of optimizing over the continuous decision variable α_{26}. To avoid a cost discontinuity caused by introducing an exchanger we must, of course, require the cost of an exchanger to approach zero as its area does.

The notion that we have converted a discrete decision problem to a continuous one is invalid here. It may be observed that hot stream V has sufficient heat content to drive cold stream I to its final temperature. However, the transfer of heat in exchanger 1 is limited because an inequality constraint in exchanger 2 has to be satisfied. This constraint is the approach temperature requirement between the inlet hot stream and the outlet cold stream ($T_{12} \geqq 533.33° + \Delta T$, where ΔT is a minimum allowed approach temperature of, say, 2.78°K). By numerical computation one finds that the overall cost can be lowered if α_{26} is increased (see Figure 2). This increase in α_{26} lowers the flows of cooling utilities IV and VII. Ultimately, when the flow of cooling utility IV is zero, an optimal structure is obtained with a cost of 16 945 \$/yr. At this point, $\alpha_{26} = 0.688$.

Note, however, that when the flow of the cold stream through exchanger 2 is zero, and the heat exchanger 2 is totally neglected, a network with a cost of 6 864 \$/yr is obtained, as shown in Figure 3. Thus, a significant discontinuity, which we had hoped we had eliminated, has reappeared. It should be emphasized that the data for the problem and its formulation are important only in that they are plausible and that they help make this point.

The main observation may be summarized as follows. When certain subsystems are rendered redundant during optimization (by the associated flow or a split fraction taking on a value of zero), and if inequality constraints are associated with these subsystems which force constrained behavior elsewhere, discontinuities very likely still exist in the problem. One must still make a discrete decision about whether or not to introduce that subsystem. This observation means that if the structural parameters are to be used for a synthesis problem, and if inequality constraints are involved, the problem has to be formulated very carefully, if indeed it can be, to make it a continuous one.

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Effect of a Surface Active Agent on the Viscosity of Suspensions

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It has long been known that the apparent viscosity of suspensions is a function of the volume fraction of suspended solids for given solids shape, size distribution, and surface properties (Ting and Luebbers, 1957; Thomas, 1963). Ting and Luebbers (1957) derived the following equation relating the volume fraction of solids x_v to the viscosity of the suspensions μ_{sp}:

$$\frac{x_v}{\mu_{sp}} = x_{v,\infty} - x_v \qquad (1)$$

where $x_{v,\infty}$ is a characteristic slurry property at a constant temperature. Ting and Luebbers measured the viscosities of suspension of glass spheres and other narrowly sized particles in dense liquid media prepared by blending different liquids to match the density of solids. The experimental slurry viscosities as measured by a Brookfield viscometer at 20°C were satisfactorily correlated with x_v by plotting x_v/μ_{sp} vs. x_v, yielding $x_{v,\infty}$ as the intercept on both axes.

Reduction of the viscosity of suspensions might be technically desirable in operations such as filtration, crystallization, and other solid-liquid separation processes. This can be done, in principle, through the interface modifying properties of surface active agents. For example, the reduction of the viscosity of colloidal suspensions by the addition of tetrasodium phosphate has been discussed by Sennett and Olivier (1964). Taki Fertilizer Company of Japan developed a phosphoric acid process via the crystallization of calcium sulfate hemihydrate that utilizes a sulfonic acid surfactant (Slack, 1968), which has the beneficial effect of significantly reducing the slurry viscosity.

The purpose of the present work is to demonstrate the effect of a surfactant in reducing slurry viscosity and to present, at the same time, an improved method of presenting slurry viscosity data.

EXPERIMENTAL

A Brookfield model LVT viscometer was used to measure the apparent viscosities of suspensions prepared from dried calcium sulfate dihydrate (or hemihydrate) and 30 to 40% P_2O_5 phosphoric acid, containing about 2% by weight of free sulfate ions. The slurry was mixed for 30 min in a 400 ml Pyrex beaker with the help of an agitator in a constant temperature bath maintained to within 0.1°C. After this time, the agitator was stopped and the beaker was placed under the Brookfield viscometer. The spindle, maintained at the temperature of measurement, was then immersed. To minimize the effect of any appreciable settling of the solid particles, the time interval between the stoppage of the agitator and the first reading was kept to a minimum, namely, 20 s. After the first set of three observations, the slurry was agitated again and a second set of viscosity readings was taken after about 10 min. Only spindle number 1 was used at 60 rev/min. The apparent viscosity increased with decreasing shear rate (revolutions per minute), but it did not change appreciably with time.

DISCUSSION OF RESULTS

An improvement in the data presentation was obtained by rearranging Equation (1) to separate the variables, thus avoiding the same variable x_v on both axes as suggested by Sherwood (1974). Thus

$$\frac{x_v}{x_{v,\infty}} = \frac{\mu_{sp}}{\mu_{sp} + 1} \tag{2}$$

which can be rearranged to

$$x_v = x_{v,\infty} \cdot \frac{\mu_{sp}}{\mu_{\text{rel}}} \tag{3}$$

A plot of x_v against $\mu_{sp}/\mu_{\text{rel}}$ should produce a straight line passing through the origin with slope $x_{v,\infty}$.

