DP-MS-87-118

METAL TOXICITY EVALUATION OF SAVANNAH RIVER PLANT SALTSTONE COMPARISON OF EP AND TCLP TEST RESULTS

By

Christine A. Langton

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

A paper proposed for presentation at the
Waste Management '88
Tucson, AZ
February 28 - March 3, 1988

and for publication in the proceedings

The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U. S. Department of Energy.

DP-MS-87-118

METAL TOXICITY EVALUATION OF SAVANNAH RIVER PLANT SALTSTONE COMPARISON OF EP AND TCLP TEST RESULTS

By

Christine A. Langton

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U. S. Department of Energy.

DP-MS-87-118

METAL TOXICITY EVALUATION OF SAVANNAH RIVER PLANT SALTSTONE COMPARISON OF EP AND TCLP TEST RESULTS

By

Christine A. Langton

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

ABSTRACT

Saltstone is the waste treatment and disposal concept for low-level defense waste at the Savannah River Plant. The waste is a sodium salt solution which has about 230 μCi/L in addition to the hazardous characteristics of corrosivity (pH > 12.5) and metal toxicity (Cr^{+6} > 100 ppm).

The design objectives for a wasteform to stabilize this solution include: 1) eliminating hazardous characteristics of the waste; and 2) minimizing the release of potential contaminants, such as NO_3^- and radionuclides, so that drinking water standards will be maintained for groundwater at the perimeter of the disposal site.

Two EPA test procedures are routinely used at SRP to evaluate metal toxicity of wastes and wasteforms. These tests are: 1) the Extraction Procedure (EP) and; 2) the Toxicity Characterization Leaching Procedure (TCLP). The EP test is required by SCDHEC and EPA. The TCLP is used to evaluate the effect of increased surface area on metal leaching from the various SRP wasteforms.

EP and TCLP test results are presented for two types of wasteforms, a cement-based saltstone and for a slag-based saltstone. The cement wasteform results in only physical entrapment of the dissolved chromate. The slag saltstone chemically stabilizes and also physically entraps the chromium. For waste solutions with low to intermediate metal concentrations (up to 5000 ppm), the TCLP extracts typically have lower metal values than the EP extracts. This is attributed to the faster neutralization of the acetic acid by the crushed TCLP sample. Crushing increases surface area and consequently releases more alkalinity from the wasteform matrix and the wasteform pore solution.

Metal concentrations in the EP and TCLP extracts are proportional to the concentrations of metals in the pore solution for both the cement or slag-based wasteforms. The pore solution concentrations for cement wasteforms are directly related to the soluble metal concentration in the waste. The metal concentration in the slag wasteform pore solutions are significantly lower than the waste because these metals are reduced lower valences and precipitated as insoluble solid phases.

INTRODUCTION

Background

Approximately 400 x 10^6 liters of radioactive alkaline salt waste will be treated at the Savannah River Plant (SRP) Defense Waste Processing Facility (DWPF) prior to disposal in an industrial waste landfill at SRP. Treatment involves removal of Cs^+ and Sr^{+2} followed by solidification and stabilization of the potential contaminants in saltstone, a hydrated ceramic wasteform. Saltstone will be emplaced in concrete vaults at SRP which are part of an engineered disposal concept.

The decontamination process results in reducing the activity to about 230 μCi/L which is within the range for Class A low-level waste disposal. However the solution still displays both corrosive (ph > 12.5) and metal toxicity (Cr > 100 mg/L) characteristics of hazardous waste. Consequently, the saltstone process was also designed to eliminate these hazardous characteristics and qualify the resulting wasteform for disposal in an industrial waste landfill.

The specific objectives of the saltstone process were: 1) to solidify the corrosive liquid; 2) to stabilize the chromium, thereby eliminating the metal toxicity characteristic; and 3) to control the release of potential groundwater contaminants, such as NO_3^-, so that drinking water standards can be maintained for groundwater at the perimeter of the disposal site.

Hazardous Characteristic Evaluation

The corrosive liquid characteristic was eliminated by chemically reacting the water in the waste with slag, cement, and fly ash to form a monolithic solid made up of hydrated precipitates.

