EP TOXICITY TESTING OF LEAD TO RESOLVE DISPOSITION OF RADIOACTIVELY CONTAMINATED LEAD[a]

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ABSTRACT

The Department of Energy (DOE), in its efforts to comply with the requirements of the Resource Conservation and Recovery Act (RCRA) of 1976, is concerned with hazardous waste which is also radioactively contaminated. There are no existing facilities to treat or dispose of these wastes. One such waste is lead, which is extensively used in the nuclear industry as shielding. This paper reports the results of leach testing of lead (both solid lead samples and lead shot) to resolve questions as to whether or not radioactively contaminated waste lead must be treated as a hazardous waste. The results of these tests showed that: some samples passed the leach test. Results of development efforts performed to date to recycle lead and those planned for the future are included in this report.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has set specific criteria in 40 CFR 261.3 for determining when a waste must be considered hazardous. The two main criteria are: (a) exhibiting any of the characteristics of a hazardous waste identified in 40 CFR 261 Subsection C or (b) being specifically listed in 40 CFR 261 Subsection D. Lead is not a listed waste, so the criteria to be used to determine if lead is a hazardous waste are in Subsection C. There are four hazardous characteristics listed in Subsection C: (1) ignitibility; (2) corrosivity; (3) reactivity; and (4) Extraction Procedure (EP) toxicity. The determing test to be used for lead is the EP toxicity leach test. A waste exhibits the characteristic of EP toxicity if, using the EP test method (described later in this report), the extract from a representative sample of the waste contains any of the contaminants in Table I in concentrations equal to or greater than the value listed.

TABLE I

Hazardous Waste Contaminants

Contaminant	Max. Concentration (mg/L)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

Currently, radioactively contaminated waste lead at the Idaho National Engineering Laboratory (INEL) is treated as a hazardous waste. Because no hazardous waste is allowed to be disposed in the Radioactive Waste Management Complex (RWMC), radioactively contaminated waste lead is being stored until a treatment or disposal method has been identified. Activities are underway at the INEL to evaluate methods to recycle the lead.

This paper reports the results of lead toxicity tests performed at the INEL, INEL waste lead volumes, and options for the disposition of the lead.

TOXICITY TEST PROCEDURE

The EPA's Extraction Procedure (EP) toxicity test (as described in SW-846--"Test methods for Evaluating Solid Waste"--Method 1310) is designed to simulate the leaching of toxic metals (and pesticides) from waste buried in a landfill. Before the extraction procedure is performed, the waste must be evaluated for particle size. If the solid waste has a surface area greater than 3.1 cm^2/g or passes through a 9.5 mm sieve (e.g., lead shot), the procedure can be started. If the material is in a single piece (e.g., a lead brick, or a solidified block), it is prepared for extraction by subjecting the material to the "Structural Integrity Procedure" described in Section 7.10 of the referenced method 1310 as follows:

Structural Integrity Procedure (SIP):

1. Cut a 3.3-cm-diameter by 7.1-cm-long cylinder from the waste material. For wastes that have been treated using a fixative process, the waste may be cast in the form of a cylinder and allowed to cure for 30 days prior to testing.
2. Place waste into sample holder and assemble the tester. Raise the hammer to its maximum height and drop. Repeat 14 times.
3. Remove solid material from tester and scrape off particles adhering to sample holder. Weigh the waste to the nearest 0.01 g and transfer it to the Extractor.

The sample (a minimum of 100 g is required) is placed in a suitable container, (at least 2 L capacity) and demineralized water is added in a weight ratio of 16 ml water to 1 g of sample. The pH

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of the solution is then adjusted to 5.0 ± 0.2 using 0.5 N acetic acid, and the container is placed in an agitator and agitated for 24 hours.

The pH of the solution must be monitored during the course of the extraction; if the pH rises above 5.2, 0.5 N acetic acid should be added to bring the pH down to 5.0 ± 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 mL of acid per gram of solid. The pH of the solution should be adjusted at 15-, 30-, and 60-min intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5 pH units.

If, at the end of a 24-h extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 mL/g of solids) has not been added, the pH should be adjusted to 5.0 ± 0.2 and the extraction continued for an additional 4 h, during which time the pH should be adjusted at 1-h intervals.

At the end of the extraction period, deionized water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = mL deionized water to be added

W = weight in g of solid charged to extractor

A = mL of 0.5 N acetic acid added during extraction

The solution is then passed through a 0.45-μm membrane filter and the filtered extract analyzed for the toxic metals shown in Table I.

