

**U.S. DEPARTMENT OF THE INTERIOR**

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**Acetic acid leachability of lead from clinoptilolite-rich rocks  
that extracted heavy metals from polluted drainage water  
in Colorado**

**by**

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## ABSTRACT

Lead removed from heavy-metal-polluted drainage (HMPD) water in Colorado by both raw and Na-exchanged clinoptilolite-rich rocks (CRRs) in 1993 and 1994, respectively, was exposed to acetic acid solutions to examine leachability or mobility of Pb. In tests of 44 CRR samples that contained between 40 and 835 parts per million (ppm) of total Pb extracted from HMPD water with 0.03-0.3 mg/L of Pb, no significant amounts of Pb could be extracted by glacial acetic acid solutions with pH of 2.7 or 2.4 during 118-120 hour tests using powdered CRRs (100% <0.2 mm) in a rock:solution weight ratio of 1:10.

Analysis of 17 acetic acid leachate solutions after exposure to powdered CRRs with 50-835 ppm of Pb showed Pb leachate concentrations of <0.1 to 2.1 mg/L; the highest amount is less than half the amount allowed by the Toxicity Characteristic Leaching Procedure of the U.S. Environmental Protection Agency (1990, EPA Method 1311) to deem the material as "hazardous waste."

## INTRODUCTION

This study was done chiefly to evaluate the potential use of clinoptilolite-rich rocks (CRRs) for sequestration of lead extracted from lead-polluted water. Because of the preferential affinity of many CRRs for Pb, rather than other cations, they can capture between about 5 to 8 parts per million (ppm) per day from flowing acidic (pH = 4.1-4.4) heavy-metal-polluted drainage (HMPD) water containing only 0.03 mg/L of dissolved Pb (Desborough, 1994, p. 9). In HMPD water (pH = 4.3-4.9) with 0.3 mg/L of Pb, five CRRs tested captured about 85-130 ppm of Pb per day for 6 days (Desborough, 1994, p. 7); Pb was removed by CRRs from HMPD water in the pH range of about 4-8.

If CRRs can capture significant amounts of Pb from Pb-polluted drainage water, industrial waste water, or soils that contain dissolved Pb, can they retain all of the captured Pb without release to solutes such as glacial acetic acid (pH = 2.88), so that U.S. Environmental Protection Agency leachate standards are met for the Toxicity Characteristic Leaching Procedure (TCLP) regarding Pb (U.S. Environmental Protection Agency, Federal Register, 1990, v. 55, no. 61, p. 11862, table 1)? The maximum concentration of Pb allowed in the leachate solution is <5 mg/L, where 100 grams of solids (<1 cm diameter) containing Pb are exposed to 1 L of the acetic acid solution of pH = 2.88 during 24 h of continuous end-over-end rotation of the extraction vessel at 30 rpm. Thus, the solid being tested could lose up to 49 ppm of Pb to the acetic acid extract solution before being classified as "hazardous waste," because the ratio of the solid:leachate is 1:10.

Because the size of the CRR samples tested for heavy-metal extraction in HMPD water was only 25 grams, it was not possible to attempt duplication of the EPA TCLP test in the laboratory. Thus, modified methods were used in an attempt to evaluate removal of Pb from 44 samples of CRR that removed between 40 and 835 ppm of Pb from HMPD water in 1993 and 1994.

The CRRs used for this study are from seven deposits in the western United States as listed in table 1 with the abbreviations used for each. Chemical and mineralogical data for all of them were given by Desborough (1994); chemical and mineralogical data for some of them were also given by Sheppard and Gude (1982).

Table 1.—Locality data and abbreviations for clinoptilolite-rich rocks used for the present study

Locality	Abbreviation
Alamito Creek, Texas	ACT
Buckhorn, New Mexico	BNM
Crisman Hill, Idaho	CHI
Fort LaClede, Wyoming	FLW
South Dakota	SD1, SDA, SDC
Tilden, Texas	TT
Castle Creek, Idaho	XYI

