all of it, may give rise to piston or plug flow. Inasmuch as the liquids in the stagnant and well agitated zones are not separated by a membrane, fluctuations or circulation may arise. Liquid in the stagnant zone may be replaced by some from the well agitated zone or from part of the feed. Such a circulation may go on steadily in the form of piston or plug flow.

Nagata and others<sup>(17, 18, 19)</sup> have studied mixing in a tubular reactor where piston flow exists, but in the absence of any short-circuit.

Mixing problems met in actual practice may involve different combinations of these three factors: effective volume, short-circuit, piston flow. Some particular combinations, more likely perhaps to be encountered than others, will now be considered.

### Theory

As for a servomechanism element, the behavior of a mixing system can be studied by means of the answer to either a step, a linear or a harmonic demand. One only of the answers being necessary to determine a transfer function, the first or step demand has been chosen on technical grounds suggested by the experimental determinations to be made. For the different systems considered, the following are the answers to a negative step demand.

#### 1. Perfect mixing

The contents of a reservoir, Figure 1, occupy a volume of  $V$  cubic feet; the initial concentration is  $c_0$  lbs./ft.<sup>3</sup>.  $q$  cu. ft./hr., of composition  $c_F$ , are assumed to be fed continuously into the reservoir. The feed composition  $c_F$  is changed suddenly at time  $t = 0$  from  $c_0$  to 0, creating a step demand. At any given time  $t$ , mixing being perfect, the tank contents are uniform throughout and of composition  $c$ , which is also that of the effluent.

A material balance for a time element  $dt$  gives:

$$qc_F dt = qc dt + d(Vc) \dots \dots \dots (1)$$

The feed composition,  $c_F$ , being then zero, and the volume of the liquid in the reservoir being constant, Equation (1) can be written:

$$\frac{dc}{dt} + \frac{q}{V} c = 0$$

Upon integration one obtains:

$$c/c_0 = e^{-\frac{q}{V} t}$$

When plotted on semi-log paper, as in Figure 1, this equation gives a straight line.

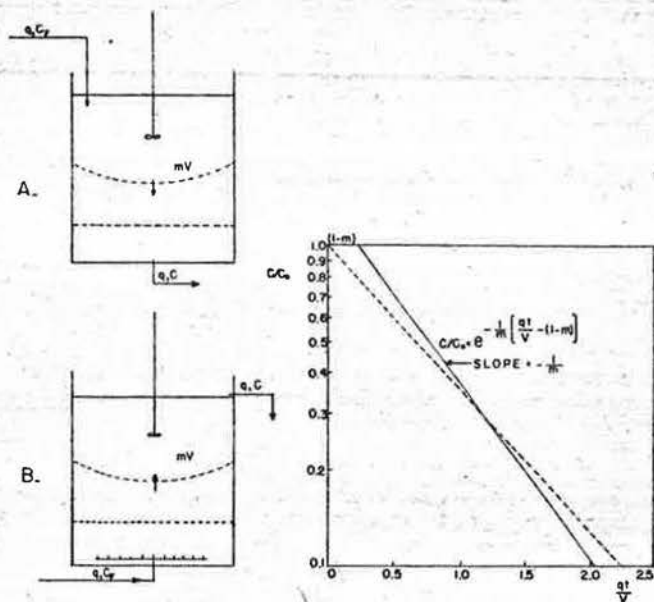


Figure 3—Partial mixing and piston flow: a fraction of the total volume is perfectly agitated; piston flow takes place before or after mixing, as shown.

### 2. Partial mixing and short-circuit

As shown in Figure 2, only a fraction  $m$  of the total volume is assumed to be well agitated. A fraction  $n$  of the feed enters the zone of perfect mixing while the other fraction  $(1-n)$  is assumed to be short-circuited directly to the outlet. The concentration, at time  $t$ , in the zone of perfect mixing is assumed to be  $c'$ . The material issuing from this zone is mixed with that portion of the feed which short-circuits the system, the mixture of the two giving a liquid of composition  $c$  at the outlet. One thus obtains:

$$nqc' dt = nqc' dt + mVdc'$$

or,

$$\frac{dc'}{dt} + \frac{nq}{mV} c' = 0$$

$$c'/c_0 = e^{-\frac{nq}{mV} t} \dots \dots \dots (2)$$

But,

$$(1-n)qc' dt + nqc' dt = qc dt$$

and,

$$c_F = 0 \therefore c = nc'$$

Equation (2) then becomes:

