PROBLEMATIC INCINERATOR ASH: A CASE STUDY IN FINDING A SUCCESSFUL TREATMENT APPROACH

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ABSTRACT

The Idaho National Engineering and Environmental Laboratory (INEEL) produces incinerator flyash and bottom ash as a consequence of burning low-level radioactive waste materials at the Waste Experimental Reduction Facility (WERF). The incineration process greatly reduces original waste volumes but concentrates the metals that are present, such as toxic metals (most notably cadmium, lead, and antimony) and nuisance metals (e.g., zinc). Anion species also become predominant in flyash produced by INEEL incineration, where chloride and sulfate are at concentrations that can approach 15-20 wt% each. In addition, treatment of the WERF flyash is further complicated by a significant fraction of ignitables composed of carbon soot and various hydrocarbon species that have been measured in some cases at 30% net by Loss-on-Ignition tests. Bottom ash produced at the WERF site is generally much less toxic, if not nontoxic, as compared to the flyash. Due to the complex composition of the flyash material, stabilization attempts at the INEEL have been only partly successful, causing the effectiveness and viability of treatment methods to be revisited. Breakthroughs in flyash stabilization came in 1998 when more complete characterization data gave us further insight into the chemical and physical nature of the flyash. These breakthroughs were also facilitated by the use of a computer model for electrolytes that allowed us to simulate stabilization options prior to starting laboratory studies.

This paper summarizes efforts at the INEEL, spanning the past three years, that have focused on stabilizing flyash. A brief history of INEEL treatability studies is given, showing that the degree of effective flyash stabilization was proportional to the amount of meaningful characterization data that was available. Various binders have been used in these treatability studies, including Portland cement type I/II, Portland cement type V, JGC Super Cement (blast furnace slag cement), a Fluid Tech binder (Aquaset II), and phosphate-bonded ceramic. In addition, a number of additives have been investigated to enhance the stabilization processes. It is demonstrated that flyash preconditioning, a cornerstone of the FY 1998 work, is essential for successful stabilization as it promotes metal precipitation and prepares the flyash for solidification with the binder material. Results and trends from the extensive experimental matrices are explained, along with a mathematical/statistical interpretation of the treatment data through the use of an INEEL-developed "effectiveness factor". Also, the outcome of computer-simulated flyash stabilization will be discussed. Finally, recommendations will be given for flyash preconditioning schemes and final treatment formulations in light of the new Universal Treatment Standards. Applicability and interest for this topic lie not only at the INEEL, but also at any other DOE and Private Sector incineration facility that produces hazardous flyash.

INTRODUCTION

Incinerator flyash is generated at the INEEL as a result of burning low-level radioactive waste materials at the Waste Experimental Reduction Facility (WERF). Bottom ash, also produced during the incineration process, is not discussed herein due to its low toxicity and ease of treatment. Waste volumes are drastically reduced during the incineration process. However, noncombustible and nonvolatile (or sparingly volatile) components such as metals are greatly concentrated within flyash. Examples of metals found in the WERF flyash include toxic metals (most notably cadmium, lead, and antimony) and nuisance metals (e.g., zinc). Also predominant in flyash produced by INEEL incineration are anion species such as chloride and sulfate, where concentrations can approach 15-20 wt% each. Treatment of the WERF flyash is further complicated by a significant fraction of ignitables composed of carbon soot and various hydrocarbon species that have been measured in some cases at 30 wt% net by Loss-on-Ignition (LoI) tests.

Due to the complex composition of this flyash material and limited characterization data, previous stabilization attempts at the INEEL have been only partly successful. As a result, further investigation was required to determine an effective, reliable treatment method for this mixed low-level waste (MLLW). Breakthroughs in flyash stabilization came in FY 1998 when more complete characterization data gave us further insight into the chemical and physical nature of the flyash. These breakthroughs were also facilitated by the use of a computer model for electrolytes that allowed us to simulate stabilization options before starting laboratory studies.

Results from treatability studies done the previous two years (FY 1996 and 1997) showed that the WERF flyash was a problematic MLLW that required more than just a simple combination with a hydraulic binder to achieve satisfactory stabilization. Flyash *preconditioning* is required for successful stabilization to promote metal precipitation (thereby diminishing the concentrations of soluble toxic metals) and to prepare the flyash for solidification with the chosen binder material. Preconditioning steps should collectively yield the bulk of stabilization for the hazardous constituents, and be followed by the final step of binder addition (solidification). Four separate preconditioning studies were performed during FY 1998 on flyash from incineration campaign 088.

Table I lists the properties of flyash materials that have been used in the INEEL treatability studies, as well as summary information for treatment methods and treatment success rates. It should be noted that each study utilized flyash from different incineration campaigns, referred to as "Burns". For example, the FY 1997 study used a flyash composite sample from Burns 073, 074, and 076 whereas Burn 088 flyash was investigated in FY 1998. Applicable treatment standards are summarized in Table II, where a comparison is made between the treatment standards defined by RCRA Characteristic, Universal Treatment Standards (UTS), and the newly promulgated UTS (1,2). Results from the Toxicity Characteristic Leaching Procedure (TCLP) are used as performance criteria for the indicated treatment standards (3).

SOLIDIFICATION/STABILIZATION MATERIALS

Description of Hydraulic Binders

Hydraulic cement-based binders have found widespread acceptance and utilization for stabilizing hazardous constituents, typically heavy metals, in a solid matrix so that the resulting solid monolith is resistant to leaching according to prevailing treatment standards. Most inorganic solids, liquids, and sludges are amenable to this treatment to some extent. Good success has been gained by using hydraulic binders to solidify MLLW samples at the INEEL, where nearly 60 mixed wastes have been included in our studies over the last seven years; case studies are discussed in reference 4. Portland cement (PC), a Type I/II formulation from Holnam, was the primary binding agent used in these INEEL treatability studies. This material has a "low alkali" designation. Type V Portland cement was also used for this work, since it was known that it performs well for high sulfate applications.