Ting and Luebbers' viscosity data (1957) of 230 μm glass spheres suspended in a mixture of Castor oil and s-tetra bromoethane were replotted in accordance with Equation (3). As shown in Figure 1, the data fit is excellent and in fact better than what was obtained by plotting x_v vs. x_v/μ_{sp} and gives an $x_{v,\infty}$ of 0.488 which compares to the approximate value of 0.5 obtained by the above authors.

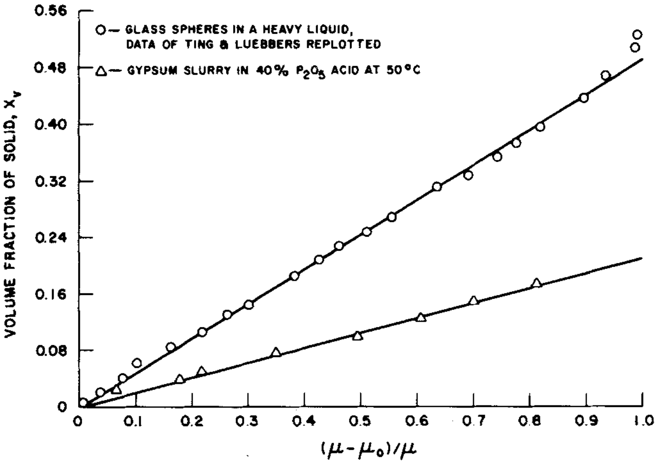

Fig. 1. Relation between slurry viscosity and volume fraction of solid.

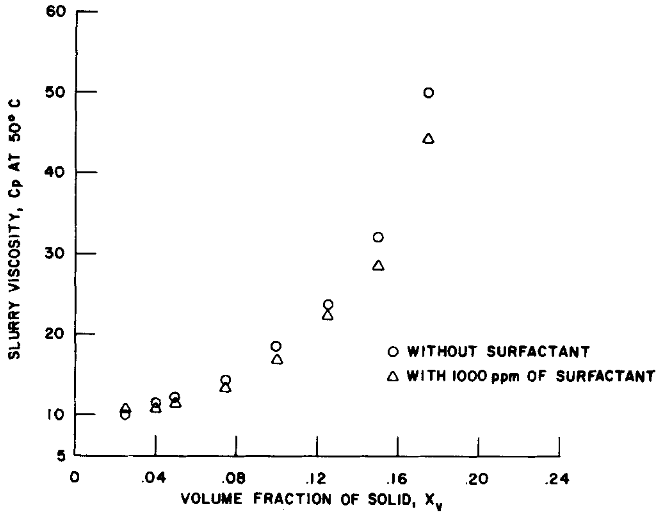

Fig. 2. Effect of solid volume on the slurry viscosity at 50°C with and without surfactant.

Figure 2 shows the strong dependence of the viscosity of gypsum slurries in 40% P_2O_5 at 50°C on the volume fraction of gypsum present, as represented by the circles. The corresponding viscosities obtained from the slurries having 1 000 p.p.m. of a surfactant are also plotted in Figure 2. The surfactant was a mixture of homologues and isomers of approximate average composition $C_{12}H_{25}SO_3Na$. The reduction of viscosity as a result of the presence of the surfactant is clearly seen. The data of Figure 2 (no surfactant) were also plotted in Figure 1, again showing good correlation between $(\mu - \mu_o)/\mu$ and x_v. Similar results were obtained for calcium sulfate hemihydrate in phosphoric acid. Unlike Ting and Luebbers' spheres, the solid phase in the present work had a very wide size distribution (5 to 90 μm) and a significantly higher density than the acid (2.37 for gypsum, 2.57 for hemihydrate compared to 1.50 for the acid).

Preliminary investigation showed that at high solid level in the suspension, where the slurry viscosity rises very rapidly with volume fraction of solid (0.10 to 0.20), the reduction of slurry viscosity as a result of a surfactant may get confounded with the effect of a concommittant drop in the solid level. A factorial design, comprising the slurry viscosity (response) as a function of x_v, percent P_2O_5 in the acid, and the parts per million of the surfactant, was implemented. Table 1 lists the variables at the two levels along with the analysis of variance obtained for the significant effects. The F ratios were calculated by comparing the mean squares with respect to an independent error mean square obtained from replication.

The number in the last column of Table 1 conclusively demonstrates that all three variables affecting the slurry viscosity of gypsum in phosphoric acid are highly significant. While x_v and percent P_2O_5 increased the viscosity, the surfactant reduced it. For example, the slurry viscosity at 50°C at $x_v = 0.20$ increased from 65.9 to 70.1 cp at percent P_2O_5 increased from 30 to 40. Also, the surfactant at 1 000 p.p.m. reduced the latter viscosity to 53.5 cp, that is, by 24%. The solid-surfactant interaction AC (a negative effect) was also found significant at 0.05 level of significance. It probably indicates that the reduction of viscosity is more pronounced at both high x_v and high surfactant levels.

