Heavy metals in cement and cement kiln dust from kilns co-fired with hazardous waste-derived fuel: application of EPA leaching and acid-digestion procedures

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Abstract

Substantial leaching from cement and cement kiln dust (CKD) of specific metals, especially Cr and Ba, resulted from application of the standard Toxicity Characteristic Leaching Procedure (TCLP). However, all TCLP concentrations are below limits for hazardous waste defined in the Resource Conservation and Recovery Act (RCRA). Four variations on the TCLP were assessed. The primary discernible enhancement of Tier-III metals release, relative to the standard TCLP, is increased leaching of Cr by chlorinated-water solutions. This likely results from enhancement of metal dissolution by chloride complexation. The final pH of each extract remained high. Thus, the capacities of these cement and CKD samples to buffer the acidity of the leaching solutions were not exceeded, even after two sequential exposures. This factor calls into question whether these high-pH solutions could represent any 'real-world' condition and implies that the TCLP is not suitable for assessing the leaching behavior of alkaline systems such as cement and CKD. The EPA SW-846 microwave-assisted, acid-soluble procedure produces only partial recovery of any metal relative to dissolution-independent concentrations obtained by X-ray fluorescence spectrometry. Our results contradict previously published statements that TCLP and acid-soluble metal concentrations showed no consistent relationship. Both current results and re-evaluation of previously published data indicate correlations between TCLP and SW-846 acid-soluble concen-

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trations, for several metals, that are significantly > 0 at high levels of confidence. © 1998 Elsevier Science B.V.

1. Introduction

Cement kilns fire raw materials at temperatures that, in the hottest zone, typically exceed 1480°C to produce clinker (raw cement product) of good quality [1,2]. Clinker is ground with gypsum to produce commercial portland cement. The traditional fuel for this energy-intensive process is conventional fossil fuels (CFF)—coal, coke, oil, and natural gas. However, over the past dozen years, the substitution of hazardous waste-derived fuel (WDF) for CFF in cement and aggregate kilns has increased considerably [2]. Solid materials discharged from cement kilns are the clinker (raw product) and cement kiln dust (CKD), fine-grained particulate matter that is trapped by air pollution control devices (APCD) to limit emigration from the kiln stacks.

WDF consumption in cement and light aggregate kilns is permitted under the Boilers and Industrial Furnaces (BIF) Act, 40 CFR (Code of Federal Regulations) 266, that was adopted on February 21, 1991. Under the BIF Rule, residues from the cement kiln process, specifically CKD, were exempted from regulation as hazardous waste under Subtitle C (40 CFR 261.22) of the Resource Conservation and Recovery Act (RCRA). This interim exemption, also known as the Bevill exemption, is codified at 40 CFR 261.4(b)(8). Materials not covered by the Bevill exemption, as published in 40 CFR Part 266.112 (Subpart H), include CKD that fails the subtitle C test for hazardous waste land disposal. The EPA Office of Solid Waste (OSW) published in 1986 the third edition of methods (SW-846) for standard leaching and analytical procedures to evaluate RCRA status [3]. The SW-846 test assigned to demonstrate compliance with the Bevill exemption for CKD land disposal is the Toxicity Characteristic Leaching Procedure (TCLP) test, method 1311 in SW-846 [3]. Additional test protocols designated in the BIF Rule, to indicate *recoverable* (acid-soluble) metals, are the SW-846 procedures for acid-soluble digestion (methods 3050 and 3051 (microwave assisted)). These acid-soluble, recoverable-metals procedures have been referred to by some as yielding 'total' metals [4], an inaccurate terminology. A proposed update to the third edition of SW-846 published more recently [5] apparently did not alter the TCLP significantly. Our results will be compared to those from a previous study [4] that applied the TCLP from this same version of SW-846 [3].

WDF-CFF fuel mixing has generated considerable debate regarding the fate of metals introduced to the kiln in WDF [6]. Most evidence indicates that only small proportions of most metals are emitted from the kiln stacks [7,8]. Metals that do not exit a kiln through stack emissions, unless they accumulate temporarily in the kiln, will be incorporated into either the cement clinker or the CKD. The more volatile metals tend to concentrate more strongly in the CKD relative to the clinker [2,6,8–10].

The primary published source that relates directly to the fate of metals in cement clinker and CKD is the Portland Cement Association (PCA) study [4]. These results are

discussed below. Additional literature, which concentrate on procedures for the stabilization and solidification (S/S) of hazardous waste, relate less directly to the question of metals behavior in cement and CKD. In those studies, metal dopants typically were introduced in the aqueous solution used to set a cement paste [11–17]. This different mechanism of incorporating metals might lead to significantly different locations of metals within the cement structure, a difference that could contribute to distinctly different leaching behavior of WDF-processed cement and S/S-processed waste materials. Nonetheless, those S/S studies provided potentially enlightening guides to the contrasting behaviors of specific metals, most notably tendencies for Pb to concentrate in pores and on surfaces of the material and for Cr to substitute preferentially into the solidified matrix [11,13–17].

The present manuscript directly addresses questions regarding the applicability of those SW-846 methods to cement and CKD processed with WDF. The effect of varying the TCLP procedure on the amount of metal leached will be addressed. In addition, absolute masses of metal derived by the various leaching and dissolution methods will be compared.

2. Toxicity characteristic leaching procedure (TCLP)

2.1. The TCLP procedure

The TCLP for alkaline materials [3] is summarized briefly in the Appendix. Prior to the third edition of SW-846 [3], the analogous test was a similar leaching procedure called the Extraction Procedure Toxicity test (EPTox) [18]. EPTox was compared to other leaching tests, for coal-preparation wastes, by Heaton et al. [19]. The primary differences between the TCLP and EPTox procedures were described by LaGrega et al. [20] and evaluated by Sorini and Jackson [21] and Bricka et al. [22]. These differences are summarized briefly in the Appendix. Generally, the EPTox appears slightly less aggressive than the TCLP.

2.2. Previously published criticisms of the EPTox and TCLP

2.2.1. General criticisms

General criticisms in the literature of the TCLP and EPTox include: (a) These tests include grain-size reduction, thus, eliminating the ability to evaluate potential advantages in waste segregation by S/S processes (encapsulation by the matrix) [20,23]; (b) The low-pH extraction fluid may not represent 'real world field conditions' [20].

2.2.2. Criticisms specific to alkaline solids (including cement and CKD)

Several references have criticized the TCLP and EPTox as insufficiently aggressive toward leaching heavy metals from alkaline solids [20,24–27]. Both these procedures are susceptible to control of the final solution pH by the alkalinity of the solid. Mix and Murphy [24] applied the data of Schock [28], which address the potential effects of dissolved carbonate on lead solubility. They argued that very high pH solutions, where

CKD is disposed, could enhance lead dissolution (high Pb solubility). This lead could precipitate as the pH then drops to the range ∼ 9–11.5, at which Pb solubility is lower, when other waters mix with the CKD-affected waters.

The limited data of Sorini and Jackson [21] indicated that the degree of TCLP leaching did not increase with decreasing solution pH, though TCLP leaching generally exceeded EPTox. Criticism by Bishop et al. [25] of EPTox referred primarily to the possible binding of heavy metals, especially Cr and Pb, in silicate compounds and to the limited solubilities of silicates at pH values below nine. Thus, low-pH release of metals bound in silicates could be limited. The solubility of calcium silicates may remain low up to pH = ∼ 11 [29].

The objections to EPTox referred to the capacity of cement to buffer solutions to very high pH [26], an effect also noted for the TCLP by Kosson et al. [27,30] and LaGrega et al. [20]. Details of the response can depend greatly on the liquid:solid ratio (LS). Because the solubility of most metals is low at higher pH (> ∼ 7), most heavy metals would be precipitated in the highly alkaline environment of the cement pore solution [26]. However, at pH below seven, the metals will become increasingly soluble. Thus, in nature, the acid-neutralizing capacity of cement eventually will be overcome, then the pH levels may fall dramatically, which may increase metal solubilities greatly. Poon [26] termed this effect the 'breakthrough point', the pH at which the solubilities of many metals may increase dramatically as the leaching water becomes more acidic.

2.3. Alternative leaching-test procedures proposed in the literature

Alternative leaching procedures, which are used as standards for other applications or which have been proposed as standards, are listed in Table 1.

EPTox (1) procedures are discussed above and in Appendix A. Both the ANSI/ANS [31] (procedure 2) and ANSI/NSF [32] (procedure 3) tests suspend a bulk sample in the leaching solution without agitation. The ANSI/NSF test [32] includes at least ten cycles of 'conditioning', during which the sample is immersed for a total of at least 14 days for a minimum of 24 h per cycle. Following this 'conditioning', the 'leaching' solutions are brought into contact with the sample. According to ANSI/NSF protocol, only these 'leaching' solutions typically are analyzed for metals, an approach that may not

Table 1
Alternative leaching protocols to the TCLP

Test	Extraction Medium
1. EP Toxicity test (EPTox)	0.5 N acetic acid
2. ANSI/ANS-16.1 [31] American Nuclear Society	distilled water
3. ANSI/NSF-61 [32] National Sanitary Foundation, drinking water recommendation	ANSI/NSF extraction water
4. Modified TCLP [25]	17.4 N (conc.) glacial acetic acid
5. Column test [25]	0.05–0.2 N acetic acid
6. Mortar-bar leach [33]	Bottled water/Deionized Water
7. Concrete-cylinder leach [34]	TCLP fluid/Deionized Water
8. Availability Leaching Test [27,30]	Two extractions, pH = 7 then 4
9. Acic Neutralization Capacity Test [27,30]	Eleven extractions, LS = 5:1

recognize all the metal released. However, Germaneau et al. [33], following a protocol virtually identical to the ANSI/NSF test, also reported metal concentrations in their 'conditioning' and disinfecting solutions. In some cases, these concentrations exceeded those in the 'leaching' solutions. Kanare and West [34] also followed ANSI/NSF recommendations. For pipe-lining procedures in the field (in situ), this 'conditioning' recommended by ANSI/NSF may be followed only rarely, because pipes must be pressed back into service as soon as possible (S. Medlar, personal communication, 1995).

A contrasting suite of leaching tests has been proposed for thorough characterization of S/S and municipal-incinerator waste [27,30]. This group proposed separate tests to address the questions of (a) release potential, (b) elemental solubility as a function of pH, and (c) release under diffusion-controlled conditions. Specific tests proposed therein include the availability leach test (ALT) and the acid neutralization capacity (ANC) test. The ALT provides a measure of the maximum amount of an element or species that could be released under aggressive leaching conditions. This test combines data from two sequential extractions at controlled pH and a high LS (100:1). The two extracts are combined for analysis. The high LS ensures that release of a contaminant is not governed by its solubility. The ANC test evaluates the solubilities of specific metals over a wide pH range by eleven separate extractions at LS = 5:1. This low LS insures that each extraction is solubility constrained for some analytes.

2.4. Variations to the standard TCLP evaluated, current study

The present study evaluates the efficacy of the standard TCLP method as applied to cement and CKD. We also have implemented four modifications to the standard TCLP procedure, to evaluate their effects on metals leaching. Variations to the standard TCLP procedure evaluated in our study include:
1. Leaching of set cement rather than of raw, nonhydrated cement,
2. Leaching in multiple-successive or serial extractions (repeated-exposure or sequential-batch tests),
3. Leaching with a chlorine-disinfectant bearing solution in reagent water,
4. Leaching for an extended duration (one week).

Results from TCLP variations (1)–(4) are reported below (Section 7). Some further potential variations could be: leaching with a similar-pH solution using a substitute acid (nitric, sulfuric), leaching with only reagent water, leaching with lower LS, controlled-pH leaching tests at high LS to provide a measure of metal availability, and leaching tests that produce titration curves to address the acid-neutralization capacity of the material.

3. Acid soluble or 'total recoverable' metals

A measure of absolute *total* metal concentrations in bulk samples is useful to apply any evaluation of leached concentrations relative either to the absolute total or to the

'available' metal in the system [27]. Although the EPA SW-846 acid-soluble methods 3050 and 3051 provide a standard measure of comparison relative to the TCLP [4], these methods produce only an *acid-soluble* metal concentration; in many matrices this may fall short of the absolute total concentrations of many metals [4,27]. Thus, these SW-846 results should not be referred to as 'total metals'. Many silicate phases tend to dissolve only incompletely in the absence of hydrofluoric acid, a relation well known in geochemistry [35]. A recent study of S/S processing found acid-soluble metal concentrations (method 3051) to fall far short of absolute total (dissolution-independent) concentrations (by instrumental neutron activation analysis, INAA) [27]. Thus, considering acid-soluble metal concentrations as equivalent to 'total' metal concentrations, in most cases, is likely to produce erroneous conclusions based on falsely low metal abundances.