Table I Characteristics and summary treatment information for MLLW incinerator flyash used in INEEL treatability studies.

INEEL Waste ID	Contaminant Level, per TCLP analysis	Physical Characteristics	Year	Applicable Treatment Standard	Treatment(s) Applied	Treatment Success Rate
147A	62.4 mg/L Cd 17.8 mg/L Pb	(Not available)	1996	RCRA characteristic	PC stabilization, Lime addition, Ferrous sulfate addition; Aquaset II stabilization	4 of 13 (30.8%)*
147A (composite of Burns 073, 074, 076)	0.34 mg/L Ag 48.7 mg/L Cd 37.4 mg/L Pb 3.89 mg/L Sb	(Not available)	1997	UTS	PC stabilization, Lime addition, "white glue" addition; PBC stabilization	1 of 16 (6.3%)*
147A (Burn 088)	705 mg/L Cd 35.3 mg/L Pb 2.05 mg/L Sb	Specific Gravity = 0.25 Moisture ≈ 2% LoI =14.2% TOC = 8.04 wt% Br^- = 3.15% Cl^- = 11.5% SO_4^{2-} = 4.38% Zn = 20.5%	1998	New UTS	Flyash preconditioning; PC stabilization; SC stabilization; PBC stabilization; Numerous additives	28 of 40 (70%)*

* Overall success rate is shown, as based on the criterion of TCLP testing per the shown treatment standard; the rate can vary according to the grouping of formulations. For example, FY 1998 monoliths that contained preconditioned flyash with PC as the sole binder saw a treatment success rate of 100%.

Table II Various Treatment Standards for toxic metals (1,2). Values are TCLP levels, mg/L.

	Sb	**As**	**Ba**	**Be**	**Cd**	**Cr**	**Pb**	**Hg**	**Ni**	**Se**	**Ag**	**Tl**
RCRA Char.	NA	5.0	100	NA	1.0	5.0	5.0	0.20	NA	5.7	5.0	NA
UTS	2.1	5.0	7.6	0.014	0.19	0.86	0.37	0.025	5.0	0.16	0.30	0.078
New UTS**	1.15	5.0	21.0	1.22	0.11	0.60	0.75	0.025	11.0	5.7	0.14	0.20

** per EPA Final Ruling of May 26, 1998 (reference 2)

NA Not Applicable

Other hydraulic binders included in this study are phosphate-bonded ceramic (PBC) and Super Cement (SC) from ADTECHS Corporation. Both PBC and SC are capable of producing very hard monolithic waste forms. PBC is a low temperature ceramic material primarily composed of $MgKPO_4 \bullet 6H_2O$. In recent years, PBC has been developed largely at Argonne-East National Laboratory as a means of treating wastes that have traditionally been less compatible with PC-based formulations. SC is proprietary alkali-activated blast furnace slag cement that can be used by itself or in combination with PC. High salt wastes having low moisture content are good candidates for stabilization by SC.

Stabilization Additives

Several additives were used in this work to determine their effect upon metal leaching, monolith hardening, and in general to improve the compatibility between the waste and the binder material. The type of stabilization additives and their relative amounts are driven by the complexity of the waste being stabilized, which should be well defined *before* treatment is attempted. Additives are used to effect a beneficial change in the waste form (e.g., pH change, metal precipitation, etc.), typically prior to the addition of the binder during the final solidification step. For example, additives were used in FY 1998 to precondition the flyash before a binder was introduced to the mixture. Specific additives are disclosed below where treatment formulations are discussed.

SOLIDIFICATION/STABILIZATION APPROACH

Experimental variables used for this work, listed in order of importance, include waste loading, stabilization additives, type of hydraulic binder, and total percent water in the treated waste form. As mentioned above, flyash preconditioning is another experimental consideration added in FY 1998.

Summary of FY 1996 and 1997 Stabilization Efforts

Table I indicates that treatment success rates were meager for the FY 1996 and 1997 treatability studies involving WERF flyash. Much of the reason for this low percentage of successful formulations is due to insufficient upfront characterization data for the raw flyash. Meaningful data covering Loss-on-Ignition and anion analysis was not known until too late in FY 1997. Accordingly, the treatment formulations used during these first two years of study centered on conventional recipes involving Portland cement, lime, or other single additives. One important observation from these studies was that the addition of lime to concrete formulations increased stabilization effectiveness. As discussed below, lime is believed to provide a benefit by supplying extra calcium to replace that which would otherwise be consumed through calcium sulfate formation due to excessively high sulfate concentrations in the flyash.

Flyash Preconditioning: One Key to Success in FY 1998

Flyash preconditioning is a slurry-phase stabilization process that occurs prior to final solidification. The aim of preconditioning is twofold: (1) to dissolve the fraction of readily soluble toxic and nuisance metals (the fraction that would leach quickly under TCLP testing), and (2) precipitate the soluble metals as highly insoluble metal compounds. Results of the flyash preconditioning work are given in Figure 1 wherein the water-soluble concentrations of metals are plotted, taking into account the various dilution factors from the preconditioning steps. The effect from each successive preconditioning step upon metal solubility can be assessed by studying Fig. 1. The separate plots within Fig. 1 show that preconditioning greatly decreases the amounts of soluble toxic metals (cadmium, lead, and antimony) and the nuisance metal zinc through chemical precipitation, thereby substantially increasing the chances for successful stabilization and solidification. The precipitated metals are eventually bound within a cementitious matrix after a hydraulic binder is added to the mixture of preconditioned flyash.

