

MIXING ALTERNATIVES FOR THE POLYESTER MICROENCAPSULATION PROCESS FOR IMMOBILIZATION OF HAZARDOUS RESIDUALS*

R. MAHALINGAM**, P.K. JAIN*** AND R.K. BIYANI†

*Department of Chemical Engineering, Washington State University, Pullman, WA99164
(U.S.A.)*

and R. V. SUBRAMANIAN

*Department of Materials Science and Engineering, Washington State University, Pullman,
WA 99164 (U.S.A.)*

(Received December 3, 1980; accepted February 1, 1981)

Summary

The evaluation of two mixing methods, as alternatives to impeller mixing in the polyester immobilization of hazardous residuals, is described. These are (1) emulsification of the toxic waste solution into the polyester resin by air sparging and (2) mixing of neat polyester resin with volume reduced wastes in a rotary drum type mixer.

The evaluation in the first method is in terms of time for emulsification, viscosity and droplet size distribution, and time for emulsion curing, as compared to low- and high-speed impeller mixing. In the second method, the discussion is limited to the time and nature of solidification.

Introduction

A basic approach in waste management is to develop processes for the conversion of hazardous residuals in the form of liquids or semi-solid sludges into solids for safe handling, transportation and storage, with minimal potential for contamination of the environment. Immobilization [1] of the waste at a plant site is primarily concerned with the incorporation of the waste into a solidification agent, the essential operations involved being waste collection, pre-treatment and mixing-in of the solidification agent, followed by packaging and handling for ultimate disposal. Pretreatment is directed towards waste volume reduction by evaporation or dewatering and

* Paper presented at the A.I.Ch.E. 89th. National Meeting, Portland, Oregon, August 1980, in the Symposium Session on "Chemical Engineering Aspects of Reprocessing, Recovered Product Conversion, and Waste Solidification".

**To whom correspondence should be addressed.

***Bechtel Corporation, San Francisco, CA 94119 (U.S.A.)

†DuPont, Fort Madison, Iowa 52627 (U.S.A.)

addition of chemicals for pH adjustment and foam prevention. The blending of the waste with the binder, followed by solidification, however, are the most important stages of the immobilization process. Some common binders used are bitumen, hydraulic cement, absorbers and organic polymers.

Background

The feasibility of immobilizing hazardous wastes in a polyester matrix has been demonstrated both in the laboratory and on the pilot plant [2–14]. By finely dispersing the waste solution, slurry or solids into a water-extensible polyester resin, each waste particle or droplet is individually encapsulated inside a thin skin of the resin matrix. Addition of an initiator polymerizes this resin matrix to produce a rigid monolithic solid suitable for land burial.

For successful commercialization of the polyester process, there is a need for studies directed towards adapting the equipment used in the existing commercial waste disposal processes to the newly developed polyester process. Furthermore, if 100% retention of a waste for its hazardous lifetime is the goal of shallow land disposal, better waste processing techniques must be adopted.

The work described here evaluates two mixing methods as alternatives to the impeller mixing used in the pilot plant. The time and nature of solidification are evaluated, and where applicable, viscosity and droplet size distribution are also evaluated. These, in turn, are used to interpret the leach characteristics of the monolith.

General description of pilot plant runs

The pilot plant (Fig.1) and the Process Flow sheet (Fig.2) are described in detail elsewhere [5, 6, 8, 10, 11]. A brief outline of the general operation scheme of the pilot plant is given here (Fig.3). To start off, a batch emulsion in the desired ratio of resin to waste is prepared in the emulsification tank (item 8, Fig.2). Continuous streams of resin and waste in the correct propor-

Fig.2. Pilot plant flow sheet — Polyester process for immobilization of hazardous wastes

- | | |
|---|--|
| 1. Waste preparation tank | 12. a, b Ball valves with pneumatic actuator |
| 2. Steam coil | 13. Resin tank |
| 3. Variable speed paddle mixer | 14. Resin metering pump |
| 4. Variable speed TEEL screw pump | 15. a, b Diaphragm valves |
| 5. Rotameter | 16. 4-Way solenoid valve |
| 6. 3-Way ball valve with pneumatic actuator | 17. Timer |
| 7. a, b Flow control valves | 18. Solidification can |
| 8. Emulsification tank | 19. Variable speed Helicone mixer |
| 9. Variable speed Turbon mixer | 20. Diaphragm pump |
| 10. Air motor | 21. Initiator tank |
| 11. Variable speed MOYNO screw pump | |