The US EPA Report to Congress on CKD [2] tabulated together results from the nitric acid-soluble PCA [4] digestions along with those from the $HF + HNO_3 + H_2O_2$ technique from Haynes and Kramer [36] ([2], Exhibit 3–18). Direct comparison of those results cannot be valid because the methods of acid dissolution to obtain acid-soluble metals are very different. The PCA study used the standard EPA SW-846 methods [37], which employ only nitric acid (method 3051) or a combination of HNO_3 and HCl (method 3050). However, in the US Bureau of Mines (USBM) study [36], Haynes and Kramer employed a much more aggressive technique that uses both nitric and hydrofluoric acids, along with hydrogen peroxide. This multi-acid technique produces much more aggressive attack, particularly on silicate phases ([35], pp. 94–98). The PCA results, in the data summary [37], were stated explicitly to reproduce incompletely the certified standard reference material (SRM) concentrations. In contrast, the USBM study reported 'good agreement between certified values and values obtained' with their method. Thus, the comparison implied by the tabular compilation in the Report to Congress [2] *should not be applied directly to two such disparate datasets*.

We compare below our results from applying the EPA SW-846 method 3051 for acid-soluble metals to analyses by dissolution-independent, X-ray fluorescence (XRF) spectrometry. XRF should provide a close measure of absolute total metal concentrations. These two types of data on the same samples will provide a distinct illustration of the incomplete metals recovery accomplished by the acid-soluble SW-846 method.

4. Evaluation of previously published results for cement and CKD

Only limited information in the published literature relates directly to the fate of metals in cement clinker and CKD. A study by the PCA [4] published acid-soluble and TCLP metal concentrations for cement and CKD samples from 79 cement plants. Some of these plants burned WDF and others did not. In part, this study was intended to update an earlier study on CKD by the USBM [36] because of process changes, most notably the increased incorporation of WDF into cement-kiln fuel. However, SW-846 acid-soluble metal results from the PCA and USBM studies cannot be compared legitimately, as mentioned briefly above and discussed in detail below (Section 8.6.).

Although acid-soluble and TCLP results were reported by the PCA, sample information notably absent from that study includes:

1. Which samples were processed with WDF;
2. What 'absolute' (either dissolution-independent or complete-dissolution) metal concentrations were present.
3. What percentage of CKD recirculation is associated with any sample (although they claimed this was the primary factor controlling metal concentration).

Some aspects of the PCA data analysis, in addition, appear inconsistent. The data summary [37] presented correlation coefficients and plots for metal concentrations, from the TCLP and acid-soluble techniques, for both cement and CKD. Although the reported correlation coefficients range as high as 0.75, with total datasets in some cases reported to exceed 180 individual measurements, the statement was made that, ''in every case, there was no consistent relationship between the total [sic] metals concentration and the TCLP result for cement and CKD'' ([4], p. 8). However, our re-evaluation of those data suggests this statement is inaccurate. We address this question in the discussion of experimental results (Section 8).

According to the BIF Rule, SW-846 methods (TCLP 1311 and acid-soluble metals 3051 or 3050) are designated to classify CKD as hazardous (or not) under RCRA. These RCRA standards typically are based on 100 times the relevant EPA primary standards for drinking water [2]. The TCLP was developed to assess leaching potential from an

Table 2
Cement and CKD samples used in the present study

Company name	Plant location	Source	WDF use	Sample designation
Continental	Hannibal, MO	PLANT	P	CCC(MO)-1
Dixie	Knoxville, TN	PLANT	A	DC(TN)-1
Giant	Harleyville, SC	JOE*	P	Giant(SC)-1
Giant		PLANT	P	Giant(SC)-2
Giant		Dennis Morris*	P	Giant(SC)-3
Holnam	Clarksville, MO	PLANT	P	Holnam(MO)-1
Holnam	Holly Hill, SC	JOE*	P	Holnam(SC)-1
Holnam	Holly Hill, SC	PLANT	P	Holnam(SC)-2
Holnam	Holly Hill, SC	Dennis Morris*	P	Holnam(SC)-3
Keystone	Bath, PA	JOE*	P	Keystone(PA)-1
Lafarge	Alpena, MI	PLANT	UK	Lafarge(MI)-1
Lone Star	Green Castle, IN	PLANT	P[a]	LSI(IN)-1
North Texas	Midlothian, TX	PLANT	A	NTXC(TX)-1
River	Festus, MO	PLANT	A	RCC(MO)-1
Texas Industries	Midlothian, TX	PLANT	P	TXI(TX)-1
Texas Industries		Sue Pope*	P	TXI(TX)-2
Unknown	SC	Dennis Morris*		[a]CKD(SC)-1
Total number rcvd.		17	10 Rcvd. directly from plants	

All samples are Cement except [a]CKD(SC)-1 is Cement Kiln Dust.
* INDIVIDUAL SOURCES: Ms. Sue Pope, Midlothian, TX; Dennis Morris, Laidlaw Env., Pinewood, SC; JOE = J.O. Eckert, Jr., Rutgers University.
WDF usage: (from ARTT list of 11/28/94) P = Primary, A = Alternate, S = Supplementary, UK = Unknown; [a] = Apparently Discontinued.

improperly disposed solid waste [2], such as in a municipal landfill environment. In practice, variations in end-point pH may control the differences in metals release where metal solubilities are dependent on pH [27,30]. Cement and CKD control strongly the pH of the extraction fluid, creating very alkaline final solutions that contrast greatly with the intended leaching medium [20]. Thus, a re-appraisal of the applicability of the TCLP to highly alkaline solids, such as cement and CKD, appears warranted. This need provided the impetus for the present study.

5. Sources of cement and CKD samples

Samples of ordinary portland cement (OPC) and CKD used for this study, along with details on sample acquisition and sample-name assignment, are listed in Table 2. A source list obtained prior to sample acquisition (Rollins Environmental, Wilmington, DE, 28 November 1994) identified cement plants that burn WDF as a primary or an alternate fuel source. Samples were requested from 22 plants indicated to manufacture cement using WDF. OPC samples were received from ten plants. Individual OPC samples either were shipped directly from each plant or were purchased by individuals in hardware outlets. The study samples were obtained from seven facilities indicated to burn WDF as a primary source and from four indicated to burn WDF in an alternate or 'unknown' capacity (Table 2). One of these primary WDF burners apparently discontinued the use of WDF prior to our receipt of samples. One specimen of CKD was analyzed. Additional details on plant operation, during which these samples of cement and CKD were generated, are not available.

6. Experimental methods

Procedures described below include the standard TCLP and variations thereof. In the discussion of variations, any part of the procedure not explicitly described was performed the same as in the standard procedure.

6.1. Standard TCLP

Standard procedures set forth in SW-846 [3], method 1311 (TCLP) were followed. A brief summary of procedures is provided in the Appendix. Our sole modification of these SW-846 procedures was the substitution of an additional tap-water rinse for the initial use of detergent in the standard cleaning procedures, to ensure no contamination by detergent (W. Johnson, EOHSI, personal communication, 1995.). Reagent-grade (ACS) HCl and HNO_3 (Fisher Scientific, Pittsburgh, PA) were used for this acid-wash cleaning procedure. Additional details may be obtained from the authors on request.

6.1.1. Initial TCLP leaching test

Prior to the arrival of specific required equipment, an initial TCLP extraction was performed at Princeton Testing Laboratories (Princeton, NJ). 199.6 g of this sample

(Giant(SC)-1) was weighed into a polyethylene bottle and transported to the laboratory. The laboratory performed the TCLP and microwave-assisted acid digestion procedures from EPA publication SW-846 (methods 1311 and 3015, respectively).

6.1.2. Raw cement and CKD

These already fine-grained powders did not require any particle-size reduction, and were loaded directly into the extraction vessels.

6.1.3. Set cement

Portions of seven cement samples were set (hydrated) prior to size reduction and extraction. 100 g of the raw cement powder was hydrated with 50% (w/w) deionized water (DIW). These were set using large hexagonal polystyrene weighing dishes (Fisher Scientific) as molds. Following initial hydration, the open top of the setting cement was monitored for dryness over a 48-h period. Throughout this time period, a small amount of additional DIW was applied when the surface was noted to be dry. Particle size was reduced to below 9.5 mm, as indicated by the method, using a masonry hammer. Fragments were prevented from contamination by enclosure within polystyrene dishes during the impacts.

6.2. Multiple exposure TCLP

The solid residues from the initial, standard TCLP leaches of four cements were subjected to a second exposure in the TCLP extraction fluid. All other aspects of the procedure followed the standard TCLP protocol.

6.3. Chlorinated water TCLP

Two raw-cement samples (TXI(TX)-2 and Holnam(MO)-1) each were exposed to leaching in chlorinated reagent water at two different Cl_2 concentrations: 4 ppm and 100 ppm. Chlorine was introduced as calcium hypochlorite ($Ca(OCl)_2$), a standard compound for the disinfection of water, to minimize the impact on the major-element chemistry of the system.

6.4. Extended exposure time TCLP

Two raw-cement samples were subjected to an extraction for which rotation lasted one week (168 h). All other aspects of the test were equivalent to the standard TCLP. These extended-time leaching tests were applied to two samples with significant Cr and Pb concentrations from the standard TCLP: TXI(TX)-1 and Holnam(MO)-1.

6.5. Digestion and analysis

6.5.1. Microwave digestion of extracts

All extracts described above were subjected to microwave-assisted acid digestion (SW-846 method 3015). Five ml of ultrapure (double distilled) nitric acid (Ultrex, J.T.

Table 3
Standard TCLP of raw cement and CKD

Concentration units: ppb		Sample							
Element	Isotope	Blank-1	Blank-2	Blank-3a	Blank-3b (Std. 1 wk)	Blank-3c (Std. 1 wk)	Giant (SC)-1	Giant (SC)-1b	Holnam (SC)-1
Beryllium	**Be 9**	**5.45**	**ND**	**0.99**	**ND**	**ND**	**0.40**		**ND**
Aluminium	Al 27	116.12	8.03	6.79	16.65	7.78	Overrange		Overrange
Titanium	Ti 49	3.93	ND	1.70	4.90	ND	5.05		4.55
Vanadium	V 51	2.18	ND	1.56	4.30	ND	ND		ND
Chromium	**Cr 52**	**12.66**	**6.27**	**7.76**	**15.74**	**7.95**	**264.97**	**(273)**	**138.05**
Manganese	Mn 55	2.01	0.70	1.28	6.61	ND	4.14		ND
Cobalt	Co 59	0.24	0.06	0.93	3.89	ND	8.15		6.96
Nickel	Ni 60	1.67	21.67	3.49	8.91	ND	104.44		104.15
Zinc	Zn 64	1.45	11.70	3.05	15.02	ND	23.85		19.97
Copper	Cu 65	0.68	1.13	1.87	10.22	ND	8.63		7.16
Arsenic	**As 75**	**0.29**	**ND**	**0.89**	**2.22**	**ND**	**0.97**	**(<10)**	**ND**
Selenium	**Se 82**	**1.22**	**1.08**	**3.43**	**8.20**	**1.55**	**4.93**	**(<5)**	**1.81**
Rubidium	Rb 85	ND	ND	0.73	0.62	ND	221.45		29.05
Cadmium	**Cd 114**	**0.06**	**0.03**	**0.32**	**2.10**	**ND**	**0.16**	**(<1)**	**0.11**
Cesium	Cs 133	ND	ND	0.73	3.64	ND	4.28		0.20
Barium	Ba 138	0.22	ND	1.52	ND	0.37	915.32		654.91
Lead	**Pb 208**	**1.92**	**1.36**	**0.84**	**2.95**	**ND**	**1.64**	**(<10)**	**ND**
Dilution factor		1.1110	1.1110	3.0525	1.1110	3.0525	1.1110		1.110
pH (final)		BLANKS	BLANKS	BLANKS	BLANKS	BLANKS	12.69		12.65
BLANK used:							Blank-1	−	Blank-1

ND = Not Detected; PTL@: Independent TLCP and analysis (GFAA) by Princeton Testing Laboratories.

