

Large Scale Preparation of Melamine-Based Superplasticizing Admixtures.

I. Process Optimization

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

Synopsis

The process for preparing novel sulfonated melamine-formaldehyde resins was studied in detail with the objective of optimizing the production cycle time. The effects of minimizing temperature differences between consecutive reaction steps and reducing reaction time of selected steps of the process were assessed. Experimental work focused on increasing the polymerization step temperature and decreasing its time, resulting in considerable savings in the process time and energy consumption. The resin of the optimized cycle was found to have excellent superplasticizing properties when added to concrete mixes.

INTRODUCTION

The development of a new chemical process passes through several stages such as laboratory and pilot plant studies, optimization, and mathematical modeling.¹ A major desire in this development is to minimize the experimental research required and use data from studies to design an optimum commercial production unit that will manufacture the chemical with the desired properties. Development of batch processes, which are generally used in resin preparation, is considerably less complicated than continuous processes. The design of commercial units for these processes is generally based on pilot plant studies by simple application of the similarity or magnitude equality principles² so that modeling studies are unnecessary.³ Very few reports have appeared about this area.

In this series of studies, we examined the problems encountered in optimizing and scaling-up a novel process for producing water-soluble sulfonated melamine-formaldehyde resins, one of the major three types of chemicals used as commercial concrete superplasticizers. Superplasticizers are considered to be of special importance because they improve concrete workability, develop early strength, improve compressive strength, and permit little shrinkage.⁴ The preparation procedure of sulfonated melamine-formaldehyde superplasticizers was reported by quite a few researchers.⁵⁻⁸

A novel four-step preparation procedure was recently developed.^{9,10} The four steps are (a) hydroxymethylation (the addition reaction between melamine and formaldehyde), (b) sulfonation [the product of step (a) is sulfonated], (c) low pH condensation [the product of step (b) is polymerized], and (d) high pH rearrangement (molecules rearrange to give a more stable product). Some of

the prepared products have excelled concrete superplasticizing properties and are superior to available commercial melamine-based superplasticizers. The effect of the preparation procedure on product dispersion ability and stability were also reported and discussed.^{11,12}

The next step in the development of the novel process is to prepare the sulfonated melamine-formaldehyde (SMF) resins on a large scale. It is generally recommended that the development procedure pass through bench scale experimentation¹³ prior to pilot plant studies. The first paper in this series describes the preparation of SMF resins on a bench scale to optimize the developed process by reducing its time duration and energy consumption and to evaluate the effect of the optimized cycle on the properties of treated concrete.

EXPERIMENTAL

Materials

Paraformaldehyde technical grade (96% prills) from Formolyderivades, Spain, was used as received. Melamine obtained from the Saudi Arabian Fertilizer Co. had the following specifications: purity, > 99.8%; moisture, 0.1%; ash, 0.01%; off-color, 20; particle size, 40% less than 50 μm . Sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) from William Blythre and Co. Ltd., Accrington, Lancs, U.K., was used as purchased. The specifications of the product were: purity, > 96.5%; SO_2 , 65%; $\text{Na}_2\text{S}_2\text{O}_3$, < 0.03%; Fe, < 10 ppm; Pb, < 10 ppm. Sodium hydroxide flakes (NaOH) technical grade and sulfuric acid (H_2SO_4) technical grade manufactured by the Petrochemical Industries Co., Kuwait, were used as received.

Commercial sulfonated melamine-formaldehyde superplasticizer (Melment) was obtained in powder form from the Kuwait Prefabricated Building Co. This commercial superplasticizer is manufactured by Suddentsche Kalkstickstoff-Werke Aktiengesellschaft (SKW), Germany.

Equipment

Experiments were conducted in a single 10-L thermostated glass reactor equipped with a variable speed stirring motor, a peristaltic pump, a pH meter, and a circulator (heater/cooler type).

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

The resins were prepared following the four step process reported earlier.¹⁰ The detailed procedure used to prepare the standard resin and optimum cycle resin follow.

