

Large Scale Preparation of Melamine-Based Superplasticizing Admixtures.

II. Pilot Plant Studies

I. S. DAIRANIEH, S. M. LAHALIH, M. ABSI-HALABI, and
A. DASHTI, *Petroleum, Petrochemicals and Materials Division,*
Kuwait Institute for Scientific Research, P.O. Box 24885, 13109-Safat,
Kuwait

Synopsis

The standard procedure for preparing sulfonated melamine-formaldehyde (SMF) resins was slightly modified to prepare an effective more concentrated resin. SMF resins were prepared on a 200-L pilot plant reactor according to the standard, optimized and slightly modified procedures. In all cases, properties of resins prepared were similar to those which were prepared in a small scale equipment. The scaling up from the 10- to the 200-L reactors was based on a constant agitator tip speed.

INTRODUCTION

From the idea to commercial production, chemical process development passes through numerous intermediate stages. Pilot plant studies are generally considered to be a major stage of process commercialization. Practically speaking, the decision to conduct pilot plant studies is usually complex and depends on economic factors as well as the state of the art in related fields. The literature on scaling-up batch processes is quite scarce,¹ and such an important aspect of chemical engineering should be covered. In the first paper of this series, we reported on the optimization of a novel process for producing sulfonated melamine-formaldehyde (SMF) resins. The optimized process cycle resulted in a considerable savings in process time and energy consumption so that the production cost of the SMF resins was cut appreciably. This paper addresses another aspect of cutting down the production cost of the developed superplasticizer, which is the preparation of a more concentrated resin. Moreover, this paper reports on the pilot plant studies of three SMF resins prepared according to the standard procedure, the optimized procedure, and the concentrated resin procedure. Finally, it is shown that process scale-up based on a constant agitator tip speed is valid since it was successfully used to prepare SMF resins on a 200-L (pilot plant) scale from the 10-L (bench scale) experiments.

EXPERIMENTAL

Materials

Technical grade paraformaldehyde, melamine, sodium metabisulfite, sodium hydroxide, and sulfuric acid were used. Details of composition and suppliers are given in the first part of this series.

Equipment

A 10-L glass reactor equipped with a variable speed stirring motor and a viscometer that was connected to a circulator and a peristaltic pump was used for laboratory scale experiments. Pilot plant experiments were conducted in a multipurpose pilot plant (Fig. 1). The major components of the pilot plant are: a 200-L stainless steel reactor equipped with a pH meter and a viscometer, a 20 kW electric heater, a cooling tower, and a 24-kW chiller.

The slump of concrete mixes was determined by the slump conical mold according to ASTM C143. Compressive strength was measured by a concrete compression testing machine made by Control, Italy, with a 200 ton capacity. Concrete mixes were prepared using a 120-L concrete mixer.

Chemical Studies

Pilot Plant Preparation of the Standard Resin. A formalin solution was prepared by adding 16.745 kg of 96% paraformaldehyde to 78 L of water. The reaction mixture was heated for 30 min at 50°C after its pH was raised by the addition of 1.0 mL of 10N NaOH solution.