TEST RESULTS

EP toxicity tests of solid lead samples (representative of lead bricks) were performed at four independent labs. Seven samples were analyzed, with a wide range of results as shown in Table II. Three samples resulted in less than the 5 mg/L limit and four were greater, with the results ranging from 1.8 mg/L to 1785 mg/L.

Following are some observations of the variances in test parameters and their possible impacts on the results:

1. Sample Preparation (see Fig. 1). Only one lab (Lab #3) cut a cylinder (3.3 cm in diameter and 7.1 cm long) as required by the EP toxicity test procedure. Lab #1 machined thin plates from a lead brick, Lab #2 cut a rectangular section from a corner of a lead brick, and Lab #4 cut a triangular corner from a lead brick. The Lab #1 plates and the Lab #3 cylinder resulted in samples with no oxidized surfaces. The Lab #4 triangular piece resulted in a sample with three of the four surfaces oxidized. The Lab #2 rectangular piece resulted in a sample with four of the six surfaces oxidized. An oxidized surface should have a different leach-rate from a nonoxidized surface. However, this cannot be verified from these tests, since the lowest and highest results came from the nonoxidized samples.

2. Surface Area. The surface of the cylinder, as specified in the procedure, is approximately 91 cm^2. Each lab cut its sample to provide this same surface area so the variance of the results of these tests cannot be explained by a varying surface area.

3. Sample Weight. A cylinder of lead exactly the size specified in the EP toxicity procedure would weigh about 700 g. The samples in these tests weighed from 100 g (the minimum allowed by the procedure) to 895 g. The weight of the sample is important, since the procedure requires the use of demineralized water in a ratio of 16 ml to 1 g of sample. The 100-g sample would therefore require 1600 mL of demineralized water; the 895-g sample would require 14,320 mL of demineralized water.

TABLE II

SOLID LEAD SAMPLE TEST DATA

Lab	Sample #	Sample Surface Area (cm^3)	Sample Weight (g)	Acetic Acid Added (ml)	Agitation Method	Results (mg/L)	Total mg Pb Dissolved
#1	1	Approx. 91	Approx. 98	137	Vibrated	1785	3499
	2	Approx. 91	Approx. 98	110	Vibrated	1584	3105
	3	Approx. 91	Approx. 98	77	Vibrated	1011	1982
#2	1	Approx. 91	622	not available	Stirred	3.5	44
#3	1	Approx. 91	895	<10	Stirred	4	72
	2	Approx. 91	895	<10	Stirred	1.8	32
#4	1	Approx. 91	116	48	Stirred	614	1424

