

6100600

AL

BNL 40384

BR-5 is
SSDP sludge.

STABILIZATION OF GEOTHERMAL RESIDUES BY ENCAPSULATION

R. P. Webster and L. E. Kukacka

September 1987

Prepared for the
Geothermal Technology Division
U.S. Dept. of Energy
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PROCESS SCIENCES DIVISION

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PROCESS SCIENCES DIVISION
DEPARTMENT OF APPLIED SCIENCE
BROOKHAVEN NATIONAL LABORATORY
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ABSTRACT

Presented are the results of a laboratory test program conducted to identify and evaluate processes which can be used to convert hazardous geothermal residues to a non-hazardous and potentially usable form. While there are a number of methods available for stabilizing hazardous materials, the emphasis of the program was directed towards two solidification techniques: coating and encapsulation.

Results of tests done to evaluate the effectiveness of the five encapsulation and three coating systems indicated that encapsulation of the geothermal residues in portland cement mortar and concrete composites is the most promising method of stabilization investigated.

A preliminary economic analysis for a 50-MW plant producing 120,000 lb/day of slurry containing 65 wt% solid residue indicates that a profit of \$638,700 can be realized if the residue is incorporated into a portland cement concrete mix which is subsequently sold as ready-mix concrete. The cost analysis does not take into account the \$1,022,000 which is saved annually by not having to dispose of the residue as a hazardous material. Nor does it take into account the reduced liability associated with the disposal of non-hazardous materials.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
TABLES	iv
1.0 INTRODUCTION	1
1.1 Background	1
1.2 Program Objectives	1
2.0 LABORATORY TEST PROGRAM	3
2.1 Background	3
2.2 Geothermal Residues	3
2.3 Laboratory Test Methods	4
2.3.1 Compressive Strength Tests	8
2.3.2 Freeze-Thaw Tests	8
2.3.3 Physical Properties	8
2.3.4 Waste Extraction Tests	8
2.4 Encapsulation Materials Evaluated	9
2.5 Coating Materials Evaluated	11
3.0 LABORATORY TEST RESULTS	12
3.1 Preliminary Evaluation of Encapsulation Systems	12
3.1.1 Composites made using Altek 78-50 Emulsifiable Polyester Resin	12
3.1.2 Composites Made Using a MMA-Based Monomer System . .	12
3.1.3 Composites Made with Sulfur	13
3.1.4 Portland Cement Mortar (PCM) Composites	14
3.1.5 Magnesium Polyphosphate Cement (MPC) Composites . .	15
3.1.6 Preliminary Evaluation of Material Costs	16
3.2 Evaluation of Coating Techniques	18
3.3 Selection of Techniques for Further Evaluation	19

TABLE OF CONTENTS (continued)

	<u>Page</u>
4.0 EVALUATION OF PORTLAND CEMENT MORTARS AND CONCRETES CONTAINING GEOTHERMAL RESIDUES	21
4.1 Physical and Mechanical Properties of PCM and PCC Composites	21
4.2 Leachability Characteristics of PCM and PCC Composites . .	24
4.3 Long-Term Durability Tests	29
5.0 ECONOMIC ANALYSIS	33
5.1 Existing Disposal Costs	33
5.2 Economic Alternatives	33
6.0 SUMMARY AND RECOMMENDATIONS	37
REFERENCES	40

TABLES

	<u>Page</u>
1. PIXE Spectroscopy Analysis of Geothermal Residues	5
2. Gamma Pulse Height Analysis of Geothermal Residues, Natural Products	6
3. Moisture Content and pH of Geothermal Residues	6
4. 48 Hour WET Analysis of "As Received" Geothermal Residues	7
5. Soluble Threshold Limit Concentration Values of Inorganic Toxic Substances in Hazardous Wastes	10
6. Encapsulation of Residue BR1 Using Altek 78-50 Emulsifiable Polyester	13
7. Encapsulation of Residues Using a MMA-Based Monomer	14
8. Encapsulation of Residue BR1 Using Sulfur	15
9. Compressive Strengths of Portland Cement Mortars Containing Geothermal Residues	16
10. 48 Hour WET Analysis of PCM Composites Containing Geothermal Residues	17
11. Compressive Strength and 48 Hour WET Test Results for MPC Mortars Containing Geothermal Residue	17
12. Materials Cost Summary	18
13. 48 Hour WET Analysis of Coated Residue BR1	20
14. Compressive Strengths of PCM Composites Containing Geothermal Residues	22
15. Compressive Strengths of PCC Composites Containing Geothermal Residues	23
16. Physical Properties of PCM and PCC Composites Containing Geothermal Residues	25
17. 48 Hour WET Analysis of PCM and PCC Composites Containing Geothermal Residues	26
18. Summary of Long-Term WET Tests	28

TABLES (continued)

	<u>Page</u>
19. Freeze-Thaw Durability of PCC Composites Containing Geothermal Residues	30
20. 48 Hour WET Analysis of PCC Composites Containing Geothermal Residues Before and After Freeze-Thaw Testing	31
21. 48 Hour WET Analysis of 28 Day and 1 Year Old PCM Composites . . .	32
22. Cost Analysis for Incorporating Geothermal Residue Into a PCM Composite	34
23. Cost Analysis for the Production of Ready-Mix Concrete	36

1.0 INTRODUCTION.

1.1 Background.

While geothermal resources are generally regarded as a relatively inexpensive and environmentally clean source of energy, compared to coal, oil, and nuclear power, they can present a variety of pollution problems. One such problem area deals with the disposal of spent brines and waste waters generated in the drilling, construction, and operation of the plant.

Geothermal fluids generally contain a variety of inorganic elements and heavy metals. The actual chemical composition of a given fluid is governed by those elements found occurring naturally in the producing reservoir and by their solubility in water at the existing ambient temperature and pressure. Elements commonly found in geothermal fluids include antimony, barium, cadmium, chromium, lead, and zinc. In addition, radioactive elements such as radium may also be present in the fluids (1,2). The elements or residues contained in these fluids can, therefore, result in the pollution of ground and surface waters, if the fluids are not disposed of properly.

The special procedures required for the handling and disposal of hazardous materials generally result in a significant increase in the cost of disposal. Considerable savings could, therefore, be realized if a method could be identified to make "hazardous" residues "non-hazardous" prior to disposal. To this end, Brookhaven National Laboratory (BNL) has conducted a program sponsored by the Geothermal Technology Division (GTD) of the United States Department of Energy (DOE), the objective of which was to identify and develop a process for the acceptable disposal of hazardous geothermal residues.

1.2 Program Objectives.

The primary objective of the program was to identify and evaluate a process or processes which could be used to convert hazardous geothermal residues to a non-hazardous form, i.e., stabilize the residues. While there are a number of methods available for use in the stabilization of hazardous materials, the emphasis of the program was directed towards the evaluation of two solidification techniques: coating and encapsulation.

Once a hazardous material has been stabilized, it is generally disposed of. However, a second objective of the program was to identify a solidification process which could be used to produce a material which could be utilized as a construction material.

2.0 LABORATORY TEST PROGRAM.

2.1 Background.

Stabilization is a process by which hazardous materials are treated in order to contain hazardous constituents and prevent dissolution of the constituents into the environment (3). While a number of stabilization processes have been developed to handle the treatment and disposal of hazardous materials (4-14), the emphasis of the GTD/BNL program was directed towards the evaluation of two solidification techniques: encapsulation and coating.

Encapsulation is a process by which a solidification agent surrounds the material particles and binds them into a single mass (3). Materials used to encapsulate the geothermal residues included; an emulsifiable polyester, methyl methacrylate-based monomer systems, sulfur, portland cement, and magnesium polyphosphate cement.

Coating of the individual residue particles prior to incorporating them into a composite system was also evaluated. Coating materials studied included a polyester resin, calcium aluminate cement, and teflon.

2.2 Geothermal Residues.

Five geothermal residues (BR1, BR2, BR3, BR4 and BR5) were obtained by BNL from various geothermal sites located in California. The residues were by-products produced during plant operations. Four of the residues were apparently shipped as sludges. However, by the time the samples arrived at BNL, the solids had settled out and compacted into the bottom of the shipping containers, with the excess liquid rising to the surface. The fifth residue, BR2, consisted of air-dried solids containing no free moisture.

Upon arrival at BNL, a series of tests were performed to analyze each of the residues. Tests conducted included the following:

- a) proton induced X-ray emission (PIXE) spectroscopy analysis was done to identify the heavy metals present in each of the residues,
- b) gamma pulse height (GPH) analysis was done to determine the presence of any naturally occurring radioactive products,

- c) pH analysis of excess fluids,
- d) moisture content of the residue solids,
- e) 48 hr waste extraction test (WET) to determine the hazard classification of the residues (see section 2.3 for a description of the test).