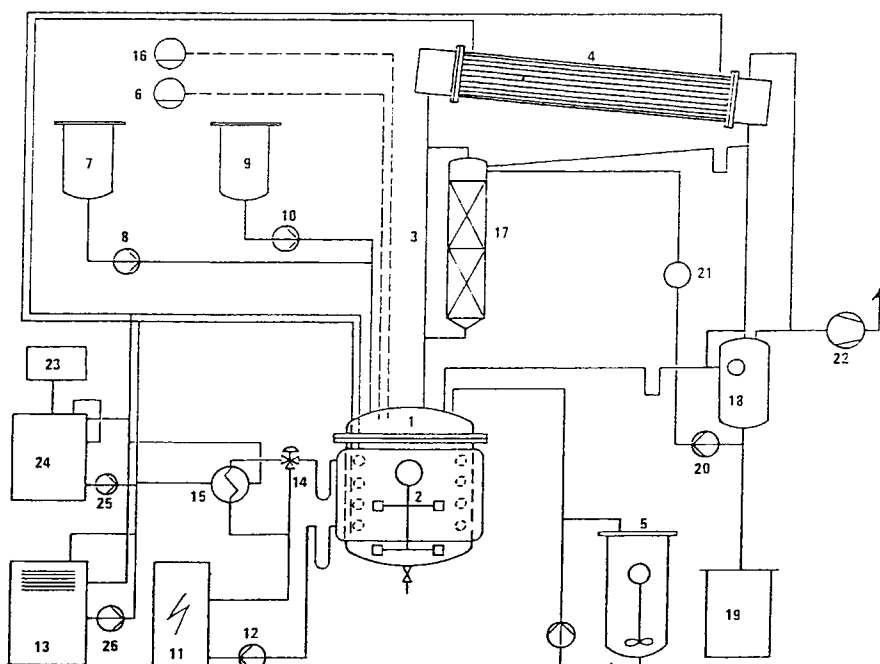


Fig. 1. Schematic diagram of the multipurpose pilot plant: (1) pilot plant reactor; (2) agitator with variable speed; (3) vapor tube; (4) main reflux condenser; (5) feed tank; (6) pH metering system; (7) NaOH solution tank; (8) NaOH pump; (9) H₂SO₄ solution tank; (10) H₂SO₄ pump; (11) heating system (thermo fluid); (12) circulation pump; (13) water chiller unit; (14) heating or cooling distribution valve and controller; (15) heat exchanger for heating and cooling; (16) viscometer; (17) packed column; (18) separator tank; (19) collecting receiver; (20) reflux pump; (21) reflux dosing meter; (22) vacuum pump; (23) water softener; (24) cooling tower; (25, 26) circulation pumps.

After the solution became clear, 30 L of H₂O was added, and the solution was again heated to 50°C. Then, the pH was adjusted to 11.35 by the addition of ~ 4 L of 10N NaOH solution (pH₁); then 16.9 kg of melamine was added immediately. The reaction mixture was heated at 50°C (*T*₁) for 15 min (*t*₁) from the time of the melamine addition. This is the first step.

Then, 12.745 kg of sodium metabisulfite was added followed by 7.5 L of H₂O. The mixture was kept at 50°C for 5 min to mix, and then its temperature was raised to 80°C (*T*₂) and kept there for 60 min. The solution was cooled to 50°C (*T*₃) and adjusted to a pH of 3.5 (pH₃) by adding 3.0 L of 14.5N H₂SO₄. The reaction mixture was kept at 50°C for 110 min (*t*₃) from the time of the H₂SO₄ addition. These are the second and third steps.

The solution pH was then raised to 7.0 (pH₄) by adding 1.5 kg of calcium hydroxide. After that, the solution was brought up to 80°C (*T*₄) and kept at this temperature for 60 min (*t*₄). This is the fourth step. Finally, the mixture was cooled to room temperature and adjusted to a pH of ~ 9.0. The solid content of such a mixture is 25–26%. When diluted to a 20% solid content, it has a viscosity of ~ 4.0–4.8 cP at 20°C.

Pilot Plant Preparation of the 40% Concentrated Resin. The quantities of materials used are different from those in the preparation of standard resin in that 19.005 kg of sodium metabisulfite are used instead of 12.745 kg so that the S/M + U is 1.2 instead of 1.0. Also, the quantity of water added is 64 L with 20.832 kg of paraformaldehyde and 21.0 kg of melamine are used. The procedure is the same except that the pH is adjusted to 11.30–11.80 and *t*₃ is 30 min instead of 110 min. Continuous cooling at 50°C is maintained on the addition of H₂SO₄ to avoid gelation. The quantities of acid and base used to adjust pH are almost doubled. The solid content of such a mixture is ~ 40%, and when diluted to 20% solid content, it has a viscosity of ~ 3–4 cP at 20°C.

Pilot Plant Preparation of the Process Optimized Resin. The quantities of materials used are the same as those in the preparation of standard resin. The procedure is also the same with the exception that *T*₃ is 70°C instead of 50°C and *t*₃ is 80 min instead of 110 min. The solid content of such a mixture is ~ 25–26% and, when diluted to 20% solid content, it has a viscosity of ~ 4–5 cP at 20°C.

Characterization and Evaluation Studies

Evaluation procedures outlined in the first part of this series were followed here.