Table 3 (continued)

Element	Isotope	Giant(SC)-2	Holnam(SC)-2	TXI(T X)-1	TXI(TX)- 2	NTXC(T X)-1	LSI(IN)-1	Lafarge(MI)1	Holnam(MO)-1
Beryllium	**Be 9**	**ND**	**ND**	**2.19**	**1.81**	**ND**	**ND**	**17.23**	**27.76**
Aluminium	Al 27	Overrange	Overrange	Overrange	Overrange	Overrange	Overrange	Overrange	Overrange
Titanium	Ti 49	2.29	1.71	6.42	6.13	1.94	0.40	0.98	1.79
Vanadium	V 51	ND	ND	ND	ND	ND	ND	ND	ND
Chromium	**Cr 52**	**235.45**	**66.66**	**329.92**	**269.99**	**48.68**	**82.18**	**38.81**	**107.45**
Manganese	Mn 55	ND	6.79	ND	ND	ND	ND	ND	ND
Cobalt	Co 59	6.09	4.07	6.64	5.48	1.98	1.99	2.96	2.60
Nickel	Ni 60	64.13	57.32	24.14	19.86	2.54	0.36	2.05	12.73
Zinc	Zn 64	13.35	16.51	2.81	0.54	ND	ND	18.26	22.72
Copper	Cu 65	5.39	8.18	2.63	2.29	0.61	0.37	0.42	1.54
Arsenic	**As 75**	**ND**	**0.92**	**0.06**	**ND**	**ND**	**ND**	**ND**	**ND**
Selenium	**Se 82**	**5.00**	**1.25**	**0.65**	**1.13**	**0.27**	**0.16**	**0.48**	**0.48**
Rubidium	Rb 85	346.68	31.85	126.30	129.57	211.52	127.46	260.19	188.79
Cadmium	**Cd 114**	**0.09**	**0.09**	**1.59**	**2.30**	**0.03**	**0.02**	**0.06**	**0.16**
Cesium	Cs 133	11.87	0.54	6.06	6.56	16.36	4.83	9.80	9.37
Barium	Ba 138	735.31	583.32	484.89	426.95	469.95	648.06	654.45	586.97
Lead	**Pb 208**	**ND**	**8.00**	**ND**	**ND**	**ND**	**ND**	**ND**	**3.15**
Dilution factor		1.1110	1.1110	1.1110	1.1110	1.1110	1.1110	1.1110	1.1110
pH (final)		12.68	12.69	12.33	12.43	12.46	12.44	12.22	12.27
BLANK used:		Blank-1	Blank-1	Blank-2	Blank-2	Blank-2	Blank-2	Blank-2	Blank-2

ND = Not Detected.

Table 3 (continued)

Concentration units:ppb		Sample					
Element	Isotope	CCC(MO)-1	Eystone(PA)-1	* Dixie(TN)-1	River(MO)-1	Giant(SC)-3	Holnam(SC)-3
Beryllium	**Be 9**	**29.74**	**9.92**	**6.94**	**ND**	**ND**	**3.21**
Aluminium	Al 27	Overrange	Overrange	183.90	4.84	312.27	ND
Titanium	Ti 49	1.29	1.30	219.31	466.58	443.77	279.75
Vanadium	V 51	ND	ND	ND	6.35	ND	0.92
Chromium	**Cr 52**	**41.12**	**82.07**	**15.41**	**986.21**	**14.14**	**215.31**
Manganese	Mn 55	ND	ND	1.82	0.90	1.56	ND
Cobalt	Co 59	2.69	1.84	4.81	7.50	9.17	4.99
Nickel	Ni 60	18.07	ND	13.04	81.40	96.91	15.68
Zinc	Zn 64	23.31	11.34	31.65	18.56	41.50	6.89
Copper	Cu 65	1.80	0.77	ND	3.43	6.30	ND
Arsenic	**As 75**	**ND**	**ND**	**ND**	**ND**	**ND**	**0.48**
Selenium	**Se 82**	**0.23**	**ND**	**ND**	**25.46**	**7.37**	**ND**
Rubidium	Rb 85	1.98	210.42	824.92	564.18	255.51	48.93
Cadmium	**Cd 114**	**0.04**	**0.07**	**0.42**	**ND**	**ND**	**0.46**
Cesium	Cs 133	ND	9.46	17.33	37.63	4.42	0.55
Barium	Ba 138	558.56	470.60	4108.91	831.63	2306.31	516.50
Lead	**Pb 208**	**ND**	**ND**	**4.56**	**17.24**	**0.13**	**ND**
Dilution factor		1.1110	1.1110	3.0525	3.0525	3.0525	3.0525
pH (final)		12.27	12.32	12.34	12.27	12.34	12.28
BLANK used:		Blank-2	Blank-2	Blank-3b	Blank-3c	Blank-3c	Blank-3b

ND = Not Detected; * Samples acid digested at QC, Southampton, PA.

Table 3 (continued)

Element	Isotope	Maximum	Drinking water standard	% of D.W. Std	PCA Avg. (TLCP, Cement)	RUTCLP MAX. % of PCA Avg.	RCRA Limit	CKD	PCA CKD (Avg. TCLP):	RUTCLP CKD % of PCA Avg.
Beryllium	**Be 9**	**(NC)#**	**4.00**	**NA**	**0.5**	**−**	**7**	**1.78**	**0.40**	**(NC)#**
Aluminium	Al 27	312.27						15.62		
Titanium	Ti 49	466.58						19.07		
Vanadium	V 51	6.35						13.88		
Chromium	**Cr 52**	**986.21**	**100.00**	**986.2**	**540.0**	**182.6**	**5000**	**217.93**	**100.00**	**217.93**
Manganese	Mn 55	6.79	200.00	3.4				ND		
Cobalt	Co 59	9.17						4.72		
Nickel	Ni 60	104.44	100.00	104.4	110.0	94.9	70,000	31.82	130.00	**24.48**
Zinc	Zn 64	41.50						26.48		
Copper	Cu 65	8.63	1300.00 *	0.7				6.49		
Arsenic	**As 75**	0.97	**50.00**	1.9	**27.0**	**3.6**	**5000**	**4.36**	**66.00**	**6.61**
Selenium	**Se 82**	25.46	**50.00**	50.9	**11.0**	**231.5**	**1000**	**144.93**	**152.00**	95.35
Rubidium	Rb 85	824.92						3954.18		
Cadmium	**Cd 114**	2.30	**5.00**	46.0	**1.9**	**121.1**	**1000**	**0.28**	**28.80**	0.97
Cesium	Cs 133	37.63						393.99		
Barium	Ba 138	4108.91	2000.00	205.4	1350.0	304.4	100,000	830.38	1040.00	79.84
Lead	**Pb 208**	**17.24**	**15.00** *	**114.9**	**9.0**	**191.5**	**5000**	**111.04**	**349.00**	**31.82**
Dilution factor			* = Action level							
pH (final)								11.79		
BLANK used								Blank-3b		

(NC)# = Detection not confirmed (Severe Spectral Overlap Noted); ND = Not Detected.

Table 4
TCLP on SET cement

Concentration units: ppb		Set Cem.-1 TXI(TX)-1	Subtract:	Set Cem.-1 TXI(TX)-2	Subtract:	Set Cem.-1 Holnam(MO)-1	Subtract
Element	Isotope	Set 1	Set-raw	Set 1	Set-raw	Set 1	Set-raw
Beryllium	**Be 9**	**11.9**		**6.4**		**4.3**	
Aluminium	Al 27	339.1	NA	227.7	NA	262.7	NA
Titanium	Ti 49	0.6	−5.8	0.4	−5.7	1.2	−0.6
Vanadium	V 51	ND	NA	ND	NA	ND	NA
Chromium	**Cr 52**	**62.6**	**−267.4**	**44.8**	**−225.2**	**15.3**	**−92.1**
Manganese	Mn 55	1.1	NA	0.4	NA	0.2	NA
Cobalt	Co 59	17.7	11.1	19.4	14.0	4.2	1.6
Nickel	Ni 60	34.0	9.9	34.2	14.3	29.9	17.1
Zinc	Zn 64	79.2	76.4	39.4	38.9	29.7	7.0
Copper	Cu 65	9.8	7.2	8.6	6.4	5.5	4.0
Arsenic	**As 75**	**0.1**	**0.1**	**0.1**	**NA**	**0.2**	**NA**
Selenium	**Se 82**	ND	**NA**	**1.1**	**0.0**	ND	**NA**
Rubidium	Rb 85	221.5	95.2	274.7	145.2	434.0	245.2
Cadmium	**Cd 114**	**0.2**	**−1.3**	**0.3**	**−2.0**	**ND**	**NA**
Cesium	Cs 133	7.6	1.5	9.4	2.8	14.7	5.3
Barium	Ba 138	1982.1	1497.2	1898.8	1471.9	2102.9	1516.0
Lead	**Pb 208**	**0.2**	**NA**	**ND**	**NA**	**1.1**	**−2.0**
	Dilution Factor	3.0525		3.0525		3.0525	
	pH	12.12		12.13		12.13	

Table 4 (continued)

Concentration Units: ppb		Set Cem. −1 Holnam (SC)-2	Subtract	Set Cem. −1 Holnam (SC)-1	Subtract	Set Cem. −1 Giant (SC)-1	Subtract	Set Cem. −1 Giant (SC)-2	Subtract
Beryllium	**Be 9**	**5.1**		**2.1**		**4.7**		**2.3**	
Aluminium	Al 27	658.1	NA	304.7	NA	365.1	NA	333.7	NA
Titanium	Ti 49	1.3	−0.4	1.8	−2.7	0.7	−4.3	2.0	−0.3
Vanadium	V 51	ND	NA	ND	NA	ND	NA	0.4	NA
Chromium	**Cr 52**	**11.9**	**−54.7**	**25.3**	**−112.7**	**27.1**	**−237.8**	**27.2**	**−208.2**
Manganese	Mn 55	0.1	−6.7	ND	NA	0.2	−3.9	0.2	NA
Cobalt	Co 59	5.9	1.8	6.2	−0.7	6.4	−1.7	7.5	1.4
Nickel	Ni 60	48.5	−8.8	50.8	−53.4	42.1	−62.3	38.1	−26.1
Zinc	Zn 64	33.7	17.2	28.8	8.8	69.2	45.3	21.7	8.4
Copper	Cu 65	12.3	4.1	5.6	−1.6	6.9	−1.7	13.5	8.2
Arsenic	**As 75**	**0.2**	**−0.7**	**0.1**	**NA**	**ND**	**NA**	**0.1**	**NA**
Selenium	**Se 82**	**ND**	**NA**	**ND**	**NA**	**ND**	**NA**	**ND**	**NA**
Rubidium	Rb 85	63.6	31.7	45.0	15.9	284.2	62.8	521.8	175.1
Cadmium	**Cd 114**	**ND**	**NA**	**ND**	**NA**	**ND**	**NA**	**ND**	**NA**
Cesium	Cs 133	0.9	0.3	0.4	0.2	5.0	0.7	14.1	2.2
Barium	Ba 138	1710.9	1127.6	1752.3	1097.4	3475.3	2560.0	3487.1	2751.8
Lead	**Pb 208**	**ND**	**NA**	**ND**	**NA**	**0.4**	**−1.2**	**1.4**	**NA**
	Dilution Factor	3.0525		3.0525		3.0525		3.0525	
	pH	12.12		12.14		12.14		12.14	

Baker) were added to 45 ml of the TCLP extract. These microwave-digested solutions were transferred to DIW-rinsed, virgin 125 ml polyethylene bottles (Nalge, Rochester, NY). These stored solutions then were diluted further with DIW before analysis; dilution factors for each extract are given in the analytical tables. Two standard TCLP samples and two of the chlorinated-water TCLP samples (100 ppm) underwent method 3015 acid digestion at QC, Inc., (Southampton, PA). Samples processed in this way are indicated in Tables 2 and 3 by an asterisk after the analytical sample designation.

6.5.2. Analysis by ICP-MS

Acid-digested extracts were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) using standard methods similar to a modified EPA method 200.8. The Fisons Plasmaquad ICP-MS instrument is housed and operated in the Environmental and Occupational Health Sciences Institute (EOHSI) of Rutgers University. Twenty-nine isotopes of 24 metals were analyzed; seventeen of these are listed in the analytical tables (Tables 6 and 7). Application of the ICP-MS method to TCLP analyses was discussed in considerable detail by Goergen et al. [38]. Calibration standards were prepared by appropriate dilutions of a 1000 mg/l (= parts per million, ppm) multi-element standard solution. Standard-solution concentrations were diluted quantitatively to 1, 3, 5, 7, 10, and 15 ppb (parts per billion). In addition to sample blanks, which correct analyses of extract solutions for any extraneous metal contributions to the leachate solutions, standard blanks also were prepared with each set of calibrant standards to ensure that any potential matrix interferences or contamination from standard preparation could be identified. Standards, blanks, and extracts for each analytical suite carried identical concentrations of nitric acid (10% or 4%) to minimize potential matrix effects. Diluted solutions were analyzed directly, no spike-procedure evaluation of recovery was performed. Observations of high signal/noise (S/N) ratios on the lowest-concentration standards indicate that quantitation of ≤ 1 ppb should be achievable at the directly measured (raw) concentrations. Taking 1 ppb as a conservative estimate of the raw quantitation limit, this can be scaled to an estimated quantitation limit for each original sample extract by multiplying 1 ppb times the value of 'Dilution Factor' for that sample (Tables 2–4). These effective quantitation limits of ~ 1.1 and ~ 3 ppb should be extremely conservative and, nonetheless, are below concentrations that typically elicit health-based concerns.