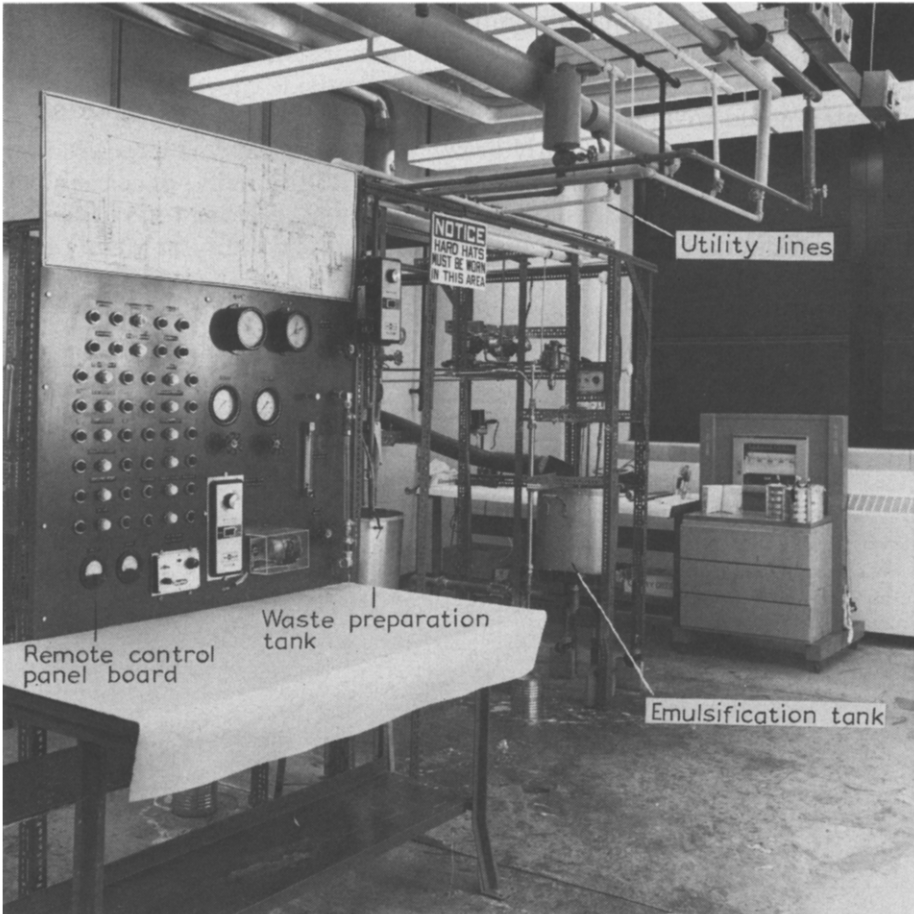
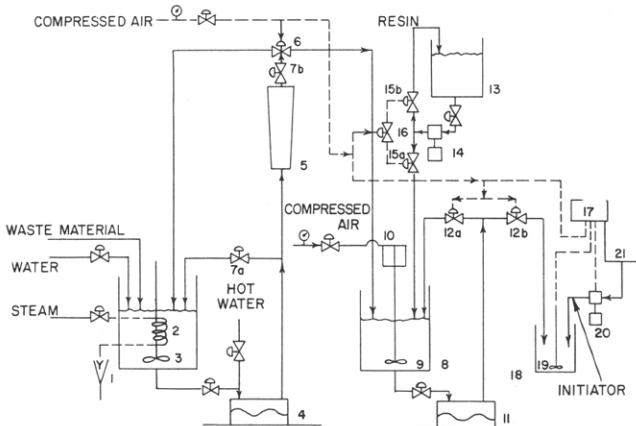
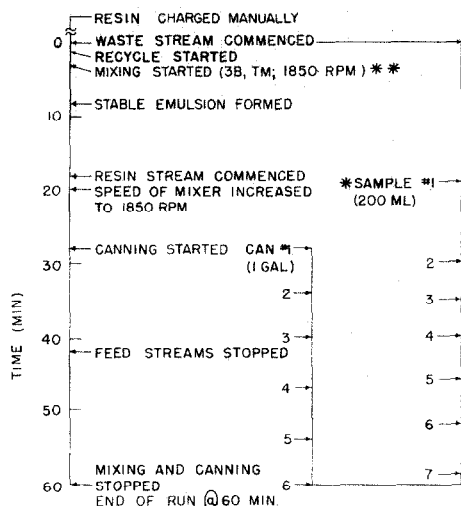


Fig.1. Pilot Plant for the Polyester Immobilization of Hazardous Wastes.



tions are then fed into this emulsion base in the emulsification tank. The initial batch emulsion preparation step here is more for convenience and in a full-scale operation, a batch emulsion prepared outside the "hot" zone, with fresh water, could well be used as a starter.