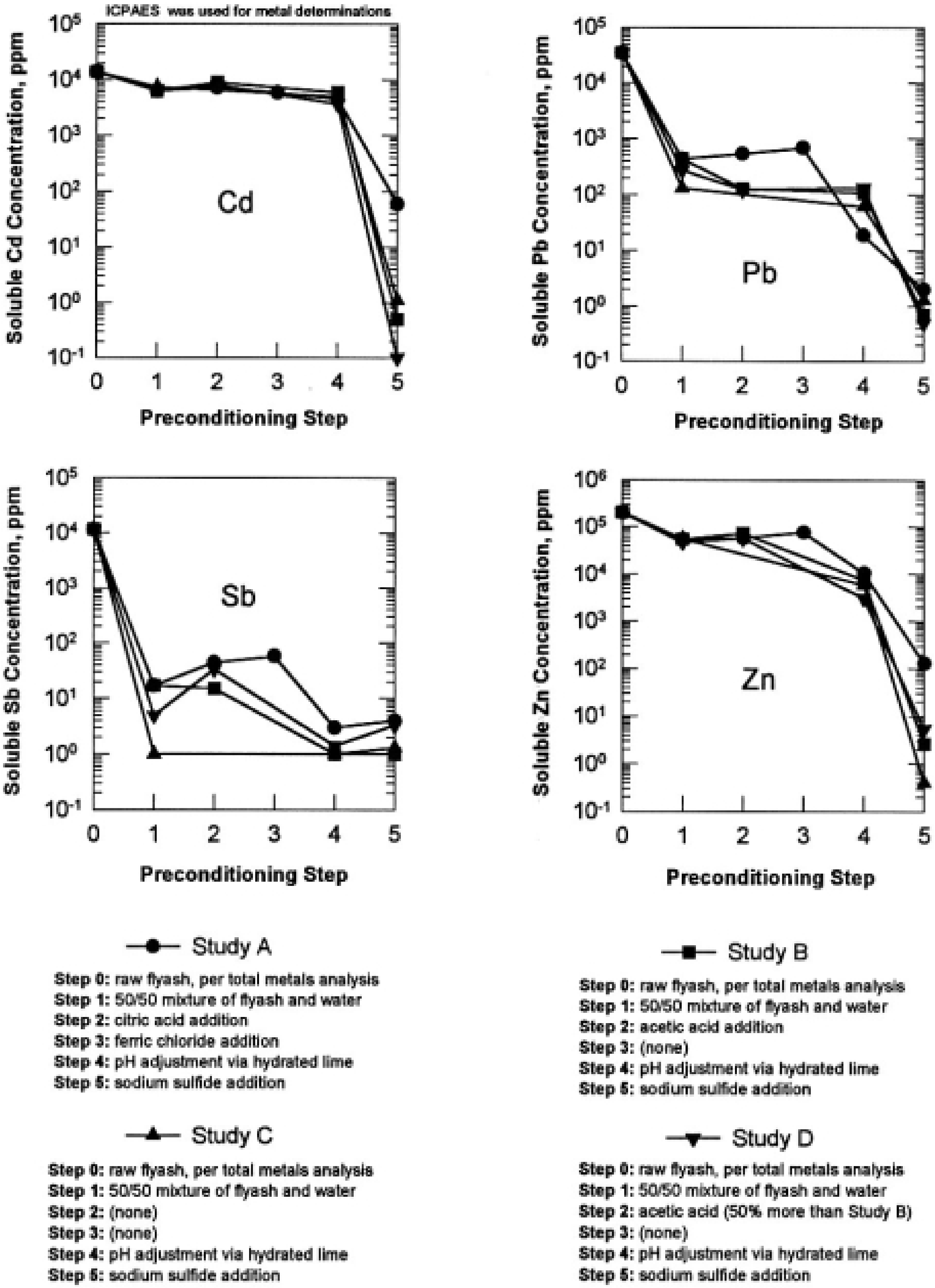


Fig. 1: Soluble metal concentrations from four preconditioning studies performed on WERF flyash, Burn 088.

The choice of additives is key to successful preconditioning of WERF flyash. Acetic acid was chosen to enhance upfront metal solubilization (it is the same acid used for the TCLP protocol) and to help disengage the organic soot layer that adheres to the flyash particles. Hydrated lime is valuable as both a pH-neutralizing agent and as a source of supplemental calcium since the abundance of sulfate in the flyash tends to consume calcium, forming slightly soluble $CaSO_4$. Calcium is a crucial element of hydraulic concretes, such as those made with PC. Finally, a sulfide-based precipitating agent was chosen because metal-sulfide compounds have very low solubilities in water, and because effective precipitation can be accomplished by adding a small amount of sodium sulfide relative to the other ingredients. Sodium sulfide gave very satisfactory results in reducing the levels of soluble toxic metals, and proved to be superior to a proprietary chelate-based precipitant. Preconditioning also drastically reduced the level of soluble zinc. Although zinc is not defined by EPA as being a toxic metal, it is a nuisance metal to solidification based on hydraulic binders, as it can interfere with the proper set and cure of concrete (some WERF incineration campaigns produce flyash having around 20 wt% zinc).

FY 1998 Results for Treatment with PC and Super Cement

The FY 1998 treatment matrix for Waste Stream ID (WSID) 147A is given in Table III, wherein it is seen that 40 monoliths were produced while investigating flyash from Burn 088. Waste loadings, defined as the weight percent of waste in the final treated form, varied between 22 to 37.4 wt%. Binders investigated include PC Type I/II, PC Type V, PBC, and ADTECHS SC. Many formulations listed contain one or more additives, as shown, where 11 different additives were used for WSID 147A during the FY 1998 study. The amount of total water in the monoliths ranged from about 28% to 47%. Overall average amounts of constituents in the monolith formulations given in Table III are as follows: flyash = 31.0 wt%, total water content = 39.6%, hydraulic binder = 20.3%, and additives = 9.1%.

