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ABSTRACT

This paper discusses the results of recent studies related to the use of polyethylene and modified sulfur cement as new binder materials for the improved solidification of low-level wastes. Waste streams selected for this study include those which result from advanced volume reduction technologies (dry evaporator concentrate salts and incinerator ash) and those that remain problematic for solidification using contemporary agents (ion exchange resins). Maximum waste loadings were determined for each waste type. Recommended waste loadings of 70 wt% sodium sulfate, 50 wt% boric acid, 40 wt% incinerator ash and 30 wt% ion exchange resins, which are based on process control and waste form performance considerations are reported for polyethylene. For sulfur cement the recommended waste loadings of 40 wt% sodium sulfate and boric acid salts and 43 wt% incinerator ash are reported. However, incorporation of ion exchange resin waste in modified sulfur cement is not recommended due to poor waste form performance. The work presented in this paper will, in part, present data that can be used to assess the acceptability of polyethylene and modified sulfur cement waste forms to meet the requirements of 10 CFR 61.

INTRODUCTION

The overall objective of the Waste Form Evaluation program, sponsored by the U.S. Department of Energy's Low-Level Waste Management Program, is to develop and test technology for the improved solidification of low-level waste (LLW) through the use of materials and processes which are not currently being used commercially or by the DOE. The initial phases of the program which included the selection of the potential solidification materials to be investigated (polyethylene and modified sulfur cement), the waste types to be used, and the process development studies, have already been reported[1,2,3]. This paper will discuss the results of waste form property evaluation studies.

The selection of polyethylene and modified sulfur cement was based on such considerations as compatibility with waste, material properties, solidification efficiency, ease of processibility, availability of materials and economic feasibility. They are both thermoplastic materials which form a monolithic solid upon cooling. Since the solidification process is not dependent upon complex chemical reactions as it is in the case of hydraulic cements and thermosetting polymers, the processing is simplified and solidification of the waste is assured. Because both materials are heated above their melt temperatures before they are combined with waste to form a homogeneous mixture, they are especially well suited for incorporation of dry wastes resulting from advanced volume reduction systems. Both materials are resistant to chemical attack and are commercially available. The optimal waste loadings for most waste types studied were usually as high or higher than the optimal waste loadings for currently used solidification agents.

The types of waste which were selected for these studies are the products of advanced volume reduction technologies and "problem wastes," which are wastes that are incompatible with conventional solidification agents. The first category includes sodium sulfate waste, boric acid waste and incinerator ash. As a typical "problem waste," a mixed bed ion exchange resin was used. The wastes were prepared to closely simulate actual wastes in both physical and chemical composition. All of the wastes were dried to facilitate mixing into the solidification materials.

WASTE FORM STABILITY TESTS

Waste form stability is considered to be an important factor in the performance of shallow land burial sites. Thus, a data base of relevant physical and chemical properties of the waste form is being acquired to help predict potential behavior in a burial site. These data are generated through the application of a series of standardized stability tests for simulated laboratory scale waste form specimens. The tests which were used in this study are listed in Table 1. All of these tests are included in the NRC's Branch Technical Position Paper on Waste Form[4]. NRC's recommended test methods and criteria by which waste form stability is determined are also included in Table 1 so that the test results reported in this study could be judged for compliance with 10 CFR 61 stability requirements.

WASTE FORM FABRICATION

Polyethylene

Low-density polyethylene (LDPE) was chosen because its processibility is less difficult than that of high-density polyethylene, which requires a higher temperature and pressure. The processing methods used were extrusion and batch mixing. Extrusion was found to be the optimal processing method for incorporating LLW in polyethylene to form a homogeneous mixture. For the production of laboratory scale simulated polyethylene waste forms a commercially available 1 1/4 inch single-screw extruder was used. The process details are given elsewhere[1,3].

Maximum waste loadings for LDPE incorporating each of the waste types investigated are: 70 wt% for sodium sulfate, 50 wt% for boric acid, 40 wt% for incinerator ash and 65 wt% for ion exchange resins. Waste loadings are presented in terms of waste which can be incorporated to form a monolithic solid, based solely on processing parameters.

Modified Sulfur Cement

The modified sulfur cement used in these studies was developed by the US Bureau of Mines and is commercially available. It contains a modifier (5 wt%) consisting of equal parts of DCPD (dicyclopentadiene) and an oligomer of CPD (cyclopentadiene). The material melts at 119°C to form a low-viscosity liquid. Process development studies were performed using two methods, a screw extruder method and a dual-action heated mixer. The low-melt viscosity of the modified sulfur cement impeded conveyance through the extruder barrel and also hampered the screw's ability to effectively mix the waste and binder constituents. More suitable processing results were achieved by using the heated batch mixer. The details of this process have previously been described[2,3].