$$c/c_0 = ne^{-\frac{nq}{mV} t}$$

Taking natural logarithms:

$$\ln c/c_0 = \ln n - \frac{nq}{mV} t$$

Thus, plotting  $c/c_0$  vs  $qt/V$  on semi-log paper as in Figure 2, the value of  $n$  can be read directly on the concentration ratio axis, at  $t = 0$ . The straight line has a slope of  $-n/m$ , from which can be derived the value of  $m$ , once  $n$  has been determined.

### 3. Partial mixing and piston flow

With a fraction  $m$  of the total volume well agitated, the feed can be considered to give piston flow in two different ways, as shown in Figure 3:

(a) The feed is introduced into the zone of perfect mixing, displacing an equal volume into the stagnant

zone: this liquid, in turn, displaces the other already present, by the mechanism of piston or plug flow.

(b) The feed, introduced into the stagnant zone, displaces an equal volume from the latter into the zone of perfect mixing which, in turn, supplies an equivalent volume of liquid to the outlet.

In either case, the composition of the liquid at the outlet would remain constant at  $c_0$  for a period of time  $t = (1-m)V/q$ , which represents the time required to displace all the material out of the stagnant zone at the prevalent rate of flow. The variation of the outlet composition with time, in either case, is obtained in the following way:

$$qc_F dt = qc' dt + mVdc'$$

$$\frac{dc'}{dt} + \frac{q}{mV} c' = 0$$

$$c'/c_0 = e^{-\frac{q}{mV} t}$$

But,  $c = c'$  at time:  $t = \frac{(1-m)V}{q}$

$$\therefore c/c_0 = e^{-\frac{1}{m} \left[ \frac{qt}{V} - (1-m) \right]}$$

$$\ln c/c_0 = -\frac{1}{m} \left[ \frac{qt}{V} - (1-m) \right]$$

Plotting this equation on semi-log paper gives a straight line of slope  $-1/m$ , as shown in Figure 3. The value of  $m$  can also be obtained from the intercept at  $c/c_0 = 1$ .

### 4. Partial mixing with piston flow and short-circuit

Among the several possible combinations, the following three have been considered.

(A) In addition to having a fraction  $m$  of the total volume well mixed and a fraction  $n$  of the feed going to the zone of perfect mixing, a fraction  $p$  of the feed gets into the stagnant zone from where it displaces an equivalent volume by piston flow into the zone of perfect mixing, as shown in Figure 4. The outgoing liquid, of composition  $c$  at time  $t$ , is made up in part of liquid of composition  $c'$  from the zone of perfect mixing, and of the fraction  $(1-n-p)$  of the feed which short-circuits the tank. Two periods have to be considered, before and after time  $t = (1-m)V/pq$ , during which all the liquid originally in the stagnant zone is displaced.

a)  $0 < t < (1-m)V/pq$

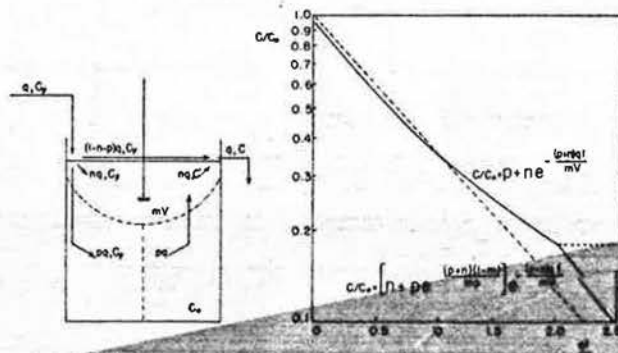


Figure 4—Partial mixing with piston flow and short-circuit: part of the feed displaces liquid from the stagnant region into the zone of perfect mixing.

