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Ion-exchange of clinoptilolite-rich rocks in Argo drain water at Idaho Springs, Colorado, and related experimental aspects

by

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ION-EXCHANGE OF CLINOPTILOLITE-RICH ROCKS IN ARGO DRAIN WATER AT IDAHO SPRINGS, COLORADO, AND RELATED EXPERIMENTAL ASPECTS

By George A. Desborough

Abstract

Clinoptilolite-rich rock (CRR) samples from six deposits were exposed to the Argo tunnel acid-rock drainage (ARD) at Idaho Springs, Colorado, to evaluate metal and nonmetal exchange capacity (cation capture or release). Sodium-rich, calcium-rich, calcium- and potassium-rich, and mixed-cation CRR samples were used in both field and related laboratory studies. Raw, sodium-exchanged, and H^+-exchanged CRR samples were studied. For raw CRR samples, copper capture ranged from 0 to 220 parts per million (ppm), and zinc ranged from 70 to 1,300 ppm for a 10-day exposure. Na-rich Fort LaClede, Wyo., CRR had the highest metal capture, and the Ca-rich CRR from Buckhorn, N. Mex., Castle Creek, Idaho, and the St. Cloud mine, N. Mex., had the lowest metal capture. Raw Tilden, Tex., and South Dakota CRR samples had intermediate capture of copper and zinc. Na-exchange of CRR significantly enhanced copper and zinc capture for the Ca-rich Buckhorn, N. Mex., Castle Creek, Idaho, and the St. Cloud mine, N. Mex., samples; however, the metal capture of these Na-exchanged CRR samples was no better than the raw Ft. LaClede, Wyo., the three raw South Dakota samples, and the raw Tilden, Tex., CRR.

For the raw Na-rich CRR in the Argo ARD, both potassium and calcium were captured from the water; this Na-rich CRR also captured more Cu and Zn than the other CRR samples. Three raw Ca-rich CRR samples captured less than one-fourth to one-half of the copper and zinc than the other three raw CRR samples. Extensive capture of calcium from metal-rich ARD is deleterious because it lowers the hardness of the water. On the other hand, those CRR samples that contribute calcium to the metal-rich water are beneficial because they increase the hardness of the water.

Laboratory exposure of most of these CRR samples to highly acidic—pH = 1.5—HCl solutions for 24 hours at 38°C did not result in significant degradation of clinoptilolite. Virtually all natural heavy-metal-rich ARD have a pH greater than 2, and most of them in Colorado range from 2.5 to 8.

Prior to this study, I thought that the heavy-metal capture of divalent copper, zinc, and lead might be related to calcium displacement from clinoptilolite in ARD. This cannot be proved from the information presented here. Copper + zinc + lead capture has some correlation with calcium + potassium loss of ARD-exposed South Dakota CRR that was studied last year. This present study shows that for some CRR, H^+ may interfere with heavy-metal capture as much as calcium.

This study of CRR exposed to a single ARD shows that the capture of heavy metals by CRR presently cannot be predicted for other ARD in the absence of adequate chemical data for dissolved heavy metals and nonmetallic cations such as calcium, potassium, sodium, strontium, and barium.

Introduction

This work was done to determine: (1) the ability of several clinoptilolite-rich rock (CRR) samples from the Western United States to capture heavy metals from the Argo acid-rock drainage (ARD), (2) the relations, if any, of heavy-metal capture (Cu and Zn) to nonmetal cation exchange by CRR in the Argo ARD, (3) the stability or degradation of clinoptilolite in solutions with low pH, (4) the effects of pre-treatment, including acidulation (acid exposure) and Na-exchange, on heavy-metal capture, (5) the response and stability of CRR to cyclical exposures to low pH (1.5 and 3) alternating with Na-exchange in saturated NaCl solutions, and (6) the influence of different water:rock ratios in acidic and Na-exchange laboratory experiments with CRR samples from six localities.