The results of these tests are presented in Tables 1 through 4.

Results of the PIXE analysis, Table 1, indicate that each of the residues contain various levels of a number of heavy metals, several of which, if present in sufficiently high quantities, are considered to be toxic to humans.

Results of the GPH analysis, Table 2, indicate that each of the residues contains very low levels of several naturally occurring isotopes, the most significant being radium (Ra)-226, thorium (Th)-228, and actinium (Ac)-228. The level of activity present is, however, extremely low and is not considered to be hazardous. The residues were, therefore, not treated as radioactive wastes.

Table 3 presents a summary of the moisture content and pH of each of the residues.

Results of the 48 hr WET analysis, Table 4, indicated that three of the five residues, BR3, BR4, and BR5, must be considered as hazardous, based upon the results of the test. Each of these residues had concentrations of one or more elements in excess of the allowable soluble threshold limit concentration (STLC). Residue BR3 contained excessive amounts of arsenic (As) and lead (Pb), residue BR4 contained excessive amounts of As, cadmium (Cd), chromium (Cr), and Pb, and residue BR5 contained excessive amounts of As.

2.3 Laboratory Test Methods.

The test methods used to evaluate the physical and mechanical properties of the composite materials cast using the geothermal residues are described below.

Table 1. PIXE Spectroscopy Analysis of Geothermal Residues.

ELEMENT ^a	CONCENTRATION, mg/liter				
	RESIDUE				
	BR1	BR2	BR3	BR4	BR5
Titanium (Ti)	12,870 ± 1,900	20,530 ± 2,300	12,500 ± 1,710	4,380 ± 160	3,900 ± 400
Vanadium (V)	7,130 ± 1,430	13,090 ± 836	7,080 ± 1,080	2,380 ± 111	1,450 ± 130
Chromium (Cr)	1,530 ± 390	1,870 ± 208	1,180 ± 202	1,070 ± 170	160 ± 20
Manganese (Mn)	1,980 ± 440	3,300 ± 79	1,530 ± 220	1,370 ± 91	2,350 ± 330
Iron (Fe)	31,310 ± 6,300	54,340 ± 9,490	22,680 ± 4,870	41,220 ± 3,390	26,100 ± 1,860
Nickel (Ni)	—	—	—	—	12 ± 2
Copper (Cu)	38 ± 6	373 ± 25	296 ± 8	635 ± 48	360 ± 60
Zinc (Zn)	65 ± 19	131 ± 7	216 ± 86	1,070 ± 145	1,200 ± 100
Arsenic (As)	—	—	—	774 ± 117	280 ± 30
Bromine (Br)	—	—	26 ± 2	—	140 ± 20
Rubidium (Rb)	79 ± 23	70 ± 14	118 ± 35	342 ± 10	520 ± 35
Strontium (Sr)	4,950 ± 1,430	5,130 ± 92	3,540 ± 700	1,660 ± 165	2,400 ± 170
Zirconium (Zr)	9,780 ± 480	1,210 ± 160	895 ± 280	340 ± 41	195 ± 40
Lead (Pb)	124 ± 35	140 ± 19	52 ± 7	1,300 ± 124	390 ± 40

^a In addition to the elements listed, the residues also contained various levels of phosphorus, sulfur, chlorine, potassium and calcium.

(5.1)

Table 2. Gamma Pulse Height Analysis of Geothermal Residues, Natural Products.

NUCLIDE	Half Life, yr	ACTIVITY, $\mu\text{Ci/gm}$				
		RESIDUE				
		BR1	BR2	BR3	BR4	BR5
K-40	20,000	3.80 E-5	4.13 E-5	5.79 E-5	2.34 E-5	3.54 E-5
Bi-211	70,000	1.06 E-3	9.42 E-4	1.15 E-3	3.07 E-4	7.17 E-5
Bi-212	14,000	1.30 E-4	4.07 E-5	5.16 E-5	1.70 E-5	—
Bi-214	1,602	2.97 E-4	2.75 E-4	3.49 E-4	8.76 E-5	1.64 E-5
Pb-212	14,000	1.58 E-4	4.90 E-5	6.63 E-5	2.20 E-5	1.99 E-5
Pb-214	70,000	4.26 E-4	3.66 E-4	4.46 E-4	1.19 E-4	2.46 E-5
Tl-208	14,000	1.25 E-4	4.07 E-5	5.16 E-5	1.71 E-5	—
Ra-224	14,000	9.89 E-4	5.70 E-4	9.76 E-4	2.57 E-4	2.28 E-5
Ra-226	1,602	3.63 E-4	2.68 E-4	3.40 E-4	8.52 E-5	1.64 E-5
Th-228	14,000	1.48 E-4	4.71 E-5	6.38 E-5	2.12 E-5	—
Th-234	70,000	2.04 E-5	2.11 E-5	4.08 E-5	4.89 E-6	—
Ac-228	14,000	3.26 E-4	3.98 E-4	4.70 E-4	1.22 E-4	—

Table 3. Moisture Content and pH of Geothermal Residues.

	RESIDUE				
	BR1	BR2	BR3	BR4	BR5
Moisture content of solids, wt %	15	10	19	39	55
pH of excess fluid after settlement of solids	1.67	— ^a	3.35	5.10	5.12

^a Residue contained no free moisture.

(5.1)

Table 4. 48 Hour WET Analysis of "As Received" Geothermal Residues.

RESIDUE	ELEMENTAL CONCENTRATION, ^a mg/l													
	Sb	As	Ba	Cd	Cr	Co	Cu	Pb	Mo	Ni	Ag	V	Zn	Hg
BR1	3	ND ^b	27	0.2	<0.1	0.2	0.8	3.5	ND	0.5	<0.1	ND	18	<<0.01
BR2	0.7	ND	29	<0.1	ND	<0.1	0.4	0.3	ND	ND	ND	ND	1	<<0.01
BR3	40	13	24	0.2	0.5	0.5	20	9.3	ND	0.8	<0.1	ND	17	<<0.01
BR4	17	77	19	2.3	96	0.9	0.1	136	ND	1.2	<0.1	ND	215	<<0.01
BR5	3.1	10	15	0.3	0.3	0.3	1.3	1.5	0.1	0.6	<0.1	9	62	<<0.01
STLC ^c	100	5	100	1	5	80	25	5	350	20	5	24	250	0.2

^a Values reported are the highest concentration measured in three separate tests.

^b ND = not determined.

^c STLC = soluble threshold limit concentration.

2.3.1 Compressive Strength Tests.

Compressive strengths were measured for 1-in. diam by 2-in. long (2.54 cm by 5.08 cm) portland cement mortar cylinders and 3-in. diam by 6-in. long (7.62 cm by 15.24 cm) portland cement concrete cylinders in accordance with ASTM C39.

2.3.2 Freeze-Thaw Tests.

The freeze-thaw durability of 3-in. diam by 6-in. long (7.62 cm by 15.24 cm) portland cement concrete cylinders was evaluated in accordance with ASTM C666, Procedure A.

2.3.3 Physical Properties.

The specific gravity, water absorption, and void volume of portland cement mortars and portland cement concretes were measured in accordance with ASTM C642. Water permeability characteristics were evaluated using a Ruska Water Permeameter and were done in accordance with Ruska's prescribed test procedures.

2.3.4 Waste Extraction Tests.

The test procedure used to determine whether a geothermal residue or a composite system made with a geothermal residue contained excessive levels of leachable hazardous materials is a procedure developed by the California Department of Health Services (DOHS) known as the 48 hr waste extraction test (WET) and is described in subsection (f) of Section 66700 of the California Administrative Code, Title 22, Division 4, Chapter 30, Criteria for Identification of Hazardous and Extremely Hazardous Wastes, R-45-78.

The test procedure involves leaching a 50 g sample, which is ground to pass a 10 mesh sieve, in 500 ml of a 0.2 M, pH 5 sodium citrate solution for a period of 48 hr. A sample is then extracted from the leachate and analyzed by means of atomic absorption (AA) spectroscopy for inorganic substances considered to be hazardous. Any material which

contains an inorganic substance listed in Table 5, at a concentration in milligrams per liter (mg/l), in excess of its listed soluble threshold limit concentration (STLC) is considered to be hazardous.

Control specimens were subjected to 48 hr WET tests to determine levels of leachable elements normally detectable in each of the systems evaluated.

The California DOHS selected sodium citrate for its leachate because it is functionally similar to naturally occurring organic and biochemical matter found in landfills and soils, it has been used by researchers to test the extractability of toxic metals in various wastes, and as a moderate complexing agent, it is more likely to provide a conservative prediction of the environmental mobility of toxic materials in wastes than other known chelating agents (15).

