

# Preferential Acidic, Alkaline and Neutral Solubility of Metallic Elements in Fly Ash

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**KEYWORDS:** Coal Utilization By-Products, leaching, pH

## ABSTRACT

In the US, over 100 million tons of coal utilization by-products (CUB) are generated annually. To determine if exposure of these materials to aqueous fluids poses an environmental threat, researchers at the National Energy Technology Laboratory (NETL) have conducted extensive leaching tests. Five 1 kg samples of 35 PC fly ashes have been leached with acid, neutral and alkaline solutions at an approximate rate of 130 mL/d for 1 to 3 months. The leachates are analyzed for pH and 19 cations. The data from this leaching experiment has shown that the release of metal ions from fly ash is related to the alkalinity of the ash and the mineral matrix of the element. However, comparing the maximum concentration in a leachate sample to its pH indicates that the dominant influence on solubility of metallic elements is pH. The pH of the leachate is determined by the soluble alkalinity of the ash and the  $H^+/OH^-$  concentration of the leachant. Those elements that form oxyanions are apparently most soluble at high pH. Heavy metals are more soluble at low pH. Only Ca, Na, and K indicate significant solubility in the circumneutral pH range. For all elements except Ca, solubility is relatively low at all pH's; generally less than 2 % of the amount present in the ash can be extracted even by long term leaching.

## INTRODUCTION

The process of generating electricity also produces over 100 million tons of coal utilization by-products (CUB) annually.<sup>1</sup> Approximately 30% of this material is beneficially used, primarily in cement. Since CUB contain a number of elements that if released to surface or groundwater could have environmental and health effects, the extent and conditions of potential solubility has been a continuing environmental concern.

The use or disposal of CUB at coal mines is regulated by state environmental agencies or the Office of Surface Mining, Regulation and Enforcement (OSMRE)<sup>2</sup>. These agencies require that the mine operator prevent contamination of the ground or surface water both on and off-sites, and ensure that there is no actual or probable threat of water pollution. Currently, the debate over use or disposal of coal combustion by-products at coal mines centers on the potential for the materials to release toxins, such as heavy metals, back into the environment. Any mine operator using CUB is required to identify measures to be taken during mining and reclamation to assure the protection of the quality and quantity of surface and groundwater systems, from adverse

effects of the mining and reclamation process; also, to assure that rights of present users of such water are protected.

Although the Environmental Protection Agency (EPA) has concluded that fossil fuel combustion wastes do not warrant regulation as hazardous under Subtitle C of the Resource Conservation and Recovery Act (RCRA), they are currently investigating whether regulations under RCRA Subtitle D are needed for coal combustion wastes disposed in surface impoundments and landfills and used as minefill.<sup>3</sup> In response to a request from Congress, the National Research Council is conducting a study to examine the health, safety, and environmental risks of using CUB for reclamation in active and abandoned coal mines.<sup>4</sup>

Since coal mines, particularly abandoned ones, can present a severely acid environment, it is reasonable to determine if heavy metals can be released from CUB at low pH. The By-Products Utilization Group at the National Energy Technology Laboratory has conducted field studies to determine the environmental effects of using CUB in mine reclamation.<sup>5</sup> Laboratory studies with a large suite of CUB samples have determined the magnitude and conditions for metal ion release from CUB.

Previous research has indicated that metal ion solubility from fly ash is generally very low.<sup>6</sup> For most cations, less than 2% of the amount in the ash can be extracted by long-term leaching. The distribution of elements in silicate and non-silicate minerals also affects solubility.<sup>7</sup> In leaching tests with acid, alkaline and neutral leachants, the pH of the leachant, as well as the alkalinity of the CUB, strongly influenced the release of metal ions. It also appears that individual elements act like independent variables, exhibiting a maximum release within a limited pH range.