## METHODS

Mean values of initial Pb concentrations were obtained using three samples from five grams of dry, powdered CRRs that were previously exposed to Pb-bearing HMPD water. These were nondestructively analyzed for Pb, Cu, and Zn using energy-dispersive X-ray fluorescence with a Li-drifted Si detector with a  $\text{Cd}^{109}$  radioisotope source and the computer program of Yager and Quick (1992). From the five grams analyzed, four grams were weighed and added to 40 ml acetic acid solutions ( $\text{pH} = 2.4$  or  $2.7$ ) for 118-120 hours in 50 ml sealed plastic containers; the pH of each solution was measured once during the first hour of exposure, and daily thereafter. Each sample was agitated manually once each day. At the end of the test period, each CRR sample was caught on filters, rinsed with 100 ml of warm water to remove dissolved salts, and dried prior to nondestructive analysis described above. For 17 experiments, 20 ml extracts obtained for quantitative Pb analysis were each filtered through separate disposable 0.8 micron cellulose acetate filters prior to acidifying the solution with two drops of concentrated  $\text{HNO}_3$  prior to refrigeration. Reagent water has  $<0.1$  mg/L of Pb. All of the analyses, reagent preparations, and experiments reported here were done in October and November 1994.

## RESULTS

Table 2 gives the initial and final concentrations of Pb, Zn, and Cu in the CRRs exposed to acetic acid solutions of  $\text{pH} = 2.4$  and  $2.7$ , respectively; the final pH of each acetic acid solution is also given. No significant amounts of Pb were lost by any of the CRRs in the four sets of tests. Concentrations of Pb in the leachate for 12 tests of sets 1 and 2 show 0.2 mg/L or less of Pb. Some Zn was lost by all of the CRRs, but the acetic acid solutions of  $\text{pH} = 2.4$  extracted much more Zn from CRRs than the acetic acid solutions of  $\text{pH} = 2.7$ . Nearly half of the Cu in the CRRs was extracted by the  $\text{pH} = 2.4$  acetic acid solutions, but only a minor amount was lost by some CRRs for solutions of  $\text{pH} = 2.7$ . Figure 1 shows the immobility of Pb for the six CRRs exposed to  $\text{pH} = 2.4$  solutions for 120 hours. Even if the apparent loss of 10 ppm is actual for XYI (fig. 1, table 2), the amount in solution would only be 1 mg/L; the leachate data show the amount lost was 2 ppm.

Table 2.—Initial and final concentrations of lead, zinc, and copper in clinoptilolite-rich rocks exposed to acetic acid solutions of pH 2.4 and 2.7, respectively

[Concentrations of lead in 12 leachate solutions are reported. The final pH of each acetic acid solution is also given; i = initial, f = final. Concentrations of lead in the leachate solutions were determined using atomic absorption spectroscopy by Skyline Laboratories, Inc., Wheat Ridge, Colo.; n.d. = not determined]

CRR	Pbi	Pbf	Zni	Znf	Cui	Cuf	pHf	Pb, leachate mg/L
-----parts per million-----								
Set 1. Na-exchanged CRRs previously exposed to Rawley tunnel water, 7/5/94-7/10/94, 4.0 g in 40 ml pH = 2.4								
ACT	80	85	1,760	1,380	600	310	3.9	0.2
BNM	135	130	1,960	1,420	700	365	3.8	0.1
CHI	55	50	1,920	1,230	710	355	3.7	0.1
FLW	100	95	2,410	2,100	570	390	3.8	0.1
SDA	75	70	2,230	1,530	1,080	510	3.9	0.1
XYI	210	200	1,480	995	1,920	980	3.7	0.2
Set 2. Na-exchanged CRRs previously exposed to Wellington drain water, 7/14/94-7/28/94, 4.0 g in 40 ml pH = 2.4								
ACT	60	70	3,310	2,440	< 10		3.6	0.1
BNM	50	65	3,480	2,400	< 10		3.7	< 0.1
CHI	50	60	3,780	2,380	< 10		3.6	0.1
FLW	85	105	4,240	3,600	< 10		3.7	< 0.1
SDA	85	95	4,070	2,900	< 10		3.7	0.1
XYI	120	135	3,220	2,310	< 10		3.6	0.1
Set 3. Na-exchanged CRRs previously exposed to Rawley tunnel water, 7/5/94-7/10/94, 4.0 g in 40 ml pH = 2.7								
ACT	70	90	1,865	1,850	595	545	4.4	n.d.
BNM	105	110	1,960	1,840	635	565	4.6	n.d.
CHI	75	80	1,840	1,750	790	720	4.1	n.d.
FLW	80	85	2,560	2,500	590	610	4.5	n.d.
SDA	75	95	2,230	2,160	1,160	1,210	5.9	n.d.
XYI	190	195	1,460	1,380	1,900	1,745	4.4	n.d.
Set 4. Na-exchanged CRRs previously exposed to Wellington drain water, 7/14/94-7/28/94, 4.0 g in 40 ml pH = 2.7								
ACT	65	80	3,065	2,820	< 20		4.9	n.d.
BNM	40	40	3,140	2,900	< 10		5.0	n.d.
CHI	60	65	3,180	2,770	< 10		4.7	n.d.
FLW	90	105	4,200	4,090	< 10		4.9	n.d.
SDA	95	120	4,160	3,940	< 10		5.3	n.d.
XYI	105	120	3,080	2,850	< 10		4.9	n.d.