2.4 Encapsulation Materials Evaluated.

Five material systems were used to encapsulate the geothermal residues. A description of each is presented below.

a) Alpha Corporation's Altek 78-50 emulsifiable polyester. This is a low viscosity (approximately 70 cP at 25°C), pre-promoted, water-emulsifiable polyester resin which was cured at ambient conditions by adding 1 wt% methyl ethyl ketone peroxide (MEKP) initiator. Selected residues were incorporated into polymer concrete (PC) mortar mixes utilizing the Altek 78-50 as a binder. Because of the high salt content of the residues, which interfered with polymerization of the resin, it was generally necessary to wash the residues prior to incorporating them into a mix.

b) Methyl methacrylate (MMA)-based monomer system. This system consisted of 75 wt% MMA and 25 wt% poly(methyl methacrylate) (PMMA) and had a viscosity of approximately 65 cP at 25°C. The monomer was cured at ambient conditions utilizing an initiator/promoter system consisting of 4 wt% benzoyl peroxide-50 and 1 wt% dimethyl-p-toluidine, respectively. Selected residues were incorporated into PC mortar mixes utilizing the monomer as a binder. The residues were washed prior to incorporation into the mixes to remove salts which interfered with polymerization of the monomer.

Table 5. Soluble Threshold Limit Concentration Values of Inorganic Toxic Substances in Hazardous Wastes.

INORGANIC SUBSTANCES	STLC, mg/l
Antimony and/or antimony compounds	15
Arsenic and/or arsenic compounds	5.0
Asbestos	—
Barium and/or barium compounds (excluding barite)	100
Beryllium and/or beryllium compounds	7.5
Cadmium and/or cadmium compounds	1.0
Chromium (VI) compounds	5
Chromium and/or chromium (III) compounds	560
Cobalt and/or cobalt compounds	80
Copper and/or copper compounds	25
Fluoride salts	180
Lead and/or lead compounds	5.0
Mercury and/or mercury compounds	0.2
Molybdenum and/or molybdenum compounds	350
Nickel and/or nickel compounds	20
Selenium and/or selenium compounds	1.0
Silver and/or silver compounds	5
Thallium and/or thallium compounds	7.0
Vanadium and/or vanadium compounds	24
Zinc and/or zinc compounds	250

(5.1)

c) Sulfur. Selected residues were incorporated into mortar mixes in which elemental sulfur was used as the binder. The composite was made by melting the sulfur at a temperature of 140°C. The preheated residue was then added to the liquified sulfur, after which, the mix was allowed to solidify.

d) Portland cement concretes and mortars. Each of the residues were incorporated into portland cement mortars (PCM) and concretes (PCC). All PCM mixes were made using Type I portland cement and blended silica sand. The residues were added to each mix as a replacement for a portion of the silica sand aggregate. The mortar mixes had a cement/filler ratio of 0.40 and a mixing water/cement ratio of 0.45. The concrete mixes had a cement/stone/sand ratio of 1.00/1.80/2.0 by weight, a mixing water/cement ratio of 0.42, and an air content of 5%. All PCM and PCC mixes were cured for 28 days before testing.

e) Magnesium polyphosphate cement mortars. Selected residues were incorporated into magnesium polyphosphate cement mortars. The residues were added to the mixes "as received" and were incorporated as a replacement for a portion of the sand filler. The mix design for the mortars consisted of 30 wt% magnesium oxide - 22 wt% ammonium polyphosphate (with 5 wt% powdered borax retarder) - 48 wt% filler (silica sand plus geothermal residue).

2.5 Coating Materials Evaluated.

Washed and oven-dried samples of residue BR1 were coated with three materials; a polyester resin, teflon, and calcium aluminate cement. The coating was done by the Fillite Company of Huntington, West Virginia, using a proprietary process.

3.0 LABORATORY TEST RESULTS.

Initial evaluation of each of the five encapsulation systems was based upon the results of compressive strength tests and 48 hr waste extract tests (WET) done using 1-in. diam by 2-in. long (25.4 mm by 50.8 mm) cylinders. Initial evaluation of each coating system was based upon 48 hr WET analyses. Upon completion of the preliminary evaluations the most promising systems were selected for further evaluation.

3.1 Preliminary Evaluation of Encapsulation Systems.

3.1.1 Composites made using Altek 78-50 emulsifiable polyester resin.

A series of PC composites were made using the Altek 78-50 as the binder. All of the composites were made using residue BR1. Composites were made using as received, dried, and washed residues. Resin contents of the composites varied between 25 and 32 wt% in order to maintain a satisfactory mixing consistency, i.e., the dryer the residue, the more resin the mix required. The results of the compressive strength and 48 hr WET tests are summarized in Table 6.

Results of the compressive strength tests indicate that drying the residue prior to incorporating it into the mix helps to improve the strength of the composite. The compressive strength is improved further if the residue is first washed to remove soluble salts which apparently inhibit the complete polymerization of the monomer. The results of the 48-hr WET tests indicate that the elemental concentrations measured for the composites were all below those measured for the unencapsulated residue, indicating that the Altek polyester is effective in partially immobilizing the leachable metals present.

3.1.2 Composites made using a MMA-based monomer system.

A series of PC composites were made with residues BR1, BR2, BR3, and BR4 using a MMA-based monomer consisting of 75 wt% MMA and 25 wt% PMMA. The results of compressive strength tests and 48 hr WET analysis are presented in Table 7.

Table 6. Encapsulation of Residue BR1 Using Altek 78-50 Emulsifiable Polyester.

MIX DESIGN	CONDITION OF RESIDUE	COMPRESSIVE ^a STRENGTH, psi	48-hr WET Analysis				
			Elemental Concentration, mg/l				
			Ba	Cr	Cu	Pb	Zn
25 wt% resin 75 wt% BR1	As Received	3695	17.0	<0.1	0.5	1.9	18.0
30 wt% resin 70 wt% BR1	Dried	5475	20.0	<0.1	0.5	1.4	10.2
32 wt% resin 68 wt% BR1	Washed & Dried	12,900	23.0	<0.1	0.3	0.5	1.9
STLC ^b	—	—	100	5	25	5	250

^a Average of three test specimens.

^b STLC = soluble threshold limit concentration.

Compressive strength test results indicate that strengths for three of the four systems tested varied between 4165 and 16,500 psi. The fourth system, the one made with residue BR4, did not cure even after being placed in an oven at 100°C for 3 hr. The 48-hr WET analysis indicates that each of the PC systems cured passed the leach test, i.e., element levels were below specified STLC concentrations.

3.1.3 Composites made with Sulfur.

Two composite systems made using residue BR1 were evaluated (Table 8). One system consisted of 60 wt% sulfur and 40 wt% residue BR1, the other consisted of 50 wt% sulfur - 30 wt% residue BR1 - 20 wt% silica sand. Compressive strengths of these systems were 3820 and 6365 psi, respectively. Results of the 48 hr WET test indicated elemental concentrations were below specified STLC values.

Table 7. Encapsulation of Residues Using a MMA-Based Monomer.

MIX DESIGN ^a	CONDITION OF RESIDUE	COMPRESSIVE STRENGTH, psi ^b	48-hr WET Analysis				
			Elemental Concentration, mg/l				
			Ba	Cr	Cu	Pb	Zn
30 wt% MMA 70 wt% BR1	Washed & Dried	4165	33	0.4	0.3	0.1	1.0
30 wt% MMA 70 wt% BR2	Washed & Dried	16,500	30	ND ^e	0.3	0.1	0.6
30 wt% MMA 70 wt% BR3	Washed & Dried	5,400	23	0.1	9.5	2.1	—
30 wt% MMA 70 wt% BR3	Washed & Dried	0 ^c	—	—	—	—	—
STLC ^d	—	—	100	5	25	5	250

^a Monomer system = 75 wt% MMA - 25 wt% PMMA with 4 wt% BFF 50 benzoyl peroxide initiator and 1 wt% dimethyl-para-toluidine promoter.

^b Average of 3 specimens.

^c Unable to cure sample.

^d STLC = soluble threshold limit concentration.

^e ND = not detectable.

3.1.4 Portland cement mortar (PCM) composites.

A series of PCM composites were made using each of the five geothermal residues. The residues were incorporated into the mixes as a replacement for a portion of the fine aggregate. Composites were cast using both "oven-dried" and "as received" residues. Presented in Tables 9 and 10 are the results of the compressive strength and 48-hr WET tests for PCM composites which contain 7 wt% residue, based upon the dry weight of the total solid content of the mix, i.e., 10 wt% of the fine aggregate was replaced with residue.