Emulsion samples are frequently drawn for rheological characterization and for droplet size distribution determination. Additionally, once canning is started, as shown in Fig.3, samples for subsequent leaching tests of the solidified product are also withdrawn and allowed to solidify in 40 ml plastic vials [8].



* Emulsion samples collected for viscosity measurements.

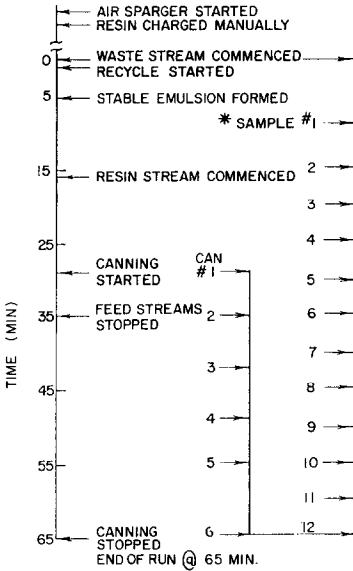
** Type of mixer, rpm

Fig. 3. Operations schedule for run 34.

Emulsification by air sparging

One of the objectives in the process development studies has been to examine alternatives with a view towards optimization on costs and operating conditions. The key step in the polyester process is the emulsification. Techniques for emulsification, involving lower capital cost and possibly less energy demand than the Turbon Mixer (as used in Run 34, Fig.3) [8, 11], are therefore sought. There is a commercial design currently available using air mixing in the urea-formaldehyde waste solidification process. Based on this precedent, an air sparger consisting of two circular turns of 1/2 inch copper tube, with 20 perforations of 0.125 inch diameter facing inward and with 1.3 inch spacing between the perforation was fabricated and installed in the emulsification tank (item 8, Fig.2). Design calculations on the air sparger are presented in the Appendix.

The effectiveness of the above air sparger was examined in Runs 00 and 37 (Tables 1 and 2). The waste used was 20% by weight sodium sulfate solution, in a waste to resin weight ratio of 65:35. The operations were similar to the general description given earlier, the only exception being the replacement of the Turbon Mixer 3B by the air sparger. The sequence of operations in Run 37 is presented in Fig.4.



* Emulsion samples collected for viscosity measurements.

Fig.4. Operations schedule for run 37.

TABLE 1

Preliminary evaluation of air sparger for emulsification

Run number	00
Waste used	Sodium sulfate, 20% by weight
Resin used	Aropol WEP 661-P
Planned waste to resin ratio (wt. basis)	50:50
Initiator used	Lupersol Delta-X
Mixer type and speed	Air sparger used
Quality of emulsion	Stable and uniform
Remarks	Batch run; air sparger for mixing; emulsification good and rapid. Large vol. of vapor evolved during emulsification.

TABLE 2

Results for run numbers 33 and 34 using Turbon mixer at different speeds and for run number 37 using air sparging

Item	Run number		
	33	34	37
Waste used	Sodium sulfate 20% by weight	Sodium sulfate 20% by weight	Sodium sulfate 20% by weight
Resin used	Aropol WEP 661-P	Aropol WEP 661-P	Aropol WEP 661-P
Planned waste to resin ratio (wt basis)	65:35	65:35	65:35
Initiator	Lupersol Delta-X	Lupersol Delta-X	Lupersol Delta-X
Temperature of waste solution, °C	55	55	41
Temperature of resin, °C	20	20	20
Flow rate of waste solution, g/min	1368 for 19.4 min then 260	1368 for 18.5 min then 260	1368 for 16 min then 260
Flow rate of resin, g/min	140	140	140
Batch of resin, kg	14.3	13.4	12.0
Flow period for waste and resin, min	25	24	19
Mixer type and speed	3B, Turbon 200 r.p.m.	3B, Turbon 1850 r.p.m.	Air sparger, 4.1 cu ft/min/ sq ft of tank cross section (Appendix)
Canning cycle time, min	6	6	6
Filling time per can, min	1	1	1
Amount of initiator per can, ml	6-14	6-14	6-14
Duration of mixing in can, min	3	3	3
Time for emulsification, min	9	8	5
Type of mixer for initiator	Helicone	Helicone	Helicone
Total number of cans	6	6	6
Density of waste, g/ml	1.14	1.14	1.14
Density of resin, g/ml	1.02	1.02	1.02
Waste to resin ratio achieved, (wt basis)	66:34	66:34	65:35

TABLE 2 (continued)