The Extraction Procedure (EP)[1] toxicity test was used in this study for evaluating metal toxicity. This test is currently required by the Environmental Protection Agency (EPA) for evaluating the characteristic of metal toxicity for non-listed waste streams and for determining whether a treatment process has stabilized a toxic metal waste to the extent that the hazardous characteristic has been eliminated.

Experimental Objectives

The objectives of this study include the following:

1) Identify wasteform design factors (ingredients and proportions) which affect toxic metal stabilization in saltstone as determined by the EP Toxicity Test.

2) Evaluate the effect of saltstone toxic metal concentrations on EP toxicity results.

3) Determine the effect of increased wasteform surface area on metal leaching. Compare results form the EP (monolithic sample) and Toxicity Characterization Leaching Procedure (TCLP)[2] (crushed sample).

4) Identify mechanisms for toxic metal stabilization in saltstone.

EXPERIMENTAL PROCEDURE

Simulated Waste

Simulated salt solution I was prepared and doped with about 100 ppm Ag, As, Ba, Cd, Hg, Pb, and Se and 2000 ppm Cr. These levels of doping were at least 1000X above the expected concentrations for the EP toxic metals except Ba (10X) and Cr (1X). In addition, simulated salt solutions II to VIII were prepared with various Cr concentrations (200 to 12,200 mg/L) to test Cr leaching as a function of source concentration. The compositions of the average DWPF salt solution and of the doped test solutions are shown in Table I.

Saltstone Preparation

Samples were mixed in a Waring blender for one minute. The resulting slurries were cast into polypropylene containers, sealed, and cured at ambient temperature for 28 days. After demolding samples were leached according to either the EP or TCLP tests. Ingredients in these wasteforms are shown in Table II.

Toxicity Evaluation

The EP and TCLP test procedures for alkaline monolithic wastes and wasteforms are summarized in Table III and schematically illustrated in Figures 1 and 2. The TCLP test also includes an extraction procedure for organic contaminants which is not summarized here.

RESULTS

Results of the EP and TCLP tests for the cement and slag-based saltstones made from solution I are tabulated in Table IV. With the exception of the Cr data, there was no significant difference between the EP and TCLP results or between the performance of cement and slag-based formulations. All extracts had toxic metal concentrations below the EPA guideline values except for Cr leached from the cement-based mix (Guideline Value = 5 ppm; EP and TCLP extracts = 16 and 12. 5 ppm, respectively). It should be noted, however, that Cr concentrations in the EP extracts were higher than those in the TCLP extracts for both the cement and slag mixes.

The impact of initial Cr loading in the waste solution on the concentration of Cr extracted in both the EP and TCLP tests was also evaluated. Data for cement and slag-based saltstones made with solutions II through VIII are listed in Table V and plotted in Figure 3. Extrapolation of the Cr EP toxic results indicate that a cement-based mix made with waste solution containing about 560 mg/L Cr would exceed the toxicity guideline value of 5 mg/L. In comparison, the slag-based mix made with solution containing about 5000 mg/L results in less than 5 mg/L Cr in the EP extract.

DISCUSSION

Chromium is the only EP toxic metal present in sufficient quantity to classify the DWPF decontaminated salt waste as having the characteristic of toxicity. The slag-based formulation stabilizes Cr at least 10X more than does the cement-based saltstone.

Lower Cr concentrations in the TCLP extracts compared to those in the EP tests were attributed to the higher pH of the TCLP extracts. Initial neutralization of the acetic acid occurred in this test. The crushed samples required by the TCLP test resulted in at least 10X more surface area compared to the monolithic samples used in the EP test. Increased surface area resulted in more leaching of the alkaline constituents in the waste, NaOH, Na_2CO_3, $NaAl(0H)_4$, and $Na_3(PO)_4$. The basic oxides, such as CaO and MgO, in the wasteform matrix also contributed to the total alkalinity of the sample. The pH of the TCLP extracts ranged between 7.5 and 10.3 for the various wasteforms tests.

The pH of the EP extracts was buffered at 5.0 ± 0.2 for the duration of the experiment. Diffusion of the soluble alkaline species and dissolution of the alkaline matrix for the monolithic samples did not occur quickly enough to neutralize the total potential acidity in the EP extraction fluid during the 24-hour test. Consequently, Cr leaching is more rapid in the acid environment of the EP test compared to the alkaline leachate in the TCLP test.