## **EXPERIMENTAL METHOD**

Leaching was carried out in a column system designed to simulate the reaction of granular materials during exposure to fluids, such as acid rain or acid mine drainage (AMD). The columns, appropriate for unconsolidated materials with a particle diameter of less than 0.5 cm, are constructed of 1 meter sections of 5 cm ID clear PVC pipe<sup>8</sup>, capped with threaded PVC pipe caps. The approximate volume of the columns is 2 L, large enough to hold a representative 1 kg fly ash sample.

The leaching solutions (Table 1) were selected to represent the broad pH range of common fluids. Deionized water is a neutral liquid, representative of exposure to surface water or groundwater. Acetic acid is a weak organic acid, and is an indicator of potential leaching during co-disposal in a municipal solid waste (MSW) landfill. Sodium carbonate is a high pH solution for elements that are caustic soluble. Synthetic precipitation is a solution simulating acid rain. Sulfuric acid is a strong mineral acid and is a component of acid mine drainage (AMD).

The 0.1 N leachant solutions are stored in 20 L reservoirs; a peristaltic pump delivers them to the columns at an average flow rate of approximately 200 mL/d. Leachate is collected in 1 L volumetric cylinders. Samples were leached for between 30 and 190 days, depending on the natural alkalinity of the Class F fly ash samples. All tests were run at ambient temperature, averaging 21 °C with seasonal variations of  $\pm 9$  °C.

Leachate samples were taken at 2 to 3 day intervals and analyzed for pH, the major elements [aluminum (Al), calcium (Ca), iron(Fe)], the minor elements [manganese(Mn), magnesium(Mg), potassium(K), and sodium(Na)], and the trace elements [antimony (Sb), arsenic(As), barium(Ba), beryllium(Be), cadmium (Cd), cobalt(Co), chromium(Cr), copper(Cu), lead(Pb), nickel(Ni), selenium (Se), and zinc(Zn)]. Metal concentration was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Thirty-five samples of Class F fly ash were obtained from pulverized coal (PC) electric power plants. The class F PC fly ash samples were analyzed by triple acid digestion and ICP-AES analysis. The major cations in the samples are Si, Al, Fe and Ca; they also contain variable amounts of the minor elements (Mg, Mn, K, Na and Ti) and trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, and Zn). A statistical description of the sample set is given in Table 2.

## RESULTS AND DISCUSSION

The pH of the leachate was initially controlled by the alkalinity of the CUB sample. The maximum pH in all leachants was between 4.0 and 13.2 (Table 3); the average maximum pH was between 8.9 (in HAc) and 11.8 (in Na<sub>2</sub>CO<sub>3</sub>). The minimum pH was a function of both the sample and the leachant. In the alkaline and neutral leachants, the minimum pH was between 2.9 and 12.0. For samples in acid leachants, the minimum pH varied from 1.0 to 12.2. The average minimum pH was between 7 and 9 for the neutral and alkaline leachants and less than 4 for the acidic leachants. For the individual samples, the pH varied by less than 1 to over 11 pH units. The average pH range was approximately 3 units in H<sub>2</sub>O and SP; in the alkaline Na<sub>2</sub>CO<sub>3</sub>, the average pH range was less than 3 units. In the acidic leachants, the average change in pH was 5 units.

The maximum soluble concentration ( $[C]_{MAX}$ ) of 19 cations was determined for 35 samples in five leachant solutions. For each of these concentration values, the corresponding pH of the leachate was determined. The distribution of the pH values at which an element was most soluble, regardless of leachant, indicates whether an element tends to be more soluble at an acidic, alkaline or neutral pH (Figure 1).

Based on this distribution of the maximum soluble concentration, the maximum solubility of Ca may occur at an acidic, alkaline or neutral pH, but it appears to be most soluble between pH 6 and pH 10. The elements Na and K have maximum solubility values over the entire pH range.

For the elements Fe, Mg, Al, Mn, Ba, Be, Cd, Co, Cr, Cu, Ni, Pb, and Zn, the maximum soluble concentration was related to an acidic pH for the majority of sample leachant combinations. For the elements that can form oxyanions, the maximum soluble concentration indicated that these elements are most soluble at alkaline pH.