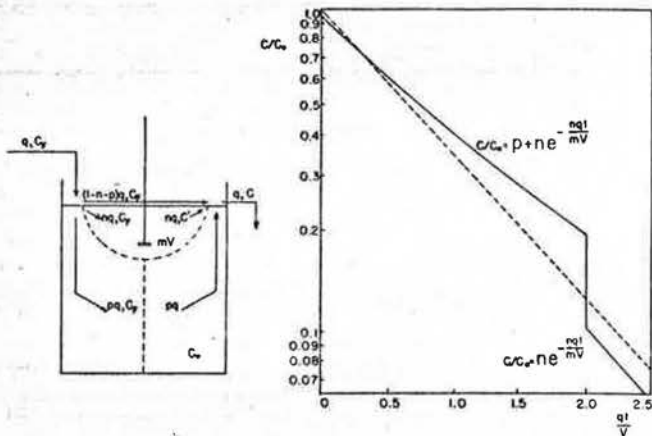


Figure 5—Partial mixing with piston flow and short-circuit: part of the feed displaces liquid from the stagnant region, around the zone of perfect mixing.

During this period, material of composition  $c_F = c_0$  enters the zone of perfect mixing from the stagnant zone. The following relations are obtained:

$$nqc_f dt + pqc_s dt = (p+n)qc'dt + mVdc'$$

$$\frac{dc'}{dt} + \frac{(p+n)q}{mV}c' = \frac{pqc_0}{mV}$$

$$c'/c_0 = \frac{p}{p+n} + Ke^{-\frac{(p+n)q}{mV}t}$$

Since

$$c' = c_0 \text{ at } t = 0, \quad K = \frac{n}{p+n}$$

$$c'/c_0 = \frac{p}{p+n} + \frac{n}{p+n}e^{-\frac{(p+n)q}{mV}t}$$

$$c = (p+n)c'$$

$$- \frac{(p+n)q}{mV}t$$

$$\therefore c/c_0 = p + ne$$

$$b) t > (1-m)V/pq$$

All the material originally in the stagnant zone has now left and liquid of composition  $c_F = 0$  enters the zone of perfect mixing from the stagnant one.

$$\frac{dc'}{dt} + \frac{(p+n)q}{mV}c' = 0$$

$$- \frac{(p+n)q}{mV}t$$

$$c' = K_1 e$$

$$+ \frac{(p+n)q}{mV}t$$

$$c/c_0 = K_1 e$$

$$\text{Now, at time: } t = \frac{(1-m)V}{pq}$$

$$c/c_0 = K_1 e^{-\frac{(p+n)(1-m)}{mp}} = p + ne^{-\frac{(p+n)(1-m)}{mp}}$$

$$\therefore K_1 = n + pe$$

$$c/c_0 = \left[ n + pe \right] e^{-\frac{(p+n)(1-m)}{mp}} - \frac{(p+n)q}{mV}t$$

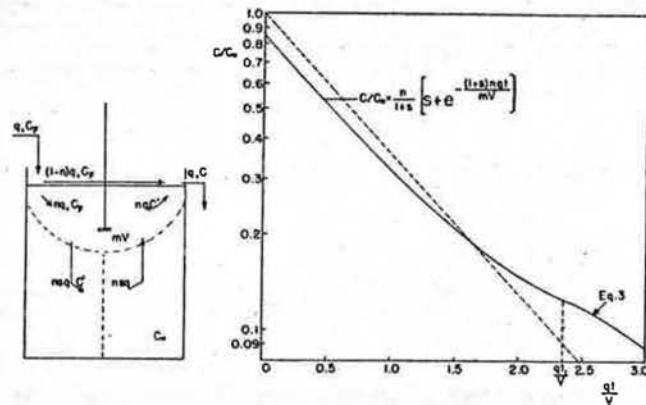


Figure 6—Partial mixing with piston flow and short-circuit: liquid from the zone of perfect mixing displaces, and is replaced by, an equal volume from the stagnant region.

Plotting  $c/c_0$  vs  $qt/V$  on semi-log paper, for the two regions of case A, gives curves such as shown in Figure 4.

(B) Part of the feed goes to the stagnant zone and displaces an equal volume by piston flow around the zone of perfect mixing, directly to the outlet, as indicated in Figure 5. The outgoing material is made up in part by this stream, in part by liquid forced out of the zone of perfect mixing and also by the part of the feed going in short-circuit.

