~~① R. Wetter~~ RAW
~~② W. Travers~~ Note Expatriation
~~③ L. Betts~~ JT
~~④ J. Lee~~
File
Solid Waste

TELEDYNE
ENERGY SYSTEMS
110 W. TIMONIUM RD.
TIMONIUM, MD. 21093
PHONE: 301-252-8220
TELEX: 8-7780
CABLE: TELISES

PROTECTIVE PACKAGING DIVISION

August 1, 1979

Refer to: PPI-WCH-181

Gentlemen:

Enclosed is a copy of our latest progress report, covering the period since the beginning of 1979. This issuance has been delayed, owing to our move to Maryland, but I believe you will find it both encouraging and enlightening.

Sincerely,

William C. Hall

William C. Hall
Division Manager

WCH:sb

TELEDYNE ENERGY SYSTEMS
PROTECTIVE PACKAGING DIVISION
Progress Report #6
July 23, 1979

The following is a chronological discussion of the continued research and development program pursued by the Protective Packaging Division (formerly PPI) of Teledyne Energy Systems.

The physical relocation of the company was accomplished during the month of February 1979. Subsequently, both laboratory and full scale experimentation was undertaken to:

1. Develop input parameters for successful solidification.
2. Upgrade successful 55-gallon drum demonstrations to successful 50 cubic foot liner demonstrations.
3. Formulate basic data for publication of a Process Control Program.
4. Investigate the effects of variances from prescribed parametric values.
5. Investigate alternate methods of agitation.

All of the above were successfully performed, and systems design has a firm bases upon which to proceed; however, additional work will continue, as it necessarily must in any dynamic program of systems optimization.

A general description of the process follows, for reference to the current state of the art, together with some description of typical laboratory experiments.

1. Chemical Solidification Components

   A. Urea-Formaldehyde Concentrate

      Component is 100.00 parts by weight of commercially available UF concentrate to which has been added 4.0 parts powdered proprietary additive. The proprietary additive aids in the gelling process and substantially reduces the water permeability of the billet. It is essentially insoluble and must be dispersed by agitation prior to using the UF concentrate mix for solidification.

1. Chemical Solidification Components (cont'd)

B. Catalyst Solution

Solution is prepared with agitation by dissolving the following chemicals in 50 parts tap water by weight:

50.0 parts technical grade prilled urea

15.0 parts standard grade granular ammonium sulfate

1.0 part proprietary additive (water-soluble powder)

When urea dissolves in water, substantial chilling occurs which prevents complete solution until the mix is heated back to ambient temperature. Pre-heating the water to about 175°F compensates for the cooling effect. The water soluble proprietary additive is a polymer modifier, and is reactive toward particular metal ions.

C. Storage

Both the UF concentrate and Catalyst Solution have indefinite shelf life under normal ambient storage conditions. The Catalyst Solution should be maintained above 60°F. to avoid precipitation of salts. The UF concentrate contains free formaldehyde which gradually vaporizes, especially at higher temperatures, so that the storage tank should be vented outside the working area. Temperatures above 100°F. may be tolerated without affecting chemical activity, but are not recommended.

2. Solidification Parameters

A. Radwaste Properties

(1) Temperature - Ambient to 120°F

Control of temperature (in conjunction with pH) is essential to assure formation of proper billet structure and adequate time for solidification chemicals to be completely added before gelation begins. Solidification in 55 gal. drums requires less time for chemical addition than for 50 cubic foot liners and cooling to ambient temperature after solidification is more rapid. These latter conditions may permit solidification of radwaste above 120°F.

A. Radwaste Properties (cont'd)

(2) pH - Moderately acid to neutral

Control of pH is best accomplished in a Waste Blending Tank to minimize the number of adjustments. Corrective reagents are technical grade aqueous 40% sodium hydroxide and 10% sulfuric acid or reasonable substitute concentrations.