Table 8. Encapsulation of Residue BR1 Using Sulfur.

MIX DESIGN	CONDITION OF RESIDUE	COMPRESSIVE ^a STRENGTH, psi	48-hr WET Analysis				
			Elemental Concentration, mg/l				
			Ba	Cr	Cu	Pb	Zn
60 wt% sulfur 40 wt% residue BR 1	Dried	3820	9.8	<0.1	0.1	1.1	3.8
50 wt% sulfur 30 wt% residue BR1 20 wt% sand	Dried	6365	8.5	<0.1	0.2	1.3	7.7
STLC ^b	—	—	100	5	25	5	250

^a Average of three test specimens.

^b STLC = soluble threshold limit concentration.

The results of the compressive strength tests indicate that the strengths of the mortars, with two exceptions, increase with the addition of residue to the mix, as compared to the controls. In addition, the strengths of the mortars containing the "as received" residues are consistently higher than those containing the dried residues.

The 48-hr WET analysis indicates that each of the PCM systems passed the leach test, i.e., element levels were measured to be below specified STLC values. In general, there was no significant difference noted in the levels measured for the systems made with the dried residue as compared to those measured for the systems made with the "as received" residue.

3.1.5 Magnesium polyphosphate cement (MPC) composites.

A series of MPC mortars were made using residues BR1, BR2, BR3, and BR4. The residues were used "as received" and were added to the mixes as a replacement for 21 wt% of the fine aggregate. Presented in Table 11 are the results of compressive strength tests and 48-hr WET tests performed on each of the composite systems.

The results of the compressive strength tests indicate that the strength of MPC mortars is reduced with the addition of 10 wt% residue. Reductions in strength varied between 15 and 60%, as compared to the controls.

The results of the 48-hr WET tests indicate that mortars made with residues BR1, BR2, and BR3 can be considered as non-hazardous, while those made with residue BR4 must be considered as hazardous since concentrations of lead (Pb) are in excess of the STLC values.

3.1.6 Preliminary evaluation of Materials costs.

A preliminary materials cost estimate (1986 cost data) was made for each of the five encapsulation systems evaluated. This cost evaluation was based strictly upon materials costs and does not take into consideration production costs such as equipment, labor, and overhead. A summary of the cost data is presented in Table 12.

Table 9. Compressive Strengths of Portland Cement Mortars Containing Geothermal Residues.

PCM SYSTEM ^a	CONDITION OF RESIDUE	28-DAY COMPRESSIVE STRENGTH, psi	CONDITION OF RESIDUE	28-DAY COMPRESSIVE STRENGTH, psi
Control - No Residue	—	4295	—	—
7 wt% BR1	Dried	4930	As Received	5160
7 wt% BR2	Dried	5530	As Received	5445
7 wt% BR3	Dried	4840	As Received	5265
7 wt% BR4	Dried	4135	As Received	4895
7 wt% BR5	—	—	As Received	3570

^a Residue content is based on dry weight of the total solid content of mix.

Table 10. 48 Hour WET Analysis of FCM Composites Containing Geothermal Residues.

FCM SYSTEM ^a	CONDITION OF RESIDUE	ELEMENTAL CONCENTRATION, ^a mg/l										
		Sb	As	Ba	Cd	Cr	Co	Cu	Pb	Ni	Ag	Zn
Control - No Residue	—	0.6	ND ^b	1.4	0.1	0.1	0.1	0.2	ND	0.1	ND	0.1
7 wt% BR1	Dried	NT ^c	ND	NT	NT	0.4	0.3	0.2	ND	0.6	ND	0.1
7 wt% BR2	Dried	NT	ND	NT	NT	0.4	0.2	0.3	0.1	0.6	ND	0.2
7 wt% BR3	Dried	NT	ND	NT	NT	0.5	0.2	0.8	0.1	0.6	ND	0.1
7 wt% BR4	Dried	NT	ND	NT	NT	1.2	0.3	2.7	1.8	0.6	ND	0.8
7 wt% BR1	As Received	0.9	ND	2.7	0.1	0.5	0.2	0.3	ND	0.4	ND	0.1
7 wt% BR2	As Received	0.8	ND	2.6	0.1	0.6	0.2	0.2	ND	0.4	ND	0.1
7 wt% BR3	As Received	0.8	ND	3.5	0.1	0.4	0.2	0.7	0.1	0.4	ND	0.1
7 wt% BR4	As Received	0.9	ND	3.0	0.1	1.5	0.2	2.6	1.4	0.5	ND	0.5
7 wt% BR5	As Received	1.7	ND	NT	0.1	0.4	0.3	2.5	1.9	0.5	0.1	1.5
STLC ^d		100	5	100	1	5	80	25	5	20	5	250

^a Residue content is based on dry weight of the total solid content of mix.

^b ND = not detectable.

^c NT = no test.

^d STLC = soluble threshold limit concentration.

Table 11. Compressive Strength and 48 Hour WET Test Results for MPC Mortars Containing Geothermal Residue.

MPC SYSTEM	COMPRESSIVE STRENGTH, psi ^b	48-hr WET Analysis								
		Elemental Concentration, mg/l								
		As	Cr	Co	Cu	Pb	Ni	Ag	Zn	
Control	4235	ND ^a	0.9	0.2	0.2	0.2	0.2	0.7	ND	6.0
10 wt% BR1	2745	ND	0.9	0.2	0.3	0.3	0.3	0.8	ND	7.0
10 wt% BR2	3600	ND	0.9	0.2	0.3	0.2	0.2	0.8	ND	6.5
10 wt% BR3	2575	ND	0.9	0.2	1.8	0.5	0.9	0.9	ND	11.5
10 wt% BR4	1770	ND	1.1	0.2	5.6	16.7	0.9	0.9	ND	15.5
STLC ^b	—	5	5	80	25	5	20	5	5	250

^a ND = not detectable.

^b STCL = soluble threshold limit concentration.

Based upon a preliminary materials cost estimate, the most economical encapsulation system is the portland cement mortar system, at a materials cost of 1.5¢/lb. The most expensive system is the PC composite made with the MMA-based monomer (38.9¢/lb). It should be noted that while the summary indicates that the materials costs for the sulfur and portland cement mortar systems are very similar, the summary does not reflect the energy costs associated with the production of sulfur composites, i.e., the energy costs for preheating the aggregates and for melting the elemental sulfur.

3.2 Evaluation of Coating Techniques.

Samples of residue B1 were sent to the Fillite Corporation, Huntington, West Virginia, to determine if it was possible to coat the individual particles of residue. This company had developed a proprietary process to coat particles that range in size from 3 microns to 2.5 mm. The residue was coated with one of three materials, a polyester resin, teflon, and calcium aluminate cement. Preliminary tests performed by Fillite indicated that it was necessary to pre-dry the residue when coating it with either the polyester resin or teflon. This was not necessary for the cement.

Table 12. Materials Cost Summary.

MATERIALS SYSTEM	RESIDUE CONTENT wt %	MATERIALS COST, ¢/lb of Composite
Polyester resin	25	38.3
MMA-based monomer	30	38.9
Sulfur	40	2.0
Portland Cement Mortar	7	1.5
Magnesium polyphosphate cement mortar	10	11.7

After coating, the samples were separated into different size fractions for evaluation in the 48 hr WET test. The polyester-coated samples were separated into two sieve size fractions, -No. 16 +No. 50 (-1.18 mm +300 μ m) and -No. 50 (-300 μ m). The cement-coated samples were also separated into two sieve size fractions, -1/4 in. +No. 8 (-6.3 mm +2.36 mm) and -No. 8 +No. 50 (-2.36 mm +300 μ m). The teflon-coated samples were not separated. Results of the 48 hr WET test are summarized in Table 13.

Results indicate that coating of the residue, in each case, reduces the concentration of material leached from the residue. The most effective coating material was the calcium aluminate cement. This is favorable since the cement is considerably less expensive than the polyester and teflon and because pre-drying of the residue is not required. The teflon coated particles exhibited the least reduction in leach rate. Microscopic examination of the particles indicated voids in the coating, and in some cases, the coating was not visible at all.

3.3 Selection of Techniques for Further Evaluation.

Based upon the results of the preliminary laboratory tests done to evaluate the effectiveness of five encapsulation and three coating techniques, encapsulation of geothermal residues in portland cement mortar and concrete was identified as the most promising method of stabilization investigated. Selection of this technique was based upon the following.