Table 1. WASTE FORM TEST METHODS

TEST	METHOD	TEST CRITERIA
Compressive strength	ASTM C-39 or D-1074	Compressive strength $\geq$ 50 psi
90-Day Immersion in Water		Compressive Strength $\geq$ 50 psi
Thermal Cycle	ASTM B-553	Compressive Strength $\geq$ 50 psi
Leach Testing (90 days)	ANS 16.1	Leachability Index > 6.0 for each isotope
Irradiation - 10^8 Rad	Gamma Irradiator or Equivalent	Compressive Strength $\geq$ 50 psi
Biodegradation		
Fungus Attack	ASTM G21	Fungal growth < 10% Compressive Strength $\geq$ 50 psi
Bacterial Attack	ASTM G22	No observed bacterial growth Compressive Strength $\geq$ 50 psi

Maximum waste loadings for modified sulfur cement waste forms as achieved during process development studies are: 80 wt% for sodium sulfate waste, 57 wt% boric acid waste and 43 wt% incinerator ash.

WASTE FORM STABILITY EVALUATION

Polyethylene

The tests outlined in Table 1 have been applied to polyethylene waste forms containing each of the waste types investigated at varying levels of waste loadings. Three radionuclides, ^{60}Co, ^{85}Sr and ^{137}Cs, were incorporated into the waste for the leaching experiments.

In general, increased waste loadings for polyethylene specimens containing sodium sulfate, boric acid or incinerator ash had little effect on the results of such tests as thermal cycling, water immersion, biodegradation and irradiation. Only specimens containing ion exchange resins showed a correlation between waste loadings and waste form failure during the water immersion test. Specimens containing 50 wt% resin swelled approximately 9% while those containing 60 wt% or more resin suffered severe cracking. Based on this test a waste loading of 30 wt% dry ion exchange resin is recommended for solidification in polyethylene.

Some of the test results for polyethylene waste forms at optimal waste loadings are summarized in Table 2. The results of the tests indicate compressive strengths which are well above the minimum 50 psi requirements.

In contrast, a clear dependence of leachability upon increased waste loadings of 10, 30 and 50 wt% for all three isotopes was established for polyethylene/sodium sulfate specimens. An example is given in Figure 1 where cumulative fraction leached of ^{60}Co is plotted as a function of time. The cumulative fraction of ^{85}Sr, ^{137}Cs and ^{60}Co leached from 50 wt% waste loaded samples after 91 days of leaching is similar ($\sim 3 \times 10^{-2}$) for all three isotopes. For a plot of these data see Figure 2.

A dependence of leachability upon increased waste loadings was also demonstrated for all three isotopes in the leaching of polyethylene specimens containing incinerator ash at waste loadings of 25 wt% and 35 wt%. An example of this can be seen in Figure 3 where the cumulative fraction leached of ^{60}Co is plotted as a function of time. At both loadings the cumulative fraction leached for ^{137}Cs after 91 days of leaching was higher (7×10^{-3} at 35 wt% loading) than that for ^{60}Co and ^{85}Sr ($\sim 1.3 \times 10^{-3}$ at 35 wt% loading). These data are shown in Figure 4.

An opposite trend in the dependence of leachability upon increased waste loadings of 10, 20 and 30 wt% of ion exchange resins in polyethylene specimens was found. The higher the waste loading the lower the leachability. An example of that can be seen in Figure 5. In this case the cumulative fraction leached for ^{85}Sr was higher (5.5×10^{-4}) than that of ^{137}Cs (1.2×10^{-4}) and ^{60}Co (2.3×10^{-4}), as shown in Figure 6.

In addition to cumulative fraction leached, all of the leaching data was calculated in terms of the "leachability index" as recommended in the ANS 16.1 leaching test. This index is a dimensionless figure of merit which quantifies the relative leachability for a given waste type-solidification agent. It can thus be used as a basis for comparison of the radionuclide retention capabilities of various solidification matrix-waste type combinations. The NRC has issued a recommended minimum leachability index of > 6 in support of 10 CFR 61 waste form stability requirements. The average leaching indices calculated for polyethylene waste forms are listed in Table 3. They all had a value greater than six. Optimal recommended waste loadings for polyethylene, which reflect a compromise between solidification efficiency and waste form performance, are summarized in Table 4.

