CEMENT AS A STABILIZATION MEDIA

J. Jeffrey, L. Garner, W. House
Chem-Nuclear Systems, Inc.
Columbia, South Carolina

ABSTRACT

Solidification of various radioactive waste streams with cement has been a common practice for many years within the nuclear industry. A significant number of waste streams have been subjected to the cementation process utilizing special additives to enhance qualities required to provide adequately stabilized waste forms.

This paper examines two of the difficult waste streams: 1) organic ion exchange resin beads and 2) borated aqueous waste. The problems that can be encountered with these streams and how these problems can be overcome with appropriate pre-treatment technology are also examined in this paper.

INTRODUCTION

Over the past decade, various radioactive waste streams have been stabilized with the use of cementitious formulations. There have been varying degrees of success because of the occasional use of formulations which were not based on a good understanding of the waste stream characteristics and their effect on the chemical reactions taking place. Each waste stream is unique. A total understanding of the various chemical constituents is required to develop an effective pre-treatment that will prevent their interference with the cementitious curing process.

Correct pre-treatment is especially important when solidifying organic ion exchange resin beads. If proper pre-treatment is not used, swelling of the beads will occur, resulting in structural failure of the waste form. The mechanism that causes resin bead swelling is well understood and cementitious chemical formulations that prevent swelling are currently being used with good results.

Borated aqueous waste also requires an understanding of the chemical constituents, how they react with chemicals included in the solidification formula, and how to pre-treat them to prevent early cure and allow for efficient waste loadings.

This paper describes these two specific waste streams, the problems involved with processing each one, and how these problems are overcome to produce a stable product that meets the waste form criteria. These "problem" waste streams are:

1. Organic ion exchange resin beads

2. Borated aqueous waste

SOLIDIFICATION OF ORGANIC RESIN BEADS

One of the major problems associated with the solidification of organic resin beads is the inability to achieve homogeneous mixing. This was solved by specific attention to design of the processing equipment. Extensive testing was necessary to develop an efficient mixing blade, one that would provide complete turnover of the volume of resin beads being processed. The proper blade speed also had to be determined. In addition, the solidification formula had to be developed with good "mixability" as one of the criteria.

Once the importance of mixing was realized and the mechanical aspects of solidifications came under control, attention was drawn to the other problems, especially inhibited cement setting. Some waste streams were found to contain "bad actors", ions that always caused trouble with the solidification process. These included: picolinate, ammonium, citrate, borate, and carbonate ions. Pre-treatment steps were developed to render these ions harmless to the cement curing before beginning the solidification. In some cases, specific agitation time periods combined with the appropriate pre-treatment chemicals are used to remove ammonia and carbon dioxide gases from the waste. This technique was effective in reducing the foaming observed in these wastes and in preventing delayed cure.

Even with the mechanical aspects and the "bad actors" under control and the waste solidified, some waste forms exhibited post solidification swell and cracking. Again, a pre-treatment process was developed to protect the resin beads from further chemical reaction once the solidification process had commenced. The use of proper mechanical mixing, pozzolanic formulations, separate additions of cement and fly ash, all lead to a solidified product with an efficient waste loading, and excellent stability. Samples of solidified waste forms immersed in water since 1987 show no indication of swell or failure.

The following Table I outlines the problems and solutions with regard to Solidification of Organic Resin Beads. Table II charts the results of 10CFR61 stabilization tests conducted.

SOLIDIFICATION OF CONCENTRATED BORIC ACID WASTES

Aqueous boric acid wastes have been a cement stabilization problem. As with organic resin bead wastes, proper mechanical mixing was part of the solution. But, even with proper mixing, it was difficult to stabilize any boric acid waste with a concentration above 12% dissolved boron. In order to meet stabilization criteria, restrictions were placed on the waste concentrations. In some cases, the waste stream had to be diluted before it could be stabilized.

TABLE I

Solidification of Organic Resin Beads

Problem	Solution
1. Failure to achieve homogeneous mixing during processing.	1. Correct selection of process equipment o Properly designed mixing blades o Correct mixing blade speed o Correct mixing blade interface with the process container o Use of improved solidification formulas designed for good mixability
2. "Bad Actor" ions (ammonium, citrate, borate, carbonate, picolinate, etc.) that interfere with cement set due to inhibiting or pH buffering reactions.	2. Correct pre-treatment and pre-treatment mixing period to release and/or render these ions harmless before binder addition is initiated. Normal pozzolanic reactions then take place to provide good product stability.
3. Resin bead swell and subsequent waste form failure after processing.	3. Correct pre-treatment and use of pozzolanic binders prevent the chemical attack on the resin beads that cause resin bead swell. No indication of product swell or failure even after years of water immersion (see sample).
4. Delayed curing of solidified resin beads due to the presence of ammonia gas.	4. Correct pre-treatment and agitation periods prior to the addition of solidification chemicals.
5. Marginal leachability and stability.	5. Use of pozzolanic formulation to provide excellent leach and stability results (see chart below). Separate addition of fly ash and cement improves process control and provides

TABLE II

Summary of Waste Form Test Results

Organic Resin Beads (72% by Volume)

Waste Form	Comp Strength "As Is" psi	After 90 Day Water Immersion psi	After Thermal Cycling psi	After 10E8R Irrad. psi	After Fungal Exposure psi	After Bacteria Exposure psi	Leach Results Cs LIX	Leach Results Sr LIX	Leach Results Co LIX
Resin 72	1850	2288	1305	2119	1408	1337	8.6	10.8	ND*

*Non Detected
Note: These results are the average of three test samples.