CONCLUSIONS

Based on EP and TCLP results, chemical stabilization rather than physical entrapment of toxic metals is preferred as the objective of a waste treatment process.

Chromium is chemically stabilized in the slag saltstone and physically entrapped in the cement saltstone. The reactions responsible for this stabilization include reduction of Cr^{+6} to Cr^{+3} followed by precipitation of the relatively insoluble $Cr(OH)_3$.[3] The mechanism is referred to as in-situ chemical stabilization of chromium in the slag-based SRP saltsone. Physical entrapment of soluble Cr^{+6} in the cement saltstone is the passive result of the cement hydration and the development of a low impermeability microstructure. (A similar microstructure develops in the slag formulation.)

In addition alkaline wastes and wasteforms are less sensitive to increased leaching due to high surface area which might result from weathering or lack of long-term structural durability. Consequently, a certain level of alkalinity may be designed into wasteforms to assure that they pass the TCLP test and can meet the requirement for land disposal.

Finally, the EP test appears to be a useful method for evaluating metal toxicity for a wide range of wasteforms. The TCLP test is also useful in ranking wasteforms which require long-term performance assessments since structural integrity is not assumed in this test.

ACKNOWLEDGMENT

The information contained in this paper was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U. S. Department of Energy.

REFERENCES

1. 10 CFR Part 216.

2. 10 CFR Part 268.

3. C. A. Langton, "Slag-Based Saltstone Formulations," Materials Research Society Meeting, Fall 1987, Boston, MA, November 30 - December 4, 1987, to be published in 1987 Proceedings of Scientific Basis for Nuclear Waste Management, in press.

Table I

Comparison of the Expected (2) Salt Solution Composition and the Composition of the Simulated Solution Used for Saltstone Metal Toxicity Evaluation

	Expected Long Term Average Salt Solution	Experimental Salt Solution I	Experimental Salt Solutions II to VII
H_2O	71 wt%	71 wt%	71 wt%
$NaNO_3$	14.1	14.2	14.2
$NaNO_2$	3.5	3.5	3.5
NaOH	3.8	3.8	3.8
Na_2CO_3	1.5	1.5	1.5
$NaAl(OH)_4$	3.3	3.3	3.3
Na_2SO_4	1.7	1.7	1.7
NaCl	0.11	0.1	0.1
Na_3PO_4	0.12	0.1	0.1
$Na_2C_2O_4$	0.28	0.2	0.2
Ag	8.5×10^{-4} ppm	96 ppm	-- ppm
As	3×10^{-4}	85	--
Ba	11	110	--
Cd	5×10^{-2}	101	--
Cr	161**	1790	196 to 12,200***
Hg	1.2×10^{-2}	94	--
Pb	2×10^{-8}	102	--
Se	7.9×10^{-1}	103	--
Spg = 1.23			
pH ~ 14			
Activity			
total	~ 230 µCi/L		
^{90}Sr	0.9		
^{99}Tc	75.3		
^{137}Cs	24.6		
Total Alpha	0.2		

* Concentrations of radioactive and organic constituents are listed elsewhere (2).

** May increase to a maximum of 1400 ppm.

*** Chromium doping in solutions II to VII were 196, 419, 955, 1540, 1990, 3620, 7060, and 12,000, respectively

Table II

Slag-Based Saltstone Formulation	
Ingredient	Wt %
Slag	25
Class F fly ash	25
Portland cement	4
Salt solution	46

Spg ~ 1.7

Cement-Based Saltstone Formulation	
Ingredient	Wt %
Cement	11.5
Class C fly ash	46
----	--
Salt solution	42.5

Table III

Comparison of EP and TCLP Procedures for Monolithic Alkaline Wastes or Wasteforms