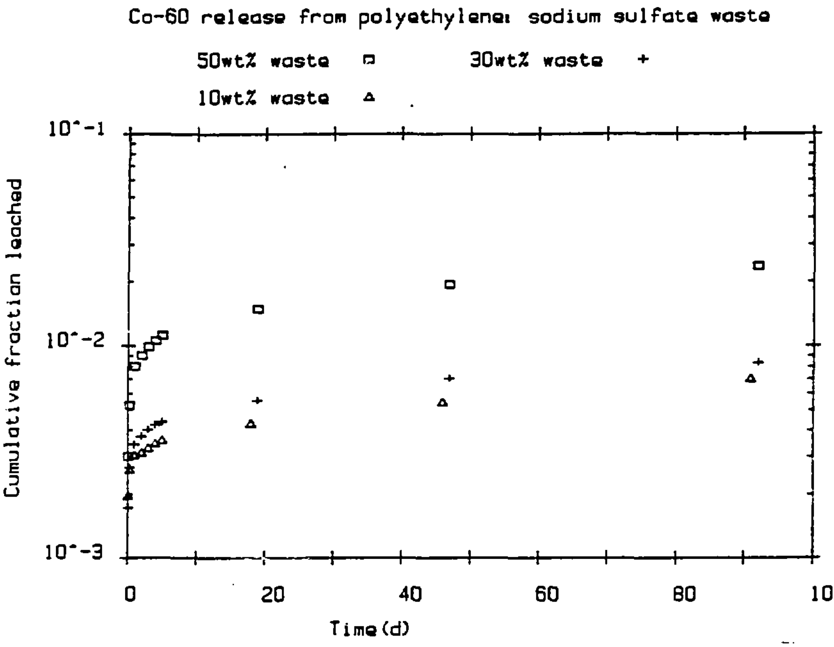

Figure 1. Cumulative fraction leached of ^{60}Co as a function of time from polyethylene waste forms containing 10, 30 and 50 wt% of sodium sulfate waste.

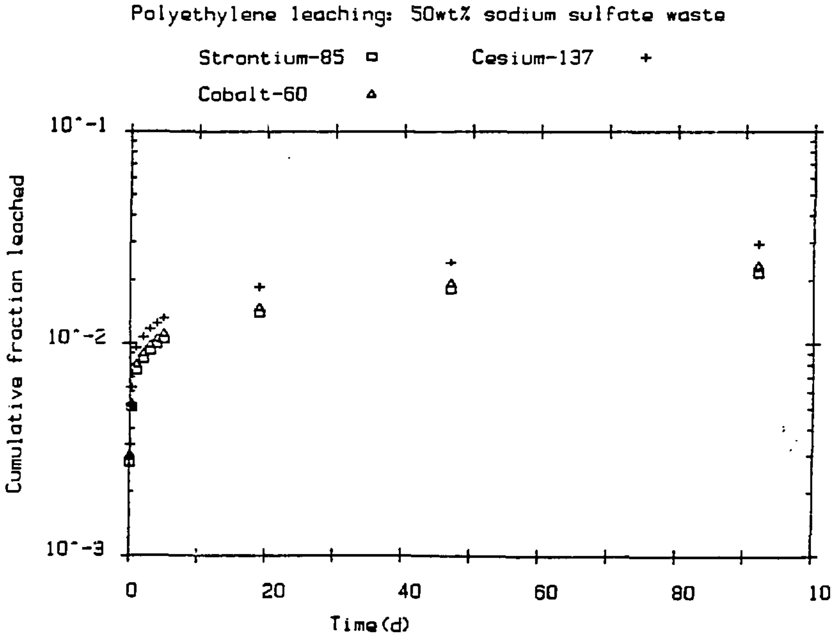

Figure 2. Cumulative fraction leached of ^{60}Co, ^{85}Sr and ^{137}Cs as a function of time from polyethylene waste forms containing 50 wt% of sodium sulfate waste.