Although this simple approach does indicate the pH at which these elements are most soluble, it can obscure other pH-related effects. For instance, Cr seems to be soluble primarily in acid solutions. However, plotting all concentration values versus pH indicates that the solubility of Cr is actually bimodal (Figure 2).

Using the distribution of pH values at which the maximum leachable concentration ( $[C_{MAX}]$ ) was measured may skew the data since acidic pH's were not reached in all solutions. For example, as shown in Table 4, the pH in H<sub>2</sub>O ranged from 12.86 to 3.43, and the average pH was 9.15 for all H<sub>2</sub>O samples. The pH for all  $[C_{MAX}]$  values for Cu in H<sub>2</sub>O is between 12.43 and 3.43, with an average of 8.61. In the acid solutions, the average  $[C_{MAX}]$  pH's for Cu were 5.04 and 4.31, indicating that Cu tends to be acid soluble.

Another disadvantage to this type of analysis is that it does not consider the magnitude of  $[C_{MAX}]$ . The pH for the Pb  $[C_{MAX}]$  values varied between 12.8 and 2.85. But the averages were 9.62 (H<sub>2</sub>O), 6.60 (HAc), 11.7 (Na<sub>2</sub>CO<sub>3</sub>), 10.14 (SP), and 4.24 (H<sub>2</sub>SO<sub>4</sub>), indicating greater solubility at neutral and alkaline pH. Over 4100 samples were analyzed in this test. Only 275 samples had Pb concentrations above the detection limit, and the majority of those were in the acid solutions. Therefore, Pb is clearly more soluble in acid solutions.

## SUMMARY

The distribution of maximum soluble concentrations  $[C_{MAX}]$  vs pH can be considered a first approximation of the preferred pH regime in which various elements can be leached from CUB. This analysis indicates that Ca, Na and K are soluble throughout a broad range of pH values. Most metallic cations appear to be more soluble in acid solutions. Those elements that form oxyanions are more soluble at higher pH.

The interpretation of the data is limited since the analysis does not detect bimodal distributions. And since it does not consider the magnitude of the maximum leachable concentration, it tends to overestimate the solubility range of elements that are only slightly soluble. However, it does indicate the preferred chemical environment in which various cations can be leached from CUB.

## REFERENCES

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Table 1. Leachant solutions for column leaching tests of PC fly ashes.

Leachant Solution	ID	pH
Sulfuric Acid	H <sub>2</sub> SO <sub>4</sub>	1.2
Acetic Acid	HAc	2.9
Synthetic Precipitation	SP	4.2
Deionized Water	H <sub>2</sub> O	5.7
Sodium Carbonate	Na <sub>2</sub> CO <sub>3</sub>	11.1

Table 2. Statistical variation in cations in PC class F fly ashes, mg/kg.

Element	Maximum	Minimum	Median	Average	STDEV
Ag	<sup>a</sup>				
Al	164695	72504	130084	127127	0.138
As	301	25	104	117	0.626
Ba	4170	121	855	1005	0.787
Be	27	2	11	11	0.501
Ca	112278	4646	19440	25378	0.839
Cd	15	0	4	7	0.952
Co	86	11	39	40	0.457
Cr	211	53	166	152	0.246
Cu	1610	50	112	160	1.705
Fe	304552	26273	102761	104245	0.545
K	21667	8468	15939	15871	0.223
Mg	23399	3438	5066	5965	0.623
Mn	542	155	232	282	0.349
Mo					
Na	18620	1039	3487	4318	0.804
Ni	1040	37	107	153	1.265
P	3237	304	1158	1288	0.605
Pb	173	12	81	83	0.440
Sb					
Se	26.9	1.4	7.6	9.127273	0.786
Si	287445	173102	228684	230244	0.103
Ti	13268	5472	9145	9007	0.196
Tl					
V					
Zn	609	16	139	158	0.737

<sup>a</sup> Blank cells indicate that all values were below the instrumental detection limit