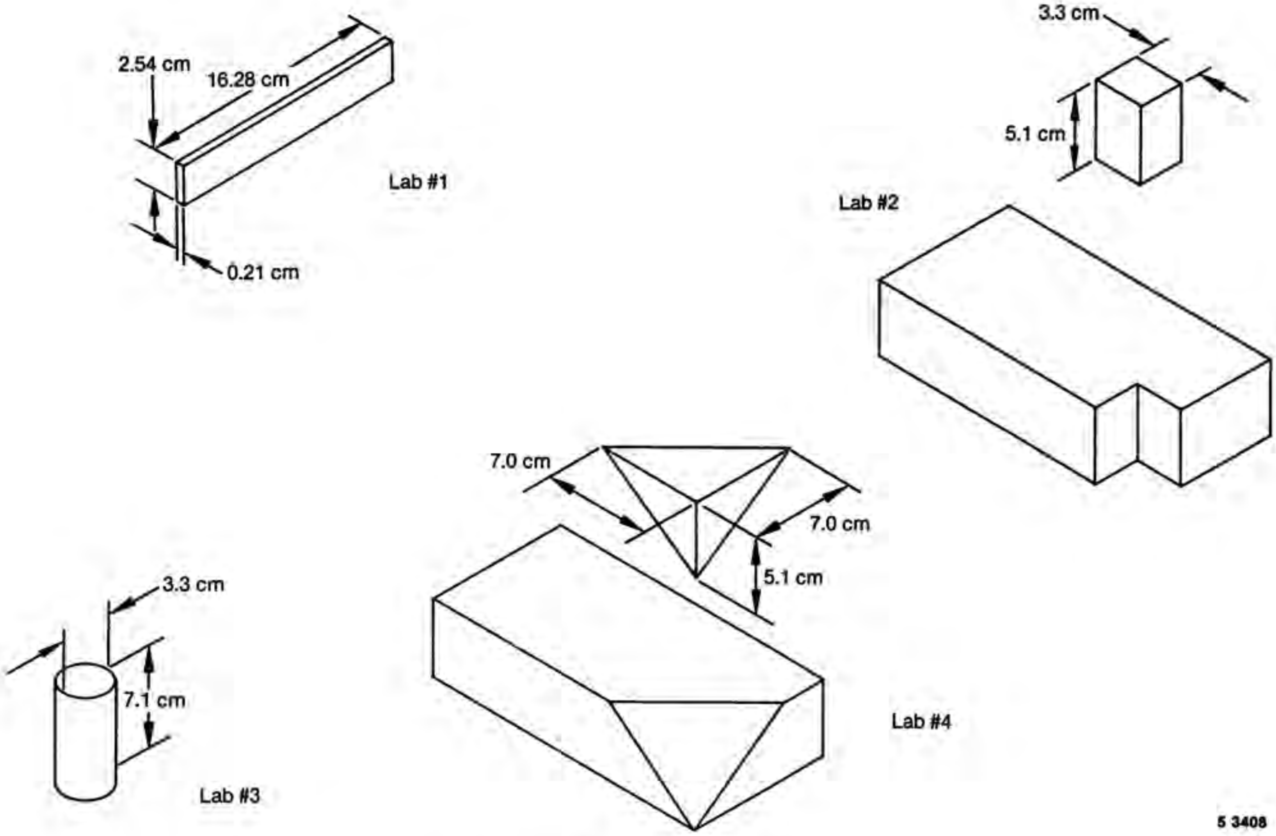

Fig. 1. Solid Lead Samples.

This is a significant difference, especially when considering that the sample surface areas are approximately the same, and this nine-fold increase in solution must have a diluting effect on the concentration of the leached lead in the final extract solution.

4. pH Control. The amount of acetic acid (0.5 N) added to each solution varied from less than 10 mL to 137 mL. The amount required to change demineralized water at a pH of 7 to a pH of 5 is very small. As the acetic acid reacts with the lead, the pH increases. When the pH rises above 5.2, more acetic acid is added to lower the pH to 5.0 ± 0.2. The largest amount of solution (14,310 mL) used less than 10 mL of acetic acid; the smallest amount of solution (1600 mL) used 173 mL of acetic acid. The sample that used only 1600 mL of acid (the largest volume used), resulted in the greatest amount of lead being leached (1,785 mg/L). The amount of acid added during the test has a profound influence on the amount of lead leached during the 24-h extraction period. Figure 2 graphically shows the amount of lead dissolved during the test as a function of the amount of acetic acid used.

   There are two additional observations that should be considered when evaluating the effect pH control has on the results of the tests.

   a. Lab #3 ran two solid-lead sample tests (using machined cylinders). During the first test, the pH was closely controlled to 5.0 but was sometimes as low as 4.8, with the result being 4 mg/L. During the second test, the pH was closely controlled and maintained at 5.2, with the result being 1.8 mg/L.

   b. When Lab #2 was informed of the large volume of acid used in the Lab #1 test to maintain the pH at 5.0 ± 0.2, they reran the extraction portion of the test using 2000 mL of demineralized water and only used about 2 mL of acid to maintain the pH at 5.0 ± 0.2. It is uncertain at this point as to why the Lab #1 tests required so much acid and why there was such a variety of results in the three tests that they performed.

5. Agitation Method. Three of the labs agitated the samples by stirring and one used a vibratory agitator. Since the tests which used the vibratory agitator had the highest leach rate, it is possible that vibratory agitation increases the leach rate. Further testing would be required to substantiate this.