Again, two periods have to be considered, before and after time:

$$t = \frac{(1-m)V}{pq}$$

$$a) 0 < t < \frac{(1-m)V}{pq}$$

$$nqc_f dt = nqc'dt + mVdc'$$

$$\frac{dc'}{dt} + \frac{nq}{mV}c' = 0$$

$$c'/c_0 = e^{-\frac{nq}{mV}t}$$

But,

$$c = nc' + pc_0$$

$$\therefore c/c_0 = p + ne^{-\frac{nq}{mV}t}$$

$$b) t > \frac{(1-m)V}{pq}$$

$$- \frac{nq}{mV}t$$

$$c'/c_0 = e$$

Now,

$$c = nc'$$

$$- \frac{nq}{mV}t$$

$$\therefore c/c_0 = ne$$

Curves of  $c/c_0$  vs  $qt/V$  on semi-log paper, for these cases, are as shown in Fig. 5.

(C) A certain amount of liquid, corresponding to a fraction  $s$  of that part of the feed which enters the zone of perfect mixing, passes out of the latter into the stagnant zone. As a result an equal volume is displaced, in piston flow, from the stagnant section into the zone of perfect mixing, as shown in Figure 6.

The two periods to be considered are before and after time:

$$t = \frac{(1-m)V}{nsq}$$

$$a) 0 < t < \frac{(1-m)V}{nsq}$$

Throughout this time period, liquid of composition  $c_0$  is displaced into the zone of perfect mixing from the stagnant one.

$$nqc'dt + nsqc_0dt = nsqc'dt + nqc'dt + mVdc'$$

$$\frac{dc'}{dt} + \frac{nq}{mV}(1+s)c' = \frac{nsqc_0}{mV}$$

$$c'/c_0 = \frac{s}{s+1} + K_2 e^{-\frac{nq}{mV}(s+1)t}$$

Since  $c' = c_0$  at time  $t = 0$

$$K_2 = \frac{1}{s+1}$$

$$\text{Also, } c = nc'$$

$$\therefore c/c_0 = \frac{n}{s+1} \left[ s + e^{-\frac{nq}{mV}(s+1)t} \right]$$

$$b) t > \frac{(1-m)V}{nsq}$$

Liquid entering the zone of perfect mixing now has the composition  $c'$  of the liquid displaced from the zone of perfect mixing into the stagnant one, at time:

$$t - \frac{(1-m)V}{nsq} \text{ or, at } t - t_1.$$

$$nqc'dt + nsqc'_{(t-t_1)} dt = nsqc'dt + nqc'dt + mVdc'$$

$$\frac{dc'}{dt} + \frac{nq}{mV}(s+1)c' = \frac{c_0 nsq}{(s+1)mV} \left[ s + e^{-\frac{nq}{mV}(s+1)\left(t - \frac{(1-m)V}{nsq}\right)} \right]$$

$$c'/c_0 = \frac{s^2}{(s+1)^2} + \frac{nsqt}{(s+1)mV} e^{\frac{(s+1)(1-m)}{sm} - \frac{nq}{mV}(s+1)t} + K_3 e^{-\frac{nq}{mV}(s+1)t}$$

$$K_3 = \frac{1}{s+1} + \left[ \frac{s}{(s+1)^2} - \frac{1-m}{m(s+1)} \right] e^{\frac{(s+1)(1-m)}{sm}}$$

$$c/c_0 = \frac{ns^2}{(1+s)^2} + \frac{n}{1+s} \left[ 1 + \left( \frac{s}{1+s} - \frac{1-m}{m} + \frac{nsqt}{mV} \right) e^{\frac{(1+s)(1-m)}{sm}} \right] e^{-\frac{nq}{mV}(1+s)t} \dots (3)$$

Curves for the last two cases are shown in Figure 6.

### 5. Design procedure for tank flow reactors when partial mixing occurs

As pointed out by Smith<sup>(20)</sup>, design procedures for tank flow reactors are still unavailable when partial mixing occurs. The problem may now be solved, in general, by introducing the concepts already mentioned.

For the particular case of partial mixing and short-circuit, as shown in Figure 7, under steady-state flow conditions, the incoming solution has a composition  $c_F$ , that in the zone of perfect mixing is  $c'$ , and the outgoing liquid has a composition  $c$ .