Of the 40 monoliths that were made for this study, 12 failed the new UTS limits for one or more of the following metals: Cd, Pb, and Sb. Of the 12 monoliths that failed, eight contained a non-PC binder (e.g., SC or PBC) and PC was excluded from the formulation. Of the other four monoliths that failed, two used PC Type V as the binder. *All monoliths that lacked PC failed the new UTS treatment standards*. One way to look at these results is that of the 32 monolith formulations that contain PC, 28 passed the new UTS for a success rate of 87.5%.

The results from the FY 1998 study are markedly different (better) from the previous two years, where the failure rate was much higher than the success rate for FY 1996 and 1997. To help make sense of all the data, an *effectiveness factor* (denoted as η) was used to assess the treatment results, which yielded some good insights. The effectiveness factor is simply a mathematical expression (based on raw waste characteristics, prevailing treatment standards, waste loading in the treated form, and a treatment criterion) that provides an unbiased assessment of treatment performance. Previous work can be consulted for details concerning the effectiveness factor (5,6). TCLP testing was used as the treatment criterion for η calculations (3). The expression for the effectiveness factor is as follows

$$\eta = \frac{X_{Waste}}{2n} \sum_{i=1}^{n} \left[\frac{(\Phi_b - \Phi_r)}{\Phi_b} \left(\frac{(\Phi_b - \Phi_a)}{\Phi_b} + \frac{(\Phi_r - \Phi_a)}{\Phi_r} \right) \right]_i \qquad (1)$$

(I) (II) (III)

Table III. FY-98 overall treatment matrix and effectiveness factor (η) values for WSID #147A, WERF flyash Burn 088. (Letters **a** through **k** represent additives or preconditioning agents, as given at the end of the table)

Monolith ID (alternate ID)	**Waste wt%**	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**PC I/II**	**PCV**	**SC**	**PBC**	**η**	**η Rank**
147A.S.SC1 (147A.1S.SC)	29.4	▨	▨	▨	▨								▨		▨		0.232	13
147A.S.SC2 (147A.2S.SC)	32.7	▨	▨	▨	▨								▨		▨		0.259	4
147A.S.SC3 (147A.3S.SC)	29.4	▨	▨	▨	▨										▨		-2.62	36*
147A.S.SC4 (147A.4S.SC)	33.1	▨	▨	▨	▨										▨		-14.67	39*
147A.S.SC5 (147A.5S.SC)	34.1	▨	▨	▨	▨										▨		-16.16	40*
147A.S.SC6 (147A.6S.SC)	37.4		▨	▨	▨										with Na_2HPO_4		-10.00	38*
147A.S.PTA1 †	36.5					▨	▨	▨	▨				▨				0.284	2
147A.S.PTA2 †	33.1					▨	▨	▨	▨				▨				0.251	9
147A.S.PTA3 †	29.9					▨	▨	▨	▨				▨				0.222	17

147A.S.PTA 4 †	36.0					▨	▨	▨	▨				▨		▨		0.256	7
147A.S.PTA 5 †	32.7					▨	▨	▨	▨				▨		▨		0.259	5
147A.S.PTA 6 †	32.2					▨	▨	▨	▨						▨		0.084	30*
147A.S.PTA 7 †	23.5					▨	▨	▨	▨				▨				0.166	29
147A.S.PTA 8 †	27.0					▨	▨	▨	▨					▨			0.213	22
147A.S.PTA 9 †	32.7					▨	▨	▨	▨					▨			0.250	11

Table III. (continued).

Monolith ID (alternate ID)	**Waste wt%**	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**PC I/II**	**PC V**	**SC**	**PBC**	**η**	**η Rank**
147A.S.HCA1	33.5							▨	▨				▨				0.193	25*
147A.S.HCA2	28.2							▨	▨				▨				0.191	26
147A.S.HCA3	23.5								▨				▨				0.186	27
147A.S.HCA3B	22.0							▨	▨				▨				0.173	28
147A.S.HCA4	36.5								▨					▨			-0.572	33*
147A.S.HCA5	34.1							▨	▨					▨			0.257	6
147A.S.HCA6	27.9							▨	▨					▨			0.221	18
147A.S.HCA7	27.9				▨			▨					▨				0.221	19
147A.S.HCA8	28.0			▨	▨			▨					▨				0.222	15
147A.S.HCA9	28.4				▨			▨						▨			0.225	14
147A.S.HCA10	36.6								▨				▨				0.284	1
147A.S.HCA11	31.6								▨				▨				0.251	10
147A.S.HCA12	34.2				▨			▨					▨				-4.239	37*
147A.S.PTB1 †	32.8							▨	▨	▨			▨				0.248	12
147A.S.PTB2 †	26.7							▨	▨	▨			▨				0.204	24
147A.S.PTC1 †	33.9							▨	▨				▨				0.255	8
147A.S.PTC2 †	26.9							▨	▨				▨				0.205	23
147A.S.PTD1 †	27.4							▨	▨	▨			▨				0.216	21
147A.S.PTD2 †	28.2				▨			▨		▨			▨				0.222	16

Table III. (continued).

Monolith ID (alternate ID)	**Waste Wt%**	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**PC I/II**	**PC V**	**SC**	**PBC**	**η**	**η Rank**
147A.S.HCA1D	33.4							▨	▨				▨				0.264	3
147A.S.HCA4D	36.5								▨					▨			-1.401	35*
147A.S.HCA7D	27.5				▨			▨						▨			0.218	20
147A.S.PBC1 †	32.8					▨	▨	▨	▨							▨	-0.077	31*
147A.S.PBC2	31.5								▨		▨	▨				▨	-0.536	32*
147A.S.PBC3	31.5								▨		▨	▨				▨	-0.837	34*

Legend:
† Indicates those monolith formulations that used preconditioned flyash from one of four studies (A, B, C, and D).
* Indicates that the monolith failed the new UTS for one or more hazardous metals.