Item	Run number		
	33	34	37
<i>Results</i>			
Quality of emulsion	Uniform, viscous, and stable.	Uniform, viscous, and stable.	Uniform, viscous, and stable.
Initiator concentration, g/100 g of resin in emulsion	0.49-1.15	0.49-1.15	0.4-1.20
Peak temperature, °C	*	54-71	46-80
Time to reach peak exotherm, min	*	22-36	18-40
Compressive strength, N/mm ²	11.6 ± 0.43	14.9 ± 0.53	12.6 ± 0.23
% leached in 84 days	0.42-1.8	0.57-0.86	**
Characteristics of the solidified product	Good encapsulation and good mechanical integrity. Good curing and hard set. Uniform appearance with no free water.	Good encapsulation and good mechanical integrity. Good curing and hard set. Uniform appearance with no free water.	Good encapsulation and good mechanical integrity. Good curing and hard set. Entrapped air bubb but no free water.

*The peak exotherm and the time to peak exotherm were not recorded since the multipoint temperature recorder was out of service.

**Leachability was not evaluated.

Immobilization by rotary drum mixing

There currently exists an integrated commercial system for the solidification of hazardous wastes, using Type II or regulated set cement. In this system, applicable for example to radwastes, the radwaste slurry is pumped to the decanting tank. Here, the solid material settles to the bottom, and the excess water is siphoned off. A predetermined quantity of water over the settled material is retained for proper mix with the cement. A tank mixer is then operated to homogenize the slurry. The operator determines the quantity of waste per disposal drum and sets the pump selector switch to the proper mode. Mixing weights are added to the drum along with the dry cement. The automatic cycle is then started. The drum is uncapped, filled, capped and transferred to a tumbling or rolling station where the contents are mixed. The drum is then weighed and its radiation level measured. Next, the drum is transferred by crane to the decay pit or directly to a truck.

In order to simulate the above system, a Model KCB-10 drum rotator, with a 1/6 h.p. motor, was used (Fig.5). The 1-gallon can, mounted on a rollers/belt-and-pulley arrangement was rotated at 45 r.p.m. Two types

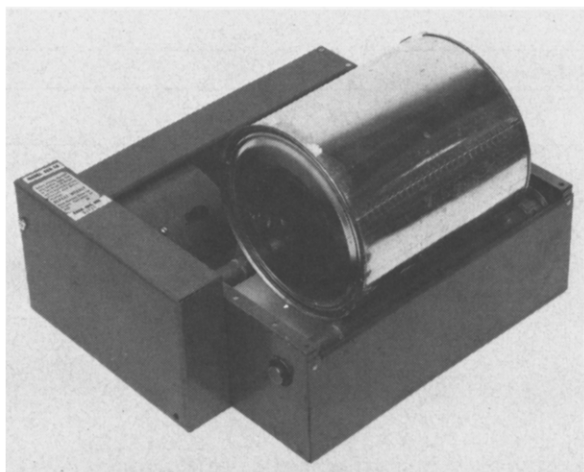


Fig.5. Set-Up for Rotary Drum Mixing.

of runs were carried out (Runs 51, 52). In run 51, the polyester resin and solid waste were premixed in the drum; next, the catalyst was added and the drum mixed again. In Run 52, all three constituents were fed in at the same time, the drum sealed and then rotated.

Results and discussion

In Table 1, the results from a feasibility run (Run 00) for emulsification by air sparging are presented. This was a batch run, with a waste to resin weight ratio of 50:50. As expected, air sparging entrains some amount of volatile constituents (styrene) from the batch.

In Table 2 the performance of the air sparger in emulsification (Run 37) is compared with that of Turbon mixers operated at low (Run 33) and high (Run 34) r.p.m. values. In all cases, the immobilization appears to be good, with uniform dispersion and with good mechanical integrity.

A comparison of the time for emulsification shows that an emulsion is formed more rapidly by air sparging than by using the Turbon mixer. This could be attributed to the absence of dead pockets as a result of complete mixing and vigorous agitation of the batch of resin by the rising air bubbles even before the waste stream addition was started.

The emulsion formed by air sparging was uniform, viscous and stable, and after polymerization, resulted in a well cured, rigid solid with good encapsulation of the waste. The encapsulation can be seen in the scanning electron micrograph shown in Fig.6b. The air sparging, however, appears to have one major drawback, in that a significant amount of air dissolves in the emulsion. This air remains trapped in the form of bubbles in the solidified product (Fig.6a) [8, 10]. The micrographs [8, 10] from Run 33 (low r.p.m.) and from Run 34 (high r.p.m.) are presented here for comparison (Fig.7 and 8). As can be seen, the droplet sizes are higher in the low r.p.m. case.