RESULTS AND DISCUSSION

Preparation of Concentrated Resins

Concentrated resins were prepared to decrease the production cost. When more resin is prepared during the same process time, the production cost per unit weight is reduced. A complication is that increasing the concentration leads to faster buildup of viscosity since molecules (macromolecules rather) have a greater chance of colliding. Thus, the polymerization time needed to attain an acceptable viscosity is shortened. When the experiments were

conducted on the 1 L scale,² it was found that increasing the concentration from 25 to 43% led to decreasing t_3 from 110 to 15 min. Moreover, the 28-day compressive strength of concrete treated with this resin was decreased by 16%. Since short polymerization times are harder to control on a larger scale, one should look for means to impede the fast viscosity buildup. Increasing the pH of the third step should lower the polymerization rate, and the viscosity buildup rate should decrease.

Resin 2 was prepared in a 10-L reactor with a pH_3 of 5.0 (compared with resin 1, which had a pH_3 of 3.5), and the gelation possibility was reduced (Fig. 2). The viscosity build up rate is cut in half, but the superplasticizing properties of resin 2 is just as poor as those of resin 1. The 28-day compressive strength of $\sim 480 \text{ kg/cm}^2$ is much less than the $\sim 550 \text{ kg/cm}^2$ strength obtained from the normal concentration (resin 4, which was prepared according to the standard procedure). Furthermore, the water reduction of the 2% dose is only 14%, compared with the 25% value of resin 4. Therefore, increasing pH_3 does not provide a viable means to obtain an effective concentrated resin, and so other means have to be investigated.

The increase of the S/M ratio leads to a higher concentration of sulfite ions that can block sites otherwise available for polymerization. Thus, the viscosity buildup will decrease. To test this idea, resin 3 was prepared with an S/M ratio of 1.2. Not only did we succeed in reducing the viscosity build up (Fig. 3) but we also improved the properties of the resin (Table I). Therefore, an effective 40% concentrated product was prepared. It must be added that

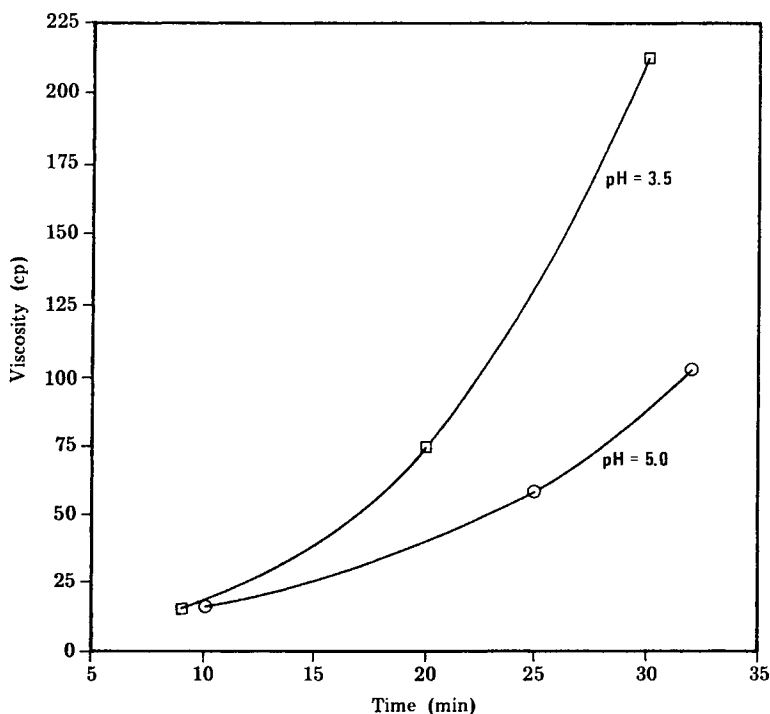


Fig. 2. Viscosity build up in the third step with different pH values.

