

Safety of Cement — Leachability of Trace Toxic Elements

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Many elements such as mercury, lead, and chromium exist in portland cements at very low levels. As the cement hydrates, these elements potentially become leachable from the concrete products. Results from studies will be presented to show the concentrations of leachable elements and implications for health effects.

(This presentation summarized material out of the previously published work "Leachability of Selected Chemical Elements from Concrete", which was first published in the Proceedings of the Emerging Technologies Symposium on Cement and Concrete in the Global Environment, Portland Cement Association Publication #SP114T, 1993. The paper is reprinted here by permission and courtesy of the Portland Cement Association.)

Summary

Eight portland cement concretes were made from four cements and two aggregates, one siliceous and one calcareous. A concrete cylinder from each was crushed according to U.S. Environmental Protection Agency SW-846 protocol and tested by the Toxicity Characteristic Leaching Procedure (TCLP). In addition to eight elements specified in the Resource Conservation and Recovery Act – arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), selenium (Se), and silver (Ag) – the concentrations of four other metals were also determined: antimony (Sb), beryllium (Be), nickel (Ni), and thallium (Tl). Analysis for most metals was performed by graphite furnace atomic absorption spectrophotom-

etry to obtain the lowest possible detection limits consistent with sample compositions and analyte concentrations. Results indicate metal concentrations in leachate are all less than one-tenth RCRA regulatory limits, and many concentrations are below detection limits. Chromium TCLP cement values correlate with concrete leachate values while lead values do not.

A second series of leaching tests was performed with deionized water in place of acetic acid solution. These tests are called "water leaching by TCLP protocol" in this paper. Four of the concretes representing both aggregates and two of the cements were tested by this procedure. Analysis of the concrete extracts was performed for the same twelve metal analytes. Concentrations of metals in water leachate are generally similar to or lower than concentrations in acid leachate.

A third series of tests was performed on all eight concretes generally following ANSI/NSF 61 to simulate leaching with drinking-quality water as would occur in a municipal water supply system. Concentrations of As, Ba, Se, and Ag were nearly all below detection limits and well below NSF specification maxima. Concentrations of Cr, fluoride, and nitrate were all below NSF specification maxima. Despite precautions to work with high-purity reagents and ultra-clean vessels, control samples showed Hg and Pb levels indicating probable contamination from the vessels used for soaking the concrete cylinders. This work points out how difficult it is to perform these tests when reporting limits are required in the sub-parts-per-billion range.

Background

This report examines two issues concerning the leachability of trace metals from concrete: leachability of crushed concrete specimens with dilute acetic

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acid and water following the U.S. EPA Toxicity Characteristic Leaching Procedure, and leachability from whole concrete specimens with synthetic drinking water following ANSI/NSF 61 procedures. The purpose of this work is to determine if selected metallic elements are leached in significant quantities and to begin to understand the differences in results from leaching tests run on the same concretes according to different protocols. Issues include 1) whether leach tests on concrete batch components are additive and whether such tests can be used to predict the leachate composition of the hardened concrete; and 2) how does particle size affect leachate concentration.

Experimental

Cement

Four cements were chosen from among the nearly 100 cements submitted for analysis and reported in the Portland Cement Association publication *An Analysis of Selected Trace Metals in Cement and Kiln Dust* (PCA Publication SP110). These cements were chosen to represent a range of leachable metal concentrations, various cement manufacturing process types, and fuels used. Cements from participants 27, 61, 82, and 84 were selected and the data for total metals and TCLP metals were obtained from that report. Table 1 indicates the types of cements, manufacturing processes, raw materials, and fuels used to make these four cements. Tables 2 and 3 show the physical and chemical properties of the cements. Cement from participant 82 is an ASTM C 150 Type IA (air entraining) cement and the other three cements are either Type I or Type II. Cements 82 and 84 were made using supplemental waste fuels.

Total and TCLP trace metal concentrations for the cements are shown in Tables 4 and 5.

Figure 1 shows the concentrations of barium, chromium, and lead in acetic acid TCLP leachate from the four cements in comparison to the range and mean concentrations in all cements from the PCA study of U.S. and Canadian cements.

Aggregates

A mixed carbonate-siliceous sand from Elgin, Illinois was used for all eight concrete batches. Two kinds of coarse aggregate were selected from among materials frequently used at CTL: siliceous coarse aggregate from Eau Claire, Wisconsin (a 60/40 ratio of two size fractions — 19 mm to 13 mm and 10 mm to 5 mm [3/4-in to 1/2-in and 3/8-in to 3/16-in] and dolomitic coarse aggregate from Thornton, Illinois 19 mm topsize [3/4-in]). The coarse and fine aggregates have well-known service histories and have been used for many years in research projects sponsored by the Portland Cement Association. TCLP tests were carried

out on the sand and each aggregate fraction. The results of these TCLP tests are shown Table 6.

Concrete Mixes

Concrete mixes were designed to obtain roughly 30 Mpa (4500 psi) compressive strength with a water-cement ratio of 0.55. Coarse aggregate: sand ratio was 60:40 and the cement content was 335kg/m³ (564 lb/cu yd) for all concretes. Municipal (Skokie, Illinois) tap water was used without additional processing. Water content was kept constant in order to keep the weight percent cement in the concretes the same while the slump was allowed to vary. Concrete mix designs are shown in Table 7. Concretes made with Eau Claire aggregate were designated EC27, EC 61, EC 82, and EC 84 and those with Thornton dolomite were designated TD 27, TD61, TD 82, and TD 84 where the number indicated the participant number of the cements. For each batch of concrete, 0.02m³ (3/4 cu ft) of concrete was mixed in a pan mixer, the air-content was obtained, and eight 75 x 150 mm (3 x 6 in) cylinders were cast in polypropylene cylinder molds (DesLauriers, Bellwood, IL) without release agent. Cylinders were consolidated by rodding except TD27 which required vibration. Three cylinders of each mix were tested at 28 days for compressive strength. Slump, air content, unit weight, and 28-day compressive strengths shown in Table 8.

Concrete cylinders were cured at 23°C(73°F) in the polypropylene cylinder molds with low-density polyethylene snap-fit covers. Samples for TCLP (acid and water) were demolded at 60–70 days of age, immediately prior to crushing for the extraction tests. Samples for the ANSI/NSF 61 drinking water tests were used at 16 months of age.

Leaching Procedures

Sample Processing

Each cylinder was demolded and broken into chunks with a steel hammer. These chunks were passed through a jaw crusher (BICO-Braun, Burbank, California) with hardened steel jaws set to produce particles mostly less than 9.5 mm (3/8 in). The crushed samples were passed through a brass 9.5 mm sieve.

The question is often asked whether crushing and grinding contaminates samples with metals from the processing equipment such as jaw crushers, disc pulverizers, or swing mills. Data from a project using clinker give some insight into possible contamination in the processing. A sample of relatively dense portland cement clinker was passed three times through the steel-plate jaw crusher (BICO-Braun, Burbank, CA) then ground with a ceramic mortar and pestle to pass a 150 µm (no. 100 U.S. Standard) sieve. A con-

trol sample of clinker was processed by grinding with a ceramic mortar and pestle to the same fineness. Flame AAS analysis for nitric acid-soluble nickel and chromium indicated small increases due to the jaw crusher processing (71.9 vs. 75.8 mg/kg Cr and 15.1 vs 16.1 mg/kg Ni). For comparison, chrome alloy disk pulverizer plates (Model UA-2000, BICO-Braun, Burbank, CA) substantially increased chromium and nickel concentrations (71.9 vs. 166.3 mg/kg Cr and 15.1 vs 22.2 mg/kg Ni). Milling 30 seconds in a tungsten carbide swing mill (W. Bleuler, Zollikon; container Cat. no. 8504 from Spex Industries, Edison, New Jersey) did not contribute significant iron, nickel, or chromium, although cobalt increased (6.6 vs. 11.3 mg/kg). We are not aware of a practical processing method that would eliminate all metal contact and permit reduction of concrete cylinders to 9.5 mm (3/8-in) size.

