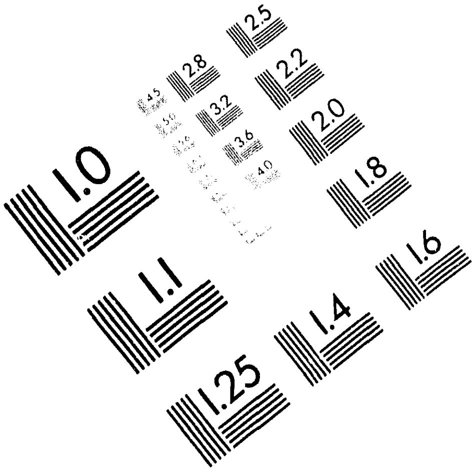
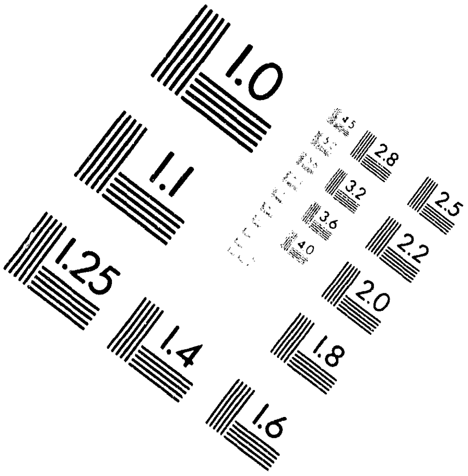
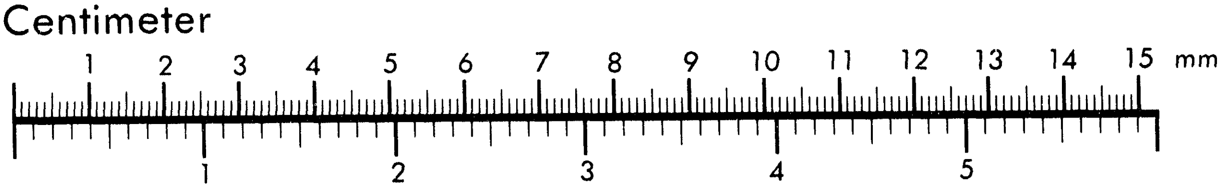


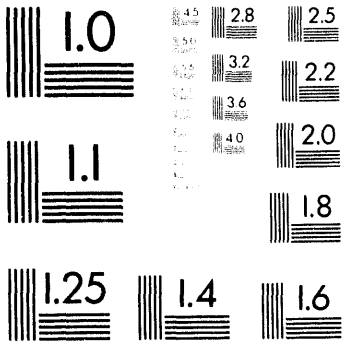
AIIM

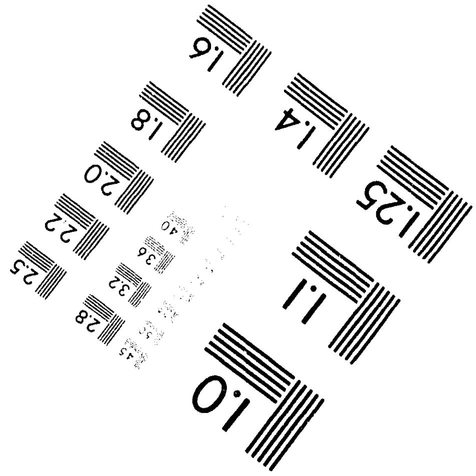
Association for Information and Image Management

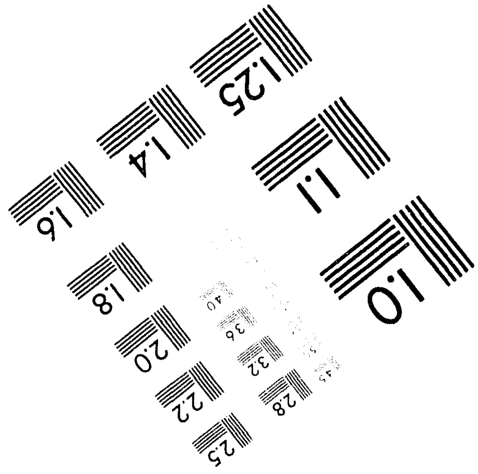
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202











MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

RFP-4825

Conf-9404126--2

CEMENTATION AND SOLIDIFICATION OF ROCKY FLATS PLANT INCINERATOR ASH

Jeffrey A. Phillips
Gary B. Semones, Ph.D.