**Table 3. Variation in maximum and minimum pH for 35 CUB samples in all leachants.**

Sample#	H2O		HAc		Na2CO3		SP		H2SO4	
	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN
FA04	12.38	8.58	12.28	3.98	12.31	9.8	12.28	9.63		
FA05	12.15	8.55	12.56	3.9	12.6	9.14	12.66	8.69	12.55	3.66
FA06	7.95	6.93	4.05	3.61	10.7	9.96	7.79	7.27	3.9	2.69
FA07	7.72	7.1	4.09	3.55	10.8	10.06	7.85	7.26	3.86	1.8
FA08	11.75	8.46	10.96	4	11.58	10.07	11.7	9.89	10.95	3.64
FA10	12.64	9.91	12.53	4	12.59	10.27	12.68	10.82	12.54	4.09
FA11	8.15	7	5.26	3.78	10.7	10	8.3	7.65	8.22	3.66
FA12	7.58	7.22	4.51	3.78	10.76	9.11	7.73	7.13	4.07	3.27
FA13	7.55	6.22	4.3	3.8	10.6	9.56	9.05	7.09	3.89	3.51
FA14	10.51	5.34	9.41	3.99	12.16	8.71	9.62	5.62	9.9	3.74
FA15	6.82	3.43	4.04	3.27	11	3.8	9.1	2.89	3.94	2.85
FA16	9.2	6.98	7.72	3.79	11.99	9.24	9.91	7.87	7.91	3.54
FA17	9.25	8.13	8.74	3.98	11.28	8.91	9.28	4.15	9.19	3.52
FA18	12.3	9.24	10.14	4.08	12.67	10.89	12.14	4.44	11.73	3.58
FA19	10.25	4.17	9.87	3.94	12.48	8.82	10.06	5.3	10.19	3.74
FA20	12.78	12.18	12.54	6.37	13.03	11.18	12.68	4.49	12.69	12.18
FA21	11.13	4.12	9.5	4.06	12.59	4.41	11.7	8.27	10.59	3.7
FA24	8.91	5.11	4.28	3.61	10.95	8.79	8.3	4.01	3.87	1.89
FA25	11.9	6.98	11.86	3.77	12.44	10.26	12.38	7.06	12.25	2.98
FA26	12.2	7.79	12.19	4.04	12.87	10.71	12.55	5.45	11.76	3.53
FA27	10.7	8.3	6.17	3.62	10.75	7.84	9.28	7.19	8.32	3.3
FA28	10.7	8.3	6.17	3.62	10.88	3.79	8.85	3.91	4.05	3.32
FA29	8.68	3.85	4.3	3.68	10.95	4.46	9.99	4.39	9.07	3.44
Fa30	9.98	8.4	6.98	3.71	10.82	8.94	10.25	7.95	9.11	3.52
FA31	9.27	7.92	8.71	3.77	10.72	7.98	8.23	7.27	7.95	3.49
FA32	8.01	6.87	6.13	3.85	13.05	10.98	12.86	8.01	12.73	3.75
FA33	12.59	7.92	12.81	3.99	12.88	10.66	12.49	7.87	12.12	3.86
FA36	11.76	7.9	12.31	4	11.58	10.82	10.38	8.03	6.25	0.93
FA38	10.49	7.91	10.07	4.24	12.93	11.21	12.49	9.15	12.53	4.1
FA39	12.63	7.69	12.28	4.19	13.22	11.03	12.74	8.76	12.79	7.25
FA41	12.86	8.09	12.7	4.32	12.88	12.08	12.48	8.44	12.46	7.97
FA44	12.48	9.5	12.09	7.9	10.87	7.91	8.58	7.55	4.08	2.38
FA46	8.19	7.11	4.8	2.17	12.83	10.51	12.38	8.29	12.33	2.66
FA49	12.4	8.05	12.24	1.18	12.81	10.39	12.31	3.71	12.31	3.58
FA51	12.37	7.84	12.15	3.85	10.77	9.15	9.36	7.99	9.27	1.04