TCLP (Acetic Acid)

EPA Method 1311 was followed. For each crushed concrete sample, 100 g was weighed into a 2 L polypropylene screw-cap jar and 2000g dilute acetic acid (pH 2.88±0.05) was added. The jars were capped and tumbled in a four-bottle rotary agitation apparatus (Analytical Testing and Consulting Services Model DC-20, Warrington, Pennsylvania) at 30 rpm for 18 hr at 23°C(73°F). Leachate was suction filtered thorough glass-fiber filters (Whatman GF/F) and transferred to polyethylene bottles. The pH of each solution was recorded. The filtered leachates were acidified to pH <2 with nitric acid.

TCLP (Water)

The procedure presented above was followed using ASTM D 1193 Type I water instead of dilute acetic acid.

Analysis

Samples were digested and analyzed according to EPA SW-846 methods by atomic absorption spectrophotometry. The methods followed procedures described in the PCA cement and kiln dust report (SP110).

Results of TCLP Tests

Estimates of Potential Metal Concentrations in Leachate

Two estimates of potential metals concentrations in leachate were obtained by using the cement TCLP result in one case (called the minimum estimate) and using the cement total metals result in the other case (called the maximum estimate). These results were combined with TCLP results from the aggregates. If

the TCLP results are additive, their sum should be a reasonable estimate of concentrations in the concrete leachate.

The minimum estimate was obtained after first calculating for each metal the contribution from the cement to the potential leachate concentration using the weight fraction of cement in the concrete (0.1397) times the cement TCLP value for each analyte. This value was then added to the weighted sum of contributions from sand (31.19% of FA TCLP) and from coarse aggregate (47.15% of CA TCLP) to give the minimum estimate. This value may be similar to actual leaching data if TCLP results are additive. As an example here is the calculation of the minimum estimate for barium in the TCLP extract concrete TD61:

$$(0.1397 \times 0.93) + (0.3119 \times 0.33) + (0.4715 \times 0.16) \\ = 0.130 + 0.103 + 0.075 = 0.31 \text{ mg/l}$$

The maximum estimate was obtained after first calculating for each metal the contribution from the cement to the potential leachate concentration using the weight fraction of cement in the concrete (0.1937) times the total metal in cement. This value was then added to the weighted sum of the contributions from sand (31.19% of FA TCLP) and from coarse aggregate (47.15% of CA TCLP) to give the maximum estimate. This value would occur if all of the metal analyte contained in the cement contributed to the concrete TCLP result. As an example here is the calculation of the maximum estimate for barium in the TCLP extract of concrete TD61:

$$(0.1397 \times 8.15) + (0.3119 \times 0.33) + (0.4715 \times 0.16) \\ = 0.139 + 0.103 + 0.075 \\ = 1.32 \text{ mg/L}$$

Leaching Results

The TCLP (acid) concrete data are shown in Table 9. The concentrations of 12 metals were determined in leachates from 8 concretes producing 96 individual measurements; fifty of those results are below detection limits. For the individual metals analyses of the concrete TCLP (acetic acid) extract, all results for arsenic, beryllium, and selenium are below detection limits and six of the eight concrete leachates for antimony, cadmium, and thallium are below detection limits. For the remaining six metals, the leachate concentrations are below detection limits for two of eight results for mercury and nickel; one of eight results is below detection limits for each of the rest of the metals. Normalized concentrations of these six metals in the eight concrete TCLP extracts are presented in Figure 2. The eight results that fall below detection limits are shown at the detection limits. Concentrations are normalized to the individual

RCRA limit for each metal and plotted on a logarithmic scale. The plot indicates all results are less than 1/10th the RCRA limits. Chromium and silver normalized concentrations (with one exception) are between 1/10th and 1/100th of their RCRA limits. Most of the normalized concentrations for barium, lead, mercury, and nickel fall between 1/100th and 1/1000th of their respective RCRA limits.

Comparison of TCLP (acid) and TCLP (water)

The TCLP water data are shown in Table 10 and a comparison of selected acid versus water results is shown in Table 11. In most instances the TCLP acid leaching result falls between the maximum and minimum estimate while the TCLP water leaching result falls near or below the minimum estimate. (See Figure 2a)

Relation Between Cement and Concrete

Approximately 15% of the crushed concrete is not recovered after filtering and drying the TCLP (acid) residue. This corresponds to the amount of cement in the concrete batches. The recovered solids consist of aggregate with little or no cement paste adhering. Whether the metals remain in solution or precipitate and become trapped in the filter residue determines the measured concentrations.

Much interest surrounds chromium and lead levels in leachates. Figure 3 indicates that TCLP chromium from the cements is correlated ($R=0.92$) with TCLP (acid) chromium from the concretes. Total chromium in the cements also correlates ($R=0.89$) with TCLP (acid chromium from the concretes (Figure 4). While leachable chromium from all eight concrete is less than one-tenth of the 5 mg/L RCRA limit, these correlations may be useful to cement producers monitoring potential leachable chromium.

No relationship appears to exist between lead levels in cement and TCLP concrete values (Figures 5 and 6).

Drinking Water Leaching

Eight 3 x 6-in concrete test cylinders were tested generally following procedures in ANSI/NSF 61-1991, "Drinking Water System Components-Health Effects." The purpose of these tests is to simulate exposure of drinking water to the interior surface of concrete pipe as the water is transported in a municipal water distribution system. These tests consist of conditioning the specimen followed by exposure to simulated drinking water containing buffering, hardness, and chlorinating agents.

Experimental

A dedicated room maintained at 23-24°C (74-76°F) was prepared by draping 0.15-mm (6-mil) polyethylene sheets to enclose a space roughly 2.5 x 3 x 2.5 m (8 x 10 x 8 ft) to minimize airborne contamination. Tacky mats (Liberty Industries) were placed immediately inside and outside the door of the room to trap particulates on workers feet. To assure sufficient supply of high-purity water, a water-polishing station (Barnstead Naopure, dual Ultrapure cartridges) fed from service deionizer cartridges was placed in the room.

Each concrete cylinder was brushed with a steel-bristle brush under cold tap water and rinsed with ASTM D 1193 Type II deionized water. Cylinders were handled throughout with latex surgical gloves. Each cylinder was placed in a 19 L (5-gal) FDA approved, white polyethylene bucket (Phillips Container Co.) which had been previously washed with soap, rinsed with tap water, washed with acid, washed with base, rinsed with tap water, and rinsed with Type II water.

Stock solutions of sodium bicarbonate (0.04 M), calcium chloride (0.04M), and sodium hypochlorite (1.5 mg/L residual total chlorine) were prepared using ACS reagent grade chemicals and Type I water. Conditioning water at pH 8 was made from the stock solutions using 260 mL 0.04 M NaHCO_3 , 260 mL 0.04 M CaCl_2 , 13.9 mL NaOCl , and Type I water to make 10.4 L. This volume gave a surface area to volume ratio of 43.7 cm^2/L based on a 910-mm (3-ft) diameter pipe.