Composition and Mineralogy of CRR Samples

Natural clinoptilolite is a hydrated aluminosilicate mineral with calcium, sodium, and potassium as major cations. These cations are present in different relative abundances in CRR of the Western United States (Sheppard and Gude, 1982, table 3). Most CRR samples may contain minor amounts of other minerals such as mica (illite), opal, quartz, potassium feldspar, plagioclase, calcite, or other zeolites (Sheppard and Gude, 1982, table 2). Consequently, the bulk chemical composition of CRR does not necessarily indicate the chemical composition of the clinoptilolite in the rock. Because most CRR samples are very fine grained (<10 micrometers), both X-ray diffraction (XRD) analysis and cation-exchange experiments aid in estimating the major cations in clinoptilolite and the major dilutant minerals.

Opal is a significant dilutant in some CRR samples, but the XRD intensity of the most intense opal peak is not proportional to the opal concentration. The intensities of clinoptilolite XRD peaks in CRR are not necessarily proportional to the clinoptilolite concentration because of the different X-ray scattering factors of the major cations (Ca, Na, and K) that are present in different amounts in each clinoptilolite of CRR.

The bulk concentrations of certain major and minor elements in the CRR samples tested in this study are given in table 1. Some of the differences in the values reported in the present study and those reported by the corporations are most likely due to differences in the analyzed samples, reflecting inhomogeneity of samples from each CRR deposit. For the first value of each CRR reported in table 1, three separate fractions from the fine (1.7-4.7 mm) sieve fraction were analyzed and averaged for all elements reported. The corporation-reported values are from their provided specifications.

For the Fort LaClede deposit, two separate beds were sampled: a pale-green bed (FLG) and a white bed (FLW). Initially, each was tested separately. Subsequently, the two were mixed in equal proportions for testing and designated FL.

In addition to the CRR samples from the six localities, six samples of CRR from the same South Dakota locality, but from different stratigraphic intervals, were tested because all have a similar, but not identical, composition (table 1).

Because of intrinsic sample inhomogeneity problems and ARD-sample interaction aspects of side-by-side samples in the Argo ARD, attention was directed to possibly significant differences in results between tests. For these reasons, some field tests of the same samples were duplicated for quality control.

Analytical Methods

The analytical methods used for this study of CRR were energy-dispersive methods that included those used by Desborough (1992), except that Ca and K were analyzed separately with an Fe^{55} radioisotope source using standards of known Ca and K. Barium concentrations were determined with an Am^{141} radioisotope source and the Superxap program of Yager and Quick (1992). For all of these analyses, about 1 g of finely powdered sample was exposed to the radioisotope X-ray emitter. For 20-g samples, three fractions were analyzed and the results were averaged. For 5- and 10-g samples, two fractions were analyzed and the results were averaged. The precision for Ca and K is about ±0.1 weight percent; the analyses for the other elements reported are within about 10-20 percent of the amount reported for values above about 100 ppm. All pH measurements were made using a digital temperature-corrected instrument.

Table 1.—*Concentrations of certain elements in raw clinoptilolite-rich rocks from six deposits*

[n.a., not analyzed; n.r., not reported]

Locality	Fe	Ca	Na	K	Cu	Zn	As	Pb	Rb	Sr	Ba
	ppm × 10^3				ppm						
Tilden, Tex.	0.6	1.6	n.a.	1.9	20	60	<10	<40	70	780	1,450
Corp. reports	0.6	1.7	n.r.	1.4							
Ft. LaClede, Wyo.											
white bed	0.6	1.3	n.a.	1.5	20	80	<10	<40	80	345	1,100
green bed	1.0	1.2	n.a.	1.3	20	70	<10	<40	90	370	1,270
Corp. reports	1.4	1.1	3.5	1.6						300	
Buckhorn, N. Mex.	1.0	2.7	n.a.	1.1	20	60	<10	<40	40	575	2,450
South Dakota, 1	2.0	3.3	n.a.	3.7	20	100	<10	<40	120	325	1,150
St. Cloud, N. Mex.	0.9	2.7	n.a.	1.9	20	70	<10	<40	80	1,700	1,030
Corp. reports	0.5	0.5	0.6	3.2							
Castle Cr., Idaho	1.5	2.5	n.a.	1.4	20	110	<10	<40	85	135	735
South Dakota Group, samples from different intervals, same locality											
SDA	1.7	2.8	n.a.	3.7	20	100	<10	<40	110	355	835
SDB	2.0	3.1	n.a.	3.8	20	100	<10	<40	110	365	1,500
SDC	2.0	1.9	n.a.	3.7	20	60	<10	<40	120	355	1,020
SDD	2.1	3.2	n.a.	4.1	20	100	<10	<40	120	360	1,400
SD91-1	1.3	2.0	n.a.	3.4	20	60	<10	<40	85	610	1,100
SD91-3	1.5	2.1	n.a.	3.6	20	60	<10	<40	100	350	1,550