EP toxicity testing of lead shot was performed at two independent labs. Sixteen samples of #6 shot

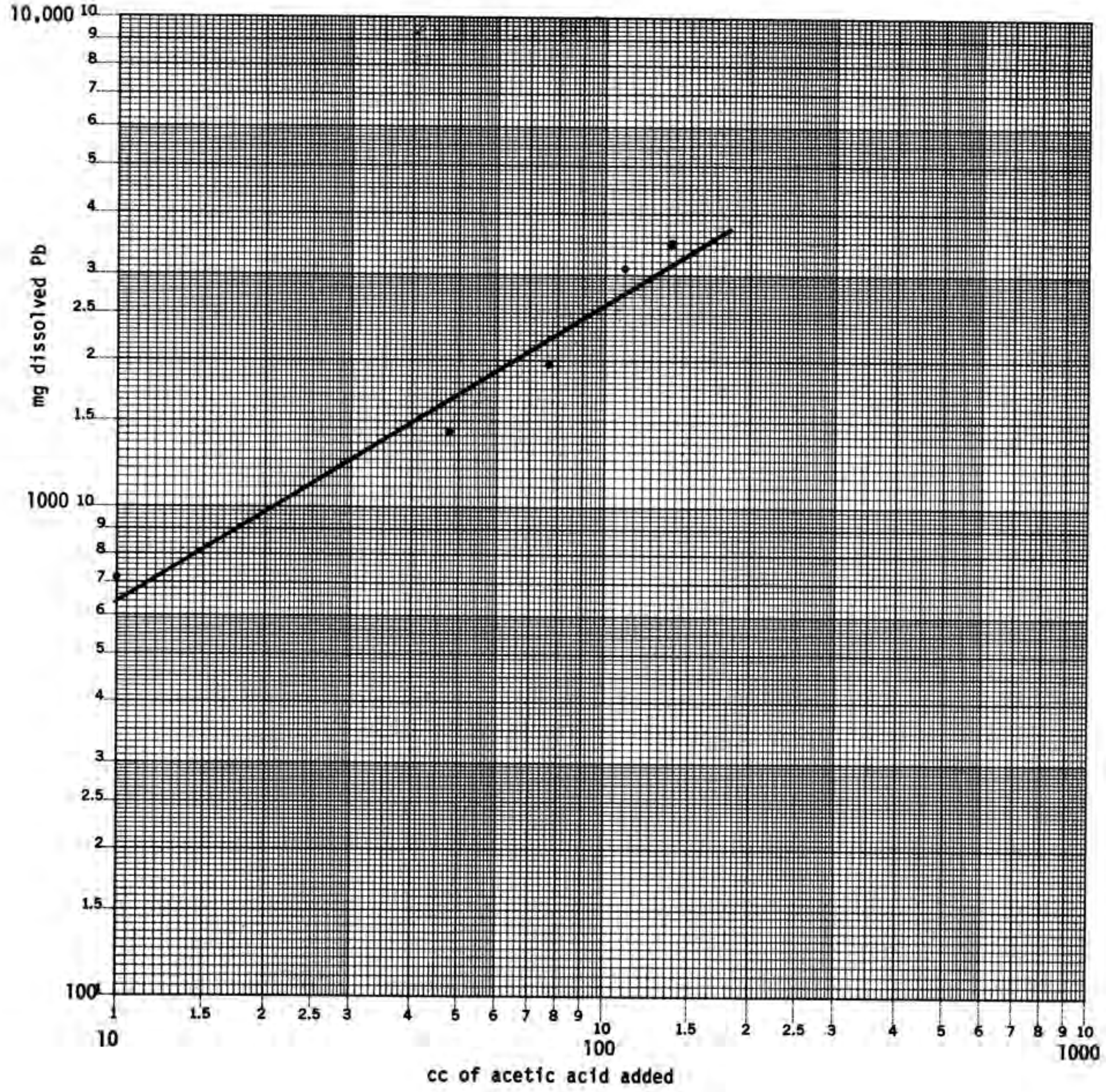

Fig. 2. Dissolved lead as a function of the amount of acid used.

and two samples of #8 shot were analyzed, and the results are shown in Table III. Test series #1 was performed using acetic acid as is currently specified in the EP toxicity procedure.

The EPA is in the process of changing the EP toxicity test, and the new procedure is called the Toxicity Characteristic Leaching Procedure (TCLP). Following is a description of the changes in the proposed TCLP:

1. All TCLP tests must be tumbled (see Fig. 3); no stirring is permitted.
2. The test is run for 18 hours instead of 24 hours.
3. A leaching solution ratio of 20 ml to 1 g of waste sample is used instead of 16 to 1 for the current EP procedure; the 16 to 1 is subsequently adjusted to 20 to 1 after the leaching process is completed.
4. After the solution has been added to the waste, the pH is not checked and adjusted.
5. A 5 g sample of the waste is mixed with 96.5 ml of demineralized water. The pH of this mixture is measured. If the pH is less than 5.0, solution A is used in the TCLP test. If the pH is greater than 5.0, 3.5 ml of 1.0 N HCl are added to the mixture,

TABLE III.