Specimens were first exposed to conditioning water/disinfecting solution containing 50 mg/L available chlorine. Subsequent exposures contained 2 mg/L available chlorine. Specimens were immersed in the conditioning water for 12 days with a change of water every 24 hours, and for two additional days with no change of water. The conditioning water was decanted and specimens were immersed in pH 8 extraction water of the same concentration as the conditioning water, at 23-24°C (74-76°F) for 16 hr.

Extract water samples were decanted into pre-cleaned 125 mL (4 oz) amber glass bottles for mercury analysis and into 2 l (64 oz) polyethylene bottles for other analytes. Nitric acid (11mL, Baker Instra-Analyzed, 70%) was added to stabilize the solutions for metals analysis at pH <2. Five mL potassium dichromate/nitric acid solution (25 mL 70% HNO_3 plus 0.068 g $\text{K}_2\text{Cr}_2\text{O}_7$, diluted to 500 mL) was added to stabilize the solutions for mercury analysis. Samples were maintained at room temperature until analysis. A separate sample of each extraction water was taken for nitrate analysis to which no stabilizing agent was added. At CTL, samples were analyzed by graphite furnace atomic absorption spectrophotometry according to EPA SW-846 methods for As, Ba, Cd, Cr,

Pb, Se, and Ag. Mercury was analyzed by cold vapor AAS. Fluoride was determined by double standard additions using a selective ion electrode. Nitrate was determined using a colorimetric test kit (Hach NI-10). Sample volumes and instrumental settings were chosen to give reporting limits generally one-twentieth or less of the Drinking Water Standards.

Split samples also were analyzed according to EPA SW-846 methods at TEI Analytical, Niles, Illinois, using GFAAS for As, Pb, and Se; inductively coupled plasma spectrometry for Ag, Ba, and Cd; and Hg by cold vapor AAS. Fluoride was determined by ion chromatography according to ASTM D 4327. Reporting limits at TEI were generally equal to or better than one-tenth of the Drinking Water Standards.

Results and Discussion

To be listed as acceptable under the ANSI/NSF 61 protocol, drinking water system components must produce leachates with analyte concentrations less than one tenth the U.S. EPA National Primary Drinking Water Standards. Results of analyses from CTL and TEI laboratories are shown in Table 12. For comparison, the relevant drinking water standards are shown following the laboratory results.

Values for As, Cd, Se, and Ag are nearly all below reporting limits. Concrete extracts contained Ba and Cr at less than one-tenth the drinking water standards.

One approach for comparing TCLP and ANSI/NSF 61 protocols is to normalize results based on surface area to volume (SAV) ratios. Sieve analysis of a TCLP (water) residue was used to calculate the surface area of the residual concrete particles, yielding a surface area of 3440 cm²/100g. (This calculation assumed spherical particles. Since most surface area is in the finest fraction, which contains nearly equal particles, this assumption is reasonable. However, surface roughness, cracks, and permeability were ignored. Thus, the calculated surface area is likely lower than the actual surface area.) In 2 L of TCLP leachate this is an SAV ratio of 1720cm²/L. The ANSI/NSF 61 tests used an SAV of 43.7 cm²/L. The ratio of SAV_{TCLP} to SAV_{NSF} is approximately 40:1. Dividing Cr TCLP (water) values by 40 yields results approximately eight times higher than the drinking water results, suggesting that permeability of the relatively small crushed concrete particles is responsible for some Cr leaching.

Lead and mercury in one control sample were higher than in any of the leachates, suggesting contamination of at least one control solution. Mercury levels were 10–20 times higher than expected in tap water and drinking water controls. To investigate the source of lead and mercury in control samples, duplicate samples of water were collected in glass bottles containing the nitric acid–dichromate preservative de-

scribed above, at the final water deionizer just before filling the polyethylene buckets. Additional samples were taken from a second deionizer used in a different part of CTL's chemistry laboratory. The samples were tested for mercury and lead by AAS, yielding the following results:

Lab:	Concentration µg/L (ppb)			
	Hg		Pb	
	CTL	TEI	CTL	TEI
deionizer 1*	0.06	n/a	<0.2	n/a
deionizer2*	0.03	n/a	<0.3	n/a
control 1†	0.9	3.2	5.8	3
control 2†	0.5	0.3	1.0	3
tap water†	0.2	0.7	2.7	n/a

* Mean of duplicate determinations. n/a = not analyzed

† Water analyzed after soaking in polyethylene buckets, with no concrete, for 16±1 hr.

We believe that contamination from the polyethylene buckets (or less likely, airborne sources) caused the concentrations of mercury and lead in controls to exceed levels in the concrete leachates. According to State of Illinois reports, the municipal water supply used to make concrete should have contained less than 0.05 µg/L (ppb) Hg. This water passed through service deionizers, plastic hoses, and the final purification deionizer before going into the buckets. A water purity meter at the final deionizer indicated resistivity greater than 18MΩ-cm at all times. These observations indicate the difficulty of performing analyses at such low levels. The use of glass containers, properly prepared, should be preferred over plastic. Some virgin plastic vessels might be suitable if they do not contain many inorganic pigments, fillers, or antioxidants.

Rather than normalize results for lab-versus-field surface area-to-volume ratios, we performed the tests at the SAV_f ratio for a 910-mm (3-ft) diameter pipe and with soaking time precisely 16±1hr. This approach was taken since concretes generally have low, but finite permeability. While leachate from steel pipe probably can be considered to come from the surface or an extremely small depth, the whole volume of a concrete specimen should be considered as potential source of leachable substances. Since the kinetics of heavy metal leaching are not precisely known and depend on individual concrete specimen permeability, we felt it would be useful to obtain results without "over-concentration" of leachate followed by normalization, if instrument detection limits were acceptable. It will be useful to have data on the changing rate of leachability of trace metals as a function of conditioning time. Due to the apparent contamina-

tion by lead and mercury in at least some samples, it would be prudent to repeat the analyses for these metals. Otherwise, it appears that metals, fluoride, and nitrate concentrations for the two aggregates and four cements tested do not present concerns in drinking water leachates from concrete.

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Appendix

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Drinking Water Standards and Health Advisories

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4	Total Chromium in Cement, mg/kg
5	Lead in TCLP Cement Extract, mg/L
6	Total Lead in Cement, mg/kg

Cement No.:	No. 27	No. 61	No. 82	No. 84
Cement Type:	Type I	Type I	Type IA	Type II
Process Type:	Preheater and precalciner with bypass	Wet	Preheater	Dry
Raw Materials:	Limestone Clay Sand Iron Oxide	Limestone Shale	Limestone Clay Sand Mill Scale Iron Dust	Limestone Clay Silica Iron
Fuels:	Coal Petroleum Coke	Natural Gas	Coal Hazardous Waste Whole Tires	Petroleum Coke Waste Solvents

Table 1 – Cements Used for Concrete Leaching Study

	Cement 27	Cement 61	Cement 82	Cement 84	
Blaine (ASTM C 204) Surface Area, cm ² /g	3380	3640	4380	4120	
L.O.I. (ASTM C 114), %	1.56	1.48	3.01	1.31	
Insoluble Residue (ASTM C 114), %	0.28	N.D.	0.61	0.49	
Mortar Strengths (ASTM C 109)	3d, MPa (psi)	22.0 (3190)	21.0 (3190)	18.1 (2630)	27.2 (3950)
	7d, MPa (psi)	30.7 (4450)	29.6 (4450)	22.9 (3200)	32.9 (4770)
	28d, MPa (psi)	43.0 (6230)	39.8 (6230)	27.1 (3930)	40.4 (5860)
Initial Vicat (ASTM C 191), hours	1:25	1:57	2:53	1:48	
Autoclave Expansion (ASTM C 151), %	0.05	<0.01	0.12	0.03	
Air Content of Mortar (ASTM C 185), %	9.4	8.8	18.9	7.8	