- a) The portland cement mortar systems did not require that the residue be washed or dried prior to incorporating it into a mix, i.e., the residue can be used "as received".
- b) Incorporation of geothermal residues into portland cement mortars appears, in many instances, to improve the 28-day compressive strength.
- c) 48 hr WET analysis indicates that elemental concentrations of hazardous elements present in the residues are well below specified STLC values, for the residue concentrations evaluated.
- d) The portland cement mortar systems were the least expensive from a standpoint of materials costs.

Table 13. 48 Hour WET Analysis of Coated Residue BRL.

COATING	PARTICLE SIZE	48-hr WET Analysis				
		Elemental Concentration, mg/l				
		Ba	Cr	Cu	Pb	Zn
Polyester resin	-No. 16 +No. 50	9.5	ND ^a	0.2	0.5	1.4
	-No. 50	14.8	ND	0.2	0.5	1.2
Teflon	As coated	18.7	<0.1	0.4	0.6	6.0
Calcium Aluminate Cement	-1/4 +No. 8	3.2	ND	<0.1	ND	ND
	-No. 8 +NO. 50	7.6	<0.1	<0.1	0.1	0.4
None	As received	27	<0.1	0.8	3.5	18
STLC ^b	—	100	5	25	5	250

^a ND = not detectable.

^b STLC = soluble threshold limit concentration.

4.0 EVALUATION OF PORTLAND CEMENT MORTARS AND CONCRETES CONTAINING GEOTHERMAL RESIDUES.

Presented in this chapter are the results of tests done to evaluate the physical, mechanical, and leaching properties of portland cement mortars (PCM) and concretes (PCC) made with each of the five geothermal residues being studied. Test methods and procedures are presented in Section 2.3.

4.1 Physical and Mechanical Properties of PCM and PCC Composites.

PCM composites containing 7 and 18 wt% residues, based upon the dry weight of the total solids content, were made with each of the five geothermal residues. PCC composites containing 5 wt% residue were also cast. The results of tests done to evaluate the compressive strengths of the PCM and PCC composites are summarized in Tables 14 and 15.

The results indicate that with the exception of the composites made with residue BR5, there is an increase in the 28-day compressive strength of PCM composites made containing 7 wt% residue. The increase in strength varies between 14 and 27%, as compared to the controls, with the greatest increase being exhibited by those composites made with residue BR2. The PCM composites made with 7 wt% residue BR5 exhibited a 17% reduction in strength.

In all cases, increasing the residue content from 7 to 18 wt% resulted in a decrease in the 28-day compressive strengths. However, the PCM composites made with residues BR1 and BR3 still exhibited compressive strengths in excess of the controls.

Compressive strength tests done at 6 mo. and 1 yr indicated a general reduction in strength with time for all but one of the PCM composites. Reductions in strength, after 1 yr, varied between 11 and 39%, compared to the 28-day strengths for composites containing 7 wt% residue and between 0.5 and 22% for composites containing 18 wt% residue. The PCM composite made with 18 wt% residue BR2 exhibited a gradual increase in strength with time, and after 1 yr, had shown a 39% increase in strength. The PCM controls exhibited a 2% increase in strength after 1 yr from a value of 4295 to 4370 psi.

Table 14. Compressive Strengths of PCM Composites Containing Geothermal Residues.

PCM SYSTEM ^a	COMPRESSIVE STRENGTH, psi ^b		
	28 DAY	6 MONTHS	1 YEAR
Control	4295	4215	4370
w/7 wt% BR1	5160	5120	4015
w/18 wt% BR1	4700	4170	4315
w/7 wt% BR2	5445	5382	4830
w/18 wt% BR2	2875	3420	3990
w/7 wt% BR3	5265	4590	3605
w/18 wt% BR3	4450	3135	4430
w/7 wt% BR4	4895	4855	3000
w/18 wt% BR4	3110	2800	2410
w/7 wt% BR5	3565	2655	3459
w/18 wt% BR5	1495	745	931

^a Residue content is a percentage of the dry weight of the total solids content.

^b Test specimen were 1-in. diam by 2-in. long cylinders.

Table 15. Compressive Strengths of PCC Composites Containing Geothermal Residues.

PCM SYSTEM ^a	COMPRESSIVE STRENGTH, psi ^b		
	28 DAY	6 MONTHS	1 YEAR
Control	4205	4090	4720
w/5 wt% BR1	4340	3650	4810
w/5 wt% BR2	4690	5190	4655
w/5 wt% BR3	4925	4645	3580
w/5 wt% BR4	4535	3465	3165
w/5 wt% BR5	3735	3100	2845

^a Residue content is a percentage of the dry weight of the total solids content.

^b Test specimen were 3-in. diam by 6-in. long cylinders.

The results of the 28-day compressive strength tests done on the PCC composites (Table 15) exhibited the same general trend as that exhibited by the PCM composites (Table 14). The PCC composites made with residues BR1, BR2, BR3, and BR4 (5 wt%) all exhibited increases in strength varying between 3 and 17%, when compared to the control. The PCC composite made with residue BR5 exhibited a 11% reduction in strength. The controls had a 28-day compressive strength of 4205 psi.

Results of six-month and one-year compressive strength tests indicated a general reduction in strength with time for the composites made with residues BR3, BR4, and BR5. The reductions in strength exhibited after 1 yr

varied between 24 and 30 percent. Composites made with residue BR1 exhibited a 11 percent increase in strength after 1 yr, while those made with residue BR2 remained relatively unchanged. Controls exhibited a 12 percent increase in strength after 1 yr.

A series of tests were performed to determine the bulk specific gravity, water permeability, water absorption, and permeable void volume of PCM composites containing geothermal residues. The results are summarized in Table 16.

The results indicate that for both PCM and PCC composites, the bulk specific gravity of the composite decreases as a result of the addition of the geothermal residue. Water absorption and permeable void volume were shown to increase with the addition of geothermal residue. In addition, both properties increased with increasing residue content. No definitive trend was noted regarding the effect of geothermal residues on the water permeability characteristics of PCM composites. Some composites exhibited increases in permeability while others exhibited decreases.

4.2 Leachability Characteristics of PCM and PCC Composites.

A series of tests were done using the 48 hr WET test to evaluate the leaching characteristics of PCM and PCC composites made with each of the five geothermal residues. A summary of the test results are presented in Table 17.

With the exception of the composites containing 18 wt% BR4, all PCM composites had element concentrations below the specified STLC values, thus making these composites non-hazardous. The composite containing 18 wt% residue BR4 must be considered hazardous, by this test, because excessive levels of arsenic (As), chromium (Cr), and lead (Pb) were detected in the leachate. In general, elemental concentrations in PCM composites tended to increase with increasing residue content.

All of the PCC composites were found to pass the 48 hr WET test, i.e., elemental concentrations in the 48 hr leachate were below specified STLC values.

Table 16. Physical Properties of PCM and PCC Composites Containing Geothermal Residues.

SYSTEM ^a	BULK SPECIFIC GRAVITY	WATER PERMEABILITY, millidarcy	WATER ABSORPTION wt %	PERMEABLE VOID VOL., %
a) PCM Systems				
Control	2.08	5.6×10^{-4}	9.22	19.21
w/7 wt% BR1	2.07	12.7×10^{-4}	10.58	21.90
w/18 wt% BR1	1.98	10.5×10^{-4}	13.71	27.14
w/7 wt% BR2	2.07	9.0×10^{-4}	9.70	20.10
w/18 wt% BR2	1.98	2.0×10^{-4}	12.59	24.91
w/7 wt% BR3	2.05	5.2×10^{-4}	11.15	22.88
w/18 wt% BR3	1.96	2.4×10^{-4}	14.55	28.49
w/7 wt% BR4	1.91	3.4×10^{-4}	15.59	29.76
w/18 wt% BR4	1.81	44.5×10^{-4}	18.54	33.49
w/7 wt% BR5	1.88	15.2×10^{-4}	15.21	28.67
w/18 wt% BR5	1.64	75.1×10^{-4}	22.65	37.15
b) PCC Systems				
Control	2.17	—	5.59	12.14
w/5 wt% BR1	2.17	—	7.39	16.07
w/5 wt% BR2	2.22(?)	—	5.64	12.54
w/5 wt% BR3	2.17	—	7.87	17.07
w/5 wt% BR4	2.10	—	9.07	19.08
w/5 wt% BR5	2.12	—	8.61	18.28

^a Residue content is based on dry weight of the total solids content.

(5.1)

Table 17. 48 Hour WET Analysis of PCM and PCC Composites Containing Geothermal Residues.