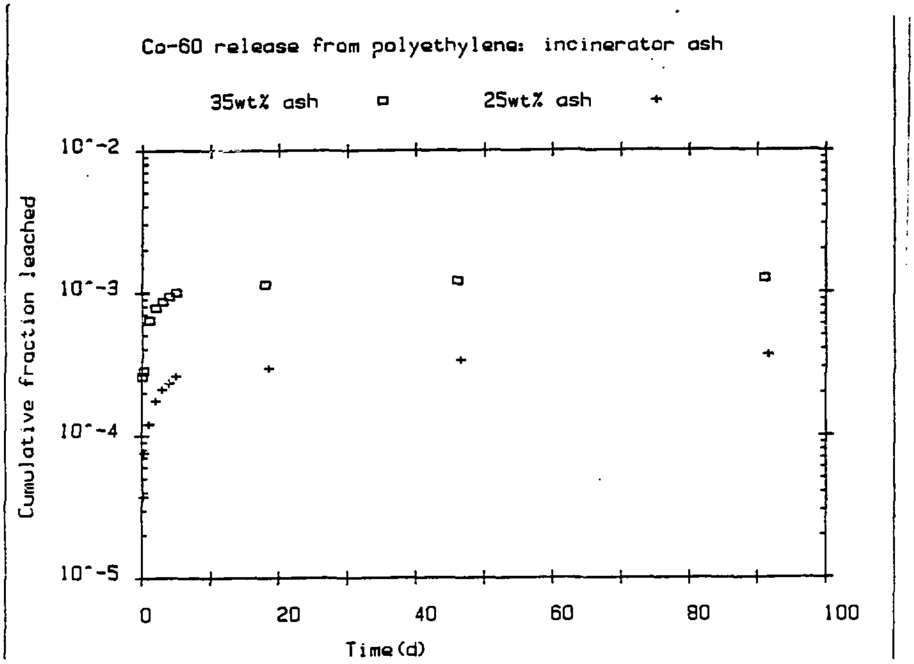

Figure 3. Cumulative fraction leached of ^{60}Co as a function of time from polyethylene waste forms containing 25 and 35 wt% of incinerator ash.

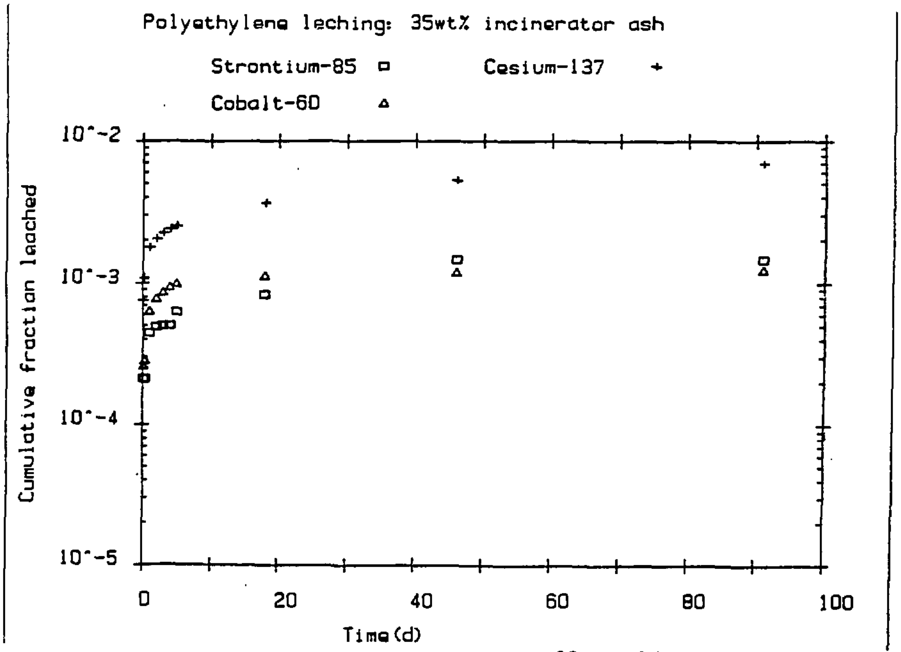

Figure 4. Cumulative fraction leached of ^{60}Co, ^{85}Sr and ^{137}Cs as a function of time from polyethylene waste forms containing 35 wt% incinerator ash.