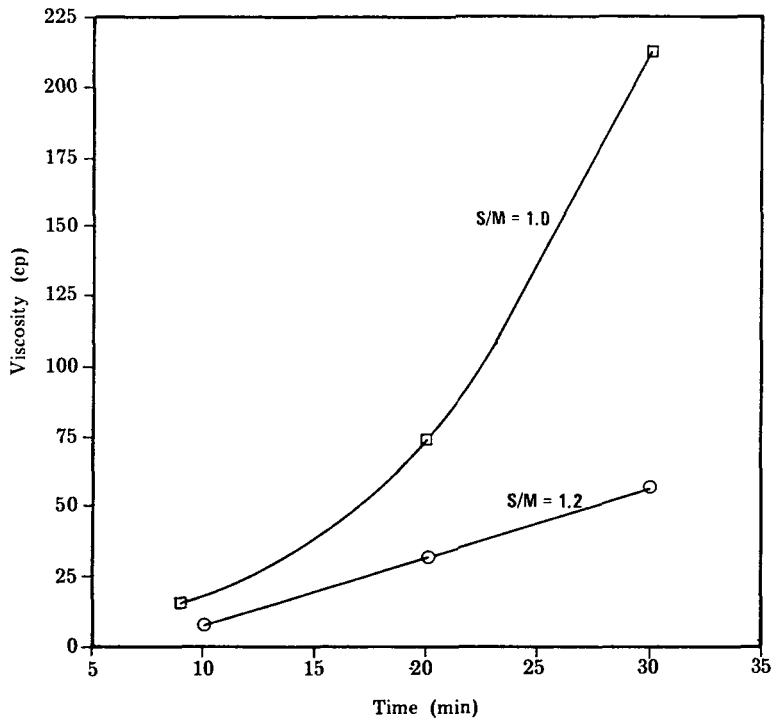


Fig. 3. Viscosity buildup in the third step with different S/M ratios, at $pH_3 = 3.5$.

various S/M ratios were investigated, and an S/M of 1.2 was found to be the optimum ratio.

Pilot Plant Studies

The strategy adopted for large scale experiments was that of fine tuning the optimum reaction conditions obtained from smaller scale experiments. Hundreds of experiments were performed on the 1-L scale to determine optimum conditions;² a fraction of that number of experiments was conducted on the 10-L scale to optimize the process cycle, leaving the product properties

TABLE I
Effect of Changing pH_3 and S/M Ratio on the Properties
of 40% Concentrated Resins

Resin no.	pH_3	S/M	2% Dose		Compressive strength (kg/cm ²)		
			Slump (mm)	Water reduction (%)	3 days	7 days	28 days
1	3.5	1.0	30	14	355	390	478
2	5.0	1.0	35	15	361	426	485
3	3.5	1.2	30	23	438	496	567
4	3.5	1.0	50	25	427	475	553

virtually unchanged. At the pilot plant scale, even fewer experiments were conducted to establish the large scale optimum reaction conditions.

In all pilot plant runs, technical grade raw materials were used. The agitator rotational velocity was 68 rpm, which is equivalent to an agitator tip velocity of 42 cm/s. The heating rate of the reaction mixture varied between 1 and 1.5°C/min, depending on the mass of the mixture, and the cooling rate was approximately 1°C/min. These numbers compare fairly well with those of the 10-L reactor (agitator tip velocity was 44 cm/s and the heating and cooling rates were approximately 1°C/min), but the two reactors had different geometries and the agitators were of different types (the pilot plant has a turbine agitator, the 10-L reactor has an anchor agitator). Therefore, the flow patterns and, consequently, shear rate distributions in each reactor were different.

The first resin to be prepared on the large scale was the standard one. It had the same superplasticizing properties as those of the resins prepared in the 1-L and 10-L reactors. The three resins resulted in a 25% water reduction at the 2% dose; at the 0.8% dose they increased the concrete mix's slump from 40 to ~ 180 mm. To ensure the reproducibility of resin 1 on the pilot plant scale, four resins (5–8) were prepared (Table II). The final viscosities of the four resins (at 20°C and 20% concentration) were 4.50, 4.61, 4.70, and 4.47 cP, respectively. All four resins gave a 25% water reduction, which is 38% higher than that of the commercial melamine-based superplasticizer (Melment). The average 28-day compressive strength of the four resins was 552 kg/cm², which is again greater than Melment's (508 kg/cm²).

Preparation of Concentrated Resin. The procedure outlined in the preparation of 40% concentrated resins on a 10-L scale (resin 3) was followed in the preparation of the concentrated resin (resin 13) on the pilot plant scale. The properties of this resin were comparable with those of resin 3; with a 0.5% dose, the slump increased from 20 to 150 mm in resin 3 and from 35 to 150 mm in resin 13.