Table 3 gives the initial and final concentrations of Pb, Zn, and Cu in the CRRs exposed to acetic acid solutions of pH = 2.7. For all of these CRRs, Pb losses were small. Lead concentrations in the leachate for the CRRs with the most Pb range from <0.1 to 2.1 mg/L (table 3). Zn and Cu losses occurred for most samples. Figure 2 shows the immobility of Pb for the CRRs exposed to acetic acid solutions of pH = 2.7 for 120 hours. Data for Pb that are slightly higher in the CRR final concentrations than in the initial concentrations reflect the relatively poor precision of the analytical method for Pb.

Figure 3 shows the rapid H<sup>+</sup> capture from the acetic acid solutions by six CRRs (table 2, set 4). Figure 4 shows the rapid H<sup>+</sup> capture from the acetic acid solutions by five CRRs (table 3, set 5).

The retention of Pb by CRRs, as compared to their lesser retention of Cu and Zn in the acetic acid solutions, can be attributed chiefly to three factors. The most important of these is the CRR preference for Pb over Zn and Cu (Desborough, 1994). A second factor is the strong H<sup>+</sup> affinity of CRRs that raises the solution pH from 2.7 to a minimum of 3.3 (fig. 4) which leads to Pb insolubility. The third factor is that the acetic acid solutions may become saturated with respect to cations such as Zn, Cu, and Ca or other cations exchanged out of the CRRs upon exposure to the fixed volume of acetic acid solution.

## **PRIOR STUDIES OF LEAD CAPTURE BY CLINOPTILOLITE-RICH ROCKS**

There have been several studies of ion-exchange capture of Pb by natural clinoptilolites (Semmens and Seyfarth, 1976; Loizidou and Townsend, 1987; Zamzow and others, 1989; Maliou and others, 1992; Kesraoui-Ouki and others, 1993). Most of the Pb-exchange studies examined capacity and heavy-metal preferences of CRRs; some also examined the effect of competing common cations such as Na<sup>+</sup>, Ca<sup>2+</sup>, and NH<sub>4</sub><sup>+</sup> (Zamzow and others, 1989). None of these studies were based on field conditions of Pb capture by CRRs in the presence of competing cations. Semmens and Seyfarth (1976) demonstrated that there was poor reversibility of exchange of captured Pb and Zn using NaNO<sub>3</sub> at a pH of 4.5, but most investigators have not examined the extractability of Pb captured by CRRs. Except for the studies of Zamzow and others (1989), all prior studies of Pb capture by CRRs used "synthetic wastewater." While the preferential capture of Pb by CRRs is well documented, what does one do with the CRR-captured Pb?

## **SUMMARY AND IMPLICATIONS**

CRRs can capture significant amounts of Pb from water with Pb concentrations as low as 0.1 mg/L, as demonstrated by field studies in heavy-metal-polluted drainage waters of Colorado. The drainage waters had a wide range in pH and a wide range in the concentrations of competing cations such as calcium and heavy metals.

This study of the acetic acid extractability of Pb from CRRs that captured Pb from chemically complex polluted water at temperatures of <16°C was done to see if it is feasible to use CRRs for Pb removal from industrial waste water and then to dispose of the Pb-bearing CRR as a nonhazardous waste. This preliminary study suggests that this application might be possible. In addition, it seems possible that soils or other media with soluble Pb might be treated for Pb-pollution remediation using CRRs.