Preparation Procedure for the Standard Resin. A formalin solution was prepared by adding 992 g of 96% paraformaldehyde to 4580 mL 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.

After the solution became clear, 1740 mL of H₂O was added, and the solution was again heated to 50°C. The pH was adjusted to 11.35 by the addition of ~ 200 mL of 10N NaOH solution (pH₁); then 1000 g of melamine were immediately added. The reaction mixture was heated at 50°C (T_1) for 15 min (t_1) from the time of the melamine addition. This is considered the first step.

Then, 754 g of sodium metabisulfite was added followed by 430 mL 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. This is the second step of the reaction. The solution was cooled to 50°C (T_3) and adjusted to a pH of 3.5 (pH₃) by adding 250 mL of 14.5N H₂SO₄. The reaction mixture was kept at 50°C for 110 min (t_3) from the time of the H₂SO₄ addition. This is the third step of the reaction.

The solution pH was then raised to 7.0 (pH₄) by adding 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 ~ 4.0–4.5 cp at 20°C. The volume of the 20% solution is ~ 10 L.

Preparation Procedure for the Process-Optimized Resin. The quantities of materials used are the same as those in the preparation of the 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 50 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. The volume of the 20% solution is ~ 10 L.

Evaluation Studies

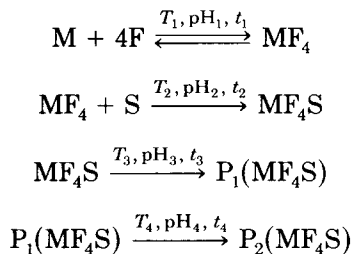
The prepared resins were tested on the following concrete mix to determine their effectiveness.

Cement	:	Water	:	Sand	:	Aggregate
1.00	:	0.53	:	1.79	:	3.43

The mix has a 28-day compressive strength of 370 kg/cm² and a slump of 30 mm. When testing the resins, cement, sand, and the aggregates are mixed dry first, then water is added with continuous mixing, and, finally, the admixture solution is added slowly. The slump of concrete (plain and treated with admixtures) was determined according to ASTM C143. The compressive strength of concrete mixes was determined using 15 cm cubes. The concrete cubes were cast and kept in high humidity conditions for 24 h. They were then removed from the molds and kept in a fresh water tank until the test age (3, 7, and 28 days). The determination of water reduction in concrete mixes when the synthesized resin solutions are added to maintain a slump value equal to the control mix was done by trial and error.

RESULTS AND DISCUSSION

A four step procedure for preparing SMF resins was fully described in earlier publication.¹⁰ The reaction proceeds as follows:



where M = melamine, F = formaldehyde, S = sodium bisulfite, MF_4S = sulfonated melamine formaldehyde, $\text{P}_1(\text{MF}_4\text{S})$ = low pH condensation intermediate, and $\text{P}_2(\text{MF}_4\text{S})$ = sulfonated melamine-formaldehyde polycondensate.

In the first step, an addition reaction between formaldehyde and melamine occurs, and the product is sulfonated in the next step. In the third step, polymerization of the sulfonated monomer takes place, and, finally, in the fourth step, the polymer rearranges to a more stable product. The reaction procedure (Table I) is cyclic (50–80°C temperature cycling) so time is lost in transient heating or cooling. It takes 20 min to increase the temperature from 50 to 80°C (second step); another 25 min are spent in lowering the condensation temperature to 50°C (third step); and 30–35 min are needed to bring the temperature of the fourth step to 80°C. Thus, the process total time becomes approximately 5.5 h, of which about 1.5 h are wasted in transient time. In an effort to reduce transient time and minimize the temperature cycle of the process, critical variables of the four steps were investigated.