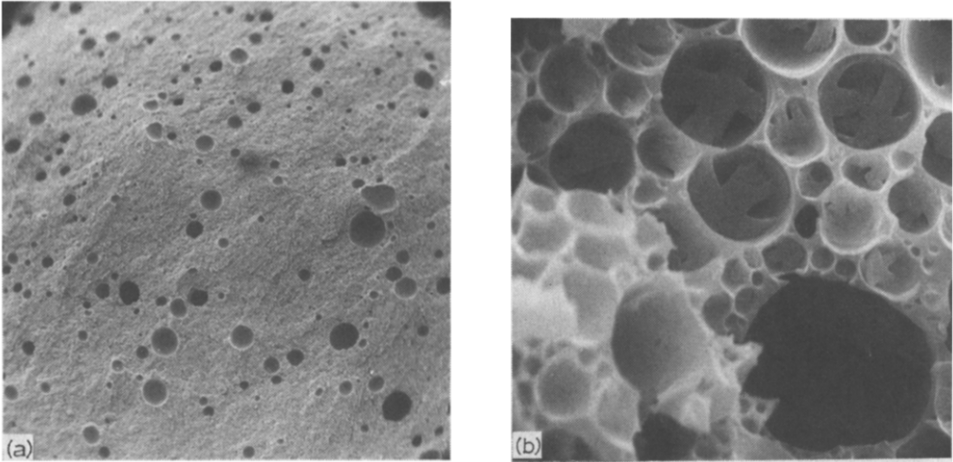


Fig. 6. Scanning electron micrographs of immobilized wastes — Emulsification by air sparging (Run 37). (a) 20% Sodium Sulfate Solution — Run 37 (Magnification 12). (b) 20% Sodium Sulfate Solution — Run 37 (Magnification 3000).

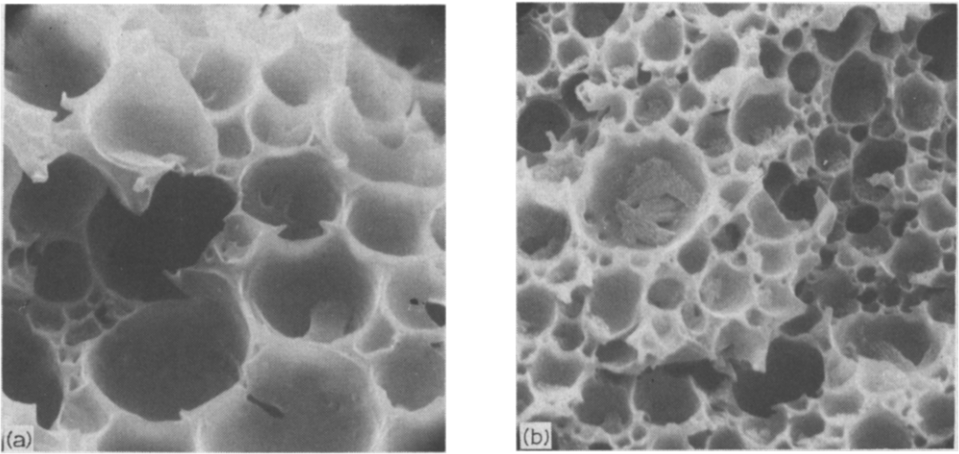


Fig. 7. Scanning electron microscopy of immobilized wastes — Emulsification by Turbon mixer (Low r.p.m.) (Run 33). (a) Sample 33-3 (Magnification 3000). (b) Sample 33-6 (Magnification 3000).

The variation in droplet size under various agitation conditions also accounts for variations in the measured viscosity [5, 6, 8, 11]. This is seen from Figs.9—11. The viscosity in Runs 33 and 37 are markedly lower than in Run 34. It is seen, however, that the viscosity in air sparging (Fig.9) is slightly higher than in low-r.p.m. Turbon mixing (Fig.10), indicating a somewhat higher shear for the conditions used in the runs.