Table 3.—Initial and final concentrations of lead, zinc, and copper in clinoptilolite-rich rocks exposed to acetic acid solutions of pH = 2.7

[Concentrations of lead in five leachate solutions are reported. The final pH of each acetic acid solution is also given; i = initial, f = final. Concentrations of lead in five leachate solutions were determined using atomic absorption spectroscopy by Skyline Laboratories, Inc., Wheat Ridge, Colo.; n.d. = not determined]

CRR	Pbi	Pbf	Zni	Znf	Cui	Cuf	pHf	Pb, leachate mg/L
-----parts per million-----								
Set 5. Raw CRRs previously exposed to upper California Gulch water, 6/4/93-6/13/93, 4.0 g in 40 ml pH = 2.7								
FLW	490	515	965	925	15	< 10	3.5	n.d.
SD1	435	425	575	320	25	35	4.1	n.d.
SDA	430	445	750	545	45	< 10	4.0	n.d.
SDC	425	470	640	470	75	15	3.8	n.d.
TT	385	400	345	295	< 10	< 10	3.4	n.d.
Set 6. Raw CRRs previously exposed to lower California Gulch water, 6/4/93-6/13/93, 4.0 g in 40 ml pH = 2.7								
FLW	550	590	1,310	1,320	< 10	< 10	3.5	< 0.1
SD1	565	580	860	575	40	45	3.9	1.4
SDA	835	825	1,110	715	35	< 10	4.1	2.1
SDC	770	785	920	620	20	20	3.7	1.2
TT	525	530	540	465	< 10	< 10	3.3	0.3
Set 7. Raw CRRs previously exposed to Rawley tunnel water, 6/17/93-7/15/93, 4.0 g in 40 ml pH = 2.7								
FLW	250	275	2,740	2,550	480	390	3.5	n.d.
SD1	315	335	1,460	935	1120	720	3.8	n.d.
SDA	270	290	2,100	1,510	845	545	3.8	n.d.
SDC	275	270	1,840	1,300	610	465	3.5	n.d.
TT	275	275	1,340	1,180	310	165	3.3	n.d.
Set 8. Raw CRRs previously exposed to Wellington drain water, 6/4/93-6/13/93, 4.0 g in 40 ml pH = 2.7								
FLW	95	110	3,460	3,260	< 10		3.4	n.d.
SD1	145	160	2,660	1,640	< 10		3.9	n.d.
SDA	180	190	3,060	2,140	< 10		3.7	n.d.
SDC	120	125	2,610	1,820	< 10		3.6	n.d.
TT	80	85	2,020	1,580	< 10		3.3	n.d.

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Pb in clinoptilolite-rich rocks before  
and after acetic acid, pH=2.4