The temperature might be increased in the first step, to decrease the 50–80°C temperature difference between the first and second steps. The time of this step is already small, as it will not be varied. The range of pH values leading to an optimum product was quite small; consequently, the pH of the first step will not be altered. The temperature of the second step cannot be reduced since sulfonation does not occur below 80°C; therefore, only the sulfonation time may be varied. All three variables of the third step may be varied; an attempt will be made to raise the temperature and reduce the time. In the fourth step, a product stabilization step, temperature, or time may be reduced, but we chose to decrease temperature since that improved the

TABLE I
Reaction Conditions of the Standard Procedure

	pH	T (°C)	t (min)
Step 1	11.35	50	15
Step 2	11.35	80	60
Step 3	3.5	50	110
Step 4	7.0	80	60

process temperature cycle. It must be stressed that these variations will be acceptable only if they do not change product effectiveness.

An experimental program was set up to study the effects of these variations on the superplasticizing properties of the resins. The prepared resins were compared with resin 10, whose preparation procedure is that of the standard resin except that it was prepared in a 10-L and not a 1-L reactor. Treating the concrete mix with a 2% dose of resin 10 resulted in a 25% water reduction and a 28-day compressive strength of 553 kg/cm². The base concrete mix (with no superplasticizer) had a 28-day compressive strength of 370 kg/cm².

Effect of T_1

The effect of the first step's temperature (T_1) on the compressive strength of concrete is shown in Figure 1. The strength is not adversely affected by the increase in T_1 nor by water reduction, which was 25% for all four tested resins. Therefore, from a process cycle viewpoint, the highest T_1 possible will be favorable. The first step is preceded by the dissolution of paraformaldehyde. When the dissolution was done at a high temperature and pH, the Cannizzaro reaction (in which 1 mol of formaldehyde is oxidized to formic acid and the other mole is reduced to methanol)¹⁴ apparently took place, as indicated by the solution's brownish color. To prevent this, the dissolution temperature had to be decreased to 50°C; therefore, the first step's temperature will be left unchanged.

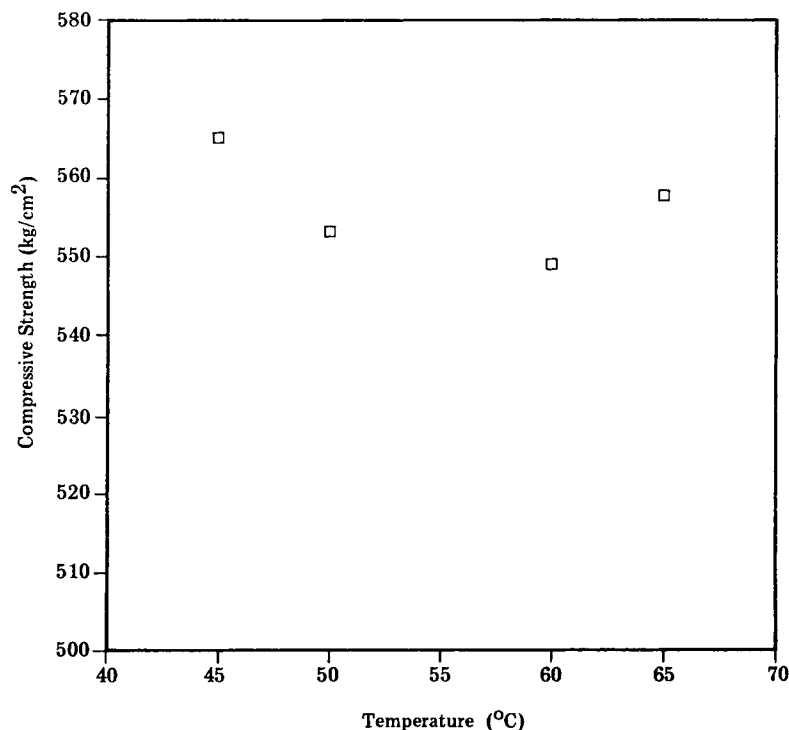


Fig. 1. The effect of changing temperature in the first step on the properties of the resins.