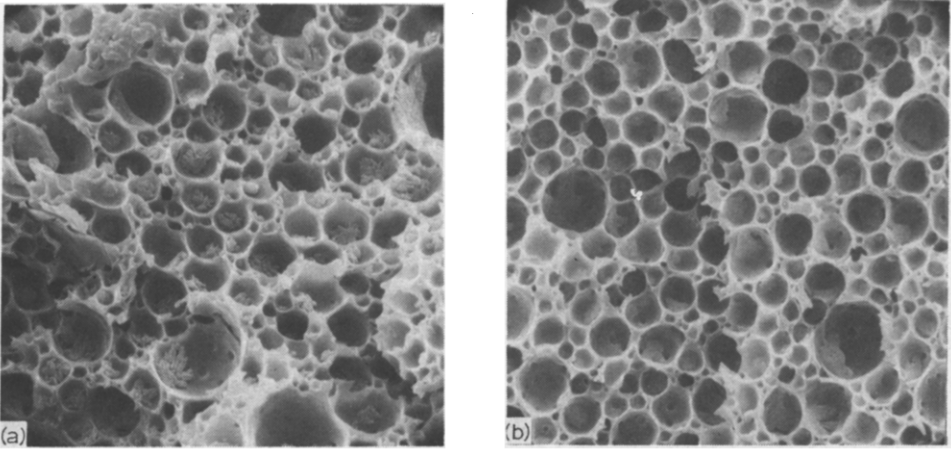


Fig.8. Scanning electron micrographs of immobilized wastes – Emulsification by Turbon mixer (High r.p.m.) (Run 34). (a) Sample 34-1 (Magnification 3000). (b) Sample 34-2 (Magnification 3000).

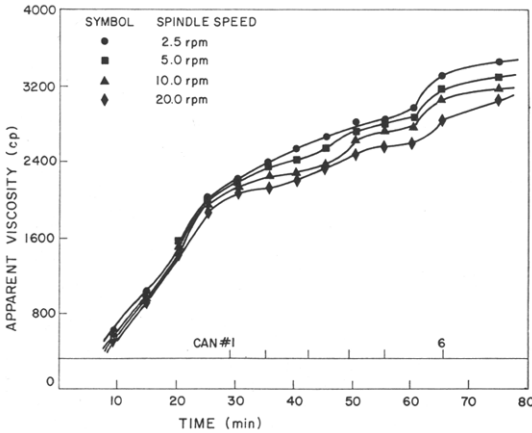


Fig.9. Apparent viscosity versus time elapsed since the commencement of emulsification – Run 37.

The droplet sizes in Runs 33 and 34, and the corresponding leach characteristics of the solidified product with respect to sodium ion, are shown in Table 3 [8, 10]. It is observed that the leach characteristics are superior for smaller particle size, i.e., for the case where emulsification has been achieved under high r.p.m. conditions. In the case of the solidified product from Run

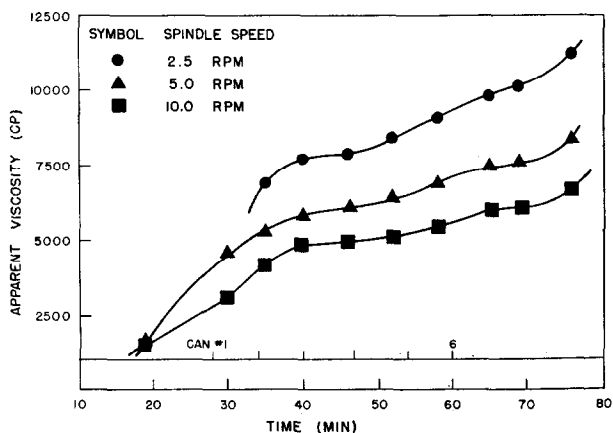
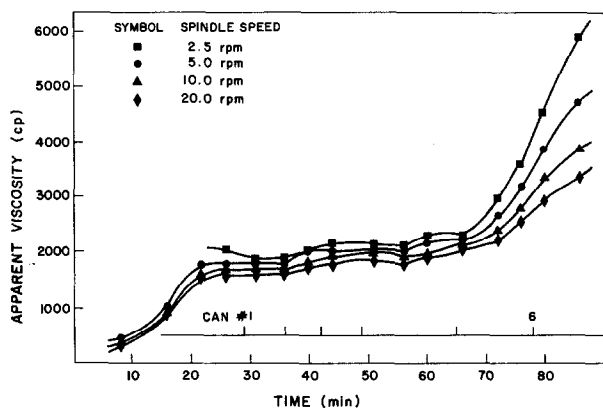
Fig.10. Apparent viscosity versus time elapsed since the commencement of emulsification – Run 33.

Fig.11. Apparent viscosity versus time elapsed since the commencement of emulsification – Run 34.