**Table 4. Range of and average leachant pH for all samples and range of and average pH's at which the maximum leachable concentration was measured for individual elements.**

	H <sub>2</sub> O Range			HAc Range			Na <sub>2</sub> CO <sub>3</sub> Range			SP Range			H <sub>2</sub> SO <sub>4</sub> Range		
	High	Low	Average	High	Low	Average	High	Low	Average	High	Low	Average	High	Low	Average
Leachant	12.86	3.43	9.15	12.81	1.18	5.80	13.22	3.79	11.06	12.86	2.89	9.20	12.79	0.93	5.57
Calcium	12.8	4.17	9.48	12.56	4.04	8.41	13.05	3.79	10.24	12.66	4.01	9.64	12.73	3.61	7.63
Magnesium	12.86	3.43	8.92	9.47	3.27	7.05	12.93	3.79	9.57	12.64	2.89	8.29	12.74	2.85	6.43
Aluminum	12.27	3.43	8.64	11.53	3.27	4.51	12.62	3.79	10.75	12.5	2.89	8.43	12.18	2.58	4.42
Sodium	12.64	3.43	9.28	12.81	3.27	8.21	13.05	4.46	10.79	12.86	2.89	9.12	12.55	2.72	7.83
Manganese	12.48	3.43	8.95	12.53	3.27	5.64	12.99	3.79	9.63	12.64	2.89	8.37	12.74	2.85	4.68
Potassium	12.64	3.43	9.23	12.81	3.27	8.47	13.05	3.79	9.97	12.86	2.89	9.16	12.55	2.85	7.91
Arsenic	12.8	3.43	7.93	12.53	3.27	5.10	12.93	9.25	11.31	12.64	2.89	8.16	12.74	1.65	4.22
Barium	12.59	3.85	9.52	12.46	3.7	5.77	13.04	3.79	10.33	12.6	3.91	9.57	12.41	1.81	7.43
Beryllium	12.8	3.43	7.78	12.41	3.27	4.82	13.22	3.79	9.73	12.32	2.89	6.68	12.39	2.85	4.38
Cadmium	12.55	3.43	8.68	12.15	3.27	5.29	12.83	3.79	8.80	12.32	2.89	6.78	12.66	2.85	4.31
Cobalt	12.23	3.43	8.25	12.15	3.27	5.46	12.88	3.79	9.00	12.6	2.89	7.58	9.26	2.85	4.33
Chromium	12.55	3.43	9.07	12.28	3.27	5.53	13	3.79	10.32	12.66	2.89	8.76	12.46	2.67	5.22
Copper	12.43	3.43	8.61	12.15	3.27	5.30	13.05	3.79	9.95	12.86	2.89	8.31	12.74	2.85	4.31
Nickel	12.86	3.43	8.60	12.07	3.27	5.04	13	3.79	9.93	12.64	2.89	8.13	9.01	2.85	4.32
Lead	12.8	3.85	9.62	11.83	3.92	6.06	12.69	10.6	11.70	12.39	7.79	10.14	12.79	1.11	4.24
Antimony	12.8	4.84	9.34	12.81	3.68	7.03	13.05	7.68	10.69	12.86	5.38	9.14	12.55	1.08	7.67
Selenium	12.54	3.85	8.82	12.21	3.27	7.59	12.68	8.84	10.90	11.83	2.89	8.60	12.39	1.09	7.59
Zinc	12.67	3.43	8.81	11.65	3.27	4.89	12.83	3.79	10.15	12.74	2.89	8.50	12.55	1.05	5.97
Iron	12.59	3.43	8.64	10.62	3.27	4.57	13	3.79	10.08	12.49	2.89	8.53	12.54	0.93	5.20