Lead Shot Sample Test Data

Test Series	Lab	Sample No.	Lead Shot Size	Sample Weight (g)	Solution Used	Agitation Method	Results (mg/L)
#1	#2	1	#6	100	a	Tumbled	130
		2	#6	100	a	"	135
#1	#3	1	#6	590	a	Stirred	9
		2	#6	590	a	"	5.3
#2	#2	1	#6	100	b	Tumbled	120
		2	#6	100	b	"	130
		3	#6	100	b	"	199
		4	#6	100	b	"	194
#2	#3	1	#6	100	b	"	5.8
		2	#6	100	b	"	6.1
		3	#6	100	b	"	7.3
		4	#6	100	b	Stirred	3.0
		5	#8*	100	b	Tumbled	1.7
		6	#8**	100	b	"	9.0
#3	#2	1	#6	100	c	"	448
		2	#6	100	c	"	426
#3	#3	1	#6	100	c	"	1145
		2	#6	100	c	"	1315
#4	#2	1	#6	100	d	"	406
		2	#6	100	d	"	429
#4	#3	1	#6	100	d	"	880
		2	#6	100	d	"	1030
#5	#3	1	#6	100	e	"	1546
#6	#3	1	#6	100	f	"	1511

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* No oxidation (new shot)

** Normal oxidation

a. EP Toxicity solution 0.5 N acetic acid

The following solutions were tested during the EPA proposed changes to the EP toxicity procedure and ultimately resulted in the presently proposed TCLP. Lead shot was tested using each solution.

b. 0.1 N sodium acetate buffer.

c. 10.5 g sodium acetate and 4.12 mL glacial acetic acid diluted to 2L with demineralized water, pH adjusted to 5.0 using 0.1 N Sodium Hydroxide solution.

d. 4.0 g sodium hydroxide and 11.4 mL glacial acetic acid diluted to 2L with demineralized water, pH adjusted to 5.0 using 0.1 N sodium hydroxide solution.

e. TCLP solution A (described in text)

f. TCLP solution B (described in text)

heated to 50°C for 10 minutes, cooled, and the pH again measured. If the pH is still greater than 5.0, solution B is used for the TCLP test.

Solution A is made by mixing 54.3 ml of sodium hydroxide and 5.7 ml of glacial acetic acid in 1 L of demineralized water (the resultant pH is 4.9); solution B is made by mixing 5.7 ml of glacial acetic acid in 1 L of demineralized water (the resultant pH is 2.9).

During the process of developing the TCLP test, other solutions were proposed. Each proposed solution was tested with lead shot. The solutions were tested in the hope that one of the solutions would not leach the lead as much as the acetic acid, which reacts with lead. The results of each test are included in Table III.

A comparison of tumbling vs. stirring was made on one test with #6 lead shot; the tumbling resulted in almost 2.5 times as much lead leaching out. Also new (nonoxidized) lead shot (#8) was compared to the normally oxidized shot, and the new shot leached about 4.5 times less than the oxidized shot.

The differences in results of lead shot tests between Lab #2 and Lab #3 are still being evaluated. The results on duplicate tests at each lab were consistent, so the differences must be in the manner in which the tests were run and in the equipment used (e.g., rpm of the tumbler, size of container, temperature, etc.).

INEL WASTE LEAD VOLUMES

There is a significant volume of radioactively contaminated waste lead at the INEL, as can be seen from Table IV. This lead is in the form of bricks, shot, sheet, and fabricated shapes made for special shielding purposes. There are about 274,000 lb of waste lead being stored and an average of 55,000 lb/yr estimated to be generated over the next seven years. In addition, there are about 720,000 lbs of contaminated lead in use which will some day also be considered excess.

OPTIONS

There are two main options for the ultimate disposition of the lead: disposal or treatment.

Disposal

There currently are no EPA-permitted facilities for the disposal of radioactively contaminated lead. One option is for an existing LLW disposal facility to obtain a permit for the disposal of hazardous waste. In addition to the cost of obtaining the EPA permit is the additional cost incurred to operate the facility under the EPA regulations. These additional costs include monitoring, EPA audits, additional reports, closure plans, etc. The other option for disposal is to build a separate EPA-approved disposal facility for mixed waste. This option would incur all of the costs described above and also the additional costs of establishing a new disposal facility including environmental evaluations, design, construction, etc. The major problem with the option of disposal of RMW is the perpetual liability that exists when any hazardous waste is disposed.