A material balance at the outlet gives:

$$(1-n)qc_F + nqc' = qc$$

$$\text{or, } c = (1-n)c_F + nc' \dots (4)$$

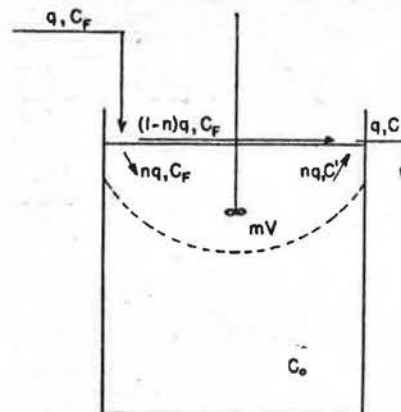


Figure 7—Partial mixing and short-circuit in a chemical reactor.

Now, taking account of the reactant in the feed and exit streams as well as that converted in the reactor, one can write<sup>(20)</sup>:

$$nqc_F - nqc' = r'mV \dots (5)$$

where:  $r'$  = reaction rate, lbs./ft.<sup>3</sup> (hr.), in the zone of perfect mixing.

$mV$  = actual volume of liquid undergoing reaction.

Equation (5) can be rewritten:

$$c' = c_F - \frac{r'mV}{nq}$$

Introducing this value of  $c'$  in Equation (4) gives:

$$c = c_F - \frac{r'mV}{q} \dots (6)$$

If mixing was perfect in the entire reactor, the concentration of the effluent would be  $c_M$  and related to  $c_F$  by the following:

$$c_F - c_M = \frac{rV}{q} \dots (7)$$

where:  $r$  = theoretical reaction rate, lbs./ft.<sup>3</sup> (hr.), based on concentration  $c_M$ .

Combining Equations (6) and (7) gives:

$$c = c_F - m(c_F - c_M) \frac{r'}{r}$$

$$m = \frac{(c_F - c)}{(c_F - c_M)} \frac{r'}{r} \dots (8)$$

While Equation (8) is a general solution for partial mixing and short-circuit, many particular solutions can

be obtained depending on the order of the reaction taking place.

Of all the possible solutions, only the following two are considered here:

a) *Zero-order reaction with partial mixing and short-circuit.*

For such a reaction, the rate is independent of concentration, so that  $r = r'$ .

Then, Equation (8) becomes:

$$m = \frac{C_F - c}{C_F - C_M}$$

Thus, one could either obtain the value of  $c$  for a given value of  $m$  or determine the effective volume by measuring feed and outlet concentrations and calculating the theoretical outlet composition. It is to be noted that in this case the short-circuit effect cancels out.

b) *First-order reaction, with partial mixing and no short-circuit.*

In a first-order reaction the rate is proportional to the concentration of the reactant. If the concentrations were  $C_M$  and  $c'$ , the reaction rates would be respectively:

$$r = kC_M$$

$$r' = kc'$$

Substituting in Equation (8), one obtains:

$$m = \left( \frac{C_F - c}{C_F - C_M} \right) \frac{C_M}{c'}$$

Now, introducing the value of  $c'$  given in Equation (4),

$$m = n \left( \frac{C_F - c}{C_F - C_M} \right) \left( \frac{C_M}{nC_F - C_F + c} \right) \dots \dots \dots (9)$$

Since the case considered here is that where no short-circuit is present,  $n = 1$  and Equation (9) becomes:

$$m = \frac{C_F - c}{c} \cdot \frac{C_M}{C_F - C_M}$$

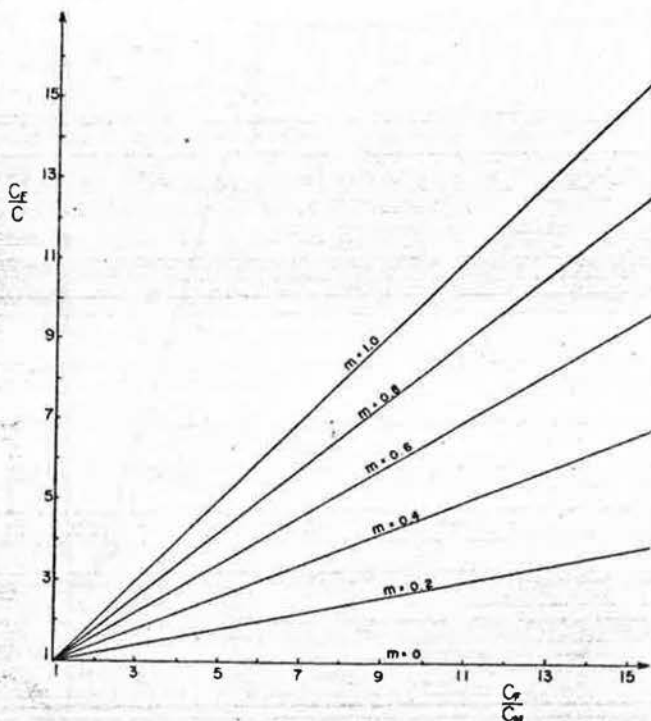


Figure 8—Relation between actual and theoretical outlet concentrations for tank flow reactors when partial mixing occurs.

which can be re-written:

$$\frac{C_F}{c} = m \left( \frac{C_F}{C_M} \right) + (1 - m)$$

The value of  $\frac{C_F}{c}$  can be obtained easily from the above expression, or from Figure 8, for given values of  $\frac{C_F}{C_M}$  and  $m$ .

The designer is thus in a position to predict the performance of a tank-flow reactor.

For cases where short-circuit is present, where higher order reactions are involved or where there is piston flow, studies are actually under way which will be the object of a future publication.

### Apparatus

Of the different cases studied theoretically, that involving partial mixing and short-circuit, as described in case No. 2, seemed to be of more immediate interest from an experimental point of view. An apparatus was set up, as shown in Figure 9, in which could be studied simultaneously the variations of effective volume and short-circuit with the level of agitation.

The tank used had an internal diameter of 30". A liquid depth of 30" was assured by a properly located outlet of  $\frac{3}{4}$ " pipe. The agitator was an experimental model by Chemineer, a 2 $\frac{1}{2}$ " simple turbine with inclined blades being used. A flow regulator and a rotameter were inserted in the  $\frac{3}{4}$ " feed line. The feed inlet was 12" from the surface of the liquid and the agitator itself was placed in between, at a distance of 6" from the surface.

The agitator speed could be adjusted at the proper value through a variable speed reducer.

### Experimental procedure

At the beginning of a run the reservoir was filled to the appropriate level with a solution of NaCl, approximately 1/20 N. After running the agitator for some time at the desired speed to allow for the mixing pattern to be fully developed, water was introduced suddenly at the required rate of approximately 1.15 gallons/min.

Samples were taken at regular time intervals of five minutes and the NaCl concentration determined volumetrically with  $AgNO_3$ , using  $K_2CrO_4$  as indicator.

### Results

The experimental results obtained were plotted, as suggested already, on semi-log paper. Figure 10 shows the

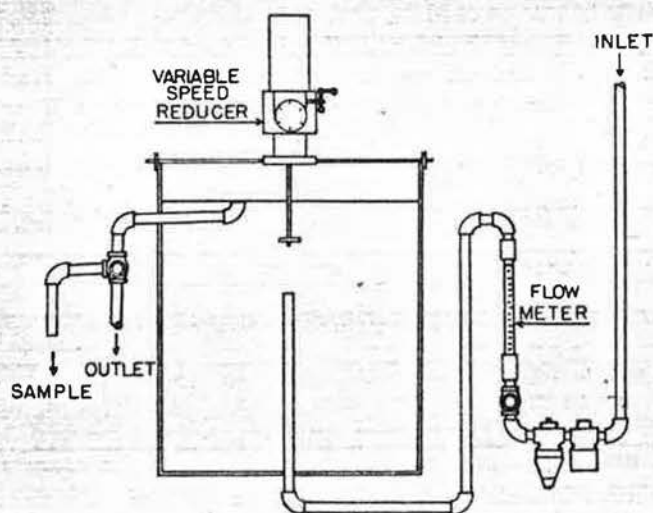


Figure 9—Experimental apparatus.

straight lines drawn through the experimental points at different levels of agitation, for values of agitator r.p.m., designated as  $N$ , ranging from 0 to 210. Values of  $m$  and  $n$  were determined from them for each agitator speed by the method described.

Even at an r.p.m. of 0 given values of  $m$  and  $n$  were obtained; they were designated as  $m_0$  and  $n_0$ . For any given value of  $N$ , then, the value of  $m - m_0$  might represent the contribution of the agitator r.p.m. to the level of mixing.