Note: N.D. = value not determined

Table 2 – ASTM Cement and Mortar Tests

Analyte	No. 27	No. 61	No. 82	No. 84
SiO ₂	20.85	21.11	20.33	20.59
Al ₂ O ₃	4.55	4.56	4.08	4.53
Fe ₂ O ₃	2.34	2.43	3.39	2.96
CaO	63.88	64.05	60.47	63.69
MgO	2.45	2.11	4.36	2.71
SO ₃	3.34	2.85	3.00	2.74
Na ₂ O	0.00	0.08	0.18	0.08
K ₂ O	0.51	0.62	0.79	0.52
TiO ₂	0.16	0.23	0.25	0.21
P ₂ O ₅	0.02	0.19	0.10	0.06
Mn ₂ O ₃	0.04	0.12	0.08	0.05
SrO	0.04	0.03	0.07	0.15
Lol	1.56	1.48	3.01	1.31
Total	99.75	99.86	100.11	99.62
<u>Calculated</u>				
<u>Compounds</u>				
C ₃ S	57	55	49	58
C ₂ S	17	19	22	15
C ₃ A	9	9	6	8
C ₄ AF	7	7	10	9

Table 3 – Chemical Analysis of Cements, wt%

Analyte	No. 27	No. 61	No. 82	No. 84
Antimony	<0.19	<0.19	<0.19	<0.19
Arsenic	<16	19.0	9.09	70.6
Barium	92.9	163	275	197
Beryllium	1.10	1.65	1.32	1.51
Cadmium	<0.05	<0.05	0.04	<0.13
Chromium	33.9	99.3	65.0	167
Lead	8.11	4.62	5.95	6.45
Mercury	<0.062	<0.004	<0.01	0.0255
Nickel	23	<12	21	76
Selenium	<3	<6	<4	<4
Silver	7.62	10.3	7.06	8.03
Thallium	<0.4	<0.2	0.20	<0.6

Table 4 – Total Trace Metals in Cements, mg/kg

Analyte	No. 27	No. 61	No. 82	No. 84
Antimony	<0.0163	<0.02	<0.02	0.0040
Arsenic	<0.010	<0.035	<0.060	<0.019
Barium	0.71	0.93	1.58	1.59
Beryllium	<0.0001	<0.0002	0.00008	0.00059
Cadmium	<0.0010	0.00107	0.00185	<0.00009
Chromium	0.371	1.05	0.713	1.22
Lead	<0.005	0.018	0.0080	0.0049
Mercury	<0.0006	<0.00012	<0.0001	0.00023
Nickel	<0.19	<0.03	<0.05	<0.08
Selenium	<0.006	<0.005	<0.02	<0.004
Silver	0.055	0.068	0.071	0.056
Thallium	<0.03	<0.004	<0.008	<0.007

Table 5 – TCLP Trace Metals in Cements, mg/L

Analyte	Elgin Sand	Eau Claire 3/4"	Eau Claire 3/8"	Thornton
Antimony	<0.0022	<0.0022	<0.0022	<0.0023
Arsenic	<0.003	<0.003	<0.003	<0.014
Barium	0.33	0.33	<0.33	0.16
Beryllium	<0.00062	0.00067	0.00047	<0.00015
Cadmium	0.00068	0.00046	<0.00021	<0.00017
Chromium	<0.04	<0.04	<0.04	<0.07
Lead	0.007	0.009	<0.007	0.018
Mercury	<0.00007	<0.0003	0.00008	0.00039
Nickel	<0.08	<0.08	<0.08	0.18
Selenium	0.011	<0.006	<0.006	<0.010
Silver	0.0522	<0.01	<0.01	0.0422
Thallium	0.006	<0.002	<0.002	<0.002

Table 6 – TCLP (acid) Extracts From Aggregates, mg/L

	<u>Siliceous Eau Claire</u>	<u>Calcareous Thornton Dolomite</u>
Cement	335 (564)	335 (564)
Water	184 (134)	184 (310)
Elgin Sand	775 (1307)	747 (1259)
Coarse Aggregate		
19–13 mm (3/4–1/2 in)	695 (1172)	
10–5 mm (3/8–3/16 in)	463 (781)	
19 mm (3/4 in) topsize		1129 (1903)

w/c = 0.55

Coarse Aggregate to Sand Ratio = 60:40

Table 7 – Concrete Mix Designs, kg/m³ (pcy)

Eau Claire Siliceous Coarse Aggregate

	<u>EC-27</u>	<u>EC-61</u>	<u>EC-82</u>	<u>EC-84</u>
Strength at 28 days, MPa (psi)	44.1 (96390)	38.1 (5520)	27.2 (3950)	33.0 (4790)
Slump, mm (in.)	120 (4.7)	115 (4.5)	200 (7.8)	195 (7.6)
Air Content, %	1.0	1.9	6.2	0.6
Unit Weight, kg/m ³ (pcf)	2409	2384 (148.8)	2291 (143.0)	2425 (151.4)

Thornton Dolomite Coarse Aggregate

	<u>TD-27</u>	<u>TD-61</u>	<u>TD-82</u>	<u>TD-84</u>
Strength at 28 days, MPa (psi)	33.2 (4810)	41.4 (6010)	19.0 (2750)	38.1 (5520)
Slump, mm (in.)	25(1.0)	90 (3.5)	180 (7.2)	160 (6.3)
Air Content, %	1.3	1.6	6.5	1.2
Unit Weight, kg/m ³ (pcf)	2384 (148.8)	2377 (148.4)	2246 (140.2)	2387 (149.0)

Table 8 – Properties of Concretes

<u>Analyte</u>	<u>EC27</u>	<u>EC61</u>	<u>EC82</u>	<u>EC84</u>
Antimony	<0.0022	<0.0025	<0.0025	0.0204
Arsenic	<0.008	<0.008	<0.005	<0.019
Barium	0.44	0.68	0.9	0.69
Beryllium	<0.0004	<0.00022	<0.00022	<0.00022
Cadmium	<0.00023	0.00153	<0.00017	<0.00017
Chromium	<0.04	0.19	0.19	0.3
Lead	<0.012	0.017	0.025	0.013
Mercury	0.000346	0.000082	0.000406	0.000416
Nickel	<0.08	,0.14	0.17	0.29
Selenium	<0.006	<0.009	<0.009	<0.007
Silver	0.0655	0.11	0.0766	0.0788
Thallium	<0.002	<0.002	<0.002	0.006

<u>Analyte</u>	<u>TD27</u>	<u>TD61</u>	<u>TD82</u>	<u>TD84</u>
Antimony	<0.0023	<0.0023	<0.0023	0.0196
Arsenic	<0.005	<0.019	<0.007	<0.013
Barium	<0.07	0.53	1.05	0.71
Beryllium	<0.00022	<0.00022	<0.0022	<0.00022
Cadmium	<0.00017	<0.00017	0.00543	<0.00017
Chromium	0.08	0.21	0.12	0.22
Lead	0.023	0.019	0.016	0.02
Mercury	<0.00006	<0.00003	0.000344	0.00032
Nickel	0.29	0.14	0.21	0.3
Selenium	<0.011	<0.005	<0.023	<0.005
Silver	0.0766	0.0821	0.071	<0.01
Thallium	0.007	<0.002	<0.002	<0.002