EG&G Rocky Flats, Inc.
Golden, CO 80402-0464

Abstract

The Rocky Flats Plant produces a variety of wastes which are amenable to encapsulation in cement. Portland cement is an inexpensive and readily available material for this application. Cements have been used for approximately 2000 years and show good durability to weathering making this an attractive technology for waste encapsulation. Cement encapsulation of radioactive and mixed waste forms, therefore, offers long term stability of the waste product and has been proven for several waste streams at the Rocky Flats Plant including a spray dried salt/brine waste and multiple analytical laboratory waste solutions.

Cementation studies on various aqueous waste streams at Rocky Flats have shown this technology to be effective for immobilizing the RCRA constituents in the waste. Cementation is also being evaluated for encapsulation of incinerator ash. Experiments will initially evaluate a surrogate ash waste using a Taguchi experimental design to optimize the cement formulation and waste loading levels for this application. Variables of waste loading, fly ash additions, water/cement ratio, and cement type will be tested at three levels each during the course of this work. Tests will finally be conducted on actual waste using the optimized cement formulation developed from this testing. This progression of tests will evaluate the effectiveness of cement encapsulation for this waste stream without generating any additional wastes.

Introduction

The Rocky Flats Plant (RFP) currently generates and/or stores mixed wastes which are subject to Resource Conservation and Recovery Act (RCRA) Land Disposal Restriction (LDR) treatment requirements. Cementation is a viable solidification process from an economic standpoint and is a widely accepted waste management method[1] for a variety of these mixed waste forms. It is one of several solidification technologies which have been proposed to bring these wastes into compliance with LDR requirements. Cement is also inexpensive, readily available, and solidifies under ambient conditions.

Cementation of wastes at Rocky Flats has focused on aqueous waste streams generated by the analytical laboratories and from the neutralization of nitric

MASTER

acid. These acidic wastes are neutralized and mixed with cement resulting in a monolithic form which meets the waste acceptance criteria for disposal. These wastes are processed directly from the laboratory; no pre-treatment of the liquids is required.

Incinerator ash is being considered for immobilization in cement. The ash in storage was produced from the fluid bed incineration of compressor oils, crank case oils, office trash, solid waste, and diesel fuel. This ash could also contain a significant amount of sodium carbonate (Na_2CO_3), which was used as an acid sorbent in the bed, and spent chromia-alumina (Cr_2O_3-Al_2O_3) oxidation catalyst. The current waste volume is 310 ft^3 of low level mixed (LLM) waste and 60 ft^3 of transuranic (TRU) material, and the composition of this waste is shown in Table 1[2]. Additional ash will result from implementing thermal treatment of combustible waste currently in storage at Rocky Flats.

History of Portland Cement

Portland cement is an inorganic and hydraulic cementitious material that hardens when mixed with water. It is a relatively inexpensive material which has proven to be an effective encapsulant material for a wide variety of waste species. The majority of the Portland cement produced in the United States (over 71 million metric tons per year in 1972) moves only 150 miles from the production site to where it is used[3]. Cement is non-toxic, nonflammable, has good durability in nature, and achieves immobilization of the waste products from both chemical and physical mechanisms. Portland cement was first produced in the early 1800's in England from a mixture of limestone and clay[3]. However, the Romans, Greeks, and Egyptians produced similar cements and mortars for construction purposes. The materials were produced from a mixture of volcanic ash, sand, and calcareous materials. Many of these materials show good stability of the calcium silicates after 1800 years[3-5] of environmental exposure. This shows promise for the durability of cement as a long-term waste encapsulant material.