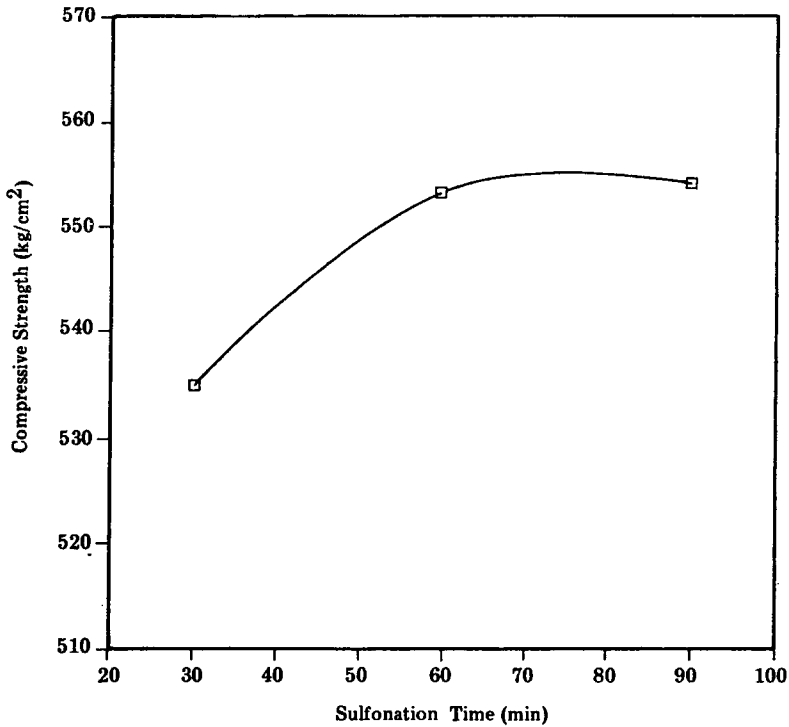


Fig. 2. Effect of sulfonation time of the second step on the properties of prepared resins.

Effect of t_2

In the second step, the sulfonation time (t_2) was varied from 30 to 90 min. Figure 2 shows the effect on the compressive strength of concrete treated with resins whose t_2 are 30, 60, and 90 min. Increasing t_2 to 90 min does not improve the 28-day compressive strength; but decreasing t_2 to 30 min results in a lower compressive strength. Therefore, t_2 will remain fixed at 60 min.

Effect of T_3 , t_3 , and pH_3

Varying the temperature, time, and pH of the third step is both critical (since polymerization occurs during this step) and challenging because of the interaction among the three variables. If one chooses three values for each variable, one has to conduct 27 experiments to get all possible permutations. But, if one resorts to the "fractional experimental design" concept, which is based on multivariate statistical analysis,¹⁵ the number of necessary experiments can be cut considerably. The basic idea here is to select an orthogonal subset of experiments that can give the needed information.

Table II shows variations in reaction conditions along with corresponding water reduction and compressive strength data obtained from a 2% dose of the resin. Increasing the reaction temperature (T_3) from 50 to 60°C leads to the reduction from (110 to ~ 80 min) in the reaction time necessary to obtain the same properties as those of the resin in the standard cycle (resin 10). When the temperature was further increased to 70°C (resin 7), the reaction

TABLE II
Effect of Varying Third Step Conditions on the Superplasticizing Properties
of Resins

Resin no.	Reaction conditions			2% Dose		Compressive strength (kg/cm ²)		
	T_3 (°C)	t_3 (min)	pH ₃	Slump (mm)	Water reduction (%)	3 days	7 days	28 days
1	60	110	3.5	50	25	465	492	580
2	60	70	3.5	30	21	409	472	542
3	60	70	4.5	35	20	405	423	514
4	60	110	4.5	30	21	398	457	518
5	70	110	3.5	50	25	438	473	568
6	70	70	3.5	75	25	456	492	574
7	70	30	3.5	55	25	402	476	543
8	70	110	5.5	35	20	405	449	539
9	70	110	4.5	35	19	423	470	525
10	50	110	3.5	45	25	427	475	553

time was even shorter; 30 min was almost enough time to reproduce resin 10's properties. Resin 7 gave the same water reduction as resin 10, but a slightly lower compressive strength. Since the reaction time reduction was so large, resin 7 was rerun; similar properties were obtained. One possible explanation for this time reduction is that the reaction rate at 70°C is much higher than 60°C. If one assumes that the viscosity build up in the third step is related to the kinetics of the reaction, then the viscosity data seems to support and confirm this explanation. Figure 3 shows the viscosity buildup in the third step when T_3 is 60 and 70°C. Obviously, a time of 50 min at 70°C is enough to build up the viscosity to the same value (8 cP) as 90 min at 60°C. Therefore, one would expect a huge decrease in reaction time.