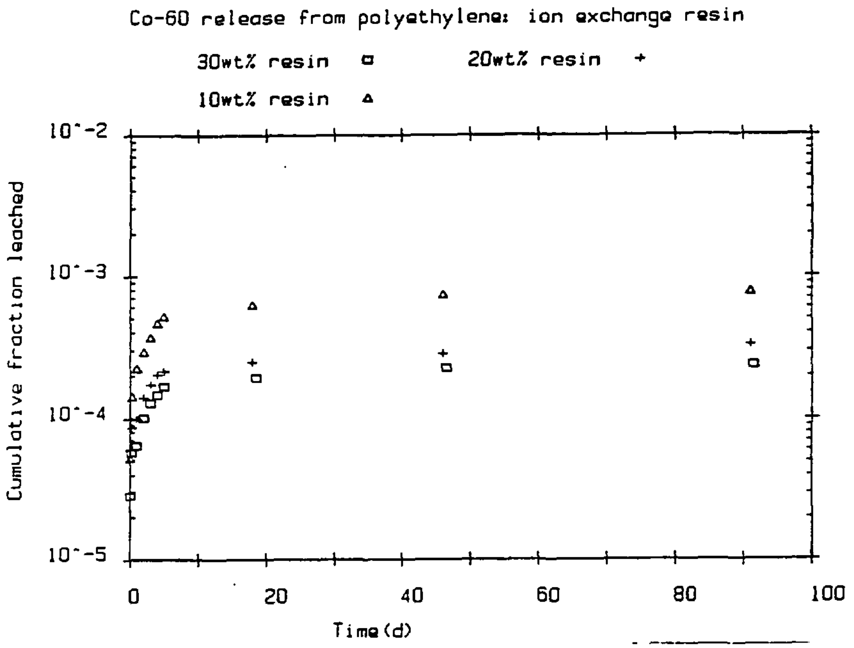

Figure 5. Cumulative fraction leached of ^{60}Co as a function of time from polyethylene waste forms containing 10, 20 and 30 wt% of ion exchange resin.

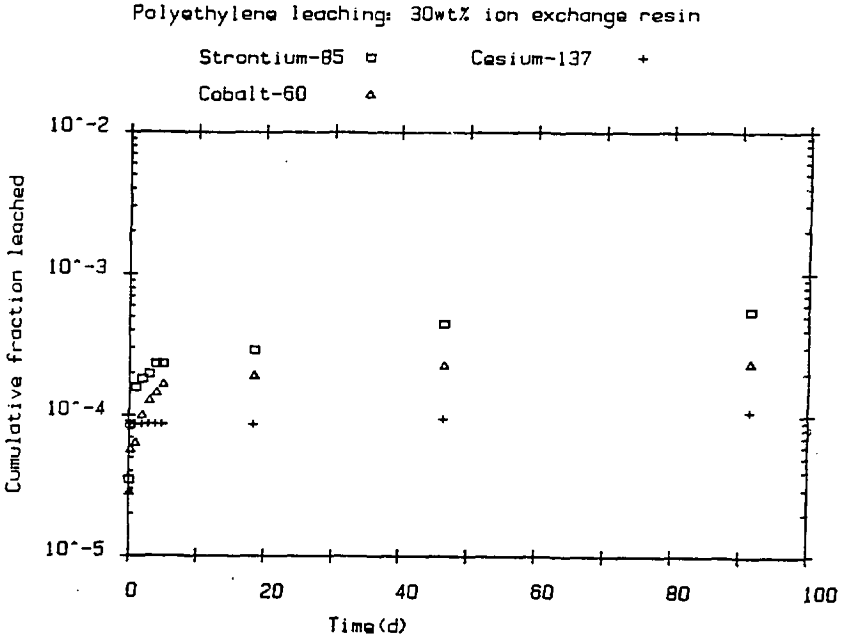

Figure 6. Cumulative fraction leached of ^{60}Co, ^{85}Sr and ^{137}Cs as a function of time from polyethylene waste forms containing 30 wt% ion exchange resin.

TABLE 2. COMPRESSIVE STRENGTHS OF POLYETHYLENE WASTE FORMS

		Compressive Strength[a] (psi)					
WASTE TYPE	WASTE LOADING WT%	INITIAL	IMMERSION	THERMAL CYCLING	IRRADIATION	BIODEGRADATION BACTERIA	BIODEGRADATION FUNGI
Sodium Sulfate	70	1600	1680	1600	1700	1300	1290
Boric Acid	50	1600	660	1600	1900	1300	1300
Incinerator Ash	40	2180	1140	2100	1820	1800	1800
Ion Exchange Resin	30	2100	1580	2100	1670	1700	1700

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a. Performed in accordance with ASTM D-1074.