List of Additives and Preconditioning Agents:
a = sodium sulfide nanohydrate, $Na_2S \bullet 9H_2O$
b = NaOH solution (25 wt% dissolved solids)
c = proprietary dispersant (35 wt% dissolved solids)
d = proprietary chelating agent (15 wt% dissolved solids)
e = citric acid
f = ferric chloride, $FeCl_3 \bullet 6H_2O$ (40% H_2O by weight)
g = hydrated lime (24% H_2O by weight)
h = sodium sulfide flakes (60%), equivalent to $Na_2S \bullet 2.89H_2O$ (40% H_2O by weight)
i = acetic acid, glacial
j = boric acid
k = $SnCl_2 \bullet 2H_2O$

Binder Legend:
PBC = phosphate-bonded ceramic
PC V = Portland cement, Type V
PC I/II = Portland cement, Type I/II
SC = JGC Super Cement (ADTECHS)

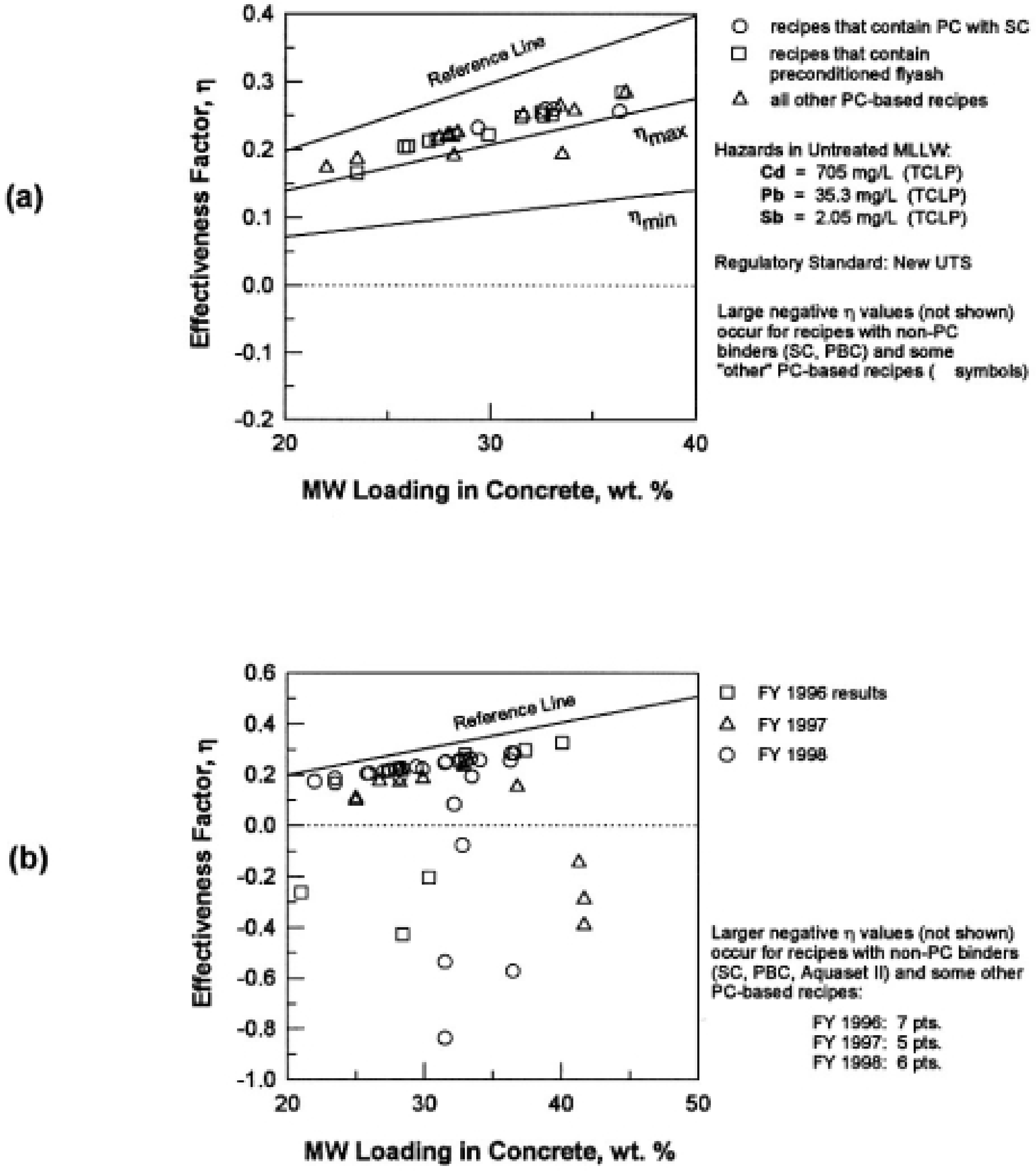
where n is the total number of hazardous components present in the waste, Φ is an arbitrary treatment criterion having a physical basis (TCLP analysis for this work), and X_{waste} is the mass fraction of waste within the treated form. Subscripts a, b, and r denote those values after treatment, before treatment, and a reference value (here, a treatment standard). Terms I through III represent the minimum change that Φ must undergo due to treatment to meet or exceed the reference value, the net change in Φ due to treatment, and the departure of Φ_a from the reference value, respectively. These three terms have been normalized in order to define mathematical limits. The theoretical maximum of η is unity as the waste loading approaches unity and as Φ_a and Φ_r tend toward zero. Larger positive values for η indicate a greater effectiveness in waste treatment, whereas near-zero or negative values may occur if a treatment has produced a detrimental effect ($\Phi_a \geq \Phi_b$), such as an increased leaching of hazardous components. In practice, most positive η values will fall within the range from 0.1 to 0.7. The waste mass fraction serves as an important upper bound, since values for η will never exceed X_{waste}. Because Eq. 1 accounts for waste loading (hence, dilution effects), multiple hazardous constituents, and treatment standards for each constituent, it balances regulatory concerns with economic concerns by considering how well a treatment has met the prevailing treatment criteria at a given waste loading.