The most common adjustment will be the addition of about 2% by weight of 40% sodium hydroxide to boric acid type radwaste. In this case, control of pH to 5.0-7.0 will prevent crystallization when cooling below 120°F. for required temperature control, and will moderate the solidification reaction rate. Also, the finished billet is less acidic and therefore, less likely to be corrosive.

Addition of 10% sulfuric acid is necessary to reduce high pH values and expend or react with certain ion-exchange resins. High concentrations of such resins, if untreated, will neutralize the acidity of the Catalyst Solution causing an unsatisfactorily slow test solidification. Corrective addition of acid reagent should be incremental and not continued after a definite decrease in pH has been accomplished.

It is to be emphasized that adjustment of the radwaste pH to a particular range should not be done automatically without regard to the composition of the material. Solutions of boric acid with significant amounts of other acidic radwaste substances such as citric acid may remain below a pH of 6 even after addition of an amount of the sodium hydroxide reagent that would normally adjust boric acid alone. A test solidification at this point should be performed to determine if more reagent is actually required.

B. Volume Ratio of Waste to Chemical Components

Tests have shown that the desired combination of billet dryness and hardness is best achieved using 1.25 volumes of aqueous radwaste to 0.5 volume each of the chemical components. This combination provides integrity of the polymer matrix even for room temperature solidifications.

Dewatered resin beads that are sufficiently spent by usage or by deliberate addition of reagent may be solidified with or without additional liquid radwaste. For the latter case, 1.5 volumes of dewatered beads are blended with 0.5 volume each of chemical components. Additional liquid radwaste should preferably be the boric acid type, with the volume of dewatered beads reduced by the volume of liquid radwaste to be added. (For example, 1.0 volume of dewatered beads mixed with 0.5 volume liquid radwaste.)

A used filter cartridge can be centrally suspended in a container before being covered by 1.0-1.25 volumes of boric acid radwaste and 0.5 volume each of chemical components. In no case should the undiluted chemical components be used to solidify the filter. Add 1.0 volume of flush water if necessary to provide the dilution needed for the desired control of the chemical reaction.

C. Mode

(1) Aqueous Liquids or Slurries

Solidification is accomplished by first transferring the required amount of conditioned waste liquid to the empty container. A short flush cycle then clears the line of waste material. Mechanical agitation or equivalent mixing is initiated, and the chemical components are sequentially added, preferably in less than 10 minutes. Agitation is continued until homogeneity is achieved and/or the viscosity is sufficient to permanently suspend any resin beads or other particulate solids. Mode variations include simultaneous addition of waste liquid and catalyst solution, or prior addition to the liner of the

catalyst in dry, granular form.

C. Mode (cont'd)

(2) Dewatered Resin Beads

Dewatered resin beads containing no other liquid radwaste cannot be effectively agitated. In this case the Catalyst Solution is first added alone to provide a fluid consistency. Agitation is initiated, and then the UF concentrate added. Continued agitation is necessary until thickening has progressed to where bead stratification will not subsequently develop.

(3) Used Filter Cartridges

Large objects such as used filter cartridges are remotely suspended in the container by means of disposable support mechanisms. Conditioned waste liquid, preferably boric acid radwaste, is then added, followed by the appropriate amount of solidification chemicals. The total volume of the mix should be sufficient to completely immerse the cartridge. Agitation is then required for a sufficient time to assure a homogeneous solidification.

3. Solidification Technology for Particular Wastes (Laboratory Observations)

A. Radwaste Chemicals

(1) Boric Acid is increasingly acidic at higher concentrations and temperatures. Addition of about 2% of 40% sodium hydroxide permits satisfactory laboratory solidification at a waste temperature of 120°F, and concentrations up to 20%, at which level some of the boric acid is present as a crystalline slurry.

(2) Sodium Sulfate interferes with desired billet formation and stability at concentrations above 12%. Solidification at 120°F. maximum, and in combination with boric acid is the preferred method of treatment at present; this is a continuing investigation.