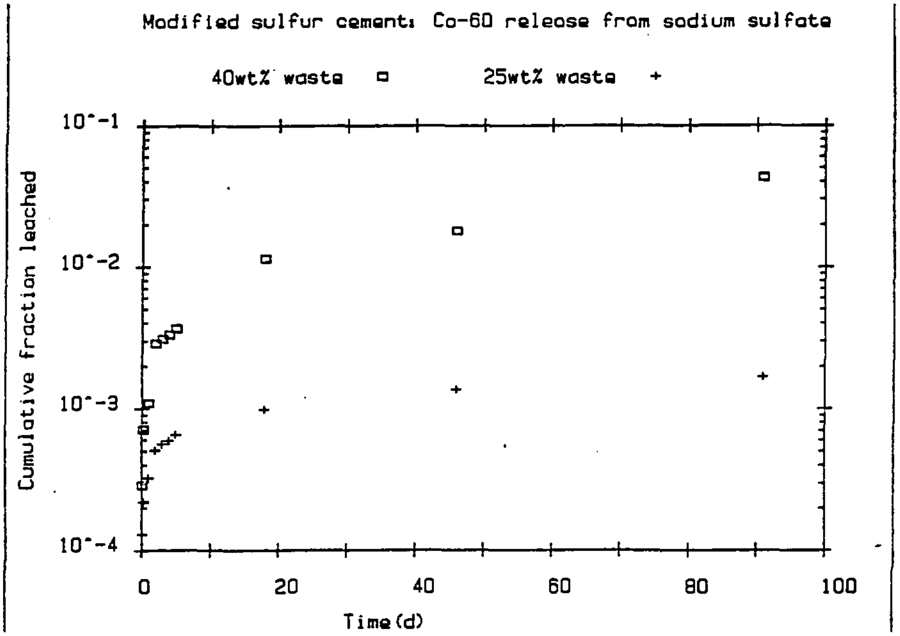

Figure 7. Cumulative fraction leached of ^{60}Co as a function of time from modified sulfur cement waste forms containing 25 and 40 wt% of sodium sulfate waste.

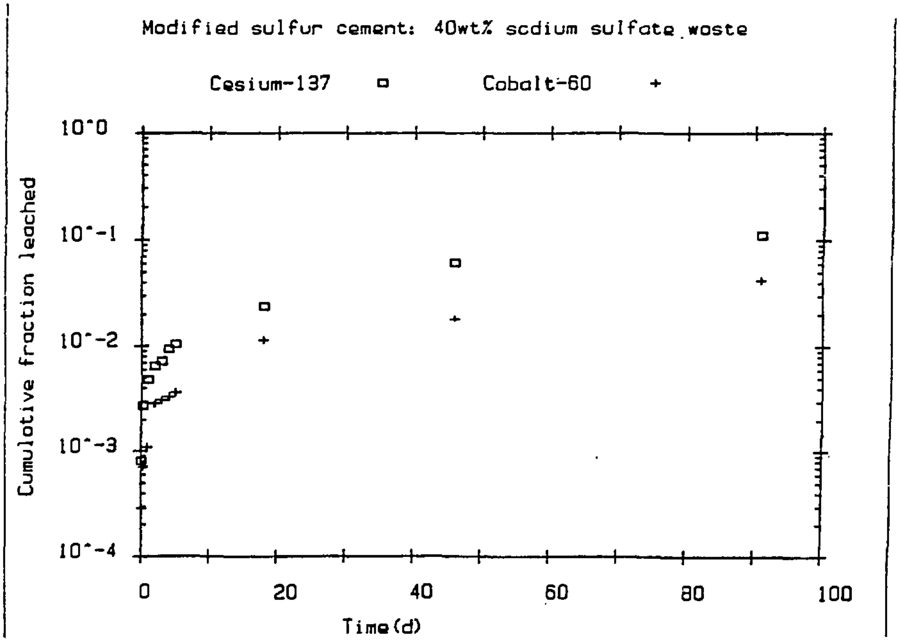

Figure 8. Cumulative fraction leached of ^{60}Co and ^{137}Cs as a function of time from modified sulfur cement waste forms containing 40 wt% of sodium sulfate waste.

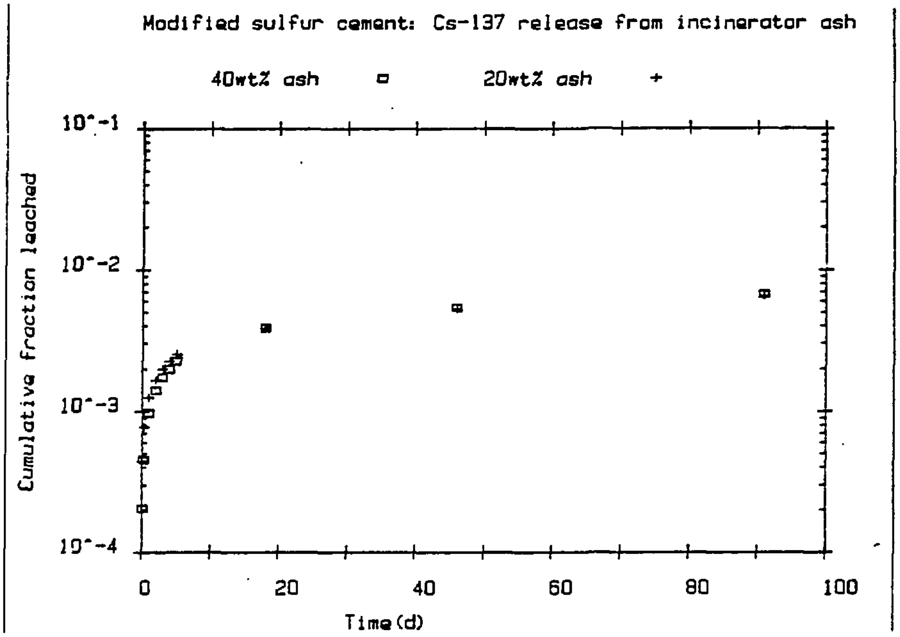

Figure 9. Cumulative fraction leached of ^{137}Cs as a function of time from modified sulfur cement waste forms containing 20 and 40 wt% of incinerator ash.