Table III lists values of the effectiveness factor for each monolith, the relative rank of each η value (out of 40), as well as a summary overview of monolith formulations. Figure 2a shows plots of the effectiveness factor values for various groupings of data points. The "reference line" represents the theoretical maximum that the effectiveness factor can have at a given waste loading. Lines shown for η_{min} and η_{max} are mathematical bounds that represent the minimum value η can have while still satisfying all applicable treatment criterion, and the maximum value for η when just one treatment criterion is narrowly missed, respectively. Together, η_{min} and η_{max} bound a gray area of η values wherein a treated waste may or may not have passed the chosen treatment criterion. Thus, it is desirable for η values to lie above the η_{max} line. No negative values for η were included in Figure 2a in order to maximize the region of the graph where the favorable (positive) values reside.

The values shown in Figure 2a indicate that most of the points lie in the favorable area above the η_{max} line, and only a few points lie in the gray area between the η_{min} and η_{max} lines. Thus, satisfactory treatment was achieved for most of the monoliths given in Table III. Overall, the η values representing monoliths that contain preconditioned flyash (denoted as symbols) are more consistent (showing less variance from the data norm) than those for monoliths containing raw flyash (△ symbols). A standard deviation of 0.07 was calculated for η values (in relation to the reference line) for the 12 recipes that contained preconditioned flyash with PC as the sole binder, where all 12 monoliths passed the TCLP testing according to the new UTS limits. In comparison, the standard deviation was 1.29 for the 16 PC-based recipes that used raw flyash, with four monoliths failing the new UTS. Looking at the top 10 recipes overall, as judged by the effectiveness factor, the following trends are seen:

- All 10 passed the new UTS.
- Waste loadings ranged from 31.6 to 36.6 wt%.
- All but one of the recipes had a total water content over 40 wt% (but none over 46%).

- All 10 recipes contained PC (9 with PC I/II, 1 with PC V), where three of these contained combinations of PC and SC.
- All 10 recipes contained a sulfide-based additive.
- Seven of the 10 recipes contained hydrated lime.
- Five of the 10 recipes contained flyash that had undergone preconditioning.



Large negative η values (not shown) occur for recipes with non-PC binders (SC, PBC) and some "other" PC-based recipes (symbols)

Larger negative η values (not shown) occur for recipes with non-PC binders (SC, PBC, Aquaset II) and some other PC-based recipes:

FY 1996: 7 pts.
FY 1997: 5 pts.
FY 1998: 6 pts.

Fig. 2: Effectiveness factor plots for INEEL 147A (WERF flyash) from (a) FY 1998 study, and (b) comparison of studies from FY 1996 through FY 1998. The reference line represents theoretical maximum values for η.

Based on the above trends, treatment formulations for WERF flyash stabilization should involve the following: waste loading between 30 and 35%, total water between 40 and 45 %, PC I/II binder, use of a preconditioning acid (glacial acetic), hydrated lime, and sodium sulfide additive. The materials should be added in the following sequence: flyash + water, then acid, then hydrated lime, then sulfide additive, then PC, where appropriate mixing times are used between additions. Based on the conclusive results gained by the preconditioning studies and related monoliths, it can be said that preconditioning is an effective insurance policy against failures, as none of the 12 monoliths that contained preconditioned flyash (with PC as the sole binder) failed the new UTS limits for toxic metals.

Figure 2b shows values of the effectiveness factor for the three years of flyash treatability studies. The new UTS limits were used as a basis for calculations. It is seen in Fig. 2b that the η values reflect the treatment success rates listed in Table I, where the FY 1998 study yielded the most consistent treatment performance. The majority of negative η data points in Fig. 2b arise from unsuccessful treatment formulations that contained binders other than PC, such as SC, PBC, and Aquaset II. This result, along with similar results given in Fig. 2a, confirm that PC is the preferred hydraulic binder for treating WERF flyash.