Table 9 – TCLP (acid) Extracts from Concretes, mg/L

<u>Analyte</u>	<u>EC82</u>	<u>EC84</u>	<u>TD82</u>	<u>TD84</u>
Antimony	<0.016	<0.016	<0.0092	<0.0092
Arsenic	<0.0035	<0.0035	<0.0035	<0.022
Barium	0.37	<0.2	0.29	<0.3
Beryllium	<0.0007	<0.0007	<0.0002	<0.0002
Cadmium	<0.0013	<0.0013	<0.0011	<0.0011
Chromium	0.0597	0.208	<0.085	<0.11
Lead	<0.022	<0.022	<0.016	<0.016
Mercury	<0.000007	0.000433	0.00078	0.000339
Nickel	<0.007	<0.007	0.0285	0.0435
Selenium	<0.01	<0.014	<0.008	<0.008
Silver	<0.086	<0.086	<0.086	<0.086
Thallium	<0.002	<0.001	<0.004	<0.002

Table 10 – TCLP (water) Extracts from Concretes, mg/L

	(concentrations in mg/L in leachate)	
	Acetic Acid	Water
Sample TD82		
Barium	1.05	0.29
Cadmium	0.00543	<0.0011
Chromium	0.12	<0.085
Nickel	0.21	0.0285
Sample EC82		
Barium	0.9	0.37
Chromium	0.19	0.0597
Nickel	0.17	<0.007
Sample TD84		
Antimony	0.0196	<0.0092
Barium	0.71	<0.3
Chromium	0.22	<0.11
Nickel	0.3	0.0435
Sample EC84		
Barium	0.69	<0.2
Chromium	0.3	0.208
Nickel	0.29	<0.007
Thallium	0.006	<0.001

**Table 11 – Summary of Differences
TCLP Extracts of Concretes
Water vs. Acetic Acid**

<u>Sample ID</u>	Arsenic (µg/L)		Barium (µg/L)		Cadmium (µg/L)	
	CTL	TEI	CTL	TEI	CTL	TEI
control 1	<2.8	<5	<1.7	<20	<0.02	<0.6
control 2	<2.8	<5	<1.7	<20	<0.02	<0.6
tap water	<2.8	n/a	18	n/a	0.08	n/a
EC27	<2.8	<5	<1.7	<20	<0.02	0.8
TD27	<2.8	<5	<1.7	<20	<0.02	<0.6
EC61	<2.8	<5	<1.7	<20	<0.02	<0.6
TD61	<2.8	<5	2	<20	<0.02	307
EC82	<2.8	<5	<1.7	<20	<0.02	<0.6
TD82	<2.8	<5	4.2	<20	<0.02	<0.6
EC84	<2.8	<5	<1.7	<20	<0.02	<0.6
TD84	<2.8	<5	<1.7	<20	<0.02	<0.6

<u>Sample ID</u>	Chromium (µg/L)		Lead (µg/L)		Mercury (µg/L)	
	CTL	TEI	CTL	TEI	CTL	TEI
control 1	0.2	<9	5.8	3	(0.9)	(3.2)
control 2	<0.2	<9	1.0	3	(0.5)	(0.3)
tap water	0.7	n/a	2.7	n/a	(0.2)	(0.7)
EC27	0.2	<9	1.1	2	(0.2)	(0.4)
TD27	<0.2	<9	21	3	(0.4)	(0.7)
EC61	0.2	<9	1.4	2	(0.4)	(0.2)
TD61	0.3	<9	0.9	2	(0.3)	(0.6)
EC82	<0.2	<9	0.9	3	(0.3)	(0.3)
TD82	0.2	<9	1.2	2	(0.2)	(0.4)
EC84	0.3	<9	0.9	3	(0.2)	(0.5)
TD84	0.3	<9	1.1	<2	(0.2)	(0.4)

<u>Sample ID</u>	Selenium (µg/L)		Silver (µg/L)		Fluoride (mg/L)	
	CTL	TEI	CTL	TEI	CRL	TEI
control 1	<0.3	<1	<0.4	<8	0.02	<0.03
control 2	<0.3	<1	<0.4	<8	0.02	<0.03
tap water	<0.3	n/a	<0.4	n/a	0.5	n/a
EC27	<0.3	<1	<0.4	<8	0.01	<0.3
TD27	<0.3	<1	<0.4	<8	0.02	<0.3
EC61	<0.3	<1	<0.4	<8	0.01	<0.3
TD61	<0.3	<1	<0.4	<8	0.01	<0.3
EC82	<0.3	<1	<0.4	<8	0.02	<0.3
TD82	<0.3	<1	<0.4	<8	0.02	<0.3
EC84	<0.3	<1	<0.4	<8	0.02	<0.3
TD84	<0.3	<1	<0.4	<8	0.01	<0.3

<u>Sample ID</u>	Nitrate-N (mg/L)	
	CTL	TEI
control 1	0.06	n/a
control 2	0.04	n/a
tap water	0.08	n/a
EC27	0.02	n/a
TD27	0.03	n/a
EC61	0.02	n/a
TD61	0.03	n/a
EC82	0.02	n/a
TD82	0.04	n/a
EC84	0.03	n/a
TD84	0.02	n/a

Table 12 – Measured Concentrations in Drinking Water Leachates

Table 12 Notes:

"n/a" indicates not analyzed Instrument settings and samples sizes were chosen to produce reporting limits generally one-twentieth or less of the Drinking Water Standards at CTL and one-tenth or less at TEI. That is the reason CTL minimum values are less than TEI's minimum values.

For comparison, the U.S. EPA national Primary Drinking Water Standards for inorganics are given here in $\mu\text{g/L}$ (ppb or mg/L (ppm). This list is based on the 1987 Drinking Water Standard found in ANSI/NSF 61-1991 Appendix F which was published in May 1991.

arsenic	50 ppb
lead	50 ppb
fluoride	4 ppm
barium	1000 ppb
mercury	2 ppb
nitrate-N	10 ppm
cadmium	10 ppb
selenium	10 ppb
chromium	xx ppb
silver	xx ppb

The Drinking Water Standards have been revised. A copy can be obtained from the EPA Safe Drinking Water Hotline at 800-426-4791 Monday-Friday 8:30-5 pm EST. The inorganic portion of the December 192 Standards are shown on the following two pages.