The effect of pH₃ on the resin properties can also be seen from Table II. When the reaction temperature is 60°C, resins whose pH₃ is 3.5 (resins 1 and 2) perform better than those with a pH₃ of 4.5 (resins 3 and 4). The same observation is repeated for a reaction temperature of 70°C (resins 5–9). Attempts to further reduce pH₃ to 2.5 were not successful since resin gelation occurred immediately after the pH₃ was lowered to below 3.0.

In this discussion, time was treated as a dependent variable, i.e., we varied T_3 and pH₃ and examined the time needed to build up the solution's viscosity to a value comparable to that of the standard preparation resin (resin 10). Such a viscosity buildup is apparently essential to obtain desirable superplasticizing properties. This conclusion is supported by the viscosity–time data collected from various resin preparations. For example, resins whose pH₃ is 4.5 (or 5.5) do not perform as well as those with a pH₃ value of 3.5, as can be seen from water reduction and compressive strength data (Table II). When the viscosity–time curves for resins of different pH₃ values are plotted (Fig. 4), it is seen that, with a pH₃ of 4.5, there is not enough viscosity buildup even at a reaction temperature of 70°C.

Based on these data, one concludes that pH₃ should be fixed at 3.5 and T_3 should be increased to 70°C, thus reducing t_3 to 50 min.

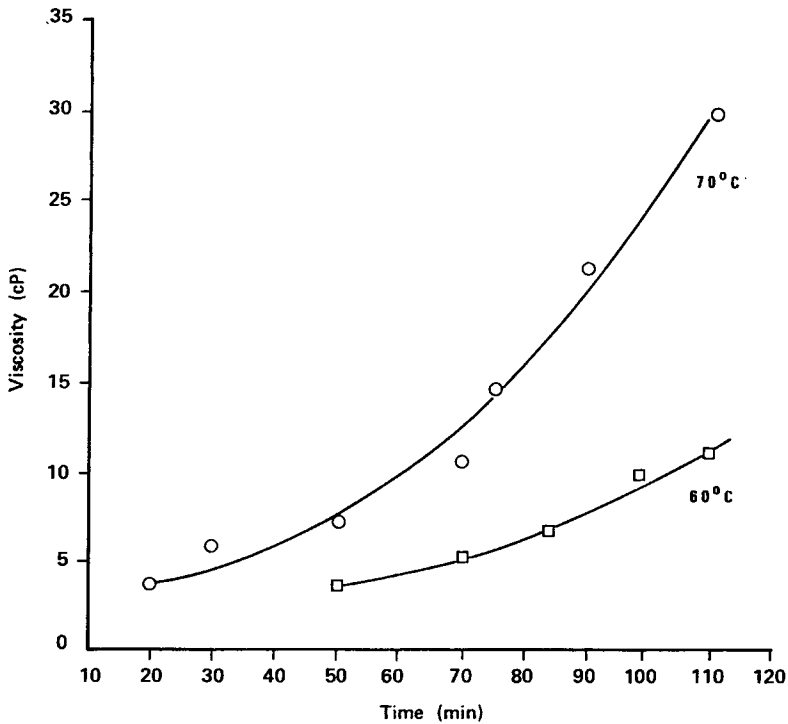


Fig. 3. Viscosity buildup in the third step with temperature changes.