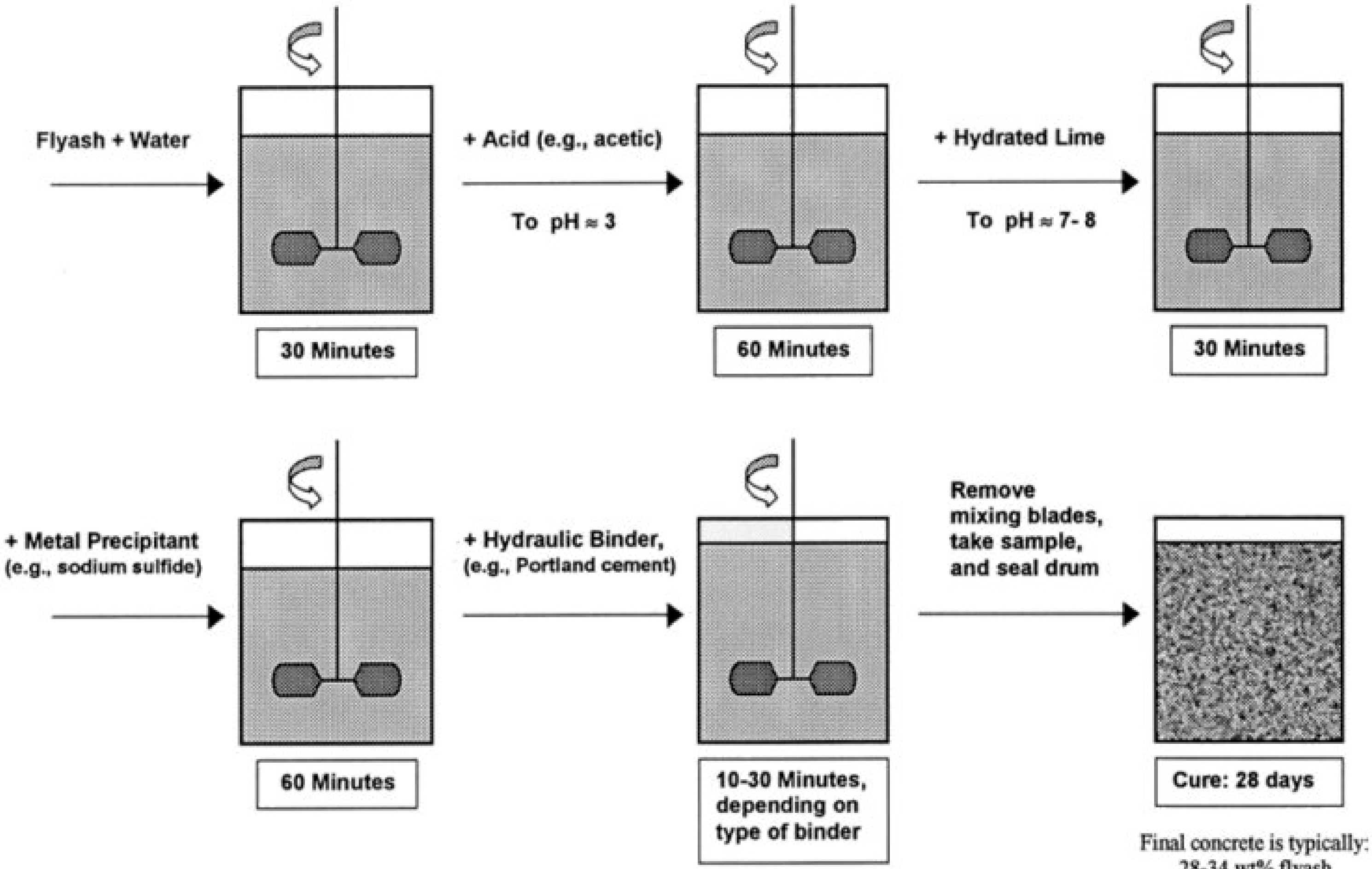
Treatment Recommendations

Based on the treatability study results for WSID 147A (Burn 088), a drum-scale process diagram (Figure 3) was designed to incorporate the essential elements of flyash stabilization, assuming that flyash preconditioning was to be done. Figure 3 shows the various chemical reagents, water, and cement that is required, as well as the range of composition of the final concrete. Note that Fig. 2 shows favorable results for flyash stabilization even where waste loadings approach 37%. However, it is recommended that the waste loading of flyash into hydraulic cement never exceed 35%. Figure 3 should be applicable to most flyash produced at the INEEL. The proportion of each ingredient should be added according to the amount of flyash to be stabilized per drum. For Burn 088 flyash the amounts of ingredients per 100 pounds of flyash are as follows: 120 lb water, 3.2 lb acetic acid, 23 lb hydrated lime, 17 lb $Na_2S\bullet 2.89H_2O$, and 75 lb PC type I/II. A variance in ingredient amounts of ±5% should be acceptable for actual drum-scale processing. Likewise, variations of ±10% for the mixing times should not compromise the effectiveness of the indicated process. The sequential addition of materials to a single drum accommodates flyash preconditioning and minimizes the likelihood of radiological contamination since the flyash is never transferred from the drum once processing has begun.

SIMULATING FLYASH PRECONDITIONING USING OLI ESP

Computer modeling was accomplished prior to laboratory studies to simulate electrochemical processes related to WERF flyash preconditioning, wherein it is desirable to produce a modified flyash that is more amenable to final solidification via hydraulic binders. This modeling capability proved to be a valuable screening tool that helped determine best options for flyash stabilization, while uncovering undesirable treatment conditions.

Environmental Simulation Program (ESP) Version 5.3 from OLI Systems, Incorporated is a steady-state (equilibrium) process simulator particularly well suited for aqueous chemical processes. Equilibrium calculations are based on Gibbs Energy minimization, which is a standard thermodynamic method for describing equilibrium properties of mixtures. Activity coefficients are obtained from a large database or through correlations.



Final concrete is typically:
28-34 wt% flyash
38-44% water
15-25% binder
8-10% additives

Fig. 3: Generalized Scheme for Preconditioning and Treating INEEL Flyash (sequential processing in a single drum)

Although the OLI Systems, Incorporated, electrolyte database was not all encompassing to cover all flyash components, it provided a satisfactory number of compounds that were collectively used to represent the raw flyash (see below). Some difficulty was had at times in achieving numerical convergence for one or more of the unit operations; such problems were usually resolved by slight modification or redefinition of an input parameter.

Of particular value to this work is the ability of the ESP software to predict when chemical compounds (e.g., sulfide forms of toxic metals) would precipitate out of solution, forming insoluble or sparingly-soluble solids. Another bonus is the ability OLI ESP has to represent chemical complexes in aqueous solutions (e.g., metal-chloride and metal-citrate complexes). Oxidation-reduction reactions can be included in the calculations if the reaction speciation is provided by the user. No rate of reaction information (kinetics) is obtained, nor is physical considerations (e.g., particle sizes) or diffusion-related limitations represented by the model. Thus, results from the thermodynamic equilibrium calculations show what would occur if all reactions were allowed to go to completion.