Chemicals	Standards			
	Status Reg*	MCLG (mg/L)	MCL (mg/L)	STATUS HA*
Inorganics				
Aluminum	L	—	—	D
Ammonia	—	—	—	D
Antimony	F	0.006	0.006	F
Arsenic	—	—	0.05	D
Asbestos (fibers/1>10 µm length)	F	7 MFL	7 MFL	—
Barium	F	2	2	F
Beryllium	F	0.004	0.004	D
Boron	L	—	—	D
Cadmium	F	0.005	0.005	F
Chloramine	L	—	—	D
Chlorate	L	—	—	D
Chlorine	L	—	—	D
Chlorine dioxide	L	—	—	D
Chlorite	L	—	—	D
Chromium (total)	F	0.1	0.1	F
Copper	F	1.3	TT**	—
Cyanide	P	0.2	0.2	F
Fluoride	F	4	4	—
Lead (at tap)	F	ZERO***	TT**	—
Manganese	L	0.2	—	D
Mercury (inorganic)	F	0.002	0.002	F
Molybdenum	L	—	—	F
Nickel	F	0.1	0.1	F
Nitrate (as N)	F	10	10	F
Nitrite (as N)	F	1	1	F
Nitrate + Nitrate (both as N)	F	10	10	F
***can't read	F	0.05	0.05	—
Silver	—	—	—	D
Sodium	—	—	—	D
Strontium	L	—	—	D
Sulfate	P	**	**	—
Thallium	F	0.005	0.002	F
Vanadium	L	—	—	D
Zinc	L	—	—	F
Zinc Chloride (measured as Zinc)	L	—	—	F
Radionuclides				
Beta particle and photon activity (formerly man-made radionuclides)	F	zero	4 mrem	—
Gross alpha particle activity	F	zero	15 pC**	—
Radium 226/228	P	zero	5 pCi/L	—
Radon	P	zero	300 pCi/L	—
Uranium	P	zero	20 µg/L	—

Drinking Water Standards and Health Advisories (December 1992)

HEALTH ADVISORIES

10-kg Child			70-kg Adult				mg/L at 10 ⁻² Cancer Risk	CANCER GROUP
One-day (mg/L)	Ten-day (mg/L)	Longer term (mg/L)	Longer term (mg/L)	RID (mg/kg/ day)	DWEL (mg/L)	Lifetime (mg/L)		
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	30	-	D
0.015	0.015	0.015	0.015	0.0004	0.015	0.003	-	D
-	-	-	-	-	-	-	0.002	A
-	-	-	-	-	-	-	700MFL	A
-	-	-	-	0.07	2	2	-	D
30	30	4	20	0.005	0.2	-	0.008	B2
4	0.9	0.9	3	0.09	3	0.6	-	*
0.04	0.04	0.005	0.02	0.0005	0.02	0.005	-	D
1	1	1	1	0.1	3.3	2.6	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
1	1	0.2	0.8	0.005	0.2	0.1	-	D
-	-	-	-	-	-	-	-	D
0.2	0.2	0.2	0.8	0.022	0.8	0.2	-	D
-	-	-	-	0.12	-	-	-	-
-	-	-	-	-	-	-	-	B2
-	-	-	-	0.14/0.005	-	-	-	-
-	-	-	0.002	0.0003	0.01	0.002	-	D
-	0.08	0.01	0.05	0.005	0.2	0.04	-	D
1	1	0.5	1.7	0.02	0.6	0.1	-	D
-	10*	-	-	1.6	-	-	-	*
-	1*	-	-	0.16*	-	-	-	*
-	-	-	-	-	-	-	-	*
-	-	-	-	0.005	-	-	-	-
0.2	0.2	0.2	0.2	0.005	0.2	0.1	-	D
-	-	-	-	-	20***	-	-	-
25	25	25	90	2.5	90	17	-	D
-	-	-	-	-	-	-	-	-
0.007	0.007	0.007	0.02	0.00007	0.002	0.004	-	-
0.08	0.08	0.03	0.11	0.003	0.11	0.02	-	D
6	6	3	12	0.3	11	2	-	D
6	6	3	12	0.3	11	2	-	D
-	-	-	-	-	-	-	4 mrem/y	A
-	-	-	-	-	-	-	-	A
-	-	-	-	-	-	-	22/26 pCi/L	A
-	-	-	-	-	-	-	2/0 pCi/L	A
-	-	-	-	-	-	-	170 pCi/L	A

*Under review

**Copper – action level 1.3 mg/L

Lead – action level 0.015 mg/L

* Under review

** Deferred

***Guidance

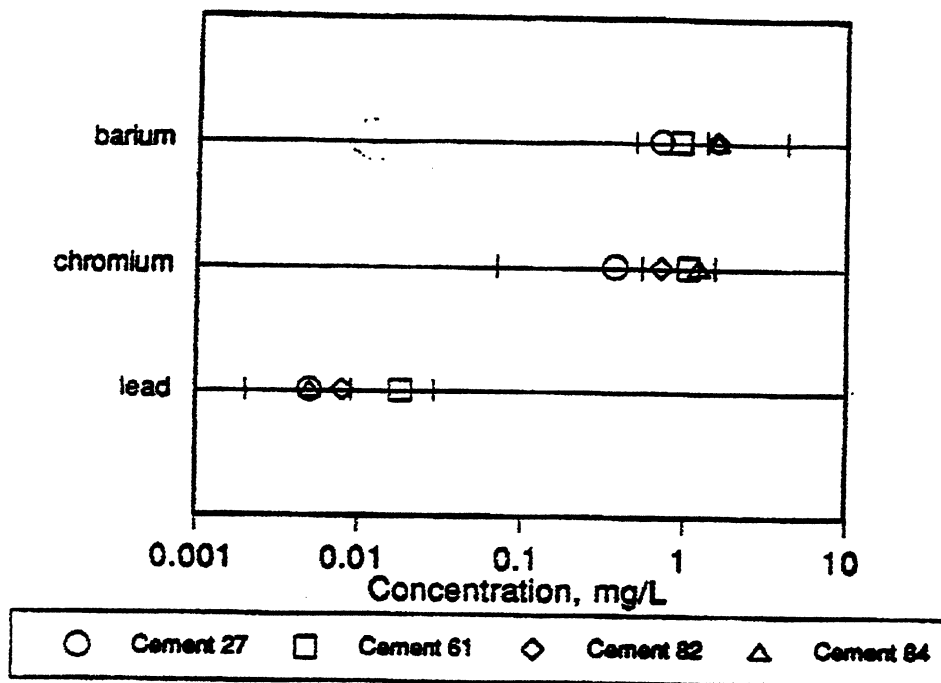


Figure 1. Concentrations of barium, chromium, and lead in acetic acid TCLP leachates from the four cements selected for this work. For comparison, the highest, lowest, and mean values for all cements in the PCA study of U. S. and Canadian cements are shown as short vertical bars. Concentrations of other elements are not shown since most are either below detection limits or far below regulatory levels.