Treatment

The best option is treatment of the lead so it is no longer considered a hazardous waste. There are basically two reasons lead is considered a waste: one is that it is radioactively contaminated to an extent that it cannot continue to be used as shielding; the second is that a specific shielding application requiring special machined shapes is no longer needed,

TABLE IV

CONTAMINATED LEAD WASTE AT THE INEL

Generator	Quantity of Contaminated Lead (lb)	Quantity of Waste Lead Stored (lb)	Amounts Generated Over Next Seven Fiscal Years (lb)						
			FY 85	FY 86	FY 87	FY 88	FY 89	FY 90	FY 91
NRF	ND	47,000	500	500	500	500	500	500	500
D&D Activities	--	--	19,400[a]	26,000[a]	52,000[a]	78,000[a]	52,000[a]	20,000[a]	59,000[a]
ICPP	150,000	--	4,000[a]	4,000[a]	4,000[a]	4,000[a]	4,000[a]	4,000[a]	4,000[a]
ANL	ND	47,000	--	--	--	--	--	--	--
LOFT	40,000	--	--	--	--	--	--	--	--
PBF	270,000	2,000	--	--	--	--	--	--	--
TAN	ND	170,000	--	--	--	--	--	--	--
TRA	360,000	50,000	--	--	--	--	--	--	--
TOTAL	720,000[b]	274,000	23,900	30,500	108,500	82,500	56,500	24,500	63,500

ND - Not Determined

a. Amounts shown for lead disposed of per year for each facility represent best-guess estimates.

b. Not yet considered waste.

and these special shapes are not suitable for use in another application. The ultimate treatment process will decontaminate the lead so that it is no longer a waste and can be recycled.

The ideal treatment process will be capable of treating all contaminated lead forms including shot, wool, sheet, bricks, and special fabricated shapes (irregular surfaces, threaded holes, etc.). The intended end result of treatment is lead which is adequately free of contamination. The methods used to determine how well the lead has been decontaminated is an important consideration in the choice of a treatment option. For example, how do you measure contamination levels of lead shot or lead wool and how would decontamination be verified?

Another important consideration is the residue resulting from the treatment process which will undoubtedly also be a radioactive mixed waste. A process that may decontaminate the lead but produce an untreatable residue would not be acceptable.

Four treatment options currently being evaluated at the INEL are: Freon decontamination; chemical decontamination (electropolishing and acid etching); mechanical cleaning; and refining. Freon decontamination was the first option to be tested due to the small amount of residue assumed to be generated (the Freon is distilled and reused). The results of Freon decontamination of lead have been very poor and therefore it does not appear to be the best treatment method. Chemical cleaning of leadsheet and lead wool appears to be difficult, unless they are totally dissolved, and then treatment of the residue becomes a problem. Mechanical cleaning (e.g. milling off the contaminated surfaces of a brick) also would not work on lead shot and lead wool, and would be costly to perform on anything but perfectly flat surfaces.

The final option being considered, refining, allows treatment of all forms of lead. It also allows for a simple radiological evaluation of the final product by taking a sample of the molten lead before casting, or a sample of the lead ingot. If it can be shown that the molten metal (or ingot) is homogenous the radiological analyses required and the manpower to verify decontamination would be significantly reduced compared to treatment techniques which decontaminate each piece of lead independently and therefore require radiological survey of each piece. Lead refining would have to be tested to determine if the contamination can indeed be removed to the lead dross (refining slag).

Testing at the INEL is under way to determine if the lead dross can be successfully treated (solidified) to render it nonhazardous. Samples of lead dross have been solidified using cement, cement and sodium silicate, and ENVIROSTONE. The initial tests did not pass the EP toxicity test; however, the results were close. The solidification formulas have been modified and additional tests performed. The solidified samples have been sent for analysis, but the results are not yet available.

Concurrently with the development of treatment processes an evaluation should be made of lead usage and why it becomes contaminated and unusable. It will be necessary to change procedures in the use of lead in the future to ensure that it does not become contaminated. Substitution of other materials for shielding may be required. Although steel does not have the high attenuation factors of lead it may be that a substitution is warranted in those cases where contamination is unavoidable to eliminate generation of a radioactive hazardous waste.