It has been found that when plotting  $(m - m_0)$  vs  $N$  on log-log paper, as shown in Figure 11, a straight line of slope 2 is obtained which can be represented by the equation:

$$m - m_0 = a N^2$$

For the particular system studied, the constants  $m_0$  and  $a$  were found to be 0.38 and  $1.25 \times 10^{-5}$  respectively.

The value of 0.38 for  $m_0$  indicates the level of mixing obtained when the agitator is at rest, through the agitation produced by the introduction of the feed. Such an effect appears to have been mentioned first by MacDonald and Piret<sup>(16)</sup>, when measuring mixing times in a vessel.

As the value of  $m$  reaches 1, when the agitator speed is increased, a maximum value of  $(m - m_0)$  is reached. This value remains constant thereafter even if the agitator speed is increased because the system behaves as one giving perfect mixing.

Proceeding in a similar way, the values of  $(n - n_0)$  vs  $N$  were plotted on log-log paper as shown in Figure 12, giving a straight line of slope 3. The values of  $n$  are thus related to the agitator r.p.m. by the equation:

$$n - n_0 = b N^3$$

where, for the particular system studied,  $n_0 = 0.77$  and  $b = 2 \times 10^{-8}$ .

When plotting, on a linear scale, the values of  $m$  and  $n$  as a function of  $N$ , as in Figure 13, both variables are found to reach a maximum value of 1 at an r.p.m. of approximately 220, indicating that the system behaves then as one giving perfect mixing.

### Conclusions

The method described to determine mixing efficiencies in continuous flow systems should prove to be a very useful tool in evaluating the actual performance of mixers. Not only is it possible to obtain optimum results with a given mixer but the relative performance of mixers of different design can be established since efficiency measurements are possible.

The contribution to the design of tank flow reactors should also be of importance because a method is now available to take into account the effects of partial mixing. Improved designs, with the best possible use of agitators, should result.

The experimental results obtained to date are very promising. While they do not draw a complete picture as yet, due to the limited extent of experimental work which could be performed, they point to a number of investigations which should lead to a comprehensive knowledge of mixing.

A new experimental set-up providing for a wider variety of investigations is nearing completion. Among others, the factors to be studied include the position, speed of rotation, shape and size of the agitator, the physical properties and the relative depth of the liquid, the location of the feed, the manner in which it is introduced, its rate and inlet velocity, and the outlet position relative to the inlet.

Other types of agitating systems will be considered, including those with internal recirculation and of the draft-tube type.

The study of systems involving chemical reactions is already under way.

### Nomenclature

- $a$  = Constant, relating effective volume to agitator speed.
- $b$  = Constant, relating short-circuit effect to agitator speed.
- $c$  = Volumetric concentration, lbs./ft.<sup>3</sup>
- $c_F$  : concentration of the feed.
- $c_M$  : concentration of the effluent if mixing was perfect, when a chemical reaction is present.
- $c_0$  : initial concentration.
- $c'$  : concentration in the zone of perfect mixing.
- $K, K_1, K'_1, K_2, K_3$  : Constants of integration.
- $m$  = Fraction of the total volume which is perfectly mixed.
- $m_0$  : value of  $m$  when the agitator is at rest.
- $n$  = Fraction of the feed entering the zone of perfect mixing.
- $n_0$  : value of  $n$  when the agitator is at rest.
- $N$  = Agitator speed, R.P.M.
- $p$  = Fraction of the feed going to the stagnant zone.
- $q$  = Rate of flow, ft.<sup>3</sup>/hr.
- $r$  = Reaction rate, lbs./((ft.<sup>3</sup>)(hr.))
- $s$  = Fraction of part  $nq$  of the feed entering the zone of perfect mixing which subsequently passes out into the stagnant zone.
- $t$  = Time, hrs.
- $t_1 = \frac{(1 - m)V}{nsq}$
- $V$  = Volume, ft.<sup>3</sup>

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# Sodium Hydroxide-Sodium Sulphate Stripping of Uranium from Amine Extracts<sup>1</sup>

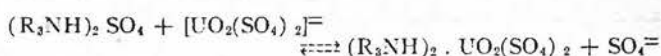
A. I. BELLINGHAM<sup>2</sup> and R. SIMARD<sup>3</sup>

Batch shake-out tests on two tertiary amines and one secondary amine to determine the effects of sodium sulphate concentration and pH on the distribution of uranium between 0.1N amine in kerosene and aqueous sodium sulphate solution showed that transfer of uranium from the solvent to the aqueous phase was favored by increasing pH values up to 5.5 and by increasing the aqueous sodium sulphate concentration up to 20% w/v Na<sub>2</sub>SO<sub>4</sub>.