Cementation of Waste

Primary development efforts for cementation technologies at the Rocky Flats Plant have focused on the treatment of radioactive nitrate salts created by the evaporation of the plant's aqueous waste in Building 374. This waste was generated from the neutralization of nitric acid. The radioactive materials in the waste were flocculated and precipitated with reagents, and the agglomerated waste was concentrated in a clarifier and the overflow sent to an evaporator. The effluent from the evaporator is a 35 weight % brine solution which is sent to a spray drier. The spray dried salt and brine were then cemented into a matrix called 'Saltcrete'.

Analytical laboratory waste solutions have also been treated using the 'Bottle Box' cementation process to immobilize RCRA listed heavy metals in this mixed waste stream. This waste is immobilized with a mixture of cement and Ramcote® 1200 and consists of an aqueous solution of salts and plutonium as well as various RCRA listed toxic metals including silver (Ag), nickel (Ni), cadmium (Cd), chromium (Cr), barium (Ba), and lead (Pb). Therefore, the treated waste must be RCRA LDR compliant and must pass Toxicity Characteristic Leaching Procedure (TCLP) tests. Management of the waste is governed by the

---

Ramcote is a trademark of Ramco Insulation, Inc., Joplin, MO.

Table 1
Rocky Flats Plutonium Recycle Surrogate TRU Ash Composition[2]

Material	Weight Percentage
Al_2O_3	3.69
BaO	0.59
B_2O_3	1.67
CaO	3.64
Cr_2O_3	2.36
CuO	0.64
Fe_2O_3	5.85
PbO	0.54
MgO	2.90
MnO_2	0.10
NiO	0.50
P_2O_5	0.59
KOH	0.50
PbO_2	2.61
SiO_2	45.00
NaOH	0.89
V_2O_5	0.64
SnO	0.15
TiO_2	2.17
C	25.00
Total	100.03

KOH substituted for K_2O
PbO_2 substituted for PuO_2
NaOH substituted for Na_2O
V_2O_5 substituted for Ta_2O_5

Comprehensive Treatment and Management Plan (CTMP) prepared as a requirement of the Federal Facilities Compliance Agreement II (FFCA II). This waste is acidic and requires neutralization prior to the waste treatment. The neutralization process causes the dissolved metals to precipitate as oxides or oxyhydroxides[6] which makes cementation a viable waste encapsulation technique because the solubility and mobility (refer to Figure 1) of the hydroxides is greatly reduced in the alkaline cement matrix[7]. The cement's alkalinity also neutralizes acidic solutions which could degrade the cement structure and thus increase the leachability of these RCRA constituents. This reduced mobility reduces the leachability of these materials from the cement into the environment. Cementation has successfully immobilized the RCRA constituents of a surrogate waste using the 'Bottle Box' process (refer to Tables 2 and 3).

The physical properties of the cement can be tailored to yield a more fluid mixture for in-drum grouting operations. It is important that the cement have sufficient water to maximize its workability. Excess water, however, can produce free standing liquid on the cement surface. This water may be