Effect of T_4

In the fourth step, reducing the temperature (T_4) might affect not only the resin's effectiveness as a superplasticizer, but it could also affect its stability.¹² Therefore, in addition to examining the compressive strength of the concrete, a stability test was conducted. The stability test involves placing a resin in an oven at 60°C for 2 weeks and continuously monitoring the changes in its pH value. Figure 5 shows that two resins whose T_4 are 80 and 75°C have a corresponding change in pH of 8 and 10.8%. The resin reduction and compressive strength data (Table III) for the two resins (resin 10, $T_4 = 80^\circ\text{C}$; resin 11, $T_4 = 75^\circ\text{C}$) show a minor drop in the compressive strength when T_4 is lowered to 75°C. Therefore, a 5°C decrease in the fourth step's temperature has an impact on the stability of the resin and the strength of the concrete. Lowering T_4 will not be profitable, so that T_4 will be left unchanged.

Thus, the optimized process cycle will preserve the first, second, and fourth step conditions of the standard process, but T_3 and t_3 will be changed from 50°C and 110 min to 70°C and 50 min, respectively. Figure 6 compares the old (standard) and the optimized process cycles. In terms of process time, a 32% savings was achieved. The old process lasted ~ 5.5 h, and the new one spans 3.7 h. In addition to time savings, energy consumption was reduced by at least 25%. Detailed energy balance calculations will not be presented here; a qualitative argument will be used instead. The basic difference between the

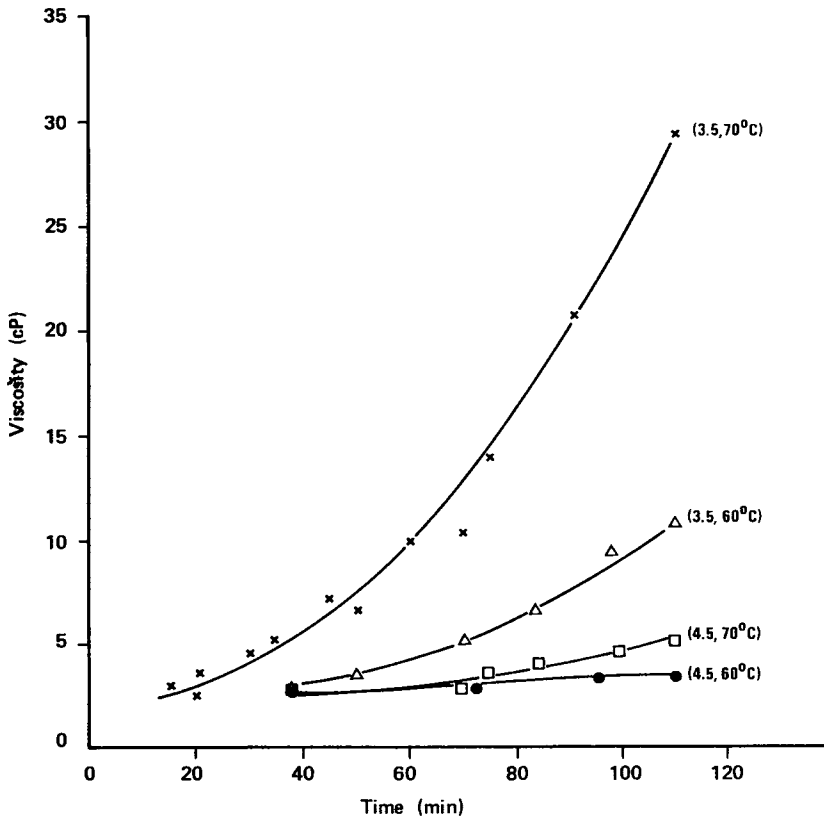


Fig. 4. Viscosity buildup in the third step with pH and temperature changes.

two processes is in the third step whose energy requirement is given by

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \quad (1)$$

$$= m \text{ cp}(T_3 - 80) + [h_i A_i (T_3 - T_w)] t_3 + m \text{ cp}(80 - t_3) \quad (2)$$

where ΔH_1 is the heat that must be removed to bring the reaction mixture's temperature from 80°C to the polymerization temperature, ΔH_2 is the amount of heat required to keep the reaction mixture at T_3 , and ΔH_3 is the heat needed to heat the reaction mixture back to 80°C . In the standard process T_3 was 50°C , and in the new process T_3 is 70°C . The cooling requirement of the new process is $1/3$ of that of the old, as can be seen below:

$$\frac{\Delta H_{1N}}{\Delta H_{10}} = \frac{T_{3N} - 80}{T_{30} - 80} = \frac{1}{3} \quad (3)$$