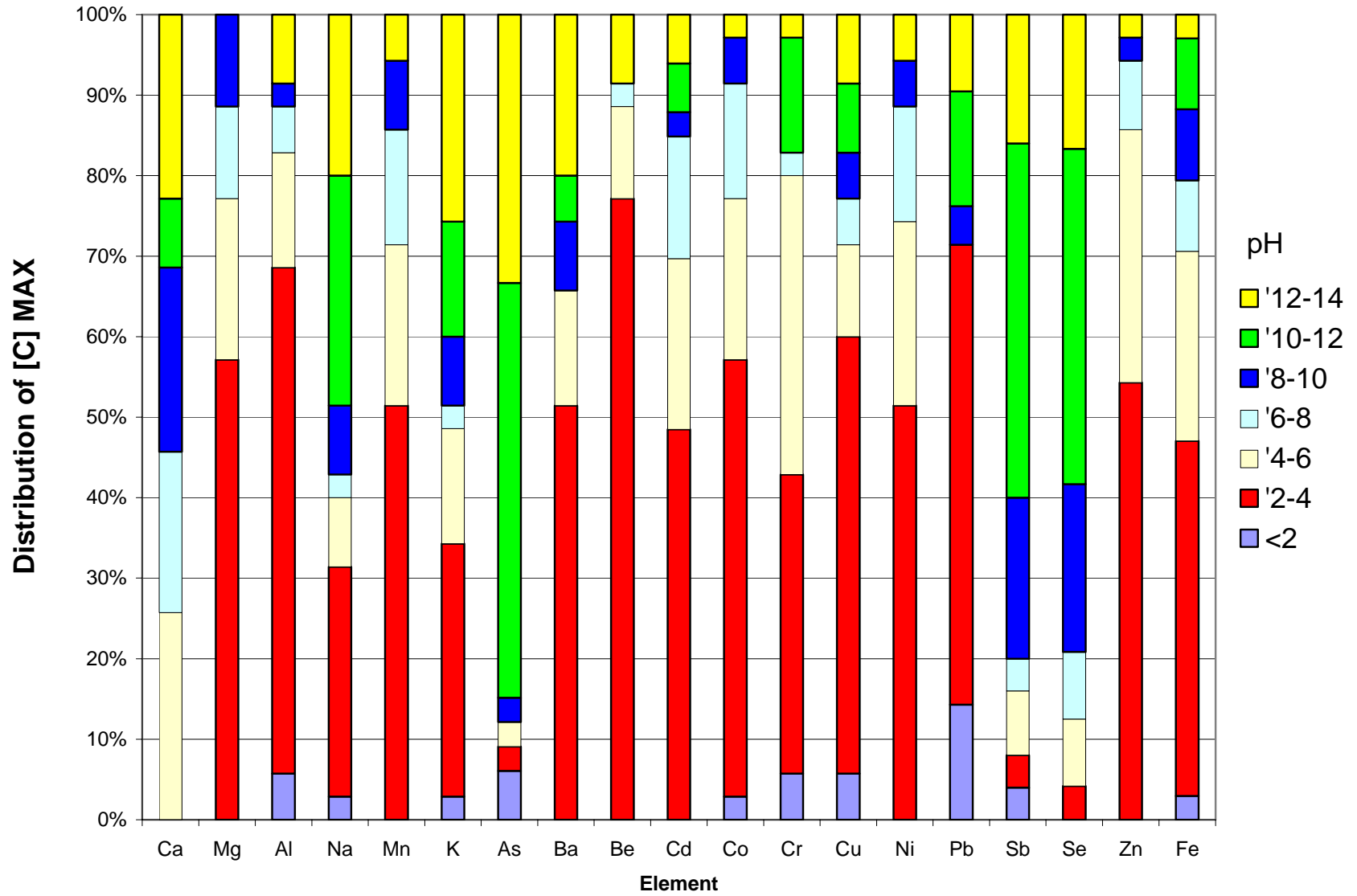


Figure 1. Distribution of [C]MAX values as a function of pH for all samples in all leachants.