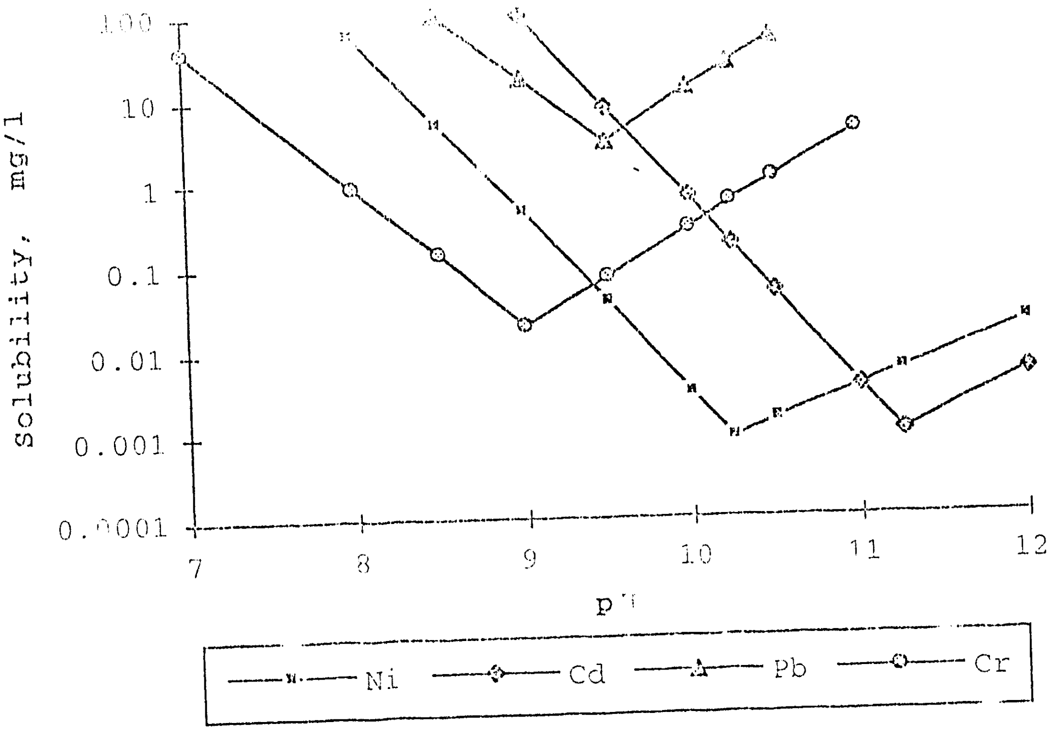


Figure 1: **Metal Hydroxide Solubility as a Function of Solution pH[7].**

sufficient to reject the waste based on the presence of free liquids. Excess water can also react with metallic species in the waste and produce hydrogen gas as a by-product. An alternative to increasing the water content is a partial substitution of fly ash or blast furnace slag for part of the cement. This substitution lowers the hydration temperature and results in a more fluid cement composition[9]. This is advantageous for applications where the additional water may degrade the waste form from physical, chemical, or radiological reactions within the waste product.

There are five primary compositions of Portland cement, two of which have been evaluated at Rocky Flats for waste encapsulation. These are type I/II and type V, respectively. Type I cement has also been evaluated, but is only available by the truckload[9]. This makes it difficult to evaluate type I cement for test purposes; type I/II cement, however, meets the specifications for both types. The various cement compositions are shown in Table 4. Type I based cements are typically used for general construction purposes[10]. This material is moderately high in tricalcium silicate ($3CaO \cdot SiO_2$ [C3S] - 45%) and dicalcium silicate ($2CaO \cdot SiO_2$ [C2S] - 27%) which allows fairly rapid hydration of the cement and thus decreases the time of set. C3S also contributes to the initial strength of the cement due to the early hydration while C2S promotes a later rise in strength from the delayed hydration reaction. This cement is also high in tricalcium aluminate ($3CaO \cdot Al_2O_3$ [C3A] - 11%) which reacts with

Table 2: TCLP Data from Surrogate Analytical Laboratory Solution Waste in Cement/Ramcote® 1200 Matrix Expressed in Parts per Million

Spike Level (ppm) Sample	Cadmium 50	Chromium 300	Barium 300	Lead 400	Silver 5	Nickel 10
1	.029	.140	2.180	< .250	< .050	< .025
2	.032	.151	2.000	< .250	< .050	< .025
3	.029	.102	1.980	< .250	< .050	< .025
4	.032	.106	2.400	< .250	< .050	< .025
5	.035	.140	2.640	< .250	< .050	< .025
6	.035	.113	2.580	< .250	< .050	< .025
7	.032	.130	2.770	< .250	< .050	< .025
8	.033	.130	2.710	< .250	< .050	< .025
9	.032	.138	2.960	< .250	< .050	< .025
9-Dupl.	.025	.132	3.14[illegible]	< .2[illegible]0	< .0[illegible]0	< .025
10	.028	.148	2.[illegible]	< .2[illegible]0	< .050	< .025
x_{avg}	.0311	.1300	2.5264	< .250	< .050	< .025
Standard Deviation	.0029	.0156	.3560	----	----	----
90% UCL	.0348	.1500	2.9822	----	----	----
TCLP Limit[11]	.066	5.2	52	.51	.072	.32