Ion-Exchange of Certain Elements in Raw CRR in Argo Tunnel ARD

A preliminary study of ion-exchange capture of copper, lead, and zinc in eight ARD's of Colorado was done in 1992 using K-rich, clinoptilolite-rich rock (CRR) from South Dakota (Desborough, 1992). Since that study, CRR samples from five other localities have been acquired and tested for ion-exchange reactions in the Argo ARD at Idaho Springs, Colo. Water in this ARD contains about 4.5 milligrams per liter (mg/l) of copper and about 30 mg/l of zinc, and it has a pH of about 3 (Ficklin and others, 1992; Plumlee and others, in press). Other data show about 6 mg/l of copper and about 50 mg/l of zinc (Williams, 1988). The water temperature is in the range of about 14°C to 18°C for the study period of July 1992 through March 1993, and the water flow rate is fast. Agglomeration or precipitation of hydrous ferric oxides (HFO) and sulfate through the drainage is extreme because of the high iron and sulfate content of the water (Ficklin and others, 1992). Because the HFO agglomeration or precipitation accumulates on any solid substrate in the ARD, immersion periods of most CRR samples were less than 10 days. Initially, 50-cc cylindrical plastic containers were used, each with vertical slits (0.5 mm wide). These narrow slits were filled with HFO in about 10-14 days, and ARD-CRR interaction was impeded or arrested. Nylon-mesh bags with 2×3-mm openings were subsequently used to improve ARD-CRR sample interactions. This met with some success, but experiments longer than about 14 days had problems with HFO agglomeration coating the bags. Thus, most of the Argo ARD CRR data reported here are for 10 days or less.

Table 2 gives the net gains and losses for certain elements after exposure of raw CRR to the Argo ARD for three different time periods, three different containers, and two different grain sizes. Because of sample availability (or not), different samples were used for several of the experiments.

Copper capture mostly varies by a factor of two or more between the best and poorest performing CRR. It ranges from 0 for Buckhorn and the St. Cloud mine CRR samples to 220 ppm for the Ft. LaClede green bed (table 2).

Zinc capture varies widely from less than 90 ppm for the Buckhorn, St. Cloud mine, and the Castle Creek CRR samples to as much as 1,300 ppm for the Ft. LaClede green bed (table 2).

It is clear that the three Ca-rich CRR samples had a poor response for copper and zinc capture in the Argo ARD (tables 1, 2). The K- and Ca-rich raw South Dakota CRR samples and the intermediate (K, Ca, and Na) Tilden CRR sample have combined copper plus zinc capture in the range of about 450 to 800 ppm. The raw Na-rich Fort LaClede (mixed green and white beds) captured about 1,100 ppm of combined copper and zinc, and it also captured significant calcium and minor potassium (table 2).

The relationships of net gain of copper and zinc to the net changes of the nonmetallic ions (Ca, K, Sr, and Ba) for raw CRR in the Argo ARD (table 2) were graphed (not shown) in order to evaluate correlations between net metal gains and nonmetallic gains or losses. The several percent (<10) of calcite in the South Dakota (SD) samples could amount to a maximum of only 0.05 weight percent (500 ppm) of the Ca in these CRR samples. Thus, Ca losses or gains greater than about 0.1 weight percent are due to cation exchange. Graphs (not shown) of Cu and Zn gains versus the losses or gains of Ca and K do not prove that Cu and Zn occupy Ca or K sites. The 775 ppm Cu + Zn capture by SD4C without detectable (±0.1 wt. %) loss of Ca or K (SD4C, table 2) for the K- and Ca-rich SD sample does not necessarily indicate that Cu and Zn do or do not occupy Ca or K sites. The uncertainty of 0.1 weight percent Ca is equivalent to 1,630 ppm of Zn (because of the atomic weight difference).