ICP-MS analyses on the Fisons Plasmaquad were run in automated mode. Groups of standards were separated by no more than eight unknown samples to insure control on the instrumental drift with time. Each set of unknowns included a quality control (QC) sample of trace elements in water, standard reference material (SRM) 1643d from the National Institute of Standards and Technology (NIST, Gaithersburg, MD). Mass spectra of all analyzed solutions were inspected to evaluate any potential interferences.

6.6. Bulk-sample metal concentrations

6.6.1. Total (dissolution-independent) metals (XRF)

Analyses by XRF were obtained from a commercial laboratory (Activation Laboratories, ACTLABS, Wheat Ridge, CO) for the Tier-III metals As, Cr, and Pb (all at 5 ppm

detection limit), as well as for major elements and for the additional trace metals V, Mn, Co, Ni, and Zn. This technique provides measurements that are independent of any dissolution or digestion and which, thus, represent absolute *total* concentrations of the metals in the samples. These total concentrations by XRF serve as reference points for acid-soluble (method 3051) results and for concentrations leached by the TCLP and variations thereof.

All available cement and CKD samples were submitted to ACTLABS for XRF analyses. A necessary component of obtaining analyses externally is the inclusion of a SRM for quality control within the likely concentration ranges of interest. A coal fly ash SRM from NIST was used for this purpose (NIST-1633b: As 136 ppm, Cr 198 ppm, Pb 68 ppm). This SRM also was proven as a reliable indicator of analytical standard reproducibility in a complex leaching study that included some matrices similar to cement [27].

6.6.2. Acid-soluble metals (method 3051 digestion)

All available samples were subjected to microwave-assisted acid-soluble digestions to analyze 'total recoverable' metals (SW-846 method 3051) [3,5,18]. This procedure is comprised of dissolving up to 0.5 g of solid in 10 ml of concentrated nitric acid during 10 min of heating by microwave oven. All method-3051 acid dissolutions of solids were carried out at QC Laboratories (Southampton, PA); solutions were analyzed by ICP-MS techniques (as discussed above). The same quality control SRM included with the samples for XRF analysis (see above) also was digested by this acid-soluble procedure, to provide further comparison of absolute total and acid-soluble metal concentrations.

6.7. Comparison of metal concentrations derived by all methods

Each method implemented in this study extracted some portion of the total metal concentration in the system. XRF results should provide the closest measure of actual total metal concentrations. To compare these various types of results, each solution-based concentration has been converted to a consistent framework of concentration (ppm) in the original solid mass.

7. Experimental results

In the tables of analytical results, rows of the primary (Tier-III) carcinogenic metals As, Be, Cd, Cr, and Pb, and in addition Se, are set off in boldface. All results presented here have been corrected for metals introduced during sample preparation by subtracting the relevant measured analytical blanks; these blank analyses also are reported in the analytical tables. Where multiple isotopes were analyzed (Cd, Pb, Se), the 'preferred' isotope (based on natural abundance, lack of interferences, and closest reproduction of SRM values) is listed. Analytical results of TCLP extractions (both standard and modified) are presented in Tables 3–7. Dissolution-independent, total-metal concentra-

Table 5
Multiple-exposure TCLP

Raw cement sample		Holnam(SC)-2			TXI(TX)-1		
		Leach #2	Subtract: Leach #2 − #1	Leached cumulative (μg)	Leached #2	Subtract: Leach 2# − #1	Leached Cumulative (μg)
Concentration units: ppb							
Element	Isotope						
Beryllium	**Be 9**	**6.7**	**NA**		**9.1**	**NA**	
Aluminium	Al 27	456.0	*NA*	841.121	257.4	*NA*	459.632
Titanium	Ti 49	3.6	1.9	9.787	1.3	−5.1	14.282
Vanadium	V 51	ND	NA	NA	ND	NA	NA
Chromium	**Cr 52**	**15.7**	**−51.0**	**150.991**	**111.3**	**−218.6**	**815.245**
Manganese	Mn 55	0.2	−6.5	12.897	0.4	NA	0.737
Cobalt	Co 59	5.1	1.1	16.944	10.5	3.8	31.139
Nickel	Ni 60	44.7	−12.7	187.313	44.5	20.4	124.587
Zinc	Zn 64	98.7	82.2	212.303	120.9	118.1	221.188
Copper	Cu 65	6.5	−1.7	26.948	6.3	3.7	16.183
Arsenic	**As 75**	**0.4**	**−0.6**	**2.346**	**0.5**	**0.4**	**0.992**
Selenium	**Se 82**	**ND**	**NA**	**2.305**	**ND**	**NA**	**1.160**
Rubidium	Rb 85	53.2	21.4	156.504	53.6	−72.7	331.775
Cadmium	**Cd 114**	**0.1**	**0.0**	**0.301**	**0.3**	**−1.3**	**3.546**
Cesium	Cs 133	0.9	0.3	2.565	2.1	−4.0	14.981
Barium	Ba 138	3535.2	2951.9	7588.448	3222.2	2737.3	6659.753
Lead	**Pb 208**	**ND**	**NA**	**NA**	**ND**	**NA**	**NA**
Dilution Factor		3.0525			3.0525		
Sample BLANK (Table 2)		Blank-3a			Blank-3a		
pH (final)		12.12			12.08		

Raw cement sample		TXI(TX)-2			Holnam(MO)-1		
Beryllium	**Be 9**	**7.9**	**NA**		**6.3**	**NA**	
Aluminium	Al 27	257.8	NA	452.528	251.7	NA	470.003
Titanium	Ti 49	1.0	−5.1	13.254	0.4	−1.4	3.985
Vanadium	V 51	ND	NA	NA	ND	NA	NA
Chromium	**Cr 52**	**59.8**	**−210.2**	**611.371**	**14.6**	**−92.9**	**221.302**
Manganese	Mn 55	0.1	NA	0.200	0.2	*NA*	0.299
Cobalt	Co 59	9.9	4.5	27.735	5.2	2.6	14.430
Nickel	Ni 60	59.8	39.9	142.194	53.1	40.4	122.091
Zinc	Zn 64	117.7	117.1	207.634	80.7	58.0	191.647
Copper	Cu 65	77.7	75.4	140.628	7.3	5.8	16.484
Arsenic	**As 75**	**0.1**	**NA**	**0.145**	**0.1**	**NA**	**0.184**
Selenium	**Se 82**	**0.2**	**−0.9**	**2.505**	**ND**	**NA**	**0.888**
Rubidium	Rb 85	62.0	−67.6	351.769	160.3	−28.4	640.347
Cadmium	**Cd 114**	**0.3**	**−2.0**	**4.830**	**0.1**	**−0.1**	**0.423**
Cesium	Cs 133	2.6	−4.0	16.820	6.9	−2.5	29.719
Barium	Ba 138	3251.8	2824.8	6509.221	3562.9	2976.0	7712.205
Lead	**Pb 208**	**0.4**	**NA**	**0.650**	**1.3**	**−1.9**	**8.078**
Dilution Factor		3.0525			3.0525		
Sample BLANK (Table 2) (Table 2)		Blank-3a			Blank-3a		
pH (final)		12.07			12.09		

NA = Not Applicable.

tions from XRF are presented in Table 8. Acid-soluble metals by method 3051 are listed in Table 9.

One interference was identified, a low mass 'tail' from a large peak at mass = 10 + 11, apparently from boron; this produced spurious values for Be. No other interferences were identified in any of the analyzed mass spectra. In no case was detection of beryllium confirmed; these peak edges showed no evidence of any shoulder that would represent actual Be. Thus, although Be values from individual analyses are presented in the analytical tables, discussion and comparison of metal concentrations will exclude Be. Although Be concentrations likely are very low, quantification of Be levels apparently will require an alternative analytical technique or a pre-analytical chemical separation.

7.1. Standard TCLP

7.1.1. Raw cement and CKD

The pH measurements of these leachates are of particular relevance to a discussion of standard TCLP applicability. Initial leachant pH values ranged from 2.82 to 2.93, corresponding closely to the range intended for the method (2.88 ± 0.05). However, for all 16 cement samples, the final pH of the standard-TCLP leachate exceeded 12 (12.22–12.69). The one CKD-sample leachate developed a pH of 11.79.

Analytical results from leaching of raw cement powder by the standard TCLP method are summarized in Table 3, where the maximum value for each metal is compared to pre-existing benchmarks, the National Primary Drinking-Water Standards (NPDWS) [32] and the average TCLP value for cement from the PCA [4] study. TCLP concentrations in CKD are compared to mean values from the PCA study in Table 3.

7.1.2. Set cement

Analytical results from TCLP extracts of set (hydrated) cement (variation #1) are compared in Table 4 to results from standard-TCLP extracts of the corresponding raw cements.

7.2. Multiple exposure TCLP

Analytical results of the repeated-exposure tests (variation #2) are compared in Table 5 to results from standard TCLP extracts of the same raw cements.

7.3. Chlorinated water TCLP

Analytical results of the chlorinated-water leach tests (variation #3) are presented in Table 6 and compared to standard-TCLP results.

7.4. Extended exposure time TCLP

Analytical results of the extended-time leach tests (variation #4) are presented in Table 7 and compared to standard-TCLP results.

Table 6
Chlorinated-water TCLP results

Element	Isotope	Blank-5	TXI(TX)@4 Cl		Holnam(MO)-1@4 Cl		Blank-6	TXI(TX)-2@100 Cl		Holnam(MO)-1@100 Cl	
		(4 ppm Cl)	4 ppm Cl	Subtract: (4 ppm Cl)-Std	4 ppm Cl	Subtract: (4 ppm Cl)-Std	100 ppm Cl	100 ppm Cl	Subtract: (100 ppm Cl)-Std	100 ppm Cl	Subtract: (100 ppm Cl)-Std
Beryllium	**Be 9**	**ND**	**ND**		**ND**		**ND**	**ND**		**ND**	
Aluminium	Al 27	96.92	ND	NA	ND	NA	248.87	ND	NA	ND	NA
Titanium	Ti 49	0.11	244.02	237.89	208.60	206.81	14.09	97.27	91.14	86.02	84.23
Vanadium	V 51	ND	3.91	3.91	0.94	0.94	6.67	2.49	NA	2.26	2.26
Chromium	**Cr 52**	**ND**	**706.33**	**436.34**	**337.88**	**230.43**	**5.55**	**517.38**	**247.39**	**82.63**	**−24.82**
Manganese	Mn 55	ND	0.49	0.49	ND	NA	6.48	ND	NA	ND	NA
Cobalt	Co 59	ND	4.20	−1.28	1.13	−1.46	3.32	2.94	−2.54	2.27	−0.32
Nickel	Ni 60	ND	38.02	18.16	34.26	21.53	5.26	5.89	−13.97	24.60	11.88
Zinc	Zn 64	ND	17.54	17.00	12.08	−10.64	9.47	16.49	15.95	46.34	23.62
Copper	Cu 65	ND	0.83	−1.46	0.53	−1.01	18.63	ND	−2.29	32.08	30.55
Arsenic	As 75	ND	ND	NA	ND	NA	2.44	0.35	0.35	0.11	0.11
Selenium	**Se 82**	**2.38**	**3.90**	**2.76**	**1.56**	**1.08**	**4.74**	**3.47**	**2.33**	**4.32**	**3.85**
Rubidium	Rb 85	ND	456.21	326.65	643.86	455.07	0.88	353.05	223.49	584.78	395.99
Cadmium	**Cd 114**	**ND**	**0.53**	**−1.77**	**ND**	**−0.16**	**2.26**	**0.63**	**−1.67**	**3.36**	**3.20**
Cesium	Cs 133	ND	11.51	4.96	16.61	7.25	3.95	10.82	4.27	15.99	6.62
Barium	Ba 138	0.78	742.82	315.87	996.64	409.67	1.93	817.66	390.71	1368.56	781.59
Lead	**Pb 208**	**ND**	**0.16**	**0.16**	**7.28**	**4.13**	**3.38**	**ND**	**NA**	**0.41**	**−2.74**
pH (final)			12.42		12.44			12.41		12.47	
Blank Used:			Blank-5		Blank-5			Blank-6		Blank-6	

NA = Not Applicable.