A reproducibility study was made of concentrated resins (9–12) with final viscosities of 3.55, 3.49, 3.82, and 2.96 cP, respectively. The properties of these resins (at the 2% dose) are given in Table III. The average water reduction and 28-day compressive strength of the concentrated resins are 23% and 537 kg/cm², which compares fairly well with the values of the normal concentra-

TABLE II
Reproducibility Study of Resins Prepared According to the Standard Procedure
Using 200-L Pilot Plant Reactor

Resin no.	Slump (mm)	Water reduction (%)	Compressive strength (kg/cm ²)		
			3 days	7 days	28 days
5	65	25	365	454	543
6	70	25	334	450	562
7	55	25	301	447	544
8	55	25	324	456	558

TABLE III
Reproducibility Study of Resins Prepared According to
the 40% Concentrated Resin Procedure Using the Pilot Plant Reactor

Resin no.	Slump (mm)	Water reduction (%)	Compressive strength (kg/cm ²)		
			3 days	7 days	28 days
9	35	23	383	489	527
10	40	22	353	458	—
11	45	22	344	450	539
12	30	23	349	457	546

tion resins (25% and 552 kg/cm²). In terms of the benefit to cost ratio, however, the concentrated resin may be better than the unconcentrated resin. It can be produced more cheaply (about half of the production cost of normal concentration) since more material can be produced in a shorter time (shorter process cycle).

Preparation of the Optimized Cycle Product. In the first paper of this series, the process for producing the standard resin was optimized by increasing the third step's temperature from 50 to 70°C and reducing the third step time (t_3) from 110 to 50 min. It was shown that, for a t_3 of 30 min, the compressive strength of the concrete mix was slightly lower than that of the standard resin, and a t_3 of 70 min gave a higher strength. Thus, t_3 was fixed at 50 min. A pilot plant run (resin 15) in which T_3 was fixed at 70°C and t_3 at 30 min was carried out. The resin did not perform as well as its 10 L counterpart (resin 14). Table IV compares the properties of these resins; for resin 15, the water reduction was lower and compressive strength was less. Increasing the time to 50 min (resin 16) did not produce significant improvement in the resin properties (Table IV). When t_3 was further increased to 80 min (resin 17), however, the water reduction and compressive strength of resin 14 were matched.

In attempting to explain this time increase from 50 to 80 min, several factors must be considered. First are the heat transfer effects. If temperature distributions are vastly different in the vessels (10 and 200 L), and if the large

TABLE IV
Effect of Reaction Time in the Third Step on Superplasticizing Properties
of Resin

Resin no.	t_3 (min)	Slump (mm)	Water reduction (%)	Compressive strength (kg/cm ²)		
				3 days	7 days	28 days
14	30	55	25	402	476	543
15	30	35	22	364	449	497
16	50	60	23	325	418	495
17	80	35	25	358	478	540

scale heating system is not as efficient as the small one, then one expects an increase of reaction time to account for temperature differences. But this was not the case. The maximum difference between the bulk and the wall temperatures in the two vessels was 2°C. Moreover, the heating rate in both the 10 L and the pilot plant reactors was approximately 1°C/min, so that thermal effects could not have caused the increase in reaction time.

The second effect to be considered is the mixing, which combines the pumping rate (blending efficiency) and velocity head (shear rate distribution) effects.³ These factors changed with the size of the vessel. It is generally accepted that the time for complete mixing must be negligible compared with reaction time.⁴ The beginning of the third step reaction is marked by the lowering of the pH from 11.4 to 3.5. This is done in 1 min when the 10-L reactor is used, but it takes 4–6 min with the pilot plant. Therefore, the process of acid blending is not the same. This problem is further complicated because, at 70°C, the reaction is fast (see Part I of this series), so that minimum blending times are essential to guarantee the same reaction kinetics.⁴

The two vessels have different geometries and different impeller characteristics, so that the shear rate distributions are different. It is known that polymerization processes are affected by the flow patterns and shear rate distribution within the reactor.⁵ If a wide range of molecular weight distribution can be tolerated, however, the shear rate distribution effect may not be significant. Therefore, the longer pH adjustment time and acid blending that violates chemical similarity in the two systems (10-L and 200-L reactors) seems to be the most reasonable explanation of the time increase in the third step. In a commercial plant, one can say that if the geometrical similarity is preserved, and if the pH adjustment and acid blending times are kept within this range, a further increase in the time of the third step is not expected.