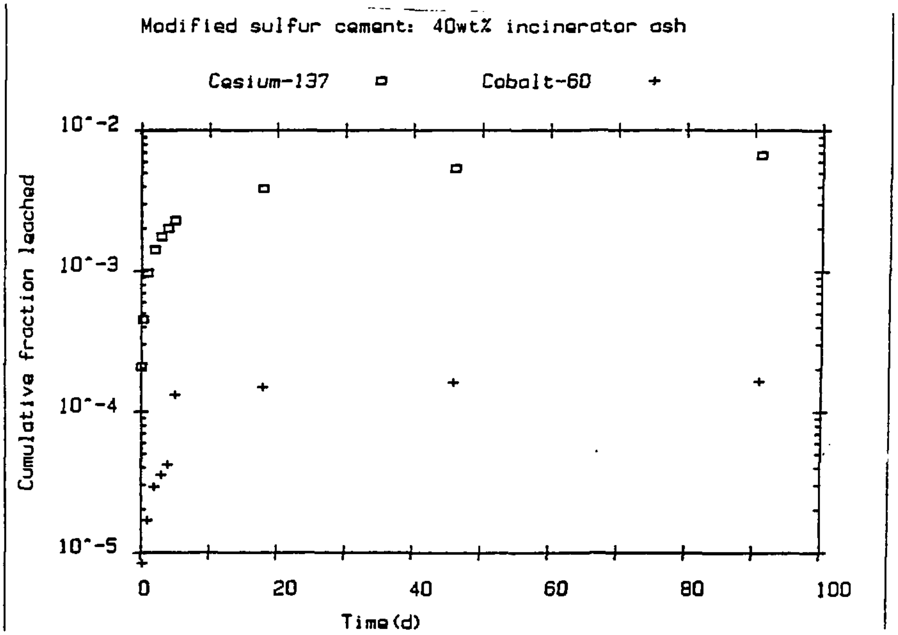

Figure 10. Cumulative fraction leached of ^{60}Co and ^{137}Cs as a function of time from modified sulfur cement waste forms containing 40 wt% of incinerator ash.

TABLE 3. AVERAGE LEACHABILITY INDICES FOR POLYETHYLENE WASTE FORMS

Waste Type	Waste Loading	Average Leachability Index, ^{60}Co	Average Leachability Index, ^{85}Sr	Average Leachability Index, ^{137}Cs
Na_2SO_4	50%	10.1	10.2	9.9
Incinerator Ash	35%	12.7	14.9	11.3
Ion Exchange Resin	30%	14.6	16.1	19.5

Modified Sulfur Cement

Increased waste loadings from 20 to 50 wt% of sodium sulfate, boric acid and incinerator ash had no significant effect on the compressive strength of the waste form.

Except in the case of water immersion tests, the initial compressive strength of the waste forms did not change after being subjected to the various stability tests, Table 5. Waste forms containing $\geq$ 50 wt% sodium sulfate and $\geq$ 57 wt% boric acid failed the water immersion test. Waste forms containing ion exchange resins < 5 wt% also failed. Use of modified sulfur cement for encapsulation of ion exchange resins is therefore, not recommended.

Two radionuclides, ^{60}Co and ^{137}Cs, were incorporated into the modified sulfur cement waste forms used in the leaching experiments. No leaching experiments have yet been performed on modified sulfur cement/boric acid waste forms. Modified sulfur cement/ion exchange resin waste forms were not tested because of incompatibility between waste and matrix material.

A dependence of leachability upon increased waste loadings was shown for modified sulfur cement/sodium sulfate waste forms. An example of this can be seen in Figure 7 where the cumulative fraction leached of ^{60}Co is plotted as a function of time for waste loadings of 25 and 40 wt%. Of the two isotopes ^{137}Cs has a higher cumulative fractional release (1.1×10^{-1}) than ^{60}Co (4.2×10^{-2}), Figure 8.