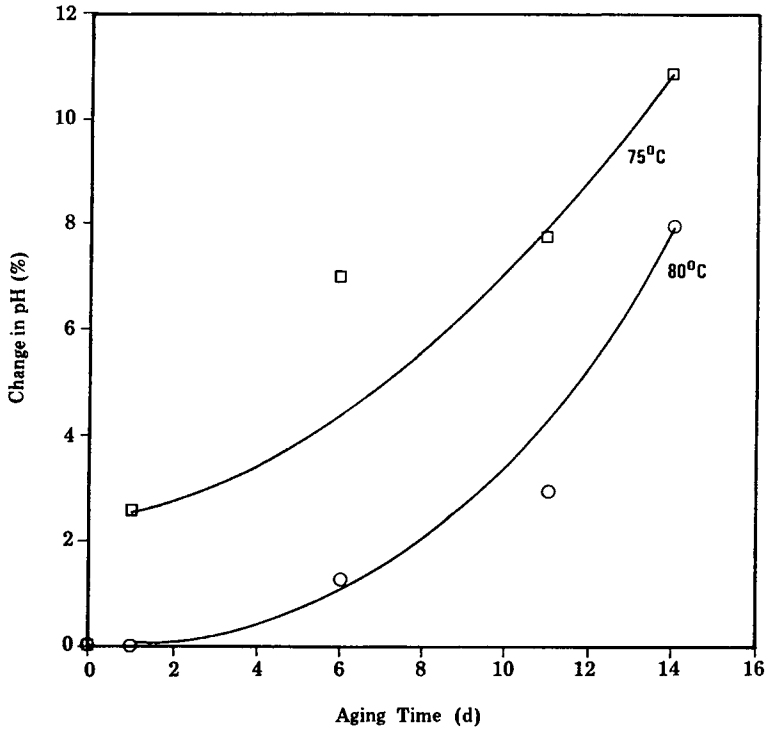


Fig. 5. Change in pH with aging time and different temperatures.

As for the heating requirement,

$$\frac{\Delta H_{2N}}{\Delta H_{20}} \sim \frac{T_{3N} - T_{wN}}{T_{30} - T_{w0}} \frac{t_{3N}}{t_{30}} = \left(\frac{2}{1.5} \right) \left(\frac{50}{110} \right) = 0.6 \quad (4)$$

and

$$\frac{\Delta H_{3N}}{\Delta H_{30}} = \frac{80 - 70}{80 - 50} = \frac{1}{3} \quad (5)$$

The wall temperatures of both processes were measured and were found to be close to that of the bulk, and h_i of the standard and the new processes

TABLE III
Effect of Lowering the Fourth Step Temperature on the Properties of Resins

Resin no.	T_4 (°C)	Slump (mm)	Water reduction (%)	Compressive strength (kg/cm ²)		
				3 days	7 days	28 days
11	75	65	25	411	460	534
10	80	45	25	427	475	553