TABLE 1. ANALYSIS OF VARIANCE OF THE VISCOSITY EXPERIMENTS

Levels of variables: A at 0.1 and 0.2; B at 30 and 40, C at zero and 1 000 p.p.m.

Variable name	Effect	Mean square	D.F.	F. ratio	Significance level
Volume fraction	A	4 136.4	1	1162.2	0.01
Solid, x_v % P_2O_5 in acid	B	81.47	1	22.69	0.05
Surfactant	C	171.03	1	47.64	0.05
Interaction	AC	102.03	1	28.42	0.05
Error		3.59	2		

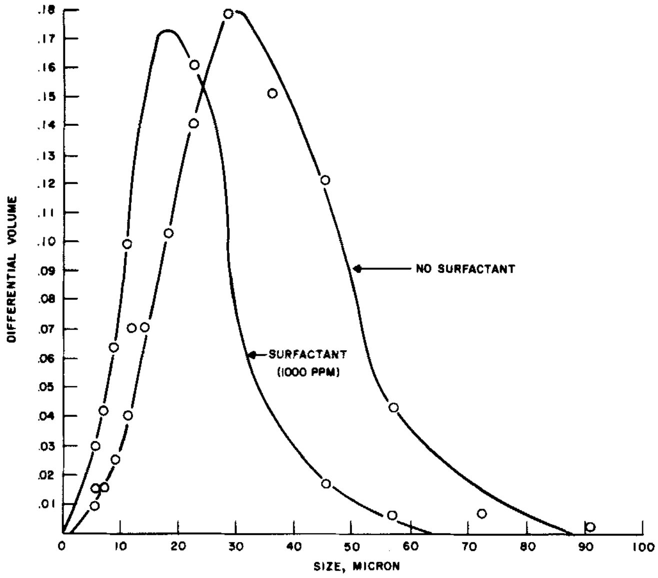

Fig. 3. Coulter counter size distributions of gypsum particles obtained from slurries with and without surfactant.

Ting and Luebbers (1957) postulated that the solid particles in a slurry form clusters or packings whose structures may be very complicated for arbitrary size distributions. Viscosity rises with increase in solid level due to occlusion of fluid in the solid structures. The probable mechanism of the influence of the surfactant is through the lubrication of the solid-liquid interface brought about by adsorption of the surfactant molecules. In other words, the surfactant molecules interfere with the packing structures and tend to increase the degree of fluidity in the suspension. In a control experiment, 60-80 mesh glass beads were suspended in phosphoric acid and the viscosities measured as a function of levels of solids and of the surfactant. No change in slurry viscosity was observed. To confirm the postulate of surface adsorption, size distribution data were obtained of the gypsum particles from both suspensions. As shown in Figure 3, the differential mass distribution measured by a Model TAII Coulter counter is shifted toward the low size for the distribution obtained from the slurry with the surfactant. Thus the formation of the solid clusters was inhibited by the action of the surfactant used in this study, as a result of which the slurry viscosity dropped.

CONCLUDING REMARKS

Following conclusions were made in the present study:

1. Viscosities of gypsum and hemihydrate slurries in wet phosphoric acid increases rapidly with the solids volume fraction, at all temperatures. Ting and Luebbers' (1957) derivation leading to Equation (3) is also valid for wide distributions with arbitrary shapes of crystals.
2. Viscosity data are well correlated by plotting x_v vs. $(\mu - \mu_0)/\mu$, and the characteristic constant $x_{v,\infty}$ is obtained from the slope of the corresponding graph.
3. The surfactant used reduced the viscosity of the phosphoric slurries significantly, presumably by facilitating the flow of solid particles past the liquid. At least in the present case, the reduction of slurry viscosity was brought about by a reduction in dominant particle size, by deagglomeration.

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NOTATION

x_v = volume fraction of solid
$x_{v,\infty}$ = volume fraction of solid in suspension for which the viscosity tends to infinity
μ = apparent viscosity measured by Brookfield viscometer, cp
μ_0 = viscosity of liquid
μ_{rel} = μ/μ_0
μ_{sp} = $(\mu - \mu_0)/\mu_0$

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Micromixing Effects on Multiple Steady States in Stirred-Tank Reactors

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Occurrence of multiple steady states in chemical reactors has been studied extensively in the last two decades, and the progress made in this area has been reviewed by Perlmutter (1972), Schmitz (1974), and Luss (1976). The problem of steady state multiplicity in isothermal reactors which in general may occur for rate expressions exhibiting a maximum at some intermediate level of reactant concentration also received attention (Denbigh et al., 1948; Matsuura and Kato, 1967; O'Neil, 1971; Bruns et al., 1973). Most of these studies investigated the behavior of an ideal stirred-tank reactor which was presumed perfectly mixed on molecular level, that is, at maximum mixedness conditions. Based on this model, uniqueness criteria and regions of multiplicity were evaluated (Matsuura and Kato, 1967; O'Neil et al., 1971). However, it is well known that reactor performance is affected not only by the residence time distribution (RTD) but also by the fluid's state of aggregation and by the micromixing paths