Parameter	EP(1)	TCLP(2)
Sample		
form	Natural form after structural integrity test	Crushed to pass -3/8 in sieve
size	Monolithic cylinder 3.3 cm x 7.1 cm	100 g minimum
age	Unspecified	Unspecified
Leachant		
volume	16 x sample wt + up to 400 ml acid	20 x sample wt
chemistry	Buffered to pH 5.0 ± 0.2 with up to 400 ml 0.5N acetic acid (0.2 moles acid) BUFFERED	0.92 N acetic acid (0.18 moles acid) NOT BUFFERED
Time	24 hr	18 hr
Analyses	8 toxic metals + Ni, CN, etc., as requested	8 toxic metals 52 organics
Apparatus	Stirred beaker	Stirred beaker + zero head extractor for organics
Criteria	Guideline values (100 x DWS)	Treatment standards target values for land and waste
Application	1) Evaluate listed or unlisted waste for EP toxic characteristics 2) Evaluate and qualify treated listed wastes for delisting	1) Qualify treated or untreated hazardous waste for hazardous landfill disposal 2) Qualify delisted industrial waste for landfill disposal

Table IV

Metal Toxicity Results for the Cement-Based and Slag-Based Saltstones Made with Solution Doped with 100 mg/L Ag, As, Ba, Cd, Hg, Pg, and Se, and 2000 mg/L Cr

	Cement-Based Saltstone		Slag-Based Saltstone	
	EP	TCLP	EP	TCLP
Ag	< 0.5	<1	<0.5	<1
As	< 0.5	< 0.5	< 0.5	< 0.5
Ba	< 0.5	< 0.5	< 0.05	0.309
Cd	< 0.02	< 0.02	< 0.02	< 0.02
Cr	16	12.5	0.113	< 0.05
Hg	<0.01	< 0.01	0.00127	0.00566
Pb	< 0.5	< 0.5	< 0.05	< 0.5
Se	< 0.5	< 1	< 0.5	< 1

Table V

Metal Toxicity Results for the Cement-Based and Slag-Based Saltstones made with Solutions Doped with Cr Concentrations From 196 to 12,200 mg/L

DWPF Salt Solution Cr doping (ppm)	Cement-Based Mix		Slag-Based Mix	
	EP Cr (ppm)	TCLP Cr (ppm)	EP Cr (ppm)	TCLP Cr (ppm)
196	1.9	2.0	0.05	0.05
419	3.6	3.3	0.20	0.05
955	7.5	5.5	0.40	0.05
1540	9.5	6.0	0.37	0.05
1990	15	12	0.05	0.05
3620	22	18	0.10	0.05
7060	30	36	7.9	1.5
12200	45	52	20	15