TABLE 3

Comparison of droplet size with viscosity and leachability — Run numbers 33 and 34

Sample number	Average particle size (μm)	Viscosity (5 r.p.m.) (cp)	Cumulative % leached out at the end of 84 days	Differential leachability between 70 & 84 days ($\text{cm} \times 10^4$)
33-1	4.9 \pm 0.7	1790 (91° F)	1.8	1.30
33-2	3.8 \pm 0.4	1800 (92° F)	1.59	0.63
33-3	4.0 \pm 0.4	2060 (91° F)	1.68	0.63
33-5	3.9 \pm 0.5	2250 (88° F)	1.75	0.78
33-6	2.0 \pm 0.5	3500 (85° F)	0.42	0.28
34-1	1.46 \pm 0.14	4000	0.57	0.28
34-2	1.20 \pm 0.10	5100	0.54	0.36
34-4	1.30 \pm 0.13	6050	0.86	0.73
34-6	1.15 \pm 0.10	7000	0.73	0.43



37, it could be expected that the leach characteristics will be similar to those from Run 34.

The presence of air (oxygen) in the emulsion could normally be expected to retard polymerization and reduce the compressive strength of the final solid. The results for Run 37, however, show that the time to peak exotherm of 18–40 minutes (Fig. 12) compares well with 22–36 minutes for Run 34 (Fig.13), for corresponding quantities of the initiator. This shows that sparging did not introduce a significant amount of oxygen to materially affect the polymerization. The compressive strength of samples from Run 37 is close to the average of those reported for Runs 33 and 34 (Table 2). Emulsion formation by sparging does not seem to have adverse effects.

In Table 4, the data obtained with tumbling mixers for the immobilization of volume-reduced wastes are presented. It is evident from Runs 51 and 52 that, for the same conditions of waste to resin ratios and r.p.m. values, a higher catalyst concentration favors uniform solidification. This is explained on the basis that this higher concentration enables rapid gelling, and hence a rapid increase in viscosity, thus preventing rapid settling out of particles which leads to a more uniform product. The results also indicate that adequate mixing does exist in such tumbling mixers.

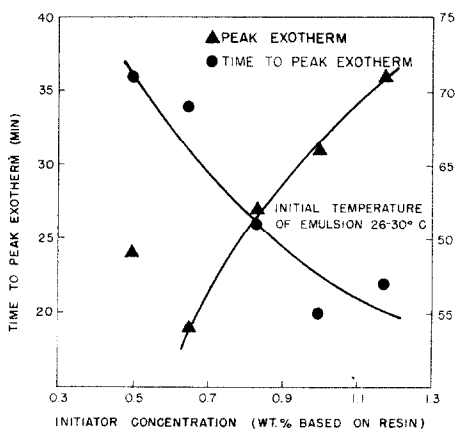
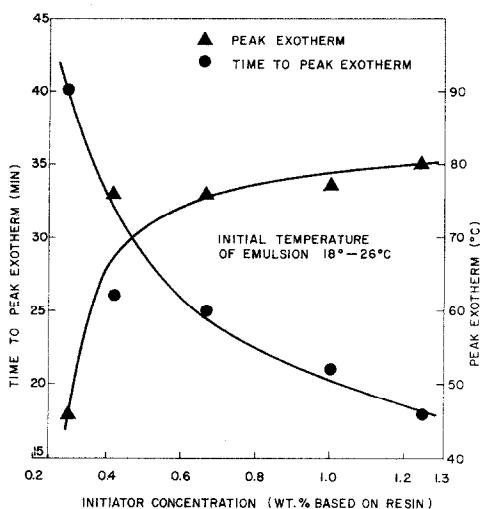


Fig. 12. Effect of initiator concentration on peak exotherm and time to peak exotherm — Run 37.

Fig. 13. Effect of initiator concentration on peak exotherm and time to peak exotherm — Run 34.

TABLE 4

Evaluation of tumbling mixer for volume reduced waste

	Run number	
	51	52
Waste	Sodium sulfate (solids)	Sodium sulfate (solids)
Resin	Aropol WEP 661-P	Aropol WEP 661-P
Planned waste to resin ratio	50:50	50:50
Initiator	Lupersol Delta-X	Lupersol Delta-X
Mixer and speed	Tumbling mixer; 45 r.p.m.	Tumbling mixer; 45 r.p.m.
Quality of emulsion	—	—
Remarks	Rotary drum type mixing of 1 gal can; pebbles of size 1/4"—1/2" used; first resin and solid waste were mixed for 15 minutes, then catalyst (5 ml) added. After 30 minutes of mixing, no solidification seen, and solids were settling down. Next day only solidified resin was seen at the top.	Rotary drum type mixing of 1 gal. can; no. of pebbles increased. This time, resin, solid waste and catalyst (7 ml) were added together and then mixed. Solidification within 20 minutes. Solids were uniformly distributed. Not much settling seen.