Table 7
Extended-time (1 week) TCLP

Cement sample		Std TCLP	TXI(TX)-1 1-Week TCLP	Subtract: 1 wk-Std	Std TCLP	Holnam(MO)-1 1-Week TCLP	Subtract: 1 wk-Std
Element	Isotope						
Beryllium	**Be 9**	#**ND**	#**ND**	−	#**ND**	#**ND**	−
Aluminium	Al 27	Overrange	381.44	−	Overrange	316.76	−
Titanium	Ti 49	6.42	414.44	408.01	1.79	438.53	436.74
Vanadium	V 51	ND	ND	−	ND	ND	−
Chromium	**Cr 52**	**329.92**	**55.79**	**−274.13**	**107.45**	**16.01**	**−91.44**
Manganese	Mn 55	ND	2.10	>	ND	2.72	>
Cobalt	Co 59	6.64	62.21	55.57	2.60	9.14	6.54
Nickel	Ni 60	24.14	72.60	48.46	12.73	100.49	87.76
Zinc	Zn 64	2.81	23.01	20.20	22.72	30.04	7.32
Copper	Cu 65	2.63	9.64	7.01	1.54	4.84	3.30
Arsenic	**As 75**	**0.06**	**ND**	−	**ND**	**ND**	−
Selenium	Se 82	0.65	6.97	6.33	0.48	5.31	4.84
Rubidium	Rb 85	126.30	438.77	312.47	188.79	146.70	−42.09
Cadmium	**Cd 114**	**1.59**	**ND**	−	**0.16**	**ND**	−
cesium	Cs 133	6.06	9.04	2.98	9.37	0.08	−9.29
Barium	Ba 138	484.89	2763.74	2278.85	586.97	1812.18	1225.21
Lead	**Pb 208**	**ND**	**0.57**	>	**3.15**	**0.13**	**−3.02**
Final pH		12.33	12.22		12.27	12.26	

#ND = Not Detected; Spectral Overlap.
> = Not detected in std TCLP, det. in 1-week.

7.5. Bulk-sample metal concentrations

7.5.1. Total (dissolution-independent) metals (XRF)

Analytical results of the dissolution-independent, total metal concentrations by XRF are presented in Table 8, in which comparison also is made of the analyzed and certified values for the quality-control SRM included with the group of XRF samples. The accuracy of these analyses is demonstrated by the close correspondence of these analyzed values to the SRM-certified concentrations. In this table, metals analyzed as trace elements in solution for the other methods, but which were reported in the XRF analyses as major-element oxides, also are repeated in the lower, trace-element section of the table. All XRF values for both major and trace elements, excluding manganese, fall within 10% of the certified values. This SRM comparison provides strong confidence in the accuracy of these XRF results.

7.5.2. Acid-soluble metals (method 3051 digestion)

Analytical results from the acid-soluble, 'total recoverable' metals technique (SW-846 3051) are presented in Table 9. As discussed below (Section 7.6.), these results are scaled to values of ppm concentrations of metals in the original solid. This scaling is accomplished by calculating the absolute mass (weight) of each metal dissolved by each method. This mass is used to calculate the concentration relative to the original mass of

the total solid. A measure is provided of the extent to which this SW-846 3051 method recovered metals from the matrix of SRM NIST-1633b by comparison to XRF values in Table 10.

Table 8
XRF data

Sample #:	Giant (SC)-1	Holnam (SC)-1	Giant (SC)-2	Holnam (SC)-2	TXI (TX)-1	TXI (TX)-2	NTXC (TX)-1
Oxide (Wt%)							
SiO_2	20.89	21.26	20.46	20.48	20.13	20.06	21.28
Al_2O_3	5.72	5.46	5.47	4.5	4.45	4.72	5.1
Fe_2O_3	2.89	2.6	2.61	3.34	3.78	4.24	3.12
MnO	0.01	0.02	0.01	0.02	0.23	0.17	0.3
MgO	1.11	1.06	1.05	1.28	1.03	0.98	0.89
CaO	68.22	66.4	68.6	67.87	67.35	65.6	67.84
Na_2O	0.17	0.16	0.16	0.13	0.28	0.27	0.14
K_2O	0.32	0.3	0.47	0.16	0.32	0.36	0.47
TiO_2	0.3	0.37	0.3	0.23	0.24	0.24	0.21
P_2O_5	0.14	0.14	0.15	0.14	0.15	0.16	0.19
LOI	< 0.01	1.32	< 0.01	0.41	0.54	0.74	0.22
TOTAL Wt.%	98.37	99.09	98.57	98.54	98.51	97.55	99.75
Element (ppm)							
Al	30273.1	28897.1	28950.0	23816.3	23551.7	24980.6	26991.8
Ti	1798.2	2217.8	1798.2	1378.6	1438.6	1438.6	1258.8
V	136.0	112.0	167.0	114.0	108.0	103.0	112.0
Cr	**87.0**	**112.0**	**118.0**	**143.0**	**315.0**	**176.0**	**63.0**
Mn	77.4	154.9	77.4	154.9	1781.3	1316.6	2323.4
Co	17.0	12.0	17.0	9.0	8.0	8.0	15.0
Ni	52.0	41.0	55.0	49.0	49.0	55.0	55.0
Cu	47.0	36.0	86.0	29.0	84.0	83.0	21.0
Zn	71.0	39.0	135.0	24.0	294.0	332.0	58.0
As	**29.0**	**9.0**	**24.0**	**13.0**	**10.0**	**10.0**	**10.0**
Pb	**< 5.0**	**< 5.0**	**< 5.0**	**< 5.0**	**< 5.0**	**< 5.0**	**< 5.0**

Sample #:	LSI (IN)-1	Lafarge (MI)-1	Holnam (MO)-1	CCC (MO)-1	Keystone (PA)-1	DC TN-1	RCC (MO)-1
Oxide (Wt%)							
SiO_2	20.86	20.77	20.62	21.16	19.49	20.81	20.59
Al_2O_3	4.35	4.69	4.74	5.11	5.87	5.13	4.96
Fe_2O_3	2.36	2.93	2.34	1.56	2.43	3.16	3.74
MnO	0.05	0.06	0.06	0.11	0.1	0.15	0.29
MgO	1.08	2.15	3.32	3.05	2.92	1.12	2.26
CaO	67.96	65.87	66.75	66.03	64.75	67.71	65.2
Na_2O	0.13	0.18	0.16	0.13	0.41	0.15	0.11
K_2O	0.4	0.61	0.56	0.1	0.64	0.74	0.61
TiO_2	0.21	0.21	0.27.	0.35	0.26	0.34	0.18
P_2O_5	0.07	0.07	0.17	0.06	0.23	0.22	0.17
LOI	1.23	0.68	< 0.01	0.5	1.07	0.09	0.81
TOTAL Wt.%	98.69	98.22	98.33	98.16	98.17	99.63	98.92

Table 8 (continued)

Sample #:	LSI (IN)-1	Lafarge (MI)-1	Holnam (MO)-1	CCC (MO)-1	Keystone (PA)-1	DC TN-1	RCC (MO)-1
Element (ppm)							
Al	23 022.4	24 821.9	25 086.5	27 044.7	31 067.0	27 150.6	26 250.8
Ti	1258.8	1258.8	1618.4	2097.9	1558.5	2038.0	1078.9
V	64.0	99.0	95.0	44.0	50.0	49.0	149.0
Cr	**92.0**	**58.0**	**88.0**	**153.0**	**95.0**	**85.0**	**230.0**
Mn	387.2	464.7	464.7	851.9	774.5	1161.7	2245.9
Co	7.0	12.0	10.0	12.0	7.0	12.0	7.0
Ni	39.0	41.0	47.0	44.0	29.0	29.0	91.0
Cu	8.0	22.0	55.0	51.0	58.0	36.0	198.0
Zn	93.0	64.0	239.0	54.0	98.0	296.0	2522.0
As	**< 5.0**	**< 5.0**	**5.0**	**< 5.0**	**< 5.0**	**10.0**	**12.0**
Pb	**< 5.0**	**< 5.0**	**39.0**	**< 5.0**	**< 5.0**	**16.0**	**140.0**

Sample #:	Giant (SC)-3	Holnam (SC)-3	CKD (SC)-1	RUCTRL-1 (SRM) Measured	NIST SRM 1633b: Reference[*]	% Recovery[*] SRM
Oxide (Wt%)						
SiO$_2$	21.27	20.19	15	49.81	49.244	101.15
Al$_2$O$_3$	5.49	4.72	5.57	27.5	28.436	96.71
Fe$_2$O$_3$	2.58	3.46	2.19	11.73	11.123	105.45
MnO	0.02	0.02	0.02	0.02	*0.017*	116.02
MgO	1.07	1.21	0.82	0.87	0.799	108.85
CaO	68.67	68.56	43.63	2.27	2.113	107.44
Na$_2$O	0.17	0.15	0.36	0.28	0.271	103.34
K$_2$O	0.34	0.2	2.96	2.23	2.349	94.93
TiO$_2$	0.36	0.23	0.41	1.33	1.320	100.79
P$_2$O$_5$	0.14	0.14	0.14	0.5	0.408	122.49
LOI	< 0.01	0.9	27.34	3.41	–	–
TOTAL Wt.%	98.87	99.76	98.42	99.95	96.081	–
Element (ppm)						
Al	29 055.9	24 980.6	29 479.3	145 543.9	150 500.0	96.7
Ti	2157.9	1378.6	2457.6	7972.1	7910.0	100.8
V	125	111.0	134.0	289.0	295.7	97.7
Cr	**110.0**	**122.0**	**81.0**	**201.0**	**198.2**	101.4
Mn	154.9	154.9	154.9	154.9	*133.5*	116.0
Co	19.0	11.0	25.0	41.0	50.0	82.0
Ni	57.0	42.0	49.0	153.0	*122.0*	125.0
Cu	63.0	36.0	175.0	109.0	*112.8*	96.6
Zn	124.0	42.0	573.0	221.0	210.0	105.2
As	**19.0**	**10.0**	**46.0**	**150.0**	*138.8*	**108.1**
Pb	**< 5.0**	**< 5.0**	**525.0**	**63.0**	**68.2**	**92.4**

[*] Italics denotes inclusion of standard deviaton in reference value.
[*] Noncertified Values = underlined.
% Recovery[*] = (Measured[*] 100)/Reference.

Table 9
Acid-soluble results by EPA method 3051 (ppm in solid)

@Sample (@All cement except CKD(SC)-1)

Element	Isotope	Giant (SC)-1	Holnam(SC)-1	Giant(SC)-2	Holnam(SC)-2	TXI(TX)-1	TXI(TX)-2
Beryllium	**Be 9**	**1.205**	**0.859**	**0.935**	**0.890**	**0.864**	**1.032**
Aluminium	Al 27	2742.890	2580.652	2464.053	2678.113	2783.554	2760.251
Titanium	Ti 49	191.212	153.479	150.863	165.585	118.545	148.723
Vanadium	V 51	15.943	12.441	16.384	14.376	9.926	12.041
Chromium	**Cr 52**	**8.539**	**11.936**	**8.742**	**16.470**	**24.200**	**17.781**
Manganese	Mn 55	38.313	21.721	30.374	23.570	207.320	187.921
Cobalt	Co 59	1.879	1.422	1.734	1.496	1.133	1.385
Nickel	Ni 60	6.383	4.752	6.449	6.471	5.112	6.638
Zinc	Zn 64	8.819	5.160	13.877	4.060	23.945	33.822
Copper	Cu 65	6.619	4.798	10.553	4.371	9.209	11.219
Arsenic	**As 75**	**4.153**	**1.836**	**4.403**	**2.148**	**1.187**	**1.596**
Selenium	**Se 82**	**0.000**	**0.000**	**1.645**	**0.397**	**0.000**	**0.000**
Rubidium	Rb 85	1.442	0.404	2.025	0.464	0.943	1.388
Cadmium	**Cd 114**	**0.017**	**0.085**	**0.063**	**0.019**	**0.031**	**0.056**
Cesium	Cs 133	0.024	0.041	0.054	0.000	0.025	0.056
Barium	Ba 138	55.419	25.196	49.874	26.929	24.578	26.552
Lead	**Pb 208**	**0.856**	**0.208**	**1.669**	**0.248**	**0.456**	**0.582**