Both Cu and Zn gains correlate positively with Sr gain. There is no correlation between the gains of Cu and Zn with the changes in Ba content of CRR.

The large gains of Ca (0.9-1.3 wt. %) by the Fort LaClede sample are the only Ca gains observed among all the CRR samples tested in Argo ARD.

The concentrations of certain elements in the Argo ARD reported by Williams (1988) are given as follows, in mg/l:

Ca	Na	K	Cu	Zn	Sr	Ba
327	22	3.4	5.7	48	1.6	0.2

The concentrations of Ca, Na, K, and Sr in the Argo ARD are an order of magnitude higher than some metal-rich ARD's in Colorado (Wetherbee and others, 1991; Smith and others, 1991). For instance, Smith and others (1991) reported the following values for the upper St. Kevin Gulch site near Leadville (mg/l):

Ca	Na	K	Cu	Zn	Sr	Ba
20	4	0.5	0.3	15	0.05	0.04

For this site, Desborough (1992) reported twice the Zn capture by South Dakota CRR in 7 days than that captured by South Dakota CRR in the Argo ARD, even though the Zn content of the St. Kevin Gulch ARD is less than half of that of the Argo ARD.

Zamzow and others (1989, table 9) observed in laboratory experiments that, for Ca at dissolved concentrations above about 60 mg/l, there are interferences with Zn ion-exchange for CRR. Na concentrations of about 700 mg/l also interfere with Zn capture. They reported that Ca concentrations of 300 mg/l inhibit Cu capture, but Na concentrations of less than about 900 mg/l do not inhibit Cu capture by CRR. The effect of dissolved K was not reported. Such interferences of the high Ca concentrations with metal capture in Argo ARD may account for some of the results shown in table 2. However, there are significant and consistent differences in the behavior of each CRR sample from six localities with the Argo ARD (table 2).

A 3-month test (Sept.-Dec. 1992) was done for an 8×10×13-cm block of South Dakota CRR in the Argo ARD to determine penetration and long-term stability of metal capture. This block was contained in a nylon bag with 2x3-mm openings. Samples were extracted afterward by drilling into the block to 0.5-, 1-, and 1-2-cm depths. Results are as follows for the upper and lower side and 1-2-cm interior or middle of the block:

	Upper side			Lower side	
	Cu	Zn		Cu	Zn
			ppm		
Outer 0-0.5 cm	135	980		90	700
Outer 0-1 cm	50	525		25	550
Middle 1-2 cm	0	0		0	0

These results demonstrate that capture of Zn continued and is more than twice that of the 10-day test for crushed and sized material (table 2). However, the capture of Cu is essentially the same as for 10-day tests for crushed and sized material. In addition, the outer 0.5 cm was the major zone of water/rock interaction. The HFO agglomeration may have impeded water/rock interaction, but apparently it did not stop capture of Zn in the outer 0.5 cm of the block. A 1-month test of very fine (0.8-1.7 mm) South Dakota CRR in a plastic cylinder captured 135 ppm of Cu and 670 ppm of Zn, but the 0.5-mm-wide opening slits for water entry were plugged with HFO when this sample was removed.