Continuous counter-current stripping of tri-iso-octylamine (TIOA) extracts with 20% w/v Na<sub>2</sub>SO<sub>4</sub> was also carried out in a three-stage mixer-settler arrangement in which the pH was controlled by the addition of 10% NaOH to the three stages. Further addition of caustic to the separated aqueous strip solution to raise the pH to 7.0-7.2 yielded a high grade uranium precipitate (88% U<sub>3</sub>O<sub>8</sub>). The continuous testing confirmed the results of the shake-out tests and showed that the procedure gave results comparing favorably with other stripping methods accompanied by a lower overall reagent cost.

AMINE solvent extraction of uranium from sulphuric acid solutions produced in the leaching of ores has been the subject of much investigation in the last few years. At the U.S.A.E.C., Oak Ridge National Laboratory, in particular, K. B. Brown, D. J. Crouse and others have made extended studies<sup>(1)</sup> of long chain amines which have proven to be efficient extractants for uranium.

The amine solvent extraction is best explained by an ion exchange mechanism which may be represented as follows:



It is well known that the loaded amine extracts can be stripped by a similar exchange using acidified solutions of chloride or nitrate salts, or with sodium carbonate, ammonium carbonate and alkalis which react irreversibly as neutralizing agents.

In the course of studies being made on the application of solvent extraction to the hydrometallurgy of Canadian uranium ores, work relating to the use of certain amines, has shown that the loaded extract can also be stripped

effectively by sodium sulphate solutions at a controlled pH favouring uranium in the aqueous phase. This led to an investigation of continuous counter-current stripping which has been incorporated in a pilot plant flowsheet.

In this work, three amines were investigated by small scale batch testing. These were (1) tertiary tri-iso-octyl amine supplied by Carbide Chemical Company, Montreal, Que., (2) a tertiary amine labelled C<sub>8</sub>-C<sub>10</sub> mixture supplied by General Mills, Inc., Kankakee, Ill., (3) a secondary dodecyl amine labelled 9D-178 supplied by Rohm and Haas Company of Canada Limited, West Hill, Ont. In the batch testing all three products responded favorably to stripping with sodium sulphate solution. However, since the tri-iso-octyl amine, at the time the work was done, appeared to have some advantages over the other two in the extraction section of the process, it was chosen for the continuous testing.

## Procedure

Batch cross-current stripping was done in open beakers with mechanical stirrers using 250 ml. of 0.1N amine (in kerosene) which had been previously saturated by contact with uranyl sulphate solutions at pH 1.4-1.5. Three or four 50-ml. fractions of sodium sulphate solution were contacted successively with the extract. For each stage of stripping 10% NaOH was used to obtain the required pH at equilibrium. The strip fractions were separated after each stage in a separatory funnel and assayed for U<sub>3</sub>O<sub>8</sub>. The final stripped solvent was also assayed for U<sub>3</sub>O<sub>8</sub>.

Two main variables to be studied were Na<sub>2</sub>SO<sub>4</sub> concentration and pH. The uranium distribution curves, Co vs. Ca expressed as U<sub>3</sub>O<sub>8</sub> g/l in organic and aqueous, were plotted as a function of pH and sulphate concentrations. From these data it was possible to predict the feasibility of an efficient continuous stripping circuit using three counter-current stages at a controlled pH. This was incorporated in a bench-scale extraction unit already treating uranium leach solutions.

## Results

### A. Batch cross-current stripping

Equilibrium data are represented graphically in Figures 1, 2 and 3. The pH as shown in Figure 1 was found to be a critical variable. For efficient stripping or for less than 0.1 g U<sub>3</sub>O<sub>8</sub>/l in the solvent, the pH should be controlled at 4.5 to 5.0. Higher pH values will cause local precipitation in the first stage where uranium concentration is high (15-20 g U<sub>3</sub>O<sub>8</sub>/l).

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