Element	Isotope	NTXC(TX)-1	LSI(IN)-1	Lafarge (MI)-1	Holnam (MO)-1	CCC (MO)-1	Keystone (PA)-1
Beryllium	**Be 9**	**1.054**	**1.160**	**1.262**	**0.678**	**0.753**	**0.966**
Aluminium	Al 27	2636.083	2440.732	2815.345	2076.671	2836.732	2865.963
Titanium	Ti 49	148.268	148.496	148.201	126.411	249.482	163.026
Vanadium	V 51	12.700	8.053	11.051	7.591	4.685	4.581
Chromium	**Cr 52**	**5.099**	**9.869**	**4.776**	**5.619**	**15.178**	**9.604**
Manganese	Mn 55	337.144	60.763	69.618	50.522	137.996	104.944
Cobalt	Co 59	1.817	0.975	1.256	0.788	1.390	1.006
Nickel	Ni 60	6.994	4.831	4.954	3.943	5.970	3.222
Zinc	Zn 64	7.470	11.471	7.780	17.493	7.852	10.835
Copper	Cu 65	2.909	1.381	3.509	5.803	7.181	7.816
Arsenic	**As 75**	**1.918**	**0.759**	**0.774**	**0.702**	**0.370**	**0.514**
Selenium	**Se 82**	**0.454**	**0.227**	**0.227**	**0.000**	**0.000**	**0.170**
Rubidium	Rb 85	2.146	1.648	2.605	1.484	0.160	2.946
Cadmium	**Cd 114**	**0.961**	**0.014**	**0.058**	**0.031**	**0.167**	**0.002**
Cesium	Cs 133	0.092	0.033	0.109	0.036	0.000	0.058
Barium	Ba 138	18.214	25.650	32.036	19.711	28.344	26.440
Lead	**Pb 208**	**0.129**	**0.242**	**0.516**	**3.808**	**0.349**	**0.681**

Element	Isotope	Dixie(TN)-1	RCC(MO)-1	Giant(SC)-3	Holnam(SC)-3	CKD(SC)-1
Beryllium	**Be 9**	**0.997**	**1.205**	**1.311**	**0.864**	**1.045**
Aluminium	Al 27	2740.090	2663.317	2962.433	2544.825	1741.812
Titanium	Ti 49	226.337	130.888	259.844	139.649	155.647
Vanadium	V 51	5.002	19.437	17.173	12.631	13.579
Chromium	**Cr 52**	**8.270**	**28.007**	**13.079**	**11.974**	**9.169**
Manganese	Mn 55	172.545	356.724	48.818	23.534	17.807
Cobalt	Co 59	1.528	1.035	2.310	1.441	2.010
Nickel	Ni 60	3.473	13.722	8.348	4.739	4.958

Table 9 (continued)

@Sample (@All cement except CKD(SC)-1)						
Element	Isotope	Dixie(TN)-1	RCC(MO)-1	Giant(SC)-3	Holnam(SC)-3	CKD(SC)-1
Zinc	Zn 64	30.010	280.280	15.935	5.464	62.127
Copper	Cu 65	5.168	31.893	9.575	4.729	30.214
Arsenic	**As 75**	**1.288**	**0.793**	**3.283**	**1.860**	**4.278**
Selenium	**Se 82**	**0.000**	**0.227**	**0.397**	**0.000**	**4.256**
Rubidium	Rb 85	3.050	2.038	1.209	0.344	22.951
Cadmium	**Cd 114**	**0.022**	**0.155**	**0.022**	**0.000**	**2.442**
Cesium	Cs 133	0.055	0.188	0.009	0.000	1.829
Barium	Ba 138	50.829	20.446	61.307	25.176	57.371
Lead	**Pb 208**	**3.822**	**23.181**	**0.777**	**0.200**	**76.749**

Element	Isotope	NIST-SRM-1633b Acid-Sol., 3051	Test SRM Certified/ Reported Values[*] NIST-SRM-1633b	%Recovery[#] of NIST SRM-1633b
Beryllium	**Be 9**	**1.493**		
Aluminium	Al 27	1351.107	1 505 000 000.000	0.00%
Titanium	Ti 49	58.603	79 100 000.000	0.00%
Vanadium	V 51	11.709	295.7	3.96%
Chromium	**Cr 52**	**4.489**	**198.2**	**2.26%**
Manganese	Mn 55	10.587	131.8	8.03%
Cobalt	Co 59	1.019	<u>50</u>	<u>2.04%</u>
Nickel	Ni 60	2.756	120.6	2.29%
Zinc	Zn 64	7.189	<u>210</u>	<u>3.42%</u>
Copper	Cu 65	4.237	112.8	3.76%
Arsenic	**As 75**	**18.255**	**136.2**	**13.40%**
Selenium	**Se 82**	**1.362**	**10.26**	**13.27%**
Rubidium	Rb 85	1.265	<u>140</u>	0.90%
Cadmium	**Cd 114**	**0.039**	**0.784**	**4.93%**
Cesium	Cs 133	0.105	<u>11</u>	0.95%
Barium	Ba 138	28.973	709	4.09%
Lead	**Pb 208**	**2.581**	**68.2**	**3.78%**
			MAX % Recovery:	**13.40%**

All values based on 0.3 g.
[*] Noncertified values = underlined.
% Recovery[#] = (Measured[*]100)/Reference.

7.6. Absolute metal released per unit mass of solid

Direct comparison of the absolute mass of each metal released, for each sample, is accomplished by scaling all results to common units. The mass of each metal released in each standard method (standard TCLP and acid-soluble 3051) has been re-scaled to a concentration (ppm) for that metal in the original solid. These values were used to calculate the ratio of each metal released by each process relative to the absolute metal content of the solid (by XRF). Results of this comparison are reported as ratios (TCLP/3051, 3051/XRF, and TCLP/XRF) in Table 10. Consistent with all previous

Table 10
Std. TCLP, acid–sol. dig., and XRF methods: Ratios for Tier III metals compared as ppm in original solid

Ratios Element	Isotope	Ratios: Giant(SC)-1 TCLP/3051	Ratios: Giant(SC)-1 3051/XRF	Ratios: Giant(SC)-1 TCLP/XRF	Ratios: Holnam(SC)-1 TCLP/3051	Ratios: Holnam(SC)-1 3051/XRF	Ratios: Holnam(SC)-1 TCLP/XRF	Ratios: NTXC(TX)-1 TCLP/3051	Ratios: NTXC(TX)-1 3051/XRF	Ratios: NTXC(TX)-1 TCLP/XRF
Chromium	**Cr 52**	0.561	0.098	5.51E-02	0.210	0.107	2.24E-02	0.177	0.081	1.43E-02
Arsenic	**As 75**	0.004	0.143	6.05E-04	0.000	0.204	0.00E+00	0.000	0.192	0.00E+00
Cadmium	**Cd 114**	0.173	–	–	0.024	–	–	0.000	–	–
Lead	**Pb 208**	0.035	0.171	5.92E−03	0.000	0.042	0.00E+00	0.000	0.026	0.00E+00
Max Tier III			0.171			0.204			0.192	

Element	Isotope	Ratios: Giant(SC)-2 TCLP/3051	Ratios: Giant(SC)-2 3051/XRF	Ratios: Giant(SC)-2 TCLP/XRF	Ratios: Holnam(SC)-2 TCLP/3051	Ratios: Holnam(SC)-2 3051/XRF	Ratios: Holnam(SC)-2 TCLP/XRF	Ratios: Lafarge(MI)-1 TCLP/3051	Ratios: Lafarge(MI)-1 3051/XRF	Ratios: Lafarge(MI)-1 TCLP/XRF
Chromium	**Cr 52**	0.486	0.074	3.60E-02	0.074	0.115	8.53E-03	0.144	0.082	1.19E-02
Arsenic	**As 75**	0.000	0.183	0.00E+00	0.008	0.165	1.29E-03	0.000	0.155	0.00E+00
Cadmium	**Cd 114**	0.027	–	–	0.086	–	–	0.020	–	–
Lead	**Pb 208**	0.000	0.334	0.00E+00	0.591	0.050	2.93E−02	0.000	0.103	0.00E+00
Max Tier III			0.334			0.165			0.155	

Element	Isotope	Ratios: TXI(TX)-1 TCLP/3051	Ratios: TXI(TX)-1 3051/XRF	Ratios: TXI(TX)-1 TCLP/XRF	Ratios: TXI(TX)-2 TCLP/3051	Ratios: TXI(TX)-2 3051/XRF	Ratios: TXI(TX)-2 TCLP/XRF	Ratios: Continental (MO)-1 TCLP/3051	Ratios: Cont.(MO)-1 3051/XRF	Ratios: Cont.(MO)-1 TCLP/XRF
Chromium	**Cr 52**	0.255	0.077	1.96E-02	0.285	0.101	2.88E-02	0.048	0.099	4.81E-03
Arsenic	**As 75**	0.000	0.119	1.16E-04	0.000	0.160	0.00E+00	0.000	0.074	0.00E+00
Cadmium	**Cd 114**	0.944	–	–	0.777	–	–	0.004	–	–
Lead	**Pb 208**	0.000	0.091	0.00E+00	0.000	0.116	0.00E+00	0.000	0.070	0.00E+00
Max Tier III			0.119			0.160			0.099	

Table 10 (continued)

Ratios Element	Isotope	Ratios: LSI(IN)-1 TCLP/3051	Ratios: LSI(IN)-1 3051/XRF	Ratios: LSI(IN)-1 TCLP/XRF	Ratios: Dixie(TN)-1 TCLP/3051	Ratios: Dixie(TN)-1 3051/XRF	Ratios: Dixie(TN)-1 TCLP/XRF	Ratios: River(MO)-1 TCLP/3051	Ratios: River(MO)-1 3051/XRF	Ratios: River(MO)-1 TCLP/XRF
Chromium	**Cr 52**	0.152	0.107	1.63E-02	0.031	0.097	3.01E-03	0.637	0.122	7.76E-00
Arsenic	**As 75**	0.000	0.152	0.00E+00	0.000	0.129	0.00E+03	0.000	0.066	0.00E+00
Cadmium	**Cd 114**	0.022	–	–	0.320	–	–	0.000	–	–
Lead	**Pb 208**	0.000	0.048	0.00E+00	0.020	0.239	4.73E-03	0.013	0.166	2.23E-03
Max Tier III			0.152			0.239			0.166	

		Ratios: Holnam(MO)-1 TCLP/3051	Ratios: Holnam(MO)-1 3051/XRF	Ratios: Holnam(MO)-1 TCLP/XRF	Ratios: Giant(SC)-3 TCLP/3051	Ratios: Giant(SC)-3 3051/XRF	Ratios: Giant(SC)-3 TCLP/XRF	Ratios: Holnam(SC)-3 TCLP/3051	Ratios: Holnam(SC)-3 3051/XRF	Ratios: Holnam(SC)-31 TCLP/XRF
Chromium	**Cr 52**	0.345	0.064	2.21E-02	0.018	0.119	2.14E-03	0.321	0.098	3.15E-02
Arsenic	**As 75**	0.000	0.140	0.00E+00	0.000	0.173	0.00E+00	0.005	0.186	8.57E-04
Cadmium	**Cd 114**	0.092	–	–	0.000	–	–	–	–	–
Lead	**Pb 208**	0.015	0.098	1.46E-03	0.003	0.155	4.18E-04	0.000	0.040	0.00E+00
Max Tier III			0.140			0.173			0.186	

		Ratios: Keystone(PA)-1 TCLP/3051	Ratios: Keystone(PA)-1 3051/XRF	Ratios: Keystone(PA)-1 TCLP/XRF	Ratios: CKD(SC)-1 TCLP/3051	Ratios: CKD(SC)-1 3051/XRF	Ratios: CKD(SC)-1 TCLP/XRF		Max 3051/XRF	Max-1 TCLP/XRF
Chromium	**Cr 52**	0.156	0.101	1.58E-02	0.429	0.113	4.85E-02		0.122	0.078
Arsenic	**As 75**	0.000	0.103	0.00E+00	0.018	0.093	1.71E-03		0.204	0.002
Cadmium	**Cd 114**	0.562	–	–	–	–	–		0.944	0.000
Lead	**Pb 208**	0.000	0.136	0.00E+00	0.026	0.146	3.81E-03		0.334	0.029
Max Tier III			0.136			0.146	Max Tier III (all)		0.334	0.078

reports, the TCLP method liberates much less metal than does the SW-846 3051 method.