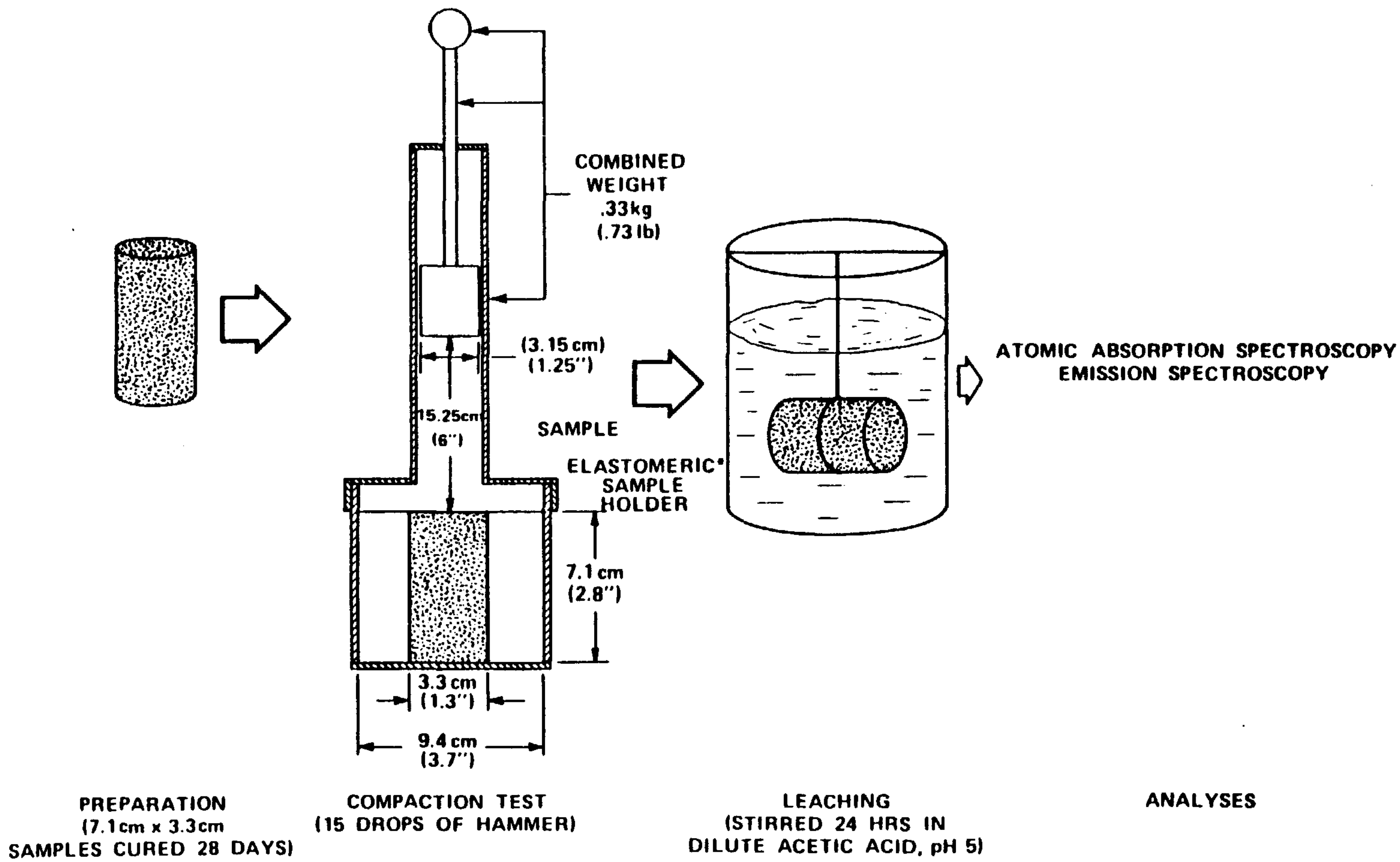

Figure 1. Schematic Illustration of the EP Toxicity Test

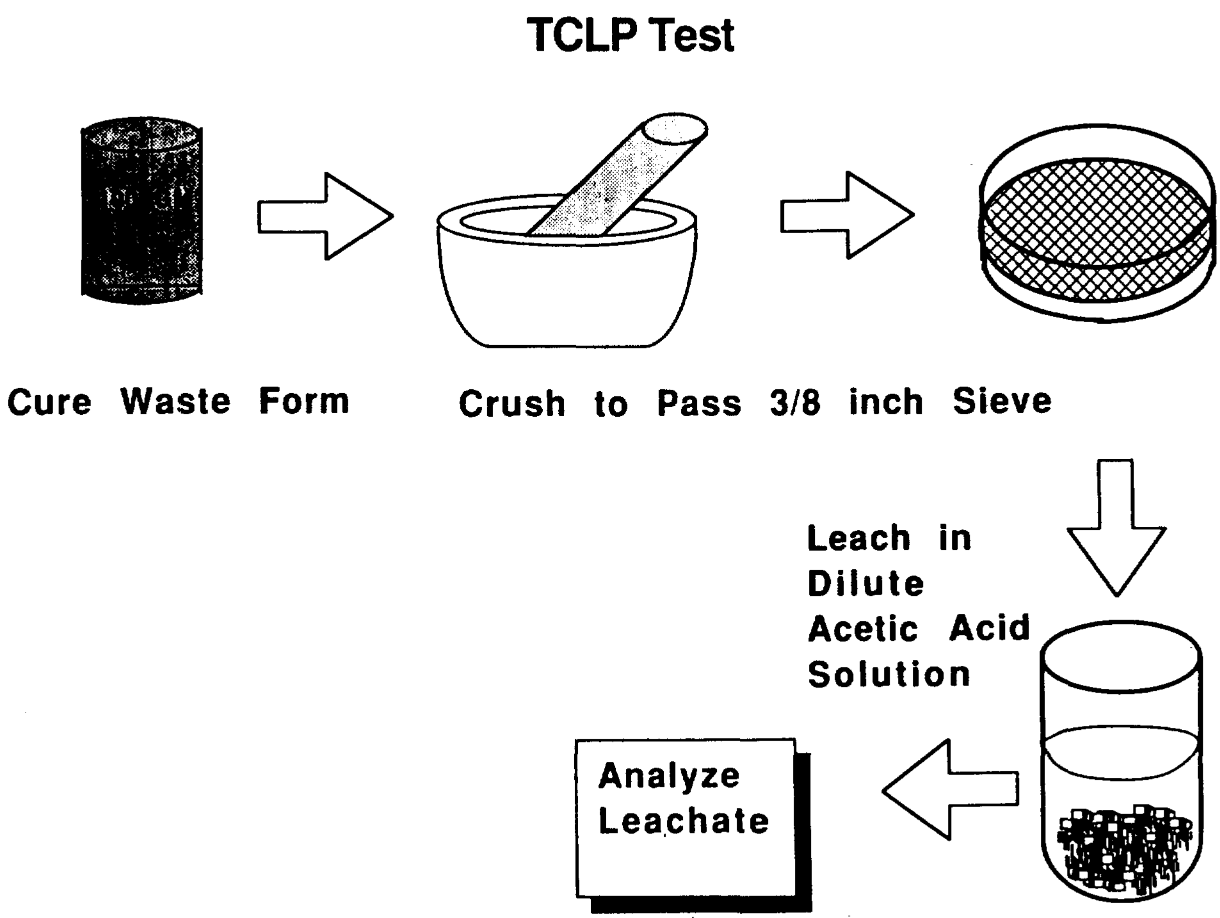