SYSTEM ^a	ELEMENTAL CONCENTRATION, ^a mg/l										
	Sb	As	Ba	Cd	Cr	Co	Cu	Pb	Ni	Ag	Zn
a) PCM											
Control	0.9	ND ^b	1.5	0.1	0.4	0.2	0.2	0.2	0.4	ND	0.1
w/7 wt% BR1	0.9	ND	2.7	0.1	0.5	0.2	0.3	ND	0.4	ND	0.1
w/18 wt% BR1	0.8	ND	2.8	0.1	0.4	0.1	0.5	0.2	2.2	ND	0.1
w/7 wt% BR2	0.8	ND	2.6	0.1	0.6	0.2	0.2	ND	0.4	ND	0.1
w/18 wt% BR2	0.7	ND	3.1	0.1	0.4	0.1	0.4	0.2	1.9	ND	0.1
w/7 wt% BR3	0.8	ND	3.5	0.1	0.4	0.2	0.7	0.1	0.4	ND	0.1
w/18 wt% BR3	0.7	ND	2.5	0.1	0.4	0.1	2.6	0.3	1.8	ND	0.1
w/7 wt% BR4	0.9	ND	3.0	0.1	1.5	0.2	2.6	1.4	0.5	ND	0.5
w/18 wt% BR4	1.4	6.6	1.8	0.2	5.0	0.2	9.0	5.4	2.2	0.1	2.5
w/7 wt% BR5	1.7	ND	—	0.1	0.4	0.3	2.5	0.9	0.5	<0.1	1.5
w/18 wt% BR5	1.2	ND	—	0.1	0.4	0.3	3.3	1.5	0.5	<0.1	6.0
b) PCC											
Control	ND	ND	0.5	0.1	0.3	0.2	1.8	0.7	0.2	<0.1	0.6
w/5 wt% BR1	ND	ND	4.0	0.1	0.2	0.3	1.8	0.8	0.3	<0.1	0.8
w/5 wt% BR2	ND	ND	4.0	0.1	0.3	0.3	1.8	0.5	0.3	<0.1	0.7
w/5 wt% BR3	ND	ND	4.0	0.1	0.2	0.3	2.6	0.4	0.3	<0.1	0.8
w/5 wt% BR4	ND	ND	2.0	0.1	1.8	0.2	4.8	3.4	0.4	<0.1	2.1
w/5 wt% BR5	0.8	ND	—	<0.1	0.2	0.1	2.0	0.4	0.2	ND	1.0
STLC ^c	100	5	100	1	5	80	25	5	20	5	250

^a Residue content is based on dry weight of the total solids content of mix.

^b ND = not detectable.

^c STLC = soluble threshold limit concentration.

(5.1)

A second series of WET tests were done to evaluate the long term leaching characteristics of each of the raw residues as well as selected PCM composites containing each of the residues.

The PCM composites tested included those made using 18 wt% residue BR1, BR2, BR3, and BR5 and 7 wt% residue BR4. The latter composite contained only 7 wt% residue because previous WET test analysis had indicated that PCM systems containing 18 wt% residue BR4 were considered "hazardous".

Extracts for AA analysis were removed for analysis from each sample after 48 hr, 1 wk, and 4 wk. An equivalent amount of sodium citrate was added to each sample to replace the extract which had been withdrawn. The leaching solution for the PCM samples was replaced every 7 days to control the pH. The leaching solutions for the raw residues were not replaced since the pH did not vary as much as those for the PCM samples. They were, however, adjusted each week to keep the pH of the solution within the prescribed range. Test results for 48 hr, 1 wk, and 4 wk are summarized in Table 18.

The test results indicate that after 48 hr, two of the five residues, BR3 and BR4, had elemental concentrations in excess of allowable STLC values, thereby making them "hazardous" materials. Residue BR3 had excessive levels of arsenic (As) and lead (Pb), and residue BR4 had excessive levels of As, chromium (Cr), and Pb. The other raw residues and all of the PCM composites passed the 48 hr WET test.

Of the samples which passed the 48 hr WET test, only residue BR5 and the PCM composite containing 7 wt% BR3 were found to fail the WET test with additional leaching. After 1 wk, residue BR5 was measured to have excessive levels of As, and after 2 wk, the PCM composite was measured to have excessive levels of Cr and Pb. The remaining PCM samples exhibited gradual increases in elemental concentrations over the 4 wk period, however, the concentrations remained below specified STLC values. The elemental concentrations measured for the raw residues appeared to decrease with time, however, this seems unlikely and is probably the result of adding new leachate to the sample after withdrawing an extract for analysis and to help adjust the pH level.

Table 18. Summary of Long-Term WET Tests.

SYSTEM ^a	LEACH TIME	ELEMENTAL CONCENTRATION, ^a mg/l									
		Sb	As	Cd	Cr	Co	Cu	Pb	Ni	Ag	Zn
Residue BR1	48 hr	3	ND ^b	0.1	0.1	0.1	0.6	3.5	0.1	<0.1	17.5
	1 wk	5	ND	0.1	0.2	0.1	0.2	4.3	0.2	ND	16.3
	4 wk	7	ND	0.1	0.4	0.1	0.1	4.0	0.2	<0.1	12.5
Residue BR2	48 hr	ND	ND	<0.1	ND	ND	0.4	0.2	ND	ND	0.9
	1 wk	1	ND	<0.1	ND	ND	0.6	0.4	ND	ND	1.1
	4 wk	1	ND	<0.1	0.1	ND	0.9	0.4	0.1	ND	1.3
Residue BR3	48 hr	40	13	0.1	0.5	0.1	20.0	8.6	0.5	<0.1	13.5
	1 wk	58	16	0.1	0.6	0.1	17.0	8.9	0.5	<0.1	14.0
	4 wk	37	11	0.1	0.8	0.2	2.7	5.4	0.4	<0.1	8.0
Residue BR4	48 hr	14	70	0.9	73	0.2	ND	68	0.3	<0.1	71
	1 wk	14	71	0.3	67	0.3	ND	27	0.3	<0.1	71
	4 wk	8	30	0.2	28	0.2	ND	7.2	0.2	<0.1	60
Residue BR5	48 hr	3	3	0.2	0.1	0.2	1.3	1.5	0.2	<0.1	59
	1 wk	3	6	0.3	0.1	0.2	6.5	1.7	0.3	<0.1	60
	4 wk	3	7	0.2	0.1	0.2	5.5	3.4	0.3	ND	55
PCM - Control	48 hr	ND	ND	<0.1	0.5	0.1	0.2	ND	0.2	ND	0.1
	1 wk	ND	ND	ND	0.6	0.1	0.2	ND	0.2	ND	0.1
	4 wk	ND	ND	<0.1	0.9	0.2	0.4	0.2	0.5	ND	1.4
PCM w/18 wt% BR1	48 hr	0.6	ND	ND	0.4	ND	0.4	ND	0.1	ND	0.1
	1 wk	0.6	ND	ND	0.5	ND	0.4	ND	0.1	ND	0.1
	4 wk	1.5	ND	<0.1	1.0	0.1	0.7	0.3	0.5	ND	2.1
PCM w/18 wt% BR2	48 hr	ND	ND	ND	0.6	0.1	0.3	ND	0.1	ND	0.1
	1 wk	ND	ND	ND	0.6	0.1	0.3	ND	0.1	ND	0.1
	4 wk	0.9	ND	0.1	1.0	0.2	0.6	0.1	0.5	ND	1.5
PCM w/18 wt% BR3	48 hr	ND	ND	<0.1	0.5	ND	2.1	ND	0.1	ND	0.1
	1 wk	ND	ND	<0.1	0.6	ND	2.3	ND	0.1	ND	0.1
	4 wk	1.0	ND	0.1	1.1	0.1	3.9	0.9	0.5	ND	2.3
PCM w/7 wt% BR4	48 hr	1.0	ND	<0.1	2.2	0.1	2.3	0.9	0.1	ND	0.3
	1 wk	1.0	ND	<0.1	2.4	0.1	2.4	2.1	0.1	ND	1.0
	4 wk	2.0	ND	0.2	5.6 ^d	0.3	4.7	8.1 ^d	0.5	ND	13.3
PCM w/18 wt% BR5	48 hr	0.5	ND	<0.1	0.2	0.1	2.8	0.7	0.1	ND	1.5
	1 wk	1.0	ND	<0.1	0.2	0.1	3.0	1.6	0.2	ND	3.5
	4 wk	1.8	ND	0.1	0.4	0.2	4.1	2.8	0.4	ND	19.2
STLC ^d	—	100	5	1	5	80	25	5	20	5	250

^a Residue contents of PCM composites are a percentage of the dry weight of the total solids content.

^b ND = not detectable.

^c STLC = soluble threshold limit concentration.

^d After 2 wk, the Cr and Pb levels were 5.5 and 7.8 mg/liter, respectively.