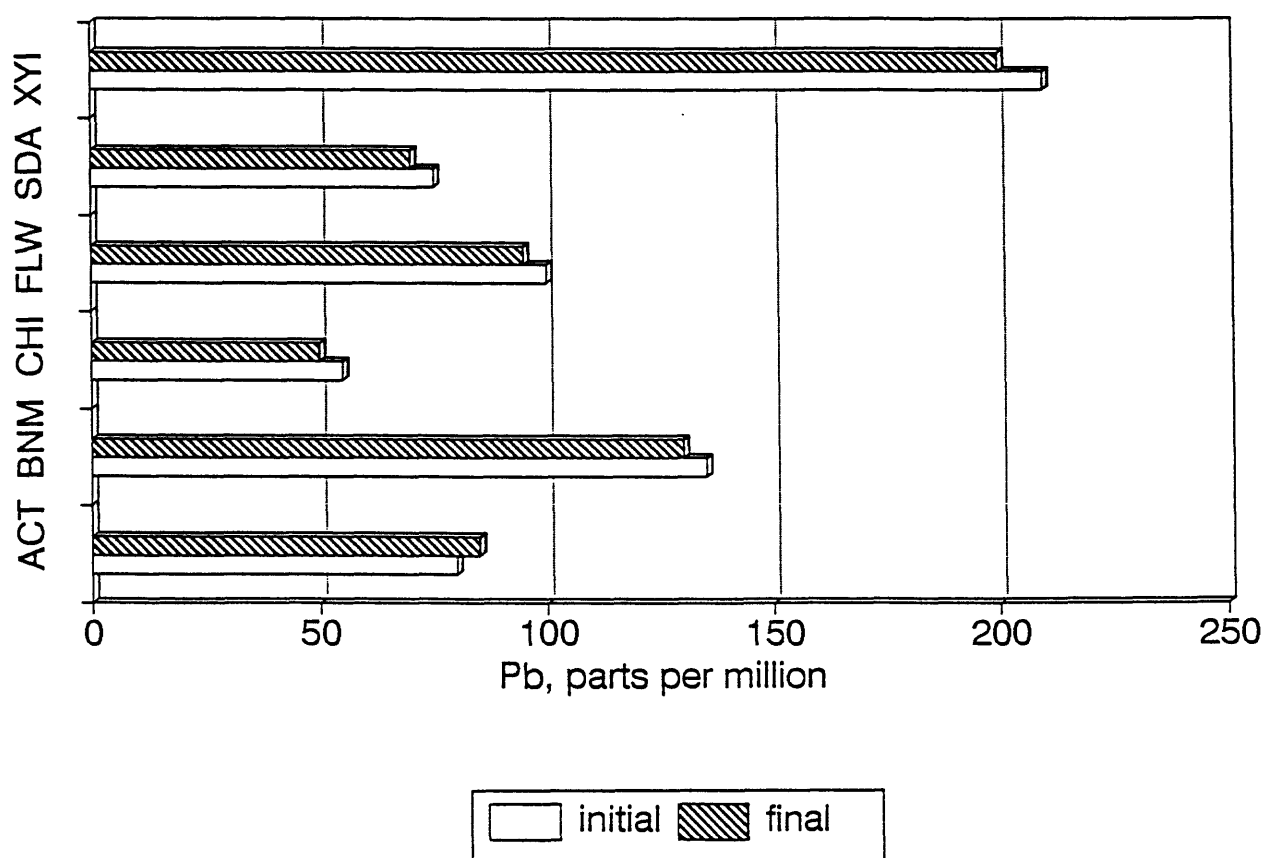


Figure 1.—Initial and final concentrations of Pb in six clinoptilolite-rich rocks exposed to pH = 2.4 acetic acid solution for 120 hours. (Set 1, table 2)

Pb in clinoptilolite-rich rocks before  
and after acetic acid, pH=2.7

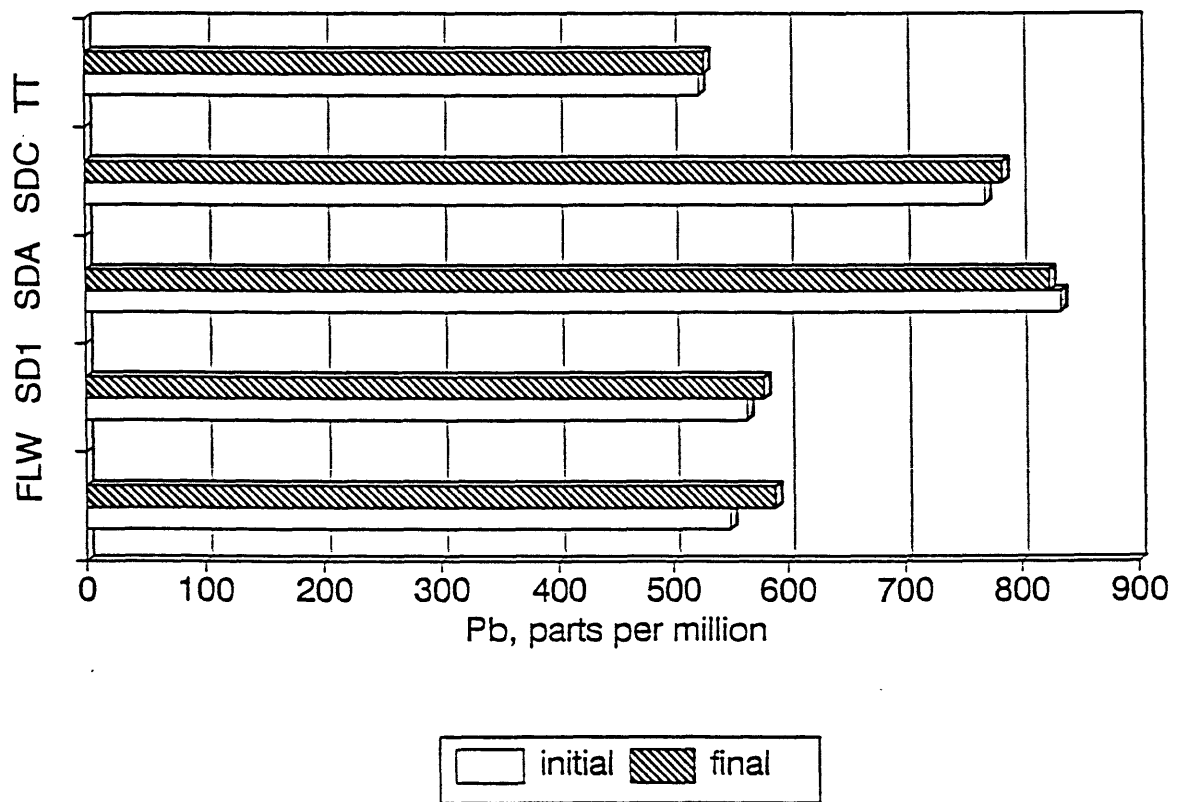


Figure 2.—Initial and final concentrations of Pb in five clinoptilolite-rich rocks exposed to pH = 2.7 acetic acid solution for 120 hours. (Set 6, table 3)