8. Discussion

8.1. Standard TCLP

8.1.1. Raw cement and CKD

High-pH leachates were generated by both the standard TCLP technique and by all the evaluated variations on the TCLP. Implications of these results include failing to exceed the acid-buffering capacity of the cement [27], control of the final leachate pH by the alkaline solid, and a possible 'breakthrough point' in metal leachability once that buffering capacity has been exceeded [24,26]; arguments regarding these factors were introduced above (Section 2). The alkalinity of the cement and CKD systems thus clearly controlled the pH of the final leachate, an effect mentioned also by Mix and Murphy [24], Poon [26], and LaGrega et al. [20]. The generation of these high pH values in TCLP leachate solutions likely will limit the solubility of most metals [24,26]. Thus, given the arguments framed in Section 2, this result alone implies that standard-TCLP leachability for alkaline solids will not represent conditions achieved in nature, especially after any exposure of substantial duration. This implication also pertains to the TCLP variations evaluated herein.

Overall, concentrations of the Tier-III, carcinogenic metals from these standard-TCLP tests are well within the range, and fairly near the mean values, reported by the PCA [4]. Our highest analyzed values exceed the PCA mean in all but one of the four Tier-III metals considered, the exception being arsenic (Table 3). Although these maxima exceed mean PCA values, they remain far below the maxima reported by the PCA; they also clearly are well below the RCRA limits for TCLP. Among all toxic metals, the highest maximum concentration in our samples is for Ba, followed by Se, Pb, Cr, and Cd. Results indicate considerable leaching of Cr from most samples, but especially the samples from the River (Festus, MO), Giant (Harleyville, SC) and TXI (Midlothian, TX) plants. River Cement also produced the greatest lead concentrations in TCLP leachates.

Metals with maximum TCLP concentrations that exceed the NPDWS include Cr, Ni, Ba, and Pb. The highest Cd concentrations are nearly half the NPDWS value. The highest seven TCLP Cr levels, though six are below the average PCA value, exceed by over threefold the current Drinking-Water standard (Table 3). The highest TCLP-leachate lead concentration exceeds the drinking water action level. Although comparison to the Drinking-Water standard may not be entirely appropriate, these values nevertheless may indicate a cause for concern. Both in the TCLP and in experiments on leaching into water from the cement-mortar lining of drinking-water pipes [39], these cements clearly control the pH of the solution. Thus, these overall solution chemistries appear similar and this comparison of TCLP results to NPDWS levels *may be* appropriate.

A primary point in question here is whether the TCLP reproduces the environmental

conditions for exposed cement or landfilled CKD. Because contact waters in the natural environment will flow past and through any cement and CKD, (1) the exposure will not be static, (2) the contact time of any given volume of water, particularly at or near the surface, may not reach 18 h, so (3) the effective LS is likely to exceed 20:1. These aspects were incorporated into the arguments of Poon [26], who referred to a 'breakthrough point' where pH drops to levels at which solubilities of most metals will increase dramatically. This pH decrease can never be attained by the standard TCLP. Only repeated, multiple exposures to acidic solutions would permit the acid neutralizing capacity of these alkaline solids to be overcome at a 20:1 LS for each exposure. However, in second exposures of cement to a standard TCLP fluid, the final pH remained over 12, so even this second exposure made limited progress toward reaching the acid neutralizing capacity of cement; metals release was not enhanced. With the greater effective LS in natural systems, the breakthrough point eventually will be attained and, if any increase in metal solubility results, increased metal leaching likely will occur [26]. The TCLP, either the standard method or the variations investigated here, cannot assess the potential for this effect.

8.1.2. Set cement

In every case, no Tier-III metals leached more strongly from set cement (variation #1, Table 4). The hydrated cements leached less of most metals, especially Cr. The most notable exception is Ba. Other metals for which set-cement leachate concentrations exceed those for the standard method on raw cement, in all evaluated samples, are cobalt, zinc, gallium, and barium. The set cement (sized according to the TCLP method at ≤ 9.5 mm) remained at a particle size much coarser than the raw cement powder; this provided less exposed surface area for attack during the set-cement leaches. This factor may partially explain the lack of more vigorous leaching in set cement (Table 4). Nonetheless, these results do not indicate a strong tendency for increased leaching of most metals in set cement relative to raw cement.

The lack of additional release of Tier-III metals from set cement over raw cement may be influenced by three primary factors: (1) larger particle size of the leached set cement, (2) stronger bonding of the metals in the set cement, and (3) slowed kinetics of dissolution or decomposition. Results from the extended-duration leach test either are inconsistent with option #3 or may indicate re-precipitation of metals during the extended-time leach. Further tests are required to differentiate among these alternatives.

8.2. Multiple exposure TCLP

The only Tier-III metal to leach more strongly into repeated-exposure leachate, relative to a single application of standard-TCLP fluid, is arsenic (variation #2, Table 5). No other Tier-III metals demonstrate increased leachability during multiple exposures. Other metals for which second-exposure leachate concentrations exceed those for the standard method, in all evaluated samples, are cobalt, zinc, copper, gallium, and barium. In all cases but one, nickel also exceeds values from the standard method. Additional repeat exposures eventually may exceed the buffering capacity of these 100-g

masses of cement and produce lower-pH extracts, but the persistence of high pH (~ 12.1) in these second-exposure leachates indicates that effect did not occur. For the Tier-III metals (As, Cr, Cd, Pb), analyses of the repeated-exposure test also indicate the extraction of less metal in these second exposures than in the initial extraction. Nonetheless, measurable Cr was extracted during all second-exposure tests. Although lower than the first-exposure concentrations, these results also produce an increase in the *cumulative* amount of Cr released across the successive extractions (Table 5). These results do not indicate a strong tendency for increased leaching of most metals during a second exposure relative to the initial exposure to the standard-TCLP test.

8.3. Chlorinated-water TCLP

In three of these four extracts, leaching of Cr exceeds that from the standard TCLP (Table 6). Note that 4 ppm total chlorine corresponds to the maximum allowable residual disinfectant concentration in the NPDWS. Except for Cr, Tier-III metal concentrations in chlorinated-water (variation #3) leachates also are lower than standard-TCLP values. Other metals consistently leached more strongly by this variation are Ni, Ga, Rb, and Ba. All these three leachates that released more Cr than the standard TCLP also exceed by more than twofold the NPDWS concentration (100 ppb, Table 4, p. 5). One possible mechanism by which increased metal dissolution may occur is complexation of metals by chloride species, an effect that may lead to increased metal solubilities [30]. Ionic aqueous species that may participate include the hypochlorite ion (OCl^-) and hypochlorous acid (HOCl). The former is more likely to predominate in high-pH environments [40]. Yet another possible cause for increased metal dissolution from cement in chlorinated systems is the well known susceptibility of concrete to attack by some chloride systems [41]. Any increased disruption of bonds to these metals in the cement phases may enhance metal leaching.

This apparent increase in Cr leachability in moderately chlorinated systems may have wide-ranging implications for safety factors that include concentrations in drinking water and chromium release into the chlorinated water of a swimming pool. This effect appears worthy of considerably more detailed evaluation by an expanded experimental program.

8.4. Extended exposure time TCLP

Finally, in most cases extended-time leachates (variation #4, Table 7), except for lead in one sample, yield concentrations of all Tier-III metals at or below the standard-TCLP results. This effect, which is particularly pronounced for Cr, seems counter-intuitive. Perhaps the leachate is better able to maintain these metals in solution at the shorter leaching time of the standard test, and that over time those metals react from soluble forms to form precipitates. In contrast, other metals that demonstrate increased leaching at the longer duration are Ti, Co, Ni, Cu, Ga, Se, and Ba.

The most striking result here is the leaching of much *less* chromium than was achieved during the TCLP of standard duration. However, the TXI(TX)-1 leachate from

the one-week test yielded measurable Pb, whereas the standard TCLP leachate for this sample did not. In neither case did any other Tier-III metal leach at levels higher those from the standard TCLP leachate. The decreased concentrations of chromium at greater exposure times may indicate a tendency, over time, for the cations to precipitate from the alkaline solutions produced during this exposure. A similar phenomenon was ascribed by Anderson et al. [42] to metal loss resulting either from rising solution pH (presumably initiating precipitation) or from adsorption back onto solids. Thus, arresting the leaching procedure after twenty hours may limit the amount of metal that can precipitate from solution, whereas at the longer duration sufficient time may be available for the solids to coalesce.

8.5. Bulk-sample metal concentrations

8.5.1. Total-sample (dissolution-independent) metals (XRF)

Dissolution-independent, absolute total metal concentrations by XRF (Table 8) provide a benchmark against which acid-soluble results can be compared. The highest XRF concentrations of Tier-III metals in cement are in samples TXI(TX)-1 (Cr), Giant(SC)-1 (As), and RCC(MO)-1 (Pb) (Table 8).

8.5.2. Acid-soluble metals (method 3051 digestion)

The highest acid-soluble concentrations of Tier-III metals in cement are in samples RCC(MO)-1 (Cr, Pb), Giant(SC)-2 (As), and NTXC(TX)-1 (Cd) (Table 9). The CKD(SC) sample yielded only 77 ppm acid-soluble Pb, a value that is rather low in comparison to PCA results (average 434, maximum 7390 ppm).

8.6. Absolute metal released per unit mass of solid

Consistent with all previous reports, the TCLP method liberates much less metal than either 3051 acid digestion or XRF total-element analyses. Although the 3051 method sometimes is referred to erroneously as providing 'total metals', results in Tables 7–9 demonstrate these 3051 results typically fall far short of the absolute total metals in the solid. Such misstatements [2,4] and erroneous comparisons to alternative methods of digestion [36] that are much more aggressive and complete, cannot be justified. Thus, comparison of SW-846 3051 metal concentrations [4] to aggressively digested estimates of total metals that demonstrated good reproduction of total-metal concentrations in reference material [36], as assembled in Exhibit 3–18 of the EPA Report to Congress [2], does not relate comparable quantities. Comparison of such nonequivalent methods should be discouraged strongly.

8.6.1. Correlations between TCLP and acid-soluble or XRF concentrations

Any attempt to predict TCLP concentrations requires an extrapolation from some other measurement, ideally from some measure of total-metal concentration. Any such

Table 11

Correlations of isotope results from TCLP vs. acid soluble (3051) and vs. XRF

TCLP vs. 3051		Correlation, Cement Only r TCLP vs. 3051	# Both Samples	t-test RATIO* T(data)/ T(Comp.) 95% Conf. that $|r| > 0$ if $|T| > \sim 1$	Confidence Level (%) that $|r| > 0$	LINEAR EQUATIONS For $y = mx + b$; y = TCLP (ppb), x = 3051 (ppm)	
Element	Isotope					Slope = m	Intercept = b
Beryllium	**Be 9**	**–**	(n)				
Aluminum	Al 27	**0.933**	6	1.864	99.34	0.927	− 2418.313
Titanium	Ti 49	**0.278**	32	0.777	87.71	1.078	− 89.559
Vanadium	V 51	**1.000**	4	–	–	0.798	− 9.158
Chromium	**Cr 52**	**0.728**	32	2.846	100.00	26.114	− 141.496
Manganese	Mn 55	**− 0.670**	10	− 1.107	96.60	− 0.012	4.519
Cobalt	Co 59	**0.521**	32	1.636	99.77	3.173	0.389
Nickel	Ni 60	**0.460**	30	1.338	98.94	7.408	− 4.697
Zinc	Zn 64	**− 0.000**	28	− 0.001	0.18	0.000	17.949
Copper	Cu 65	**0.077**	28	0.191	30.22	0.031	3.276
Arsenic	**As 75**	**0.792**	8	1.300	98.09	0.264	− 0.009
Selenium	Se 82	**0.112**	26	0.268	41.50	1.734	3.309
Rubidium	Rb 85	**0.736**	32	2.917	100.00	171.298	− 36.445
Cadmium	Cd 114	**− 0.162**	28	− 0.407	58.97	− 0.443	0.449
cesium	Cs 133	**0.892**	30	5.094	100.00	173.601	0.247
Barium	Ba 138	**0.640**	32	2.232	99.99	44.412	− 499.761
Lead	**Pb 208**	**0.886**	12	2.706	99.99	0.624	2.383
		Max r: **1.000**					

Table 11 (continued)

TCLP vs. XRF	Isotope	Correlation Cement Only r, TCLP vs. XRF	# Both Samples	t-test RATIO * T(data)/T(Comp.) 95% Conf. that $|r| > 0$ if $|T| > \sim 1$	Confidence Level (%) that $|r| > 0$	LINEAR EQUATIONS For $y = mx + b$; y = TCLP(ppb), x = XRF (ppm)	
						Slope = m	Intercept = b
Beryllium	**Be 9**	−	(n)				
Aluminum	Al 27	**0.956**	6	2.337	99.71	0.103	− 2664.721
Titanium	Ti 49	**0.027**	32	0.072	11.57	0.012	70.562
Vanadium	V 51	**1.000**	4	−	−	0.143	− 14.943
Chromium	**Cr 52**	**0.611**	32	2.072	99.98	2.185	− 96.059
Manganese	Mn 55	**− 0.632**	10	− 1.001	95.01	− 0.002	4.276
Cobalt	Co 59	**0.416**	32	1.227	98.21	0.257	1.928
Nickel	Ni 60	**0.427**	30	1.220	98.14	1.224	− 19.743
Copper	Cu 65	**0.067**	28	0.168	26.68	0.004	3.276
Arsenic	**As 75**	**0.673**	8	0.912	93.29	0.031	0.121
Lead	**Pb 208**	**0.873**	12	2.540	99.98	0.102	2.204
		Max r: **1.000**					

T-test calculated as $\{r * \mathrm{sqrt}(n-2)/\mathrm{sqrt}(1-r^2)\}$, compared to T-table values to derive confidence level.