FIGURE 2

CONCRETE LEACHATE RELATIVE CONCENTRATIONS

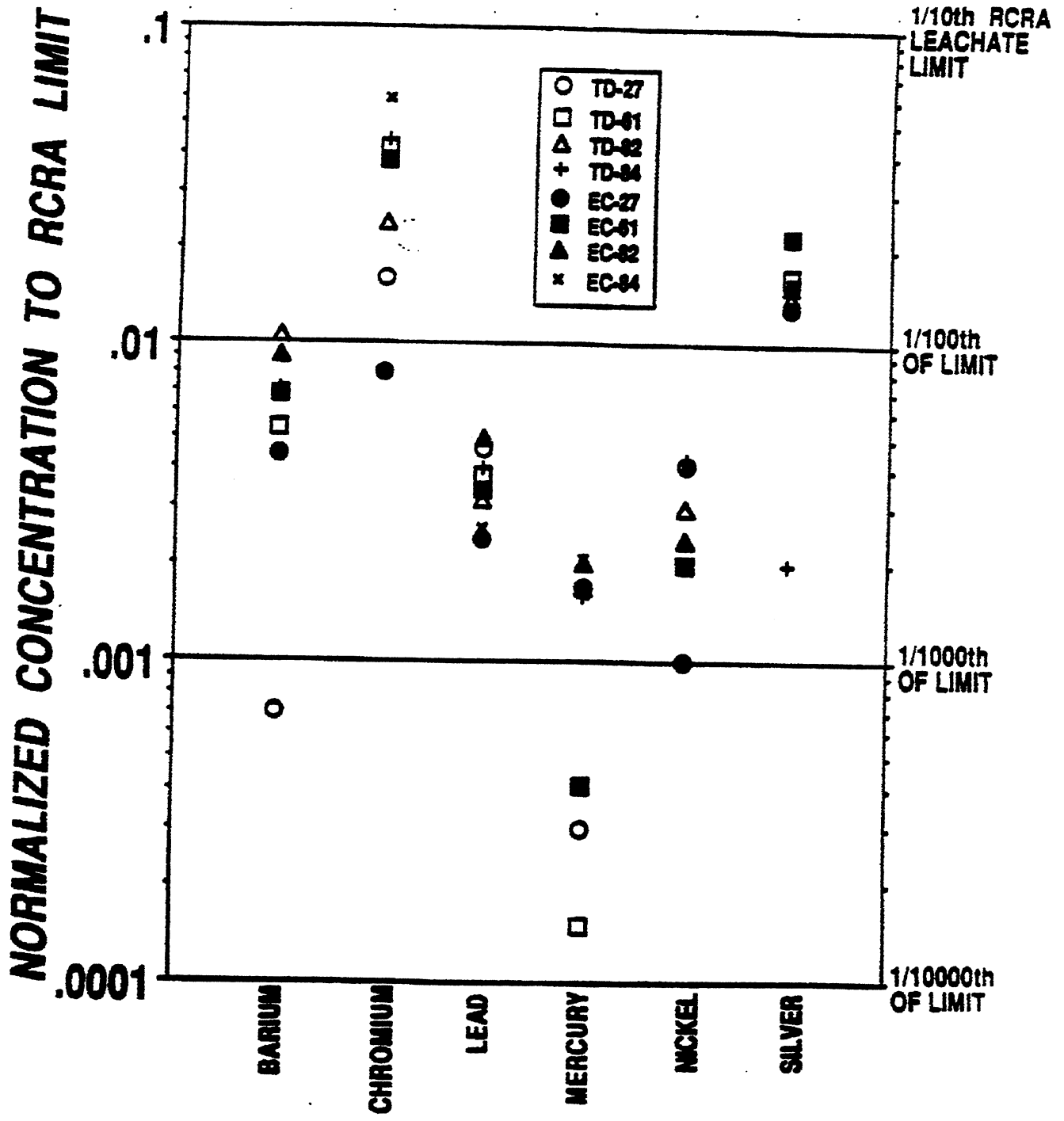
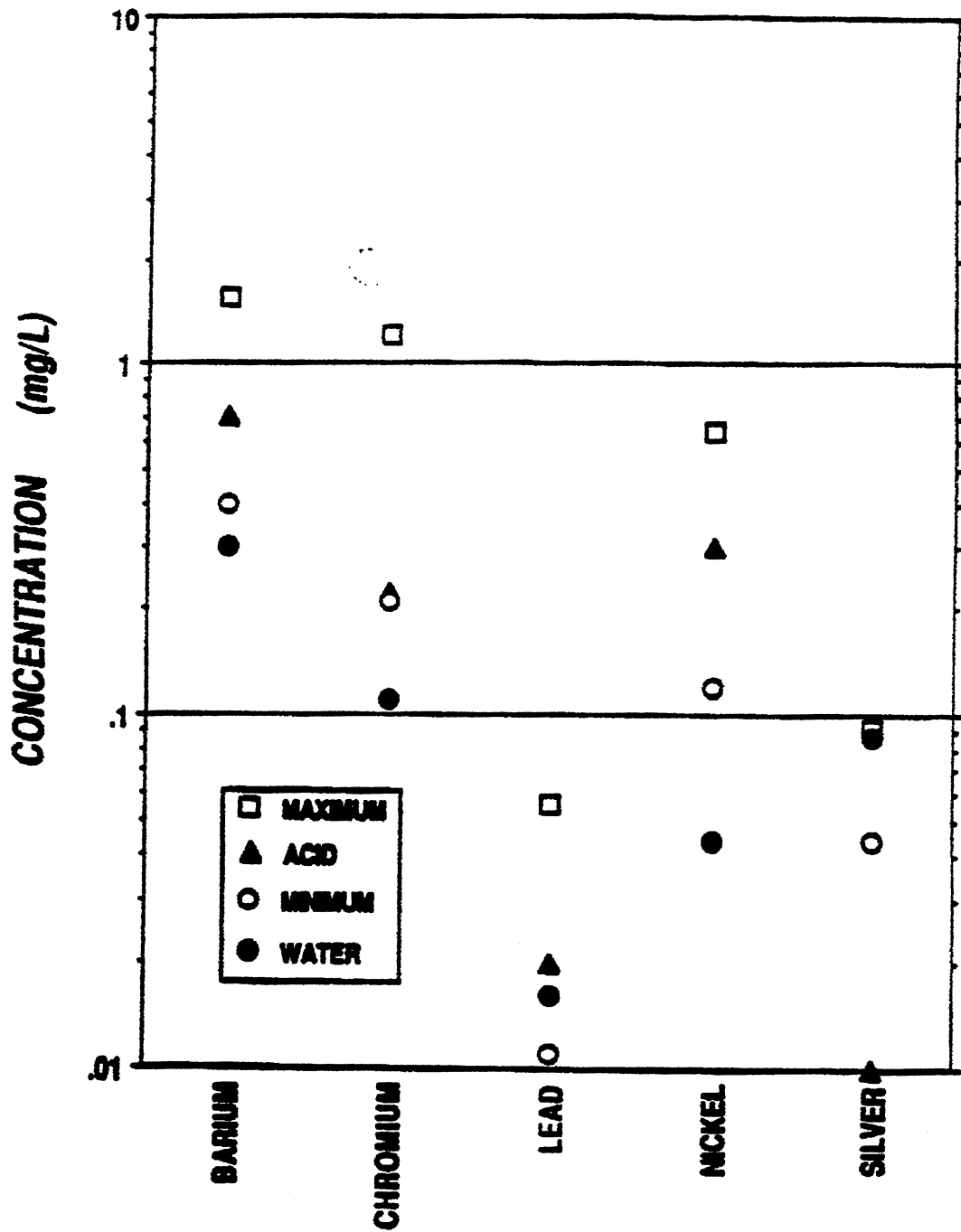


FIGURE 2a

CONCRETE TD-84 LEACHATES AND ESTIMATES OF EXTREMES



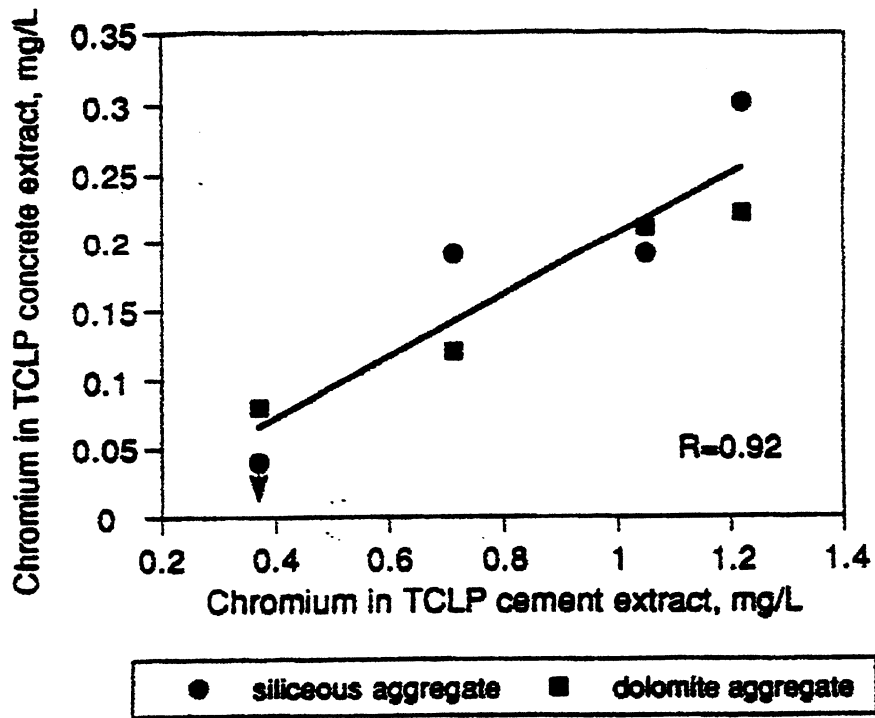


Figure 3.