Conclusions

The data from Runs 00, 33, 34, 37, 51 and 52 show that viable alternative methods of mixing the binder with the waste are available, and that existing commercial processes for waste immobilization, using these mixing techniques, could easily and profitably be switched over to the polyester process.

Acknowledgement

Portions of this research were supported by the National Science Foundation, under Grant Number ENV 76-06583.

Appendix

Design calculations for the air sparger

For a liquid depth of 3 ft (91.44 cm), Perry [15] recommends for "complete agitation," an air flow rate of about 3 (cu ft/min)/sq ft of tank cross-section and, for perforated-pipe spargers, an orifice size of 0.125 inch—0.5 inch. For our pilot plant, the orifice size chosen was 0.125 inch (0.32 cm).

A pipe size of 0.5 inch (1.27 cm) was chosen to ensure that the pressure drop down the length of the pipe was negligible compared with the pressure drop at the orifices — another design criterion.

To determine the number of orifices required, an exit air velocity of 2000 ft/min (610 m/min) was taken as the basis. The emulsification tank (1.25 ft diameter) has a cross section of 1.23 sq ft. Thus, the total air flow rate required is 3.69 cu ft/min. Each orifice has a cross section of 8.5×10^{-5} sq ft; therefore, if N represents the number of orifices:

$$N \times 8.5 \times 10^{-5} \text{ sq ft} \times 2000 \text{ ft/min} = 3.69 \text{ cu ft/min}$$

$$\text{or } N = 22$$

The sparger was designed with 30 orifices for the following reasons:

1. The liquid depth might be less than 3 ft.
2. At the start of the emulsification, the sparger is not completely submerged.
3. Conservative design in case the line air pressure dropped during experimentation, consequently reducing the exit air velocity.

References

- 1 R.M. Neilson Jr., Immobilization of set solid wastes at nuclear power plants. Paper presented at the Reactor Radwaste Management Workshop, New Orleans, Louisiana, January 1977.
- 2 R.V. Subramanian and R.A.V. Raff, Immobilization of low-level radioactive wastes, 80th National A.I.Ch.E. Meeting, Boston, September 7–10, 1975.
- 3 M. Juloori, Semi-continuous pilot plant studies on polymeric encapsulation of hazardous wastes, M.S. Thesis, Washington State University, 1976.
- 4 W.P. Wu, Encapsulation of hazardous wastes in a polyester matrix, M.S. Thesis Washington State University, 1978.
- 5 P.K. Jain, Pilot plant evaluation of polyester process for immobilization of hazardous wastes, M.S. Thesis, Washington State University, 1978.
- 6 R. Mahalingam, M. Juloori, R.V. Subramanian and W.P. Wu. Pilot plant studies on the studies on the polyester encapsulation process for hazardous wastes. Proceedings of the National Conference on Treatment and Disposal of Industrial Waste Water and Residues, Houston, Texas, April 26–28, 1977.
- 7 R.V. Subramanian, W.P. Wu, R. Mahalingam and M. Juloori. Polyester encapsulation of hazardous industrial wastes, Proceedings of the National Conference on Treatment and Disposal of Industrial Waste Waters and Residues, Houston, Texas, April 26–28, 1977.
- 8 R.K. Biyani, Optimization of process parameters and economic evaluations in polyester immobilization of hazardous wastes, M.S. Thesis, Washington State University, 1977.
- 9 Workshop on the Polyester Process for the Immobilization of Hazardous Wastes, Washington State University, 1977.
- 10 R.V. Subramanian and R. Mahalingam in: R.B. Pojasek (Ed.), Toxic and Hazardous Waste Disposal, Vol. I, Ann Arbor Science, 1979, Chap. 14.
- 11 R. Mahalingam, R.K. Biyani and J.T. Shah. Simulation of solidification temperature profiles in the polyester process for immobilization of hazardous wastes, Ind. Eng. Chem. Proc. Design Dev., 20 (1981) 85–90.

- 12 R.K. Biyani, R. V. Subramanian and R. Mahalingam, Polymerization with redox initiators, *J. Appl. Polym. Sci.*, 25 (1980) 1257—1260.
- 13 R. Mahalingam, R.K. Biyani, P.K. Jain and R.V. Subramanian, A techno-economic evaluation of current hazardous waste solidification processes, Report No. 78/13/27, Department of Chemical Engineering, Washington State University, 1978.
- 14 W.J. Bailey and R. Mahalingam, Immobilization of decontamination chemicals, Research Report, Department of Chemical Engineering, Washington State University, 1980.
- 15 R.H. Perry and C.H. Chilton, *Chemical Engineers' Handbook*, McGraw-Hill Inc., N.Y., 1973.