T-Test RATIO * = ratio of T-test value from sample data to the comparative T-table value to provide 95% confidence that the correlation coefficient is > 0.

potential relationship can be evaluated for the current dataset by regressing TCLP concentrations relative to acid-soluble concentrations or relative to absolute metal concentrations by XRF. Parameters to evaluate these potential correlations are listed in Table 11. Elements that exhibit significant correlations of TCLP with SW-846 3051 results also show strong covariation of TCLP and XRF results. The significance that each correlation coefficient differs from zero is evaluated by the standard *t*-test for the correlation coefficient *r* at *n* degrees of freedom. The test statistic computed for this evaluation is $|t_0|$, where:

$$t_0 = \frac{r\sqrt{(n-2)}}{\sqrt{(1-r^2)}} \tag{1}$$

this calculated value is compared to the Student *t* distribution for $(n-2)$ degrees of freedom [43,44]. The confidence of this approach depends on the individual element. For our data, correlation coefficients between the TCLP and SW-846 concentrations evaluate as different from zero at a significance level $> 95\%$ for Al ($r = 0.93$), Cr ($r = 0.73$), Mn ($r = -0.67$), Co ($r = 0.52$), Ni ($r = 0.46$), Ga ($r = 0.57$), As ($r = 0.79$), Rb ($r = 0.74$), Cs ($r = 0.89$), Ba ($r = 0.64$), Tl ($r = -0.82$), and Pb ($r = 0.89$). These positive correlations include several metals for which XRF data were not obtained. These correlations for lead and are chromium illustrated in Figs. 1 and 2. Correlation
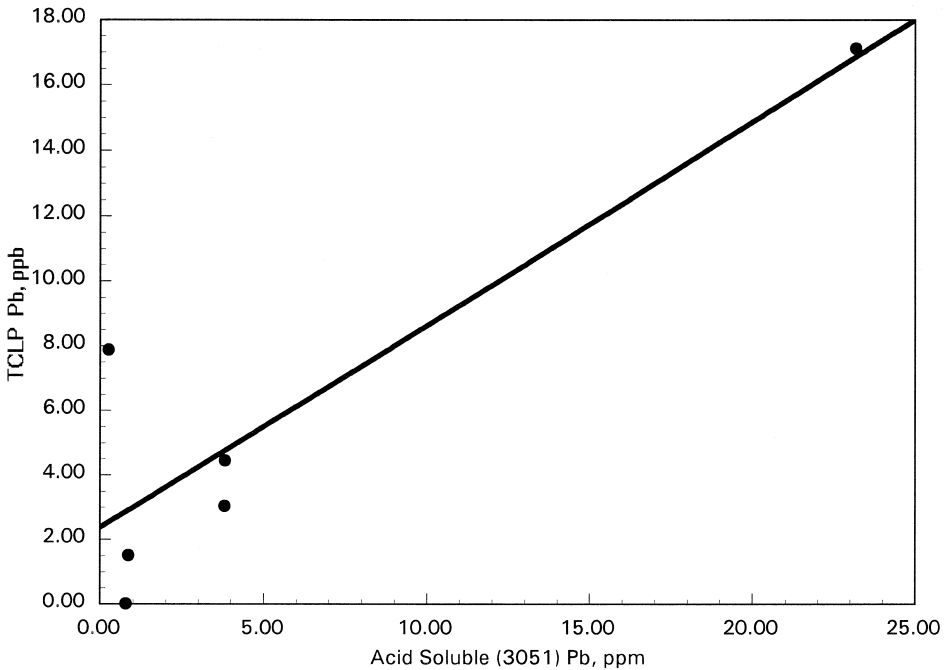
Fig. 1. Covariation of TCLP vs. 3051, Pb, cement samples only; $r = 0.886$.
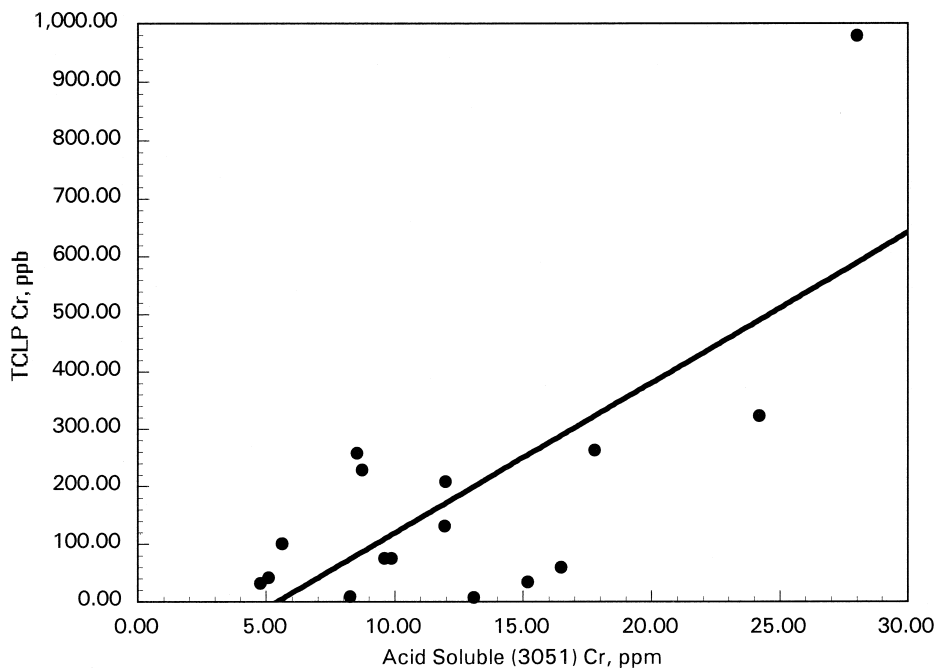
Fig. 2. Covariation of TCLP vs. 3051, Cr, cement samples only; $r = 0.728$.

coefficients between the TCLP and XRF values evaluate as different from zero at a significance level $> 95\%$ for Al ($r = 0.96$ XRF), Cr ($r = 0.61$), Mn ($r = -0.63$), Co ($r = 0.42$), Ni ($r = 0.43$), and Pb ($r = 0.87$), and $> 93\%$ for As ($r = 0.67$). For TCLP vs. XRF, only titanium, copper, and zinc fail in significance. The apparently significant correlations for Mn and Tl (SW-846 only) indicate *negative* covariation, a relationship for which a reliable explanation is not self evident.

The PCA study [4] claimed that (p. 8) ''in every case, there was no consistent relationship between the total [sic] metals concentration and the TCLP result for cement and CKD'' and that (p. 1) ''the tests showed no consistent correlation between the total [sic] concentration of a metal in CKD or cement and the amount of the metal brought into solution using the TCLP''; however, our re-analysis based on Eq. (1) yields a different conclusion. For cement, we derive levels of significance $> 99\%$ that $r \neq 0$ for Cr ($r = 0.68$, $n = 184$), and silver ($r = 0.26$, $n = 186$). In addition, As ($r = 0.18$, $n = 73$), Ba ($r = 0.10$, $n = 186$), Pb ($r = 0.11$, $n = 123$), and Hg ($r = 0.20$, $n = 53$) also give levels of significance over 75% (over 87, 82, 77, and 84%, respectively) that $r \neq 0$. Further, for TCLP vs. SW-846 acid soluble concentrations in CKD, we derive $> 95\%$ levels of significance that $r \neq 0$ for *every* correlation except Sb, As, Ba, Cd, and Ni; these Cd and Ni correlations still produce levels of significance $> 94\%$ and $> 93\%$, respectively. Thus, our significant dependence of TCLP and SW-846 acid soluble concentrations for most metals is fully consistent with the PCA data; their data evaluation apparently was incomplete.

8.7. Additional considerations

The metals gallium and barium exhibit a consistently increased tendency to leach under the conditions of every alternative TCLP modification applied here.

Although SW-846 acid-soluble procedures sometimes are mistakenly referred to as 'total' metals, our comparison of SW-836 3051 and XRF results shows this terminology to be in error. The maximum percentage of absolute total metal released by SW-846 3051 is 49.5% for manganese. This high level of SW-846 recovery for Mn may result from the wide variety of oxidation states available for this metal. The maximum percentage of absolute total metal released for a Tier-III metal is 33.4% for lead in one sample. Most fractions released by SW-846 3051, for these and other metals in most samples, are considerably lower. The SW-846 3051 method is *not intended as an aggressive, complete dissolution technique*, but rather as a *more* aggressive method than the TCLP for preliminary evaluation of RCRA status. Thus, *any consideration of SW-846 acid-soluble concentrations as representing total metals is inaccurate and should be avoided.*

9. Conclusions

Results presented here indicate substantial leaching of specific metals, especially Cr and Ba, from all samples of cement and CKD. This statement applies to extractions both by the standard TCLP and by the four variations applied here. The TCLP variation of chlorinated water, in three of four samples, leached Cr in greater concentrations than the standard TCLP; these three concentrations also exceed the National Primary Drinking Water Standard by more than twofold. The indication here of enhanced chromium leaching in a chlorinated-water system indicates that additional research on this relationship is worthy of pursuit.

Although TCLP leaching of some metals is considerable, the high pH of the final extracts demonstrates that the capacity of these samples to buffer the acidity of the leaching solutions has not been exceeded, even after two sequential exposures. Coupled with concerns about the metal-leaching ability of high pH solutions [24–27], this factor calls into question the likelihood that these high pH solutions may represent any 'real world' condition. These considerable concerns indicate that the TCLP is likely not a suitable procedure for characterizing the leaching behavior of alkaline systems such as cement and CKD.

The EPA SW-846 microwave-assisted acid-soluble procedure produces only partial recovery of any metal relative to dissolution-independent concentrations obtained by XRF spectrometry. The maximum percentage of absolute total metal released for a Tier-III metal is 33.4% for lead in one sample. SW-846 methods are not intended to provide a complete acid dissolution; any statement or implication that SW-846 acid-soluble concentrations represent total metals is inaccurate and should be avoided.

We disagree with previous statements that TCLP and SW-846 acid-soluble metal concentrations showed 'no consistent correlation' ([4], p. 1). Both current results and re-evaluation of the PCA data indicate correlations between TCLP and acid-soluble concentrations that are significantly different from zero for most metals. We present the

regression parameters for our correlations of TCLP vs. acid-soluble metal concentrations.

Appendix A. Procedures, TCLP (EPA Method 1311, SW-846)

(Parenthetical references cite the chapter of EPA SW-846 [3,5] or the section of method 1311 in which the procedure is described in full).

A.1. TCLP procedure (1311 sect. 7.2 [7.2.10] ff.)

Acid wash the extraction vessels by EPA SW-846 methods (Section 3)
Determine the appropriate extraction fluid (1311 sect. 7.1.4) if pH > 5.0, use
extraction fluid #2, pH = 2.88 ± 0.05
Prepare extraction fluids (1311 sect. 5.7)
Crush solids to < 9.5 mm if nec.
Maintain ambient temperature at 23 ± 2°C
Secure in rotary agitator, rotate at 30 ± 2 rpm for 18 ± 2 h.
Filter the extract
Acidify metal aliquots with nitric acid to pH < 2. If pptn obs., do not acidify remainder
Acid digest the extract (procedure 3051 [microwave] or 3050 [normal])
Analyze the extract (by appropriate procedure)

Analytical blanks were prepared by identical methodology to the TCLP extraction, except the rotation step was omitted.

A.2. Differences, EPTox procedure

Relative to the TCLP, the EPTox procedure uses a weaker acetic-acid solution (pH = 5), a lower liquid:solid ratio (LS, 16:1), longer contact time (24 h), and extractions are agitated in open containers rather than rotated in sealed containers.

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