4.3 Long-Term Durability Tests

A series of tests were run to evaluate the freeze-thaw durability of PCC composites in which 5 wt% of the total solids content was replaced with "as received" geothermal residues (residues BR1, BR2, BR3 and BR4). The tests were run using 3-in. diam by 6-in. long cylinders. Evaluation of the composites was based upon compressive strength and 48 hr WET tests and visual observations. The results are summarized in Tables 19 and 20.

Results of the compressive strength tests indicate that the PCC composites containing the geothermal residues exhibited reductions in compressive strength varying between 3 and 23% after exposure to 100 freeze-thaw cycles. The PCC composite containing no residue exhibited a 4% reduction in strength. Prior to freeze-thaw testing, each of the PCC composites containing residue exhibited a compressive strength in excess of the control which had a strength of 4205 psi. After 100 cycles of freeze-thaw, only the PCC composite made with residue BR2 exhibited a compressive strength in excess of the controls, which had a compressive strength of 4035 psi.

Results of the 48 hr WET tests before and after freeze-thaw testing indicates that while there is a slight increase in some of the elemental concentrations after 100 cycles of freeze-thaw, all values are still below recommended STLC values, thereby making the composites "non-hazardous".

WET tests were also run on PCM composites containing 7 wt% residue which had been stored for 1 yr in air at room temperature. These composites were made using "as received" samples of residues BR1, BR2, BR3 and BR4. The test results are summarized in Table 21.

The WET test results indicate that the elemental concentrations remain relatively stable after the first year, with no significant increases or decreases being noted in any of the elemental levels. These results indicate that the decreases in strength with time observed in the compressive strength tests (Section 4.1), do not necessarily imply an increase in elemental leaching rates. After 1 yr, each of the PCM composites tested passed the 48 hr WET test.

Two year compressive strength and 48 hr WET tests will be run on PCM and PCC composites presently being stored in air at room temperature.

Table 19. Freeze-Thaw Durability of PCC Composites Containing Geothermal Residues.

PCC SYSTEM ^a	COMPRESSIVE STRENGTH, psi		PERCENT CHANGE
	INITIAL ^b	AFTER 100 CYCLES	
Control	4205	4035	-4
w/5 wt% BR1	4340	3810	-12
w/5 wt% BR2	4690	4555	-3
w/5 wt% BR3	4925	3770	-23
w/5 wt% BR4	4535	3550	-22

^a Residue content is a percentage of the dry weight of the total solids content.

^b 28-day compressive strength.

VISUAL OBSERVATIONS

1. After 25 cycles. No evidence of deterioration in any sample.
2. After 58 cycles. In general, all cylinders are in very good condition. Some very light surface scaling was noted on PCC specimens made with residue BR4.
3. After 73 cycles. No significant changes were noted in the condition of PCC specimens made with residue BR4. Some of the other composites are starting to show very slight evidence of surface scaling.
4. After 100 cycles.
 - PCC controls - some minor surface scaling over <10% of the surface area.
 - PCC w/BR1 - minor surface scaling over 10 to 20% of the surface area. Some aggregate popouts were noted in cut surfaces on the ends of the cylinders.
 - PCC w/BR2 - no significant damage noted.
 - PCC w/BR3 - minor surface scaling over 10 to 20% of the surface area. Some aggregate popouts noted in cut surfaces at the ends of the cylinders.
 - PCC w/BR4 - significant surface scaling over 25% of area. Paste, in some areas, has been removed and aggregate has been exposed.

Table 20. 48 Hour WET Analysis of PCC Composites Containing Geothermal Residues Before and After Freeze-Thaw Testing.

PCC SYSTEM ^a	ELEMENTAL CONCENTRATION, mg/l										
	Sb	As	Ba	Cd	Cr	Co	Cu	Pb	Ni	Ag	Zn
Before Freeze-Thaw											
Control	ND ^b	ND	0.5	0.1	0.3	0.2	1.8	0.7	0.2	<0.1	0.6
w/5 wt% BR1	ND	ND	4.0	0.1	0.2	0.3	1.8	0.8	0.3	<0.1	0.8
w/5 wt% BR2	ND	ND	4.0	0.1	0.3	0.3	1.8	0.5	0.3	<0.1	0.7
w/5 wt% BR3	ND	ND	4.0	0.1	0.2	0.3	2.6	0.4	0.3	<0.1	0.8
w/5 wt% BR4	ND	ND	2.0	0.1	1.8	0.2	4.8	3.4	0.4	<0.1	2.1
After Freeze-Thaw											
Control	ND	ND	—	0.1	0.4	0.3	2.0	0.8	0.5	<0.1	1.0
w/5 wt% BR1	ND	ND	—	0.1	0.3	0.2	2.1	0.7	0.5	<0.1	1.0
w/5 wt% BR2	ND	ND	—	0.1	0.4	0.3	2.2	0.7	0.5	<0.1	1.4
w/5 wt% BR3	ND	ND	—	0.1	0.3	0.3	2.7	0.8	0.5	<0.1	1.0
w/5 wt% BR4	ND	ND	—	0.1	2.2	0.3	4.8	4.4	0.5	<0.1	11.
STLC ^c	100	5	100	1	5	80	25	5	20	5	250

^a Residue content is based on dry weight of total solids content.

^b ND = not detectable.

^c STLC = soluble threshold limit concentration.

(5.1)

Table 21. 48 Hour WET Analysis of 28 Day and 1 Year Old PCM Composites.

SYSTEM ^a	ELEMENTAL CONCENTRATION, ppm								
	Sb	Cd	Cr	Co	Cu	Pb	Ni	Ag	Zn
At 28 DAYS									
PCM/Control	0.9	0.1	0.4	0.2	0.2	0.2	0.4	ND	0.1
w/7 wt% BR1	0.9	0.1	0.5	0.2	0.3	ND ^b	0.4	ND	0.1
w/7 wt% BR2	0.8	0.1	0.6	0.2	0.2	ND	0.4	ND	0.1
w/7 wt% BR3	0.8	0.1	0.4	0.2	0.7	0.1	0.4	ND	0.1
w/7 wt% BR4	0.9	0.1	1.5	0.2	2.6	1.4	0.5	ND	0.5
After 1 Yr									
PCM/Control	ND	ND	0.8	ND	0.1	ND	ND	ND	0.1
w/7 wt% BR1	ND	ND	0.8	ND	0.1	ND	ND	ND	0.1
w/7 wt% BR2	1.0	ND	0.9	0.1	0.2	ND	ND	ND	0.2
w/7 wt% BR3	ND	ND	0.8	0.1	0.5	ND	ND	ND	0.2
w/7 wt% BR4	ND	ND	2.6	<0.1	2.0	ND	ND	ND	0.6
STL ^c	100	1	5	80	25	5	20	5	250

^a Residue content is a percentage of the dry weight of the total solid content.

^b ND = not detectable.

^c STL^c = soluble threshold limit concentration.

5. ECONOMIC ANALYSIS.

5.1 Existing Disposal Costs.

Currently, there are three major costs associated with the disposal of hazardous, solid geothermal residues in California. These are: hazardous-waste site acceptance fees, transportation costs, and a state tax on hazardous waste generation. Waste site acceptance fees presently vary between \$55/yd³ and \$90/yd³ for regulated solid waste, depending upon the site. Trucking costs are about \$55/hr (16). For a 50-MW plant which produces 120,000 lb/day of slurry containing 65% solid residue, disposal costs are about \$1,022,000/yr. This cost does not include the long-term liability associated with the disposal of hazardous waste, which must be assumed by the generator of waste and is likely to be very significant. Nor does it include increased transportation costs which are likely to occur as hazardous waste sites are located further and further from populated areas.

5.2 Economic Alternatives.

There are a number of economic alternatives available regarding the utilization and/or disposal of geothermal residues which have been classified as hazardous. These alternatives include, incorporating the residue into a PCM system which is disposed of as a non-hazardous material, selling (or giving away) the residue for use as a fine aggregate in PCM and PCC systems, and setting up a mobile concrete plant at the well site for the purposes of manufacturing ready-mixed concrete and/or concrete block.

Incorporating 18 wt% residue into a PCM system for subsequent disposal costs about \$2,129,100/yr for a 50-MW plant producing 120,000 lb/hr slurry containing 65 wt% solids (Table 22). This cost analysis does not take into account the \$1,022,000 which is saved by not having to dispose of the residue as a hazardous material. Nor does it take into account the reduced liability associated with the disposal of non-hazardous materials.

Selling the residue to a concrete manufacturer for use as a fine aggregate could result in a profit of as much as \$123,000/yr if it is sold for \$8.415/ton (17). This is the average cost of sand in California. Selling of the residue also results in a savings of \$1,022,000/yr, the disposal cost of the residue. This disposed cost could also be saved if the residue were given away for use as a fine aggregate.