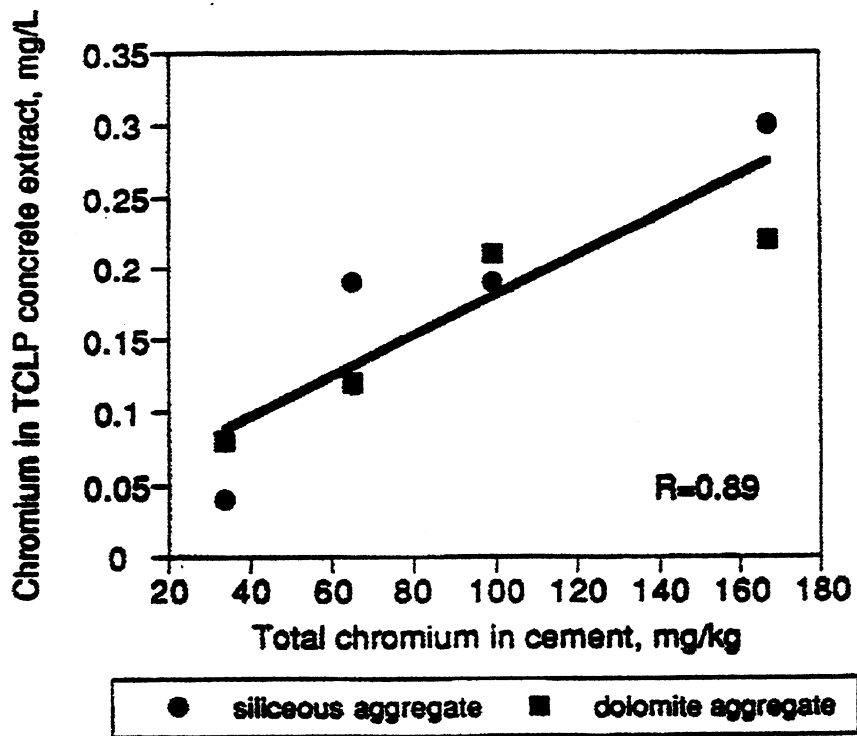


Figure 4.

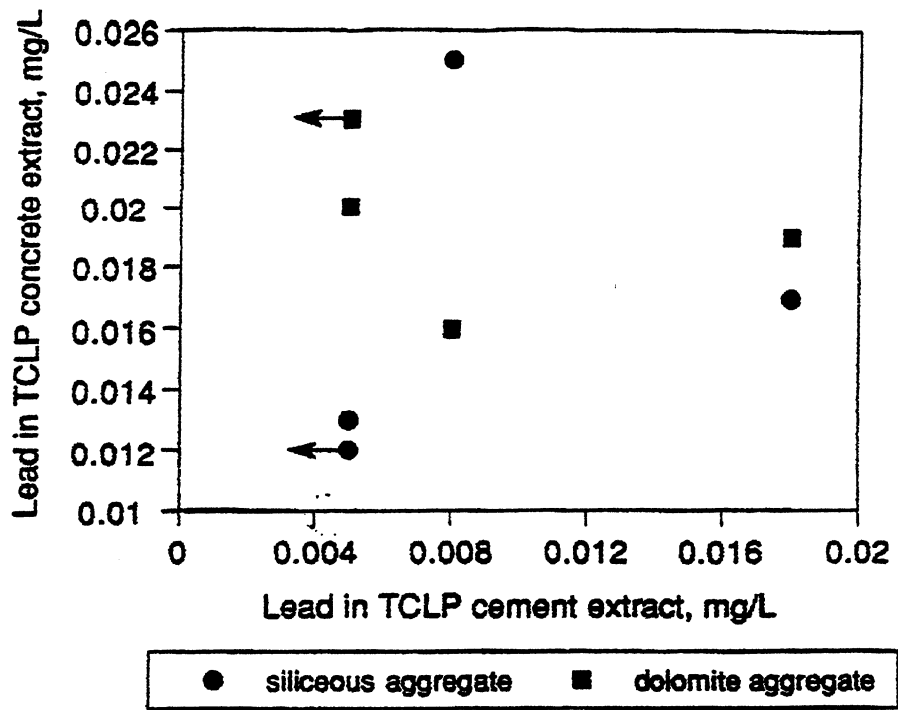


Figure 5.

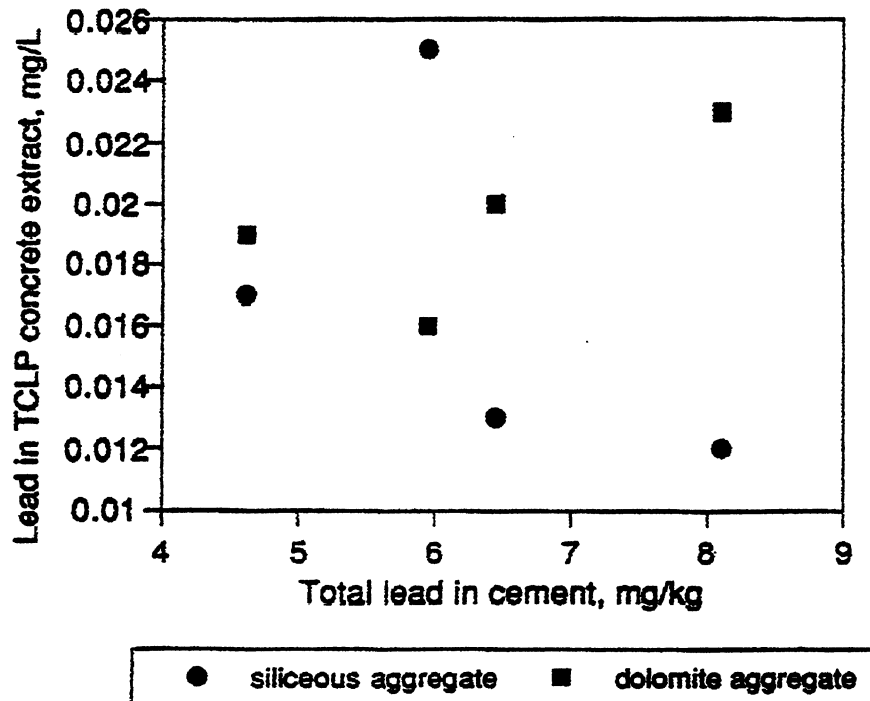


Figure 6.