A. Radwaste Chemicals (cont'd)

(3) Ion-Exchange Resin Beads when uniformly dispersed in a billet reinforce strength and absorb heat to reduce the exotherm during the gelling reaction. Unspent alkaline beads retard the polymerization reaction and may require direct neutralization by addition of sulfuric acid, or co-solidification with boric acid solutions.

(4) Potassium Chromate added at the 5% level to 10% boric acid solution did not affect solidification at 100°F. except to produce a blue-green color.

(5) Citric Acid as a 10% aqueous solution was adjusted to a pH of 3 with about 2.5% of 40% sodium hydroxide, and then solidified satisfactorily at 100°F. Adjusting to a pH of 4 required over 6% of the reagent and resulted in a slow solidification. Based on this behavior it will be necessary to check the laboratory solidification of waste liquids containing significant levels of citric acid before making any major pH adjustment.

(6) Potassium Chlorate added at the 5% level to 8% boric acid solution did not affect solidification at 100°F.

(7) "Tide" commercial detergent added at 2% concentration to 12% boric acid adjusted to 5-6.5 and a temperature of 115°F. did not affect solidification.

(8) "Turco 4502" (containing Potassium Permanganate) in 2.5% concentration in a solution of 10% boric acid and 4% sodium sulfate gelled very slowly at 115°F. Correction of pH to 5 with sulfuric acid permitted good solidification in 15 minutes.

(9) "Turco 4324" in 2.5% concentration in a solution of 10% boric acid and 4% sodium sulfate did not affect solidification at 115°F.

(10) Hydrocarbon Oil was solidified at room temperature without substantial fluid separation by mixing 1 volume of oil with 0.5 volume water and 0.5 volume each of chemical components.

During the month of June, a pilot plant was set up for full-scale 50 cubic foot solidifications. This involved the portable tanks utilized in the August 1978 testing performed at Three Mile Island. Since we are contracted to provide a modified solidification system, complete with Waste Blending Tank and the two-component UF process to several customers, it was an utmost necessity to demonstrate the ability to solidify in a full-scale liner.

Realizing that the ultimate installation would require immobilization by solidification of a disposable filter cartridge, analytical work was undertaken to determine the feasibility of air agitation of the solidification process, thereby avoiding the physical interferences which would be encountered by a mechanical agitator and the filter. This was reduced to hardware in the final demonstration.

A liner was modified to permit removal of sides and bottom following solidification to verify the billet integrity.

The air agitation was successful to the extent that adaptions were employed in our pilot plant to aid in mixing the simulated radwaste solution, in combining the powdered additive with the UFC liquid, and in preparing the urea-ammonium sulfate component.

During early June, several solidifications were undertaken, some successful, some not so successful, owing to variations in either equipment or parameters. For example, in two cases the air agitator came loose in the liner prior to completion of agitation, resulting in inadequate mixing of components. This was of benefit, in that it showed how essential proper mixing is, and indicated that many past problems in urea-formaldehyde field experiences could well be the result of inadequate mixing.

A sample of boric acid solution with 10% resin beads, when solidified with air agitation in a 50 cubic foot liner produced a dry solid, which, when cut open and broken up, revealed a uniform dispersion of resin beads, indicating thorough mixing.

High temperatures of radwaste in the liner verified what we had observed in the laboratory; namely, that high temperature hastens the reaction and produces the "doming" phenomenon seen before.

Reduction of the temperature parameter reduces or eliminates this tendency.

On 19 July, a demonstration was performed in accordance with the test procedures of Appendix A. The following visitors were present

Mr. A. Alvarez - South Carolina Electric & Gas Co.

Mr. D. Klinkseik - Gilbert Commonwealth

Mr. A. Mann - Gilbert Commonwealth

Mr. P. Lynch - King Overseas of Florida

Mr. J. Prado - U.S. Testing, Inc.