Table 3: TCLP Data from Surrogate Analytical Laboratory Solution Waste in Cement/Fly Ash Matrix Expressed in Parts per Million

Spike Level (ppm) Sample	Cadmium 50	Chromium 300	Barium 300	Lead 300	Silver 5
1	.026	.050	6.410	< .250	< .050
2	.026	.088	5.160	< .250	.092
2-Dupl.	.025	.055	6.930	< .250	< .050
3	.025	.041	6.130	< .250	< .050
4	.025	.063	5.930	< .250	< .050
5	.027	.103	1.260	< .250	< .050
6	.025	.026	5.690	< .250	< .050
7	.025	.069	5.090	< .250	< .050
8	.025	.079	2.700	< .250	< .050
9	.025	.043	5.320	< .250	< .050
10	.028	.145	1.040	< .250	< .050
x_{avg}	.0256	.0693	4.6964	< .250	.0538
Standard Deviation	.0010	.0320	1.9636	----	.0121
90% UCL	.0269	.1103	7.2105	----	.0693
TCLP Limit[11]	.066	5.2	52	.51	.072

Table 4

Chemical Composition of Portland Cements[10]

	C3S	C2S	C3A	C4AF	CSO	MgO	CaO
Type I	45	27	11	8	3.1	2.9	0.5
Type II	44	31	5	13	2.8	2.5	0.4
Type III	53	19	11	9	4	2	0.7
Type IV	28	49	4	12	3.2	1.8	1.9
Type V	38	43	4	9	2.7	1.9	0.5

C3S - $3CaO \cdot SiO_2$

C2S - $2CaO \cdot SiO_2$

C3A - $CaO \cdot Al_2O_3$

C4AF - $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

CSO - $CaSO_4$

the sulfate (SO_4^{2-}) ions in the waste to form the expansive crystal ettringite ($6CaO \cdot Al_2O_3 \cdot 3SO_4 \cdot 32H_2O$). This reaction evolves heat and accelerates the hydration reaction, but the increased thermal energy may lead to waste form degradation. Setting properties of the cement are also influenced by cement particle size (larger particle size decreases the reactivity of the cement chemical reaction with the water and thus lengthens time of set) and mixing characteristics.

Type II cements are also used for general construction purposes, but in conditions where the cement must withstand moderate sulfate attack. The decreased amounts of C3S and C3A in the cement (refer to Table 4) decrease the hydration temperature of the cement and increase the time required for the cement to set. Blending type I and II cements, however, improves the sulfate resistance while decreasing the time of set for the mixture.

Type V cements are commonly used for applications that require resistance to sulfate attack. These cement compositions gain strength more slowly than type I cement due to an increase in the time of set. The increased quantity of C2S and decreased levels of C3S and C3A (refer to Table 4) slow the hydration rate. This has been shown on experimental testing of the Building 374 spray dried salt waste. Additions of other materials (e.g., class C fly ash), however, may offset the slower hydration rate.

Fly ash is a material which may also be added to the cement to act as an absorbent and a lubricant. This material is typically high in silica (SiO_2) and lime (CaO) and is therefore similar in chemical composition to Portland cement. Fly ash also reacts with water to form calcium silicate hydroxide and calcium hydroxide and gives the cement additional strength. Fly ash also enables the cement to set more quickly and improves the mechanical and chemical properties (improved strength, improved corrosion resistance, reduced porosity) of the resultant product and considerably reduces the raw material costs[1]. Class F fly ash has been shown to be successful for eliminating cement swelling when combined with Type V Portland cement in demonstration scale tests of aqueous wastes at Rocky Flats. Class C fly ash will set up when mixed with water[12], but is more susceptible to degradation following environmental cycling.