It is important at this point to compare the properties of resins prepared under the standard and the optimized (resin 17) process cycles using the 200-L pilot plant. When the concrete mix is treated with a 0.8% dose of resin 5, its slump is increased from 50 to 185 mm; the same increase is obtained from the same dose of Resin 17. Comparing these resins with the commercially available, melamine-based superplasticizer (Melment), one finds that a 0.8% dose of Melment increases the concrete's slump from 50 to 135 mm only. Similar

TABLE V
Comparison of Superplasticizing Properties of Resins Prepared
in Standard and Optimized Process Cycles

Resin no.	Slump (mm)	Water reduction (%)	Compressive strength (kg/cm ²)		
			3 days	7 days	28 days
5	65	25	365	454	543
17	45	25	358	478	540
Melment L-10	55	18	324	457	508
—	40	—	160	270	370

behavior is obtained with other doses. Table V compares the water reduction and compressive strength data of resin 5, resin 17, and Melment when a 2% dose of each superplasticizer is used. Again, the water reduction and compressive strength of resins 5 and 17 surpass those of Melment. Complete performance evaluation studies of these resins can be found elsewhere.⁶ It was shown that, irrespective of the cement type, cement brand, and with or without other admixtures, our resins outperformed the commercial superplasticizer. Also, it was shown that, when concrete was aged (cured) under fresh water, sea water, air or humidity chamber conditions, our resins performed better than Melment.

Process Scale-Up

In going from a small to a large scale, several approaches are possible.⁷ These include mathematical modelling, pilot plant work, similarity principle, and magnitude equality.¹ In complex processes (such as polymerization), scale up is normally based on a combination of the last three approaches.

From the chemical standpoint, four similarity states are important: geometrical, mechanical, thermal, and chemical. In general, it is not possible to preserve all four types of similarity when the scale up is done. Which similarity is maintained and which is violated depends on the particular process in question.⁸ Experiments should be conducted to examine the most pertinent and controlling factors affecting the process results, so that the scale-up criteria that will be kept constant when going from a small to a large scale can be chosen. For a batch process in which a homogeneous chemical reaction is taking place in an agitated vessel, various scale up rules were suggested.^{5,9} These include scale up based on constant:

1. agitator rotational speed (N);
2. agitator pumping capacity (Q);
3. agitator power consumption (P);
4. agitator power consumption per reactor volume (P/V);
5. agitator tip speed (U_T);
6. Reynolds Number (N_{Re});
7. convective heat transfer coefficient (h);
8. convective heat transfer rate per reactor volume (q/V).

Out of these eight criteria, 4, 5, and 7 are the most widely used.⁹

In the present study, SMF resins were prepared in 10- and 200-L reactors; when moving from the small to the large scale, criterion 5 (constant tip speed) was utilized. To examine the effect of holding U_T constant on other scale-up variables, the dimensions of 10- and 200-L reactors and the physical properties of the reaction mixture are given in Table VI. The density (ρ) and heat capacity (cp) of the reaction mixture were experimentally measured and the thermal conductivity (k) was taken to be that of water. The viscosity buildup was found to be different in the two reactors. Since viscosity changes throughout the reaction period, the highest viscosity attained during the reaction will be used since it is the one that will give the smallest N_{Re} and it will indicate if

TABLE VI
Reactor Dimensions and Physical Properties of Reaction Mixture

	Symbol	10 L	200 L
Reactor diameter (m)	D	0.18	0.64
Reactor height (m)	H	0.38	0.64
Agitator diameter (m)	d	0.11	0.37
Agitator speed (s^{-1})	N	4.0	1.13
Agitator tip speed (m/s)	U_T	0.44	0.42
Density (kg/m^3)	ρ	1130.0	1130.0
Thermal conductivity (W/m K)	k	0.6	0.6
Heat capacity (J/kg K)	cp	3386.0	3386.0
Viscosity (mPa s)	η	10.0	15.0

there is a change in the flow regime. Recently, Henderson¹⁰ pointed out the importance of such parameter (highest viscosity) on mixing during polymerization studies. Table VII shows the effect of a constant U_T on some of the commonly used scale-up rules such as P/V (power per unit volume) and h (heat transfer coefficient). When obtaining the ratio of h in the 10- and 200-L reactors, N_{Re} and N_{Pr} (Prandtl Number) had to be calculated, and h was obtained from the general relationship

$$\frac{dh}{k} = CN_{Re}^{2/3}N_{Pr}^{1/3}$$

The geometrical constant C depends on the type of agitator. For an axial agitator in an unbaffled jacketed vessel (pilot plant reactor) equipped with a cooling coil, Nagata¹¹ gives a general equation from which C was found to be 0.224. As for an anchor mixer in an unbaffled vessel (10-L reactor), Uhl¹² found C to be 0.36. As can be seen from Table VII, h is decreased on scale up. However, this is compensated by the increase in the heat transfer area, which is 0.24 and 1.61 m^2 for the 10- and 200-L reactors, respectively, and the properties of resins in the two reactors will not be different. In fact, scale up based on a constant agitator tip speed proved to be valid as can be seen from data presented showing correspondence in superplasticizing properties prepared in the small and large reactors.