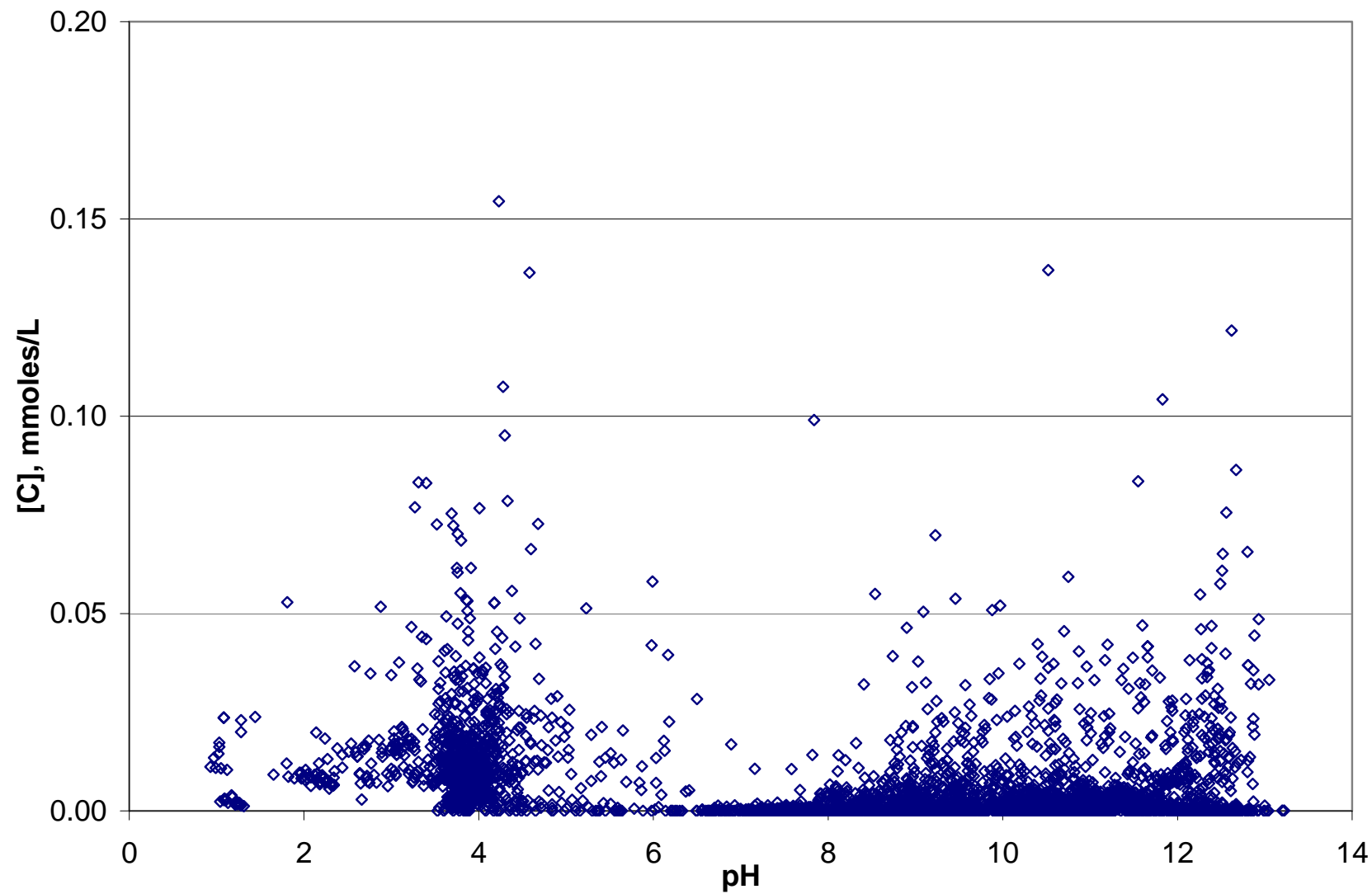


Figure 2. Distribution of measured concentration values for Cr as a function of pH.