Table 2.—*Net gains and losses (-) of certain elements for raw clinoptilolite-rich rock exposed to Argo tunnel drain at Idaho Springs, Colorado*

[plcyl = 50 cc plastic containers with 12 0.5-mm vertical slits; nylbg = 2×3-mm mesh nylon bags; pipe = 19-mm dia. i.d. PVC with 2×3-mm mesh nylon; n.d., not determined]

Locality	Time	Ca	K	Cu	Zn	Rb	Sr	Ba
	hrs.	× 10^3				ppm		
Container: plcyl		**Fine grain size** (1.4-4.7 mm)						
Tilden, Tex.	72	n.d.	n.d.	35	430	20	125	n.d.
Ft. LaClede, Wyo.-w*	72	n.d.	n.d.	135	790	25	145	n.d.
Buckhorn, N. Mex.	72	n.d.	n.d.	80	135	30	110	n.d.
South Dakota, 1	72	n.d.	n.d.	100	350	15	110	n.d.
Tilden, Tex.	168	n.d.	n.d.	35	480	0	30	n.d.
Ft. LaClede, Wyo.-w	168	n.d.	n.d.	130	920	20	130	n.d.
Buckhorn, N. Mex.	168	n.d.	n.d.	0	150	30	75	n.d.
South Dakota, 1	168	n.d.	n.d.	120	450	25	145	n.d.
Container: nylbg								
Tilden, Tex.	168	-0.7	0	55	520	20	115	n.d.
Ft. LaClede, Wyo.-w	168	1.2	0.2	75	880	25	160	n.d.
Buckhorn, N. Mex.	168	0	0	0	170	25	75	n.d.
South Dakota, 1	168	-1.4	0	100	430	25	140	n.d.
Tilden, Tex.	168	-0.1	-0.6	100	525	10	95	-280
Ft. LaClede, Wyo.-m*	168	1.3	0.1	160	945	20	145	-185
South Dakota, 1	168	-1.0	-0.2	105	460	0	125	-195
South Dakota, 4A	168	-0.6	-0.3	130	690	15	145	0
South Dakota, 4C	168	0	-0.3	190	625	10	135	-25
Castle Creek, Idaho	168	-0.2	-0.1	30	80	20	45	-50
Container: pipe								
Tilden, Tex.	240	-0.1	-0.2	55	475	10	100	n.d.
Ft. LaClede, Wyo.-w	240	1.3	0.2	120	1,030	15	170	n.d.
Ft. LaClede, Wyo.-g*	240	1.4	0.3	220	1,300	15	275	n.d.
Buckhorn, N. Mex.	240	0	0.4	25	145	25	125	n.d.
South Dakota, 1	240	-1.4	0	135	490	20	150	n.d.
St. Cloud mine, N. Mex.	240	-0.6	-0.2	0	70	0	0	n.d.
Container: nylbg		South Dakota Group						
SD4A	168	-0.6	-0.3	135	700	10	125	-20
SD4B	168	-1.0	-0.6	90	425	10	80	-655
SD4C	168	0	0	115	660	0	115	230
SD4D	168	-1.2	-0.4	120	420	15	75	-530
91-1	168	-0.1	-0.2	65	400	0	25	-55
91-3	168	-0.1	-0.5	90	590	10	100	-245
Container: pipe		**Coarse grain size** (4.7-12.7 mm)						
Tilden, Tex. - coarse not available								
Ft. LaClede, Wyo.-w	240	0.9	0.2	100	800	15	100	-200
Buckhorn, N. Mex.	240	-0.4	0	30	200	10	60	-250
South Dakota, 1	240	-1.5	-0.5	70	485	10	120	-250
St. Cloud mine, N. Mex.	240	-0.4	0	10	75	0	-50	-100

w*, white bed; g*, green bed; m*, 1:1 mix of white and green beds.

Calcium Removal from Raw CRR by Acidulation Before Exposure to ARD

I thought that removal of calcium from CRR prior to ARD exposure would enhance the exchange of copper and zinc because both are presumed to be divalent ions. Five 25-g CRR samples were treated in 100 ml of HCl solution (pH = 1.5) for 70 minutes at 38°C; samples were then rinsed and dried at 38°C. Five grams were removed from each for quantitative analysis; the remaining 20 g were placed in the Argo ARD for 7 days. Table 3 shows the amounts of certain cations lost during laboratory acidulation exposure of the five CRR samples. Significant calcium loss occurred for three of the five samples, whereas two samples showed no calcium loss. The net cation exchanges (gains of losses) for the five acidulated CRR samples exposed to Argo ARD for 7 days are also shown in table 3. The net cation exchanges for 20-g raw CRR samples also exposed to Argo ARD for 7 days are given in table 3 for comparison with the acidulated samples. There is very little difference in copper and zinc capture between the acidulated and raw samples, even though acidulation removed some calcium from three of the samples. This suggests that captured copper and zinc may have exchanged onto monovalent, rather than divalent, sites.