TABLE VII
Effect of a Constant U_T on Other Scale-up Rules

Variable	Equation	Variable in 200-L Reactor
		Variable in 10-L Reactor
U_T	$U^T = Nd$	0.95
P/V	$P \propto N^3d^5/D^2H$	0.44
N_{Re}	$N_{Re} \propto Nd^2/\eta$	2.05
N_{Pr}	$N_{Pr} \propto \eta$	1.50
h	$h = cd(N_{Re})^{2/3}(N_{Pr})^{1/3}$	0.56

CONCLUSIONS

Prior to the large scale preparation of any chemical, the process for making it must be optimized. For the case of sulfonated melamine-formaldehyde resins, the optimization studies focused on (1) minimizing the process's temperature cycling, which led to a considerable savings in time and energy, and (2) producing an effective concentrated resin, which reduces the production cost of the superplasticizer. After completing (1) and (2), SMF resins were successfully prepared on the pilot plant scale. These resins were just as effective as their counterparts prepared in 1- and 10-L reactors. The reaction time in the laboratory and pilot plant reactors were the same when the polymerization temperature was 50°C. But for the higher polymerization temperature (70°C), the time needed to build up the pilot plant solution's viscosity to a value comparable with the laboratory-prepared counterpart was extended from 50 to 80 min. This was attributed primarily to the pH adjustment time, which was long compared with the reaction time, leading to the violation of chemical similarity between the two scales. This should not present any difficulty on a commercial scale since the problem is due to lack of the proper pH control and is not inherent in the process.

The scale up from the 10- to 200-L reactor was based on a constant agitator speed. Although this scale-up rule leads to a decrease in the heat transfer coefficient, a moderate increase in heat transfer area can compensate for it.

The financial support of the Kuwait Foundation for the Advancement of Sciences is greatly appreciated. This is publication No. KISR 2380, Kuwait Institute for Scientific Research, Kuwait.

APPENDIX: NOMENCLATURE

c	geometrical constant
c_p	heat capacity (kJ/kg K)
d	agitator diameter (m)
D	reactor diameter (m)
h	convective heat transfer coefficient (kJ/m ² K h)
H	reactor height
k	thermal conductivity (kJ/m K h)
N	agitator speed (s ⁻¹)
N_{Re}	Reynolds number
N_{Pr}	Prandtl number
P	power (kJ/s)
V	volume (m ³)
U_T	tip speed (m/s)
η	viscosity (mPa s)
ρ	density (kg/m ³)

References

1. R. R. Corpstein, R. A. Dove, and D. S. Dickey, *Chem. Eng. Progr.*, **75**(2), 66 (1979).
2. M. Absi-Halabi, S. Lahalih, and T. Al-Khalid, *J. Appl. Polym. Sci.*, **33**, 2975 (1987).
3. J. Y. Oldshue, *Fluid Mixing Technology*, McGraw-Hill, New York, 1983.
4. L. M. Rose, *Chemical Reactor Design in Practice*, Elsevier, Amsterdam, 1981, p. 201.
5. J. Y. Oldshue, in *Scaleup of Chemical Processes*, A. Bisio and R. Kabel, Eds., Wiley-Interscience, New York, 1985.

6. S. Lahalih, I. S. Dairanieh, M. Absi-Halabi and A. Ali, unpublished manuscript, 1987.
7. P. Trambouze, *Chem. Eng.*, **72**, 122 (1979).
8. A. Bisio, in *Scaleup of Chemical Processes*, A. Bisio and R. Kabel, Eds., Wiley-Interscience, New York, 1985.
9. H. F. Rase, *Chemical Reactor Design for Process Plants*, Wiley, New York, 1977.
10. L. S. Henderson III, *Chem. Eng. Progr.*, **83**(3), 42 (1987).
11. S. Nagata, *Mixing: Principles and Applications*, Halstead, Tokyo, 1975.
12. V. W. Uhl, *Chem. Eng. Progr. Symp.*, **51**(17), 93 (1955).

Received January 25, 1988

Accepted April 14, 1988