Increased waste loadings (from 20 wt% to 40 wt%) had little effect on the leaching of waste forms containing incinerator ash as shown in Figure 9. The ^{137}Cs cumulative fraction leached (6.7×10^{-3}) is higher than for ^{60}Co (1.6×10^{-4})as shown in Figure 10.

Leaching indices were also calculated for modified sulfur cement waste forms. Again, all of the values are > 6. These results are shown in Table 6.

Table 4. COMPARISON OF OPTIMAL WASTE LOADINGS FOR POLYETHYLENE, MODIFIED SULFUR CEMENT AND HYDRAULIC CEMENT BASED ON PROCESSING AND WASTE FORM STABILITY CONSIDERATIONS

	Waste Type			
	Sodium Sulfate	Boric Acid	Incinerator Ash	Ion Echange Resins
Solidification in Polyethylene:				
Wt% Waste[(a)]	70	50	40	30
Drum Wt., kg[(b)]	358	225	270	210
(lbs)	(789)	(496)	(595)	(463)
Waste/Drum, kg[(c)]	250	133	108	63
(lbs)	(552)	(248)	(238)	(139)
Solidification in Modified Sulfur Cement:				
Wt% Waste	40	40	43	Not recommended
Drum Wt., kg	415	287	384	
(lbs)	(915)	(633)	(846)	--
Waste/Drum, kg	166	115	182	
(lbs)	(366)	(253)	(360)	--
Solidification in Hydraulic Cement:(d)				
Wt% Waste	9	15	40	13
Drum Wt., kg	307	296	318	318
(lbs)	678	(653)	(700)	(700)
Waste/Drum, kg	28	44	127	41
(lbs)	(61)	(98)	(280)	(91)

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a. Based on dry solid weight.
b. 55 gallon drum size waste form.
c. Equivalent quantity of waste which can be incorporated in 55 gallon drum size waste form.
d. Based on previous BNL waste form development studies for waste forms which satisfied free-standing monolithic solid and two-week water immersion criteria[6,7,8].

TABLE 5. MODIFIED SULFUR CEMENT WASTE FORM COMPRESSIVE STRENGTHS[a]

		Compressive Strengths (psi)[b]					
Waste Type	Waste Loading (wt %)	Initial	Immersed[c]	Thermal Cycled	Irradiated[b]	Biodegraded Bacteria	Biodegraded fungi
Blank	0	1800 ± 200	d	d	3000 ± 400	d	d
Sodium Sulfate	20	d	d	d	3000 ± 400	d	d
	30	3700 ± 500	2500 ± 900	2800 ± 1000	4110 ± 40	e	e
	40	4360 ± 60	3000 ± 900	3600 ± 600	3300 ± 1100	e	e
	50	4600 ± 200	failed	3700 ± 1200	d	d	d
Boric Acid	20	2200 ± 100	3100 ± 600	2200 ± 1200	2600 ± 300	d	d
	30	2000 ± 200	2600 ± 200	3400 ± 400	3040 ± 80	e	e
	40	2000 ± 100	1400 ± 200	2200 ± 200	2100 ± 700	e	e
Incinerator Ash	10	5400 ± 300	2900 ± 800	4100 ± 1000	d	d	d
	20	4300 ± 300	4000 ± 600	4400 ± 900	4400 ± 400	d	d
	30	4200 ± 2100	3900 ± 1600	3800 ± 1700	4600 ± 1000	e	e
	40	6400 ± 100	4100 ± 200	4700 ± 950	7200 ± 1300	e	e
	43	4400 ± 300	5400 ± 1100	5400 ± 2900	d	d	d

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a. Performed in accordance with ASTM C-39. 1 psi = 6.98 kPa.
b. Results reflect average of 3 replicate samples ± one standard deviation.
c. Results reflect average of 2 replicate samples.
d. Test not performed.
e. Test in progress.

TABLE 6. AVERAGE LEACHABILITY INDICES FOR MODIFIED SULFUR CEMENT WASTE FORMS

Waste Type	Waste Loading	Average Leachability Index, ^{60}Co	Average Leachability Index, ^{137}Cs
Na_2SO_4	40%	10.7	9.7
Incinerator Ash	40%	11.1	14.6

The optimal recommended waste loadings based on both, processing and waste form stability considerations as tested above, are listed in Table 4. For comparison Table 4 also includes recommended waste loadings in polyethylene and hydraulic cement.

The work described in this paper demonstrates the feasibility of polyethylene and modified sulfur cement as potential solidification agents for various types of low-level radioactive wastes. In addition, the results of stability testing to date indicate compliance with the NRC Technical Position Paper on Waste Form.

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