Figure 2. Schematic Illustration of the TCLP Test

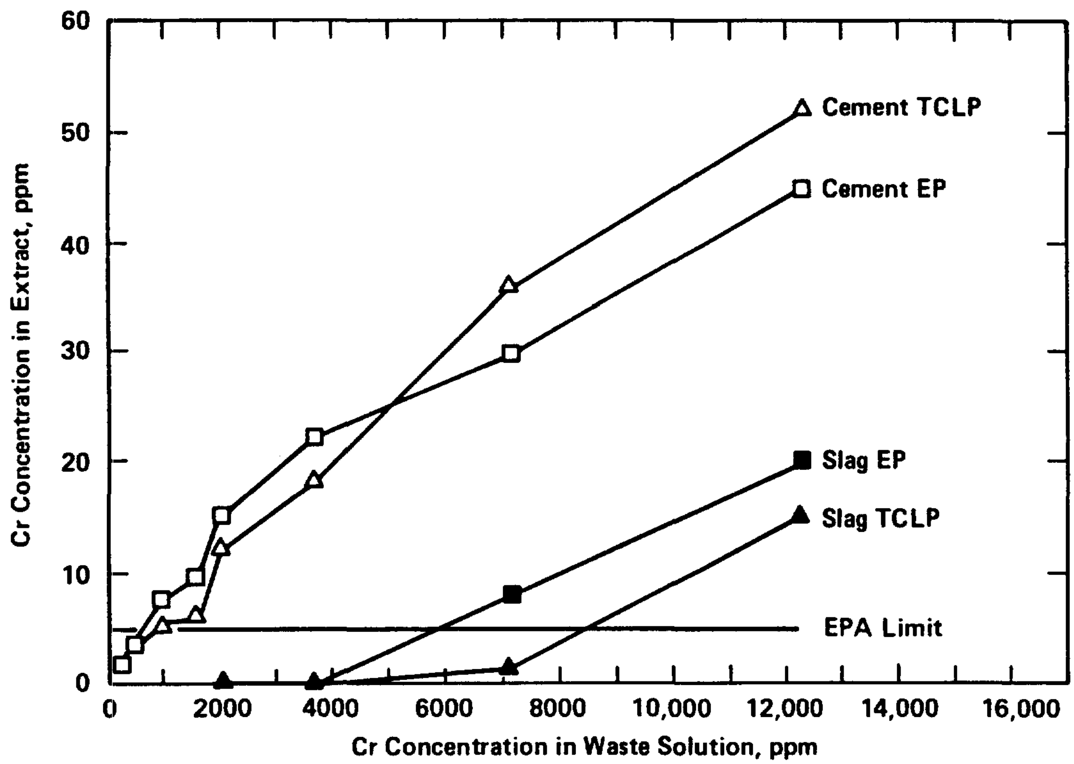

Figure 3. Cr Toxicity Results for Slag- and Cement-Based Saltstones