Summary of Waste Form Curing Regimen and Waste Loading Data

Waste Form	Cure Temp	Cure Time	%Waste Packaging Efficiency (By Vol.)
Resin-72	140°F	2 1/2 days	72

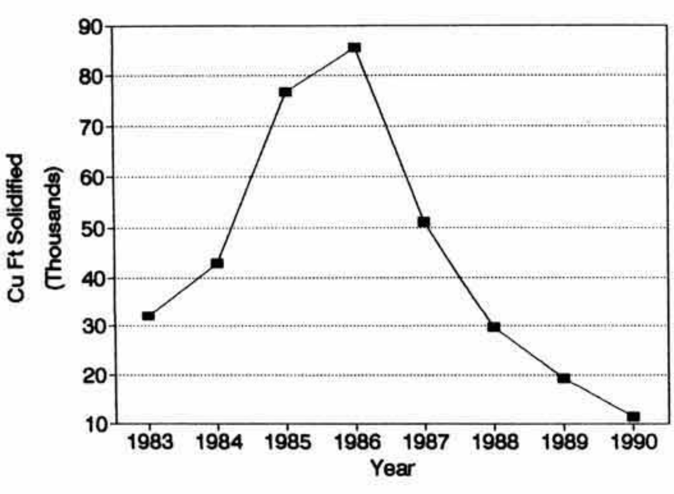

Fig. 1. Utility waste solidified by Chem-Nuclear Systems, Inc.

Although this approach gave an acceptable product, it was inefficient as far as waste packing was concerned.

Another problem with concentrated boric acid wastes was premature thickening resulting from the lime addition, which was added for pH control. A modified formulation was developed to partially neutralize the waste, and required less cement. This had the added benefit of reducing the phenomenon of "boil over" that resulted when excessive cement was used.

However, the real solution to the boric acid waste problem is the development of a CNSI patented formulation in conjunction with a pre-treatment additive that allowed processing of up to 30% dissolved boron in the waste. This is a significant improvement over the original 12% ceiling that could be tolerated. In fact, by customizing the pre-treatment specifically to the waste stream being processed, waste loadings of up to 85% by volume, with 50% dissolved boron, were achieved, with test results far exceeding waste form stability and disposal site criteria.

The following Table III summarizes the development of the current approach to boric acid waste treatment. Table IV charts the results of 10CFR61 stabilization tests conducted.

CONCLUSION

Cement based solidified and stabilized waste continues to be a useful and fully acceptable waste treatment process. Over the years, solidified wastes have decreased in volume (see following two pages, Table V and Fig. 1). This reduc-

TABLE III

Solidification of Concentrated Boric Waste

Problem	Solution
1. Concentration limited to 12% dissolved boron, with typical cement formulation.	1. Initial solution was to decrease waste loading and increase the amount of cement used. See item 3, below, for a better solution.
2. Pre-mature thickening from lime addition and occasional boil over due to excessive amount of cement usage.	2. Developed a formula which partially neutralized hot boric acid, requiring less cement. This prevented boil over but extended cure time.
3. Boric acid concentrated to greater than 12% dissolved boron is difficult to set within a practical time frame.	3. Developed a new proprietary and patented binder (PMC Process) o Pre-treatment additive immobilized soluble borates so that concentrations of 30% were processed and set hard in 24 hours. Test results far exceed waste form stability and disposal site criteria (see chart below). o Waste loading of up to 85% with 50% dissolved boron were achieved at one plant with a custom developed pre-treatment additives selected to prevent pre-mature set.

Note: The solidification of radioactive borated waste with PMC chemistry is a CNSI patented process.

tion is due to a combination of factors; shut down of evaporators at the plants, a shift to more efficient portable ion exchangers, and a shift to more efficient dewatering technology.

However, the need for cement based solidification waste processing technology continues. The waste streams that remain to be solidified are a relatively small fraction of former wastes that are not suitable for dewatering and/or packaging in High Integrity Containers (HIC's). These remaining waste streams are the former "problem" streams that can now be easily and economically processed with proper pre-treatment and new formulations. These waste streams are being processed into acceptable, fully stable waste forms and meeting currently accepted criteria, as well as the new criteria being proposed.

TABLE IV

Summary of Waste Form Test Results

Neutralized Boric (74% by Volume)

Waste Form	Comp Strength "As Is" psi	After 90 Days Immersion psi	After Thermal Cycling psi	After 10E8R Irrad. psi	After Fungal Exposure psi	After Bacteria Exposure psi	Leach Results Cs LIX	Leach Results Sr LIX	Leach Results Co LIX
PWR 74	1300	1412	716	1575	1000	1310	6.5	7.8	ND*

*Non Detected
Note: These results are the average of three test samples.

Summary of Waste Form Curing Regimen and Waste Loading Data

Waste Stream	Waste Form	Cure Temp	Cure Time	% Waste Packaging Efficiency (By Volume)
30 Wt% neutralized Boric	PWR-74	140°F	3 days	74

TABLE V

Utility Waste Solidified by Chem-Nuclear Systems, Inc.
(Cubic Feet)

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
1983	2680	1745	3325	2073	2780	3410	2544	2124	2461	1973	3181	3849	32,145
1984	4813	3821	3389	2068	1885	2388	2365	3154	2607	2976	5790	7701	42,957
1985	4260	3977	2825	7244	6429	6880	6336	5709	4779	7470	11399	9537	76,845
1986	6371	5848	8208	8523	6251	6330	5419	5702	7603	7811	10964	6567	85,597
1987	5346	5240	3890	2249	2378	2904	4754	5050	3721	4675	6382	4444	51,033
1988	3158	3912	2730	2934	3276	3066	2027	2448	1297	1390	1563	1834	29,635
1989	1705	2074	1047	1268	1359	2005	2850	1985	1044	1149	1478	1291	19,255
1990	911	946	983	937	802	914	514	912	844	1623	1032	1731	12,149