Table 3.—*Relationships of acidulated and raw CRR and ion-exchange in Argo ARD*

[n.d., not determined]

	Ca	K	Cu	Zn	Rb	Sr	Ba
	ppm × 10^3			ppm			
Cations **lost** (-) from CRR in 38°C, HCl solution (pH = 1.5) by raw CRR for 70 minutes (25 g of 1.7-4.7 mm in 100 ml solution):							
Tilden, Tex.	-0.2	0	0	0	0	0	-110
Ft. LaClede, Wyo.	0	0	0	0	0	0	-25
Buckhorn, N. Mex.	-0.2	0	0	0	0	0	-125
South Dakota 1	0	0	0	0	0	0	-310
St. Cloud mine, N. Mex.	-0.4	0	0	0	0	0	-40
Cations **gained or lost** (-) by above acidulated CRR during 7 days exposure to Argo ARD:							
Tilden, Tex.	0.2		80	465	0	90	-190
Ft. LaClede, Wyo.	1.1		170	960	15	180	-200
Buckhorn, N. Mex.	0		55	130	25	50	-240
South Dakota 1	-1.1		105	360	0	125	-255
St. Cloud mine, N. Mex.	-0.2		0	40	0	-165	-160
Cations **gained or lost** (-) by raw CRR during 7 days exposure to Argo ARD:							
Tilden, Tex.			55	520	20	115	n.d.
Ft. LaClede, Wyo.			160	930	25	160	n.d.
Buckhorn, N. Mex.			0	170	25	75	n.d.
South Dakota 1			100	430	25	140	n.d.
St. Cloud mine, N. Mex.			10	75	0	-50	n.d.

Degradation of Clinoptilolite by Acid Solutions and Displacement of Captured Copper and Zinc by Sodium Exchange

Barrer and Makki (1964) demonstrated that highly acid solutions (pH = <1), in addition to cation replacement by H^+, cause loss of aluminum from clinoptilolite. The amount of aluminum loss is small (for example, 5 mol %) for 0.25 N HCl, but experiments were run for only 4 hours at 100°C. Significant loss of aluminum would decrease the ion-exchange capacity. Barrer and Makki (1964) noticed decreased intensities of X-ray diffraction lines for the clinoptilolite after acidulation but did not explain the cause.

To evaluate the loss of aluminum from clinoptilolite after exposure to ARD, the average intensities of the following nine X-ray reflections of clinoptilolite were measured for both raw and ARD-exposed CRR: 020, 200, $20\bar{1}$, 111, $13\bar{1}$, (400,330), $22\bar{1}$, (151,350), and $(62\bar{1},530,260)$. These particular lines were selected to avoid line interferences from other minerals in the CRR. Average intensity losses for ARD-exposed CRR were in the range of about 8 to 35 percent (table 4). Some of these X-ray intensity losses were thought to be due to the much lower scattering factor of hydrogen that replaced the original cations (mostly Na). Three-gram samples of 10 ARD-exposed CRR were mixed with 100 ml of 5 weight percent of NaCl for 18 hours at 38°C. The samples were then dried at 38°C and X-rayed again. Average peak intensities were measured for the Na-exchanged CRR; the average peak intensities, compared to raw CRR, ranged from 76 to 97 percent (table 4). Thus, it appears that most of the apparent CRR degradation, as measured by peak intensities, was due to H^+ exchange, except for the Buckhorn, N. Mex., sample.