The general flyash preconditioning scheme is represented by the mixing steps in the following order, which in practice would be done in succession within the same drum before final solidification with a hydraulic binder (see Fig. 3):

Step 1. Water addition to flyash to produce a slurry phase
Step 2. Acid addition for pH modification (optional)
Step 3. Addition of a ferric salt (only if citric acid has been added)
Step 4. pH neutralization to pH 7–9 via base addition
Step 5. Addition of chemical precipitating agents to convert toxic metals into insoluble compounds.

The following compounds were used collectively in the model to represent raw flyash:

$CaSiO_3$	= 2 wt%	KCl	= 1	$PbCl_2$	= 4.5
$CaSO_4$	= 1	K_2SiO_3	= 4	Sb_2O_3	= 1
Cd	= 1	K_2SO_4	= 4	$ZnCl_2$	= 30
$CdCl_2$	= 1.5	NaCl	= 2	$ZnSiO_3$	= 2
$FeSO_4$	= 3	Na_2SO_4	= 8	$ZnSO_4$	= 5

In addition, the flyash was assumed to have a carbon/hydrocarbon fraction ("soot") at 30 wt%, wherein this fraction was assumed to be an inert component that went through the simulated processes unchanged.

Results from this modeling work suggest that:

- Sufficient water must be added to the flyash to promote electrochemical interactions between flyash and chemical reagents. The specific amount of water that is required ultimately depends on the chemical composition of a flyash batch, the preconditioning scheme, and the hydraulic cement that is chosen for final solidification. Too much water will result in lower waste loadings and poor concrete, whereas too little water can result in ineffective or incomplete preconditioning.

- Lime would be a preferred neutralizing agent (acidic pH to near-neutral) over NaOH.

- Na_2S or NaHS are superior precipitating agents for decreasing levels of soluble toxic metals in the flyash slurry before final solidification. Material safety data sheet (MSDS) information indicates that Na_2S is safer to use and store than NaHS.

Also, upfront addition of acid to the flyash slurry would no doubt accelerate the solubilization of toxic metals and may help to detach the carbon soot that coats many of the flyash particles. Best choices for acid addition include acetic acid or citric acid, where the resultant acidified flyash slurry would have a pH of approximately 3.

Because the OLI ESP model represents an idealized scenario that does not account for contributions from reaction kinetics, physical restraints (e.g., particle sizes), and diffusion-related limitations, the results from this modeling effort were used only as qualitative guidelines for preconditioning WERF flyash under laboratory conditions. Laboratory studies were performed to confirm the trends observed in this modeling work, and to establish operating conditions for drum-scale preconditioning of WERF flyash. Results from the laboratory-scale studies (discussed earlier) and this modeling effort show that flyash preconditioning causes a dramatic decrease of soluble toxic metals, as well as a substantial decrease of soluble zinc, which is a nuisance metal.

CONCLUSIONS

Treatability studies involving INEEL incinerator flyash have shown the importance of tailoring the treatment approach according to the physical and chemical characteristics of the flyash. When such characterization data is lacking the proposed treatments will inevitably retain a high risk of unsuccessful stabilization. Such was the case for studies done in FY 1996 and 1997, where the overall treatment success rates were 30.8% and 6.3%, respectively. It was not until adequate characterization data was known beforehand that substantial treatment success was had in FY 1998.

Solidification formulations based on PC yielded high treatment performance for flyash generated at the INEEL. In many cases the stabilized waste forms reduced the leachable (TCLP) concentration of toxic metals to at or below detection limits. The success seen in the third year of treatability studies was due in part to the intelligent choice of stabilization additives and waste preconditioning schemes. Portland cement, long established as a preferred binding agent for stabilizing hazardous and mixed low-level wastes, proved to be very effective for INEEL flyash stabilization. Alternate hydraulic binders were also investigated in FY 1998, including SC and PBC, with neither providing any noteworthy advantage over PC-based formulations. Use of these or other alternate binders should be done only case-by-case where an obvious benefit has been determined beforehand through treatability studies.

The use of electrochemical modeling was invaluable for predicting the performance of preconditioning schemes for WERF flyash (WSID 147A, Burn 088). The OLI ESP software allowed us to determine the feasibility of using various preconditioning and stabilization agents before performing actual laboratory studies. As a consequence, time was saved in laboratory studies, and secondary waste generated during these studies was minimized.

In summary, the success in flyash stabilization gained in FY 1998 was due to electrochemical modeling of flyash preconditioning done beforehand, laboratory studies involving flyash preconditioning, the use of sulfide additives for metal precipitation, and the use of PC Type I/II. Results from this work should see applicability not only at the INEEL, but at other DOE and Private Sector incineration facilities that produce hazardous flyash.

REFERENCES

1. U.S. Code of Federal Regulations, 40 CFR 268, subpart D, as given in *RCRA Regulations and Keyword Index, 1998 Edition*, Elsevier Science, Inc., New York, 1998.

2. Federal Register, Vol. 63, No. 100, "Final Rule Promulgating Treatment Standards…", May 26, 1998.

3. U.S. EPA Test Method 1311, "Toxicity Characteristic Leaching Procedure", Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Publication SW-846.

4. K. L. Gering and G.L. Schwendiman, "Results from Five Years of Treatability Studies Using Hydraulic Binders to Stabilize Low-Level Mixed Waste at the INEEL," *Waste Management '97, Tucson, Arizona, March 2–6, 1997.*

5. K.L. Gering, "Using an Effectiveness Factor as a Decision-Making Tool for Mixed Waste Solidification/Stabilization," *Technology: Journal of the Franklin Institute*, Vol. 334A, No. 1, 1997.

6. K.L. Gering, "Developing a Dependable Approach for Evaluating Waste Treatment Data," *Waste Management '98, Tucson, Arizona, March 1998.*