Development efforts at Rocky Flats with the Saltcrete waste have shown both [illegible] and type V cement [illegible] [illegible] [illegible]. Type I/II cement with a waste loading exceeding 30-[illegible] weight % resulted in moderate swelling of the waste form. Type V cement used in conjunction with class F fly ash reduced or eliminated the swelling, but resulted in a significant increase in the time of set when tested at RFP. Similarly, development efforts with the analytical laboratory solution waste have shown type I/II cement used with Ramcote® and with class F fly ash to be effective for immobilizing the RCRA constituents of a surrogate waste.

Experimental Test Plan for Incinerator Ash

Demonstration of cementation treatment of ash wastes will involve two basic activities: a test with surrogate materials followed by a test using actual mixed waste. This test plan addresses the first task with the objective to demonstrate encapsulation of an ash waste and to optimize the cementation formulation using non-radioactive materials as surrogates. These surrogates will be selected to be as consistent as possible with real wastes based on available waste characterization data.

Cementation development for a waste stream generally takes place in two phases. Phase I work is oriented towards optimizing a cement formulation (freeze/thaw performance, mixing characteristics, waste loading, etc.) while phase II work evaluates the optimized formulation for leach resistance. Variables are tested to increase the waste loading while decreasing the amount of water added to the cement. For the incinerator ash, a Taguchi experimental design has been selected and will evaluate fly ash content (0%, 25% and 50%), waste loading level (10%, 20%, and 30%), water/cement ratio (1.00, 1.25, and 1.50), and cement type (type I/II and V). This will require nine experimental runs to complete the test phase (refer to Table 5). Data collected during the series of experiments will include packed bulk density, viscosity, and freeze/thaw performance of the product. An optimized formula is then selected based on a statistical analysis of the data, and the optimized formula is tested to confirm the experimental results. If cementation appears to merit further examination for waste encapsulation, additional experiments are planned and conducted to evaluate the leach resistance of a spiked surrogate waste. Finally, after all testing on the surrogate waste is completed, a decision can be made as to whether to continue testing using an actual mixed waste.

Waste Acceptance Criteria

The final waste product must meet the disposal site waste acceptance criteria (WAC), including Department of Transportation (DOT) and RCRA requirements for LDR wastes. The WAC includes but is not limited to the following:

- low level mixed waste must have an activity < 100 nCi;
- the waste requires immobilization if,
    - 1 wt% of the waste has a particle diameter of < 10 μ, or
    - 15 wt% of the waste has a particle diameter of < 200 μ;
- the waste must not contain free liquids;

"Mixed waste" is a mixture of chemically hazardous and radioactive waste.

Table 5: Taguchi Experimental Design for
Cement Formulation Evaluation

Experiment	Fly Ash	Waste Loading	Water/ Cement	Cement Type
1	0%	10%	1.00	I/II
2	0%	20%	1.25	I/II
3	0%	30%	1.50	V
4	25%	10%	1.25	V
5	25%	20%	1.50	I/II
6	25%	30%	1.00	I/II
7	50%	10%	1.50	I/II
8	50%	20%	1.00	V
9	50%	30%	1.25	I/II

- waste shall be treated to reduce the volume and provide a more physically and chemically stable waste form where practical;
- waste shall not react significantly with the packaging during normal storage, shipping, and handling;
- mixed waste prohibited from land disposal under 40 CFR § 268 will not be accepted unless treated as specified under 40 CFR § 268, Subpart D; and
- cyanide or sulfide-bearing wastes in concentrations greater than 10 wt% as CN^- or S^{2-} will not be accepted.

A visual inspection for the presence of free liquids and dipsersible fines using a 'PASS-FAIL' criteria will be used in this preliminary testing. Any samples showing the presence of free liquids or dispersible fines will be rejected. TCLP testing will be conducted in a Phase II experimental test plan.