The tests were considered successful, and duplication is within the capability of existing technology. The important thing observed after removal of the solids from their containers is that it was not possible to squeeze water out of the solid with direct pressure applied. It is recognized that in a closed system, with fluid temperatures above the ambient conditions, and hence above the container temperature, there will be a tendency for water vapor to condense upon the inner container surfaces until a thermal equilibrium is reached. From our observations this volume is dependent upon the free space in the liner, and would probably be less than 500 ml in a 1400 liter container when solidification is undertaken at a nominal 120°F radwaste temperature with an 80°F surrounding ambient. If this proves to be objectionable, provision can be made to purge the free space with dry air or nitrogen while the reaction is terminating.

We recognize the objections that may arise with our proposing a 120°F parameter, when waste streams as high as 170°F are possible. This can be accommodated in several ways:

1. The combination of several waste streams in the waste blending tank will dilute the boric acid concentration, and will lower temperatures.

2. The addition of small amounts of sodium hydroxide increases boric acid solubility at low temperatures.

3. Advantage may be taken of the endothermic reaction of dry prilled urea as it would occur upon contact with hot liquid waste. Tests will be conducted in the near future to quantify this phenomenon.

APPENDIX A

50 Cubic Foot Liner Solidification

I. Initial Conditions

A. Radwaste

12% Boric acid solution

Adjusted to pH - 5-7 with NaOH

120°F

190 gallons

B. Urea Catalyst Solution

50 parts water

50 parts prilled urea

15 parts ammonium sulfate

1 part water-soluble additive

75 gallons

C. UFC solution

100 parts UFC

4 parts additive

D. Physical arrangement

1. Three tanks set up, each holding one of A, B, C, above.
2. Liquids have been mixed and agitated with ring type air sparger.
3. Tanks are equipped with 2L3 Moyno pumps, manually controlled.
4. 50 cubic foot "breakaway" liner set up in truck pit, equipped with ring-type air sparger for agitation.
5. Liner connections suspended over liner for liquid injection.

II. Procedure

A. Radwaste

1. Pump 190 gallons of radwaste into liner. Record temperatures by minute when thermocouple immersed.

B. Catalyst solution

1. Start air agitator in liner
2. Pump 75 gallons by time into liner, continuing agitation.

II. Procedure (cont'd)

C. UFC solution

1. Pump 75 gallons by time into liner, continuing agitation.
2. When mixture gets thick following completion of pumping, stop agitation.
3. Observe solidification.

D. Disconnect air line and prepare for drum procedure.

55 Gallon Drum Solidification

I. Initial Conditions

A. Radwaste

Composition

10% Boric acid

0.1% Sodium Chloride

0.01% Potassium permanganate

0.1% Powdex resin

0.1% Tide detergent

7% Resin beads

0.01% Citric acid

1% Ferric oxide

0.1% Potassium chromate

.1% Oil

.01% Anti-foam agent

.01% Decontaminating Solution

25 gallons

75°F

B. Urea Catalyst Solution

50 parts water

50 parts prilled urea

15 parts ammonium sulfate

1 part water soluble additive

C. UFC solution

100 parts UFC

4 parts additive

D. Physical arrangement

1. Two tanks set up, each holding B and C above
2. Liquids have been mixed and agitated with ring type sparger.
3. Tanks are equipped with 2L3 Moyno pumps, manually controlled.
4. 55-gallon drum in pit, loaded with A above.
5. Connections suspended over drum for liquid injection.

II. Procedure

A. Radwaste

1. Heat radwaste to approximately 100° with immersion heater. Start recording temperatures.

2. Initiate air agitation of drum.

B. Catalyst solution

1. Pump 10 gallons by time into drum

C. UFC solution

1. Pump 10 gallons by time into drum

2. When mixture gets thick following completion of pumping, stop agitation

3. Observe solidification