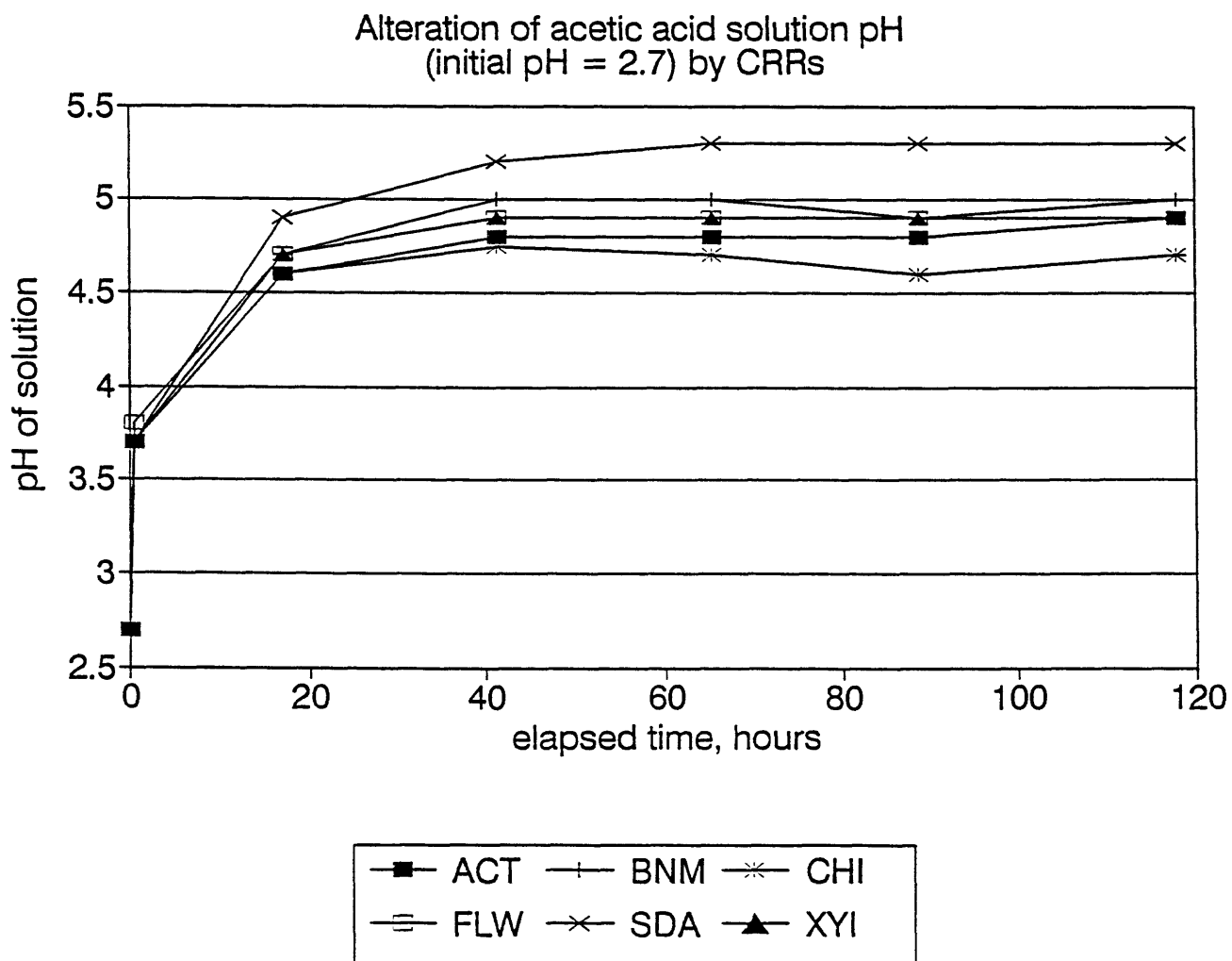


Figure 3.—Relations of initial acetic acid solution pH = 2.7 to the clinoptilolite-rich rocks (CRRs) pH alteration of the solution during exposure for 118 hours. (Set 4, table 2)