The physical stability of the waste form will be evaluated through freeze/thaw cycling experiments. This will measure the weight and dimensional changes over multiple thermal cycles to determine whether the waste form is suitable to long-term storage at RFP. The viscosity will be measured as a function of waste loading for each formulation. This will determine whether the cement-waste mixture is amenable to mixing in standard equipment.

Conclusion

Cement encapsulation of radioactive waste is a viable processing technology that offers long term stability of the waste product. Cement encapsulation has been shown to be effective for several waste streams at the Rocky Flats Plant, including a spray dried salt/brine waste and multiple analytical laboratory waste solutions.

The evaluation of cement for incinerator ash encapsulation will initially focus on a surrogate ash waste and use a Taguchi experimental design. These experiments will determine the effectiveness of cement as a waste encapsulant [illegible] proves to be [illegible] compared to alternative technologies (polymer encapsulation, microwave melting), the decision can be made as to whether to proceed to the next level of testing by evaluating a surrogate waste spiked with RCRA constituents for TCLP. Finally, actual wastes will be tested using the optimized cement formulation developed from this testing. This progression of tests will evaluate the effectiveness of cement encapsulation for this waste stream without generating any additional waste streams.

References

1. W. Jiang, X. Wu, and D. M. Roy, "Alkali-Activated Fly Ash-Slag Cement Based Nuclear Waste Forms," Scientific Basis for Nuclear Waste Management XVI Symposium Proceedings, Materials Research Society, Vol. 94, Boston, MA, Nov. 30 - Dec. 4, 1992, pp. 255-260.

2. R. M. Neilson, Jr. and P. Colombo, "Solidification of Simulated Transuranic Contaminated Ash Wastes Using Portland Type I Cement," Brookhaven National Laboratory Report BNL 50954, May, 1978.

3. J. Skalny and K. E. Daugherty, "Everything you always wanted to know about portland cement* but did not ask," Chemtech, January, 1972, pp. 38-45.

4. F. Rassineux, J. C. Petit, and A. Meunier, "Ancient Analogues of Modern Cement: Calcium Hydrosilicates in Mortars and Concretes from Gallo-Roman Thermal Baths in Western France," Journal of the American Ceramic Society, Vol. 72, No. 6, 1989, pp. 1026-1032.

5. M. E. Stokely and L. Newland, "Pozzolana-Induced Reductions in the Environmental Availability of Cadmium from Fly and Bottom Ash," Chemosphere, Vol. 24, No. 11, 1992, pp. 1591-1596.

6. E. J. Reardon, "Problems and Approaches to the Prediction of the Chemical Composition in Cement/Water Systems," Waste Management, Vol. 12, 1992, pp. 221-239.

7. B. A. Scheetz, "Chemistry of Cementitious Waste Forms," presented at the Third International Symposium on Stabilization/Solidification of Radioactive, Hazardous, and Mixed Wastes, Williamsburg, VA, Nov. 1-5, 1993.

8. G. A. Fairhall, "Effect of Process Operational Variables on the Product Properties of Encapsulated Intermediate Level Wastes," Radioactive Waste Management and the Nuclear Fuel Cycle, Vol. 9, 1987, pp. 51-70.

9. R. Trujillo, Southwestern Portland Cement, Personal Communication, February 22, 1994.

10. R. A. Haber and P. A. Smith, "Overview of Traditional Ceramics," Ceramics and Glasses, Vol. 4, Engineered Materials Handbook, ASM, 1991, pp. 3-15.

[illegible]
Ignitable and Corrosive Characteristic Wastes Whose Treatment Standards Were Vacated; Interim Final Rule," 40CFR 268 et al.

12. A. T. C. Goh and J. H. Tay, "Municipal Solid-Waste Incinerator Fly Ash for Geotechnical Applications," Journal of Geotechnical Engineering, Vol 119, No. 5, 1993, pp. 811-825.

DATE
FILMED
6/29/94

END