Table 22. Cost Analysis for Incorporating Geothermal Residue Into a PCM Composite^a.

A. Capital Costs			
1. Direct Costs (DC)			\$ 390,000
	Purchased equipment (PE)	\$300,000	
	portable transit mix plant and operating equipment		
	Installed equipment	30% PE	\$ 90,000
2. Indirect Costs (IC) (Contingency)	20% DC		\$ 78,000
3. Fixed Capital (FC)	IC+DC		\$ 468,000
4. Working Capital (WC)	25% FC		\$ 117,000
5. Total Capital Cost (TCC)	FC+WC		\$ 585,000
6. Ammortized Capital Cost (ACC) (Based on a 30-yr plant life and 10% interest rate)			\$ 62,100
B. Annual Operating Expenses			
1. Material Costs (cement, gravel, etc.)			\$1,817,000
2. Labor			\$ 150,000
3. Overhead (insurance, power, etc.)			\$ 100,000
4. Total Operating Costs (TOC)			\$2,067,000
C. Total Operating Expenses (TOE)	ACC+TOC		\$2,129,100

^a It is assumed that all residue produced is incorporated into a PCM composite. Analysis is based on 1987 price data.

Another option is to set up a mobile concrete batch plant or block plant, at the geothermal plant site, for the production of ready-mix concrete or concrete block. The potential profit produced by incorporating the residue into PCC ready-mix is about \$638,700 (Table 23). This is based upon the assumption that all of the residue produced by the plant is incorporated into a PCC mix. The PCC mix design used in the analysis consists of 21 wt% type I portland cement, 37.5 wt% crushed siliceous gravel, 36.5 wt% silica sand, and 5 wt% geothermal residue, with a mixing water to cement ratio of 0.42 and an entrained air content of $5 \pm 1\%$.

Approximately 144,175 yd³ of ready mix can be produced annually at a cost of \$41.14/yd³. The average market price for 3000 psi ready mix concrete, in California, is \$45.57/yd³ (17). If the ready mix is sold at this price, a profit of \$4.43/yd³ is realized. In addition, there is an additional savings of \$1,022,00/yr, the annual cost for disposing of the residue in a hazardous waste site.

Table 23. Cost Analysis for the Production of Ready-Mix Concrete^a.

1. Capital Costs		
1.1 Direct Costs (DC)		\$ 390,000
Purchased equipment (PE)	\$300,000	
portable transit mix plant		
and operating equipment		
Installed equipment	30% PE	\$ 90,000
1.2 Indirect Costs (IC)	20% DC	\$ 78,000
(Contingency)		
1.3 Fixed Capital (FC)	IC+DC	\$ 468,000
1.4 Working Capital (WC)	25% FC	\$ 117,000
1.5 Total Capital Cost (TCC)	FC+WC	\$ 585,000
1.6 Ammortized Capital Cost (ACC)		\$ 62,100
(Based on a 30-yr plant life and 10% interest rate)		
2. Annual Operating Expenses		
2.1 Material Costs		\$5,620,000
(cement, sand, gravel, etc.)		
2.2 Labor		\$ 150,000
2.3 Overhead		\$ 100,000
(issurance, utilities, etc.)		
2.4 Total Operating Costs (TOC)		\$5,870,000
3. Total Operating Expenses (TOE)	ACC+TOC	\$5,932,100
4. Total Annual Plant Production (ready-mix)		\$ 144,175/yd ³
5. Average Annual Production Costs		\$ 41.14/yd ³
6. Average Market Price for 3000 psi Ready Mix Concrete		\$ 45.57/yd ³
7. Potential Profit (per yd ³ of ready mix)		\$ 4.43/yd ³
8. Annual Profit (all ready mix is sold)		\$ 638,700

^a It is assumed that all residue produced is incorporated into a PCC ready-mix. Analysis is based on 1987 price data.

6.0 SUMMARY AND RECOMMENDATIONS.

Under contract to the United States Department of Energy (DOE), Brookhaven National Laboratory (BNL) has conducted a program, the objective of which was to identify and develop a process for the acceptable disposal and/or utilization of hazardous geothermal residues.

The primary objective of the program was to identify and evaluate a process or processes which could be used to convert hazardous geothermal residues to a non-hazardous form. While there are a number of methods available for stabilizing hazardous materials, the emphasis of the program was directed towards two solidification techniques: coating and encapsulation.

Once a hazardous material has been stabilized, it is generally disposed of conventionally. However, a second objective of the program was to identify a process which could be used to produce a material which could be utilized as a construction material.

Five geothermal residues were obtained from various geothermal sites located in California. Forty-eight hour waste extraction tests (WET) indicated that three of these residues contained leachable levels of various elements, such as arsenic, cadmium, chromium and lead, in excessive of the allowable limits, thereby causing them to be classified as hazardous.

Five materials were used to encapsulate the geothermal residues. They were Alpha Corporation's Altek 78-50 emulsifiable polyester resin, a methyl methacrylate-based monomer system, sulfur, portland cement concretes and mortars, and magnesium polyphosphate cement mortars. Three coating materials were evaluated, a polyester resin, teflon, and calcium aluminate cement.

Results of the preliminary laboratory tests done to evaluate the effectiveness of the five encapsulation and three coating techniques indicated that encapsulation of the geothermal residues in portland cement mortar and concrete composites was the most promising method of stabilization investigated. Selection of the technique was based upon the following:

a) The portland cement system did not require that the residue be washed or dried prior to incorporating it into a mix, i.e., it could be used "as received".

b) Incorporation of geothermal residues into portland cement mortars appeared, in many instances, to improve the 28-day compressive strength, as compared to controls.

c) Forty-eight hour WET analysis indicated that leachable concentrations of hazardous elements present in the composites are well below specified levels.

d) The portland cement mortar systems were the least expensive from a materials cost standpoint.

Results of extensive laboratory tests done to evaluate the physical, mechanical, and leaching properties of portland cement mortars (PCM) and concretes (PCC) made with each of the five geothermal residues indicated the following.

a) There is, in general, an increase in the 28-day compressive strength of PCM and PCC composites made with 7 and 5 wt% residue, respectively.

b) The 28-day compressive strength of PCM composites containing geothermal residues decreases as the residue content is increased from 7 to 18 wt%.

c) Compressive strengths of PCM and PCC composites measured after 6 mo. and 1 yr indicate a general reduction in strength with time. The decreases in strength, however, are not accompanied by significant increases in elemental leachability rates.

d) The bulk specific gravity of PCM and PCC composites decreases as a result of adding geothermal residue to the mixes while water absorption and permeable void volume were shown to increase.

e) Forty-eight hour WET analysis of PCM and PCC composites containing 7 and 5 wt% residue, respectively, indicated leachable concentrations of hazardous materials present in the composites were below specified levels, thereby making the composites non-hazardous. Four of the five PCM systems made with 18 wt% residue passed the WET while one system was found to contain excessive levels of arsenic, chromium and lead, thereby making it hazardous.

f) Continuous long-term (28-day) WET tests indicate that while measurable levels of leachable elements do increase slightly with time, only one of the PCM systems tested was found to contain excessive elemental levels after 4 wk.

g) Compressive strength test results indicate that PCC composites containing 5 wt% geothermal residue exhibit reductions in strength varying between 3 and 23% after exposure to 100 cycles of freeze-thaw. Results of 48-hr WET tests indicate only a slight increase in the concentration of leachable elements with all levels still below recommended STLC values.

Based upon the results of the 48-hr WET tests, it has been shown that hazardous geothermal residues can be stabilized by incorporating them into PCM and PCC mixes as a replacement for a portion of the fine aggregate. The feasibility of using the resultant PCM and PCC composites as structural materials would at this time, however, appear to be impractical due to the diminishing strength properties exhibited by the composites tested. It is felt that more research is required to properly define the strength characteristics of PCM and PCC composites containing geothermal residues before they be considered for use in structural applications.

Suggested areas of research include:

1. A detailed cement chemistry analysis to determine the effects of various hazardous elements, such as arsenic, cadmium, chromium and lead, commonly found in geothermal residues upon the hydration products of portland cement composites.

2. An investigation to determine optimum residue contents for PCM and PCC composites with respect to leaching and strength characteristics.

3. Investigate the use of additives to chemically bond selected elements to the cement matrix.

4. Investigate the long-term chemical and physical stability of portland cement composites containing geothermal residues.

5. Investigate the use of biochemical accumulation processes to remove selected elements from the residues prior to incorporating the residues into a portland cement composite. By selectively removing the more concentrated elements, it may be possible to increase the amount of residue added to the mix.

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