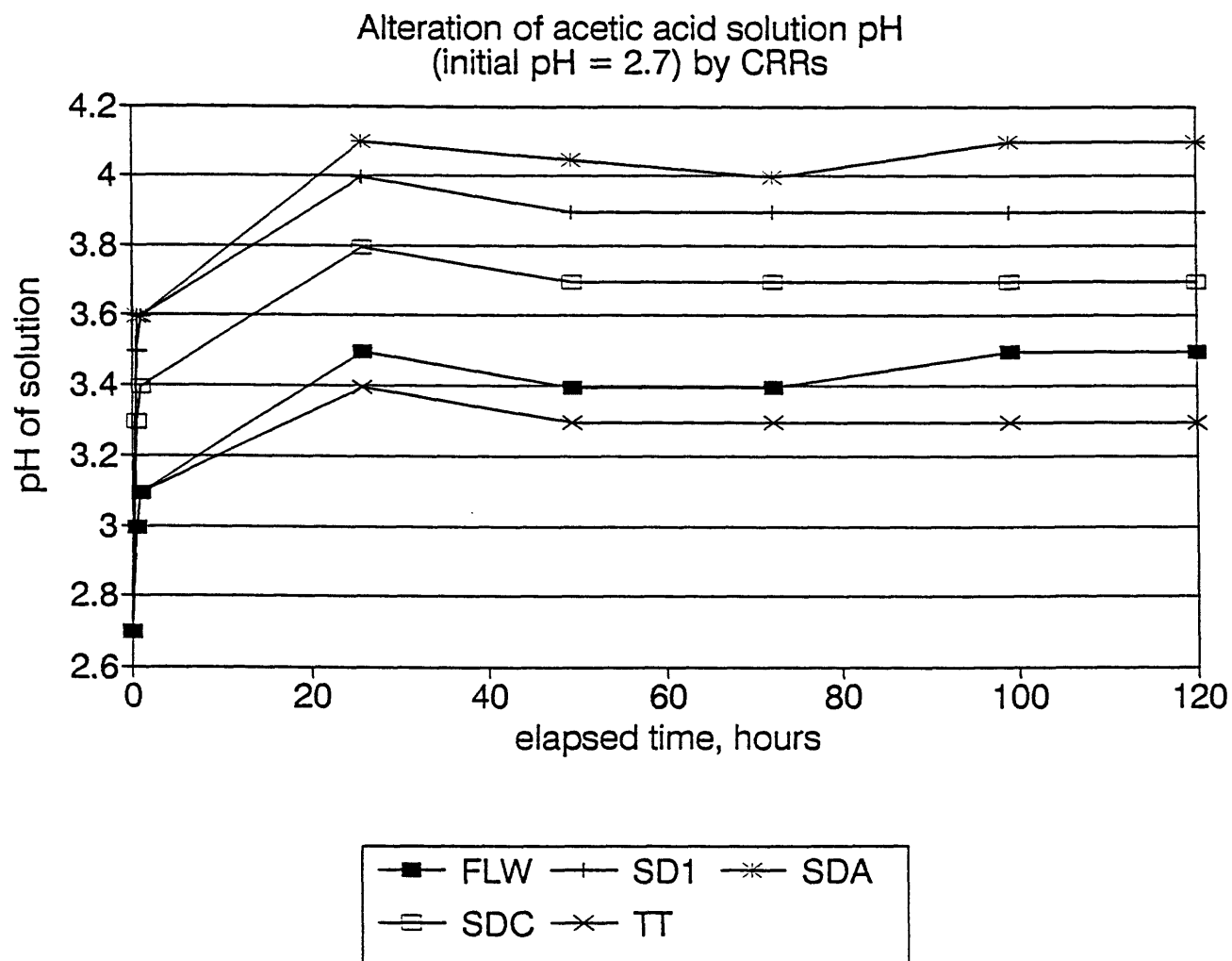


Figure 4.—Relations of initial acetic acid solution pH = 2.7 to the clinoptilolite-rich rocks (CRRs) pH alteration of the solution during exposure for 118 hours. (Set 5, table 3)