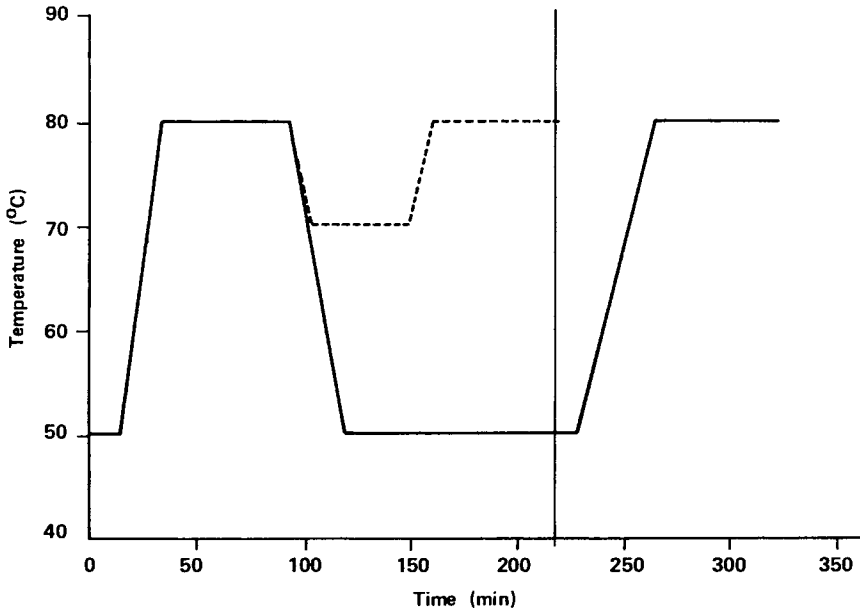


Fig. 6. The standard (—) and the optimized (---) process cycles.

were assumed to be equal. Again, the heating requirement of the optimized process is less.

CONCLUSIONS

The sulfonated melamine-formaldehyde preparation procedure was carried out successfully in a 10-L reactor. The process for producing this resin was optimized by increasing the third step's temperature and decreasing its time. Thus, the transient cooling and heating times, which accounted for 25% of the standard process's time, were significantly reduced and process energy consumption was considerably decreased. In terms of its superplasticizing properties, the product of the optimized cycle was as effective as the resin from the standard process.

APPENDIX: NOMENCLATURE

A_i	surface area of the reactor based on the inside diameter (m^2)
c_p	heat capacity of the reactor contents ($kJ/kg \text{ } ^\circ C$)
h_i	convective heat transfer coefficient of the reactor contents ($kJ/m^2 \text{ } ^\circ C \text{ h}$)
ΔH_i	enthalpy change during the i th step (kJ)
ΔH_{iN}	enthalpy change during the i th step of the optimized (new) process (kJ)
ΔH_{i0}	enthalpy change during the i th step of the saturated process (kJ)
m	mass of the reactor contents (kg)
T_i	temperature of the i th step ($^\circ C$)
T_w	wall temperature ($^\circ C$)
t_3	time duration of the third step (h)

The authors acknowledge with appreciation the financial support of the Kuwait Foundation for the Advancement of Sciences. This is Publication No. KISR2379, Kuwait Institute for Scientific Research, Kuwait.

References

1. P. Trambouze, *Chem. Eng.*, **72**, 122 (1979).
2. R. R. Corpstein, R. A. Dove, and D. S. Dickey, *Chem. Eng. Prog.*, **75**(2), 66 (1979).
3. R. Katzen, *Chem. Eng.*, **61**, 95 (1968).
4. Cement and Concrete Association, *Superplasticizing Admixtures in Concrete*, Slough, U.K., 1978.
5. A. Aigensberger and P. Bornmann, U.S. Pat. 3,941,739 (1976).
6. R. W. Auten, *Pap. Trade J.*, **127**, 45 (1948).
7. S. Pieh and H. Czepel, U.S. Pat. 4,272,430 (1981).
8. G. E. Sheldrick, U.S. Pat. 4,444,945 (1984).
9. S. M. Lahalih and M. Absi-Halabi, U.S. Pat. 4,677,159 (1987).
10. M. Absi-Halabi, S. Lahalih and T. Al-Khalid, *J. Appl. Polym. Sci.*, **33**, 2975 (1987).
11. S. M. Lahalih, M. Absi-Halabi and K. F. Shuhaibar, *J. Appl. Polym. Sci.*, **33**, 2997 (1987).
12. S. M. Lahalih and M. Absi-Halabi, *J. Appl. Polym. Sci.*, **33**, 3005 (1987).
13. J. G. Lowenstein, *Chem. Eng.*, **78**, 62 (1985).
14. I. L. Finar, *Organic Chemistry, Vol. 1, The Fundamental Concepts*, Longmans, London, 1967.
15. R. E. Miller, *Chem. Eng.*, **79**, 113 (1986).

Received January 25, 1988

Accepted April 14, 1988