After the Na-exchange, the amounts of Cu and Zn remaining in CRR were measured for these 10 CRR samples. The percentages of metals remaining after Na-exchange are shown in table 4. It may be significant that most of the Cu and Zn were removed from the samples, except the South Dakota CRR which retained all of the Cu and most of the Zn (table 4).

A second experiment with Na-exchange was done for coarse CRR exposed to the Argo ARD for 10 days; however, this experiment was done at a water:rock ratio of 4 (instead of 33 as in the first experiment) and a lower temperature of 27°C. Generally, it appears that the X-ray intensity ratios indicate poor Na-exchange and less metal removal from ARD-exposed CRR. This was first thought to indicate that equilibrium was not reached at the lower temperature and the lower water:rock ratio. This same material was subsequently exposed to the same Na-exchange solution conditions, except that the temperature was at 38°C for 24 hours (table 4). The intensities after the second Na-exchange at a higher temperature may indicate that there was permanent degradation of all these CRR samples during ARD exposure because the Na-exchange after ARD-exposure did not improve the peak intensities (table 4). The Buckhorn and the St. Cloud mine CRR samples had the greatest XRD intensity losses, and the South Dakota CRR sample had the least intensity loss. These results are not clearly understood, but the difference may be in the lower water:rock ratio of 4 for the second experiments.

Sodium and Hydrogen Ion Exchange in CRR: Laboratory Studies

A series of laboratory experiments was done on several CRR samples to evaluate the relationships between hydrogen- and sodium-exchange capacity in the absence of competing ions.

Table 4.—*Ratio of clinoptilolite XRD peak intensities of ARD-exposed samples compared with raw clinoptilolite, and ratio clinoptilolite XRD peak intensities of ARD-exposed samples with subsequent exposure to pH = 7, saturated NaCl solution compared with raw clinoptilolite*

[Percentages of metals remaining after Na-exchange are given. i.s., insufficient sample]

CRR	ARD dwell time, hr.	Mean XRD intensity ARD/raw	Mean XRD intensity ARD+NaCl/raw	Metals remaining in ARD-exposed CRR after NaCl exchange	
				Cu, %	Zn, %
Grain size tested in ARD = 1.7-4.7 mm, pH = 7, **water:rock = 33** 3 g finely ground CRR in 100 ml solution, 38°C, 18 h					
Tilden, Tex.	168	84	97	0	15
Ft. LaClede, Wyo.w	168	75	94	90	15
Buckhorn, N. Mex.	168	65	82	0	0
South Dakota 1	168	92	92	100	55
Tilden, Tex.	240	75	95	0	10
Ft. LaClede, Wyo.					
white bed	240	76	89	0	5
green bed	240	80	93	0	10
Buckhorn, N. Mex.	240	72	76	0	0
South Dakota 1	240	75	95	100	70
St. Cloud mine, N. Mex.	240	84	97	0	30
Grain size tested in ARD = 4.7-12.7 mm, pH = 7, **water:rock = 4** 10 g finely ground CRR in 40 ml solution, 27°C, 24 h					
First Na-exchange					
Ft. LaClede, Wyo.w	240	62	67	20	28
Buckhorn, N. Mex.	240	54	52	0	25
South Dakota 1	240	74	69	57	93
St. Cloud mine, N. Mex.	240	i.s.	52	0	0
Second Na-exchange, pH = 7, **water:rock = 4** 10 g finely ground above CRR in 40 ml solution, 38°C, 24 h					
Ft. LaClede, Wyo.		63	63		
Buckhorn, N. Mex.		54	53		
South Dakota 1		74	74		
St. Cloud mine, N. Mex.		i.s.	-		

Sets 1 and 2

These experiments were done in parallel; all conditions were at 38°C (that is, solutions and CRR samples were at this temperature both initially and during the experiments). Water:rock ratios were 4, and the CRR grain size was 1.7-4.7 mm. After each 24-hour test, CRR was rinsed in 100 ml of 38°C water (pH = 7) for 20-30 minutes. Four experiments were done for each of two CRR sample sets. For the first three experiments, CRR samples were dried (after rinse) at 38°C. For the fourth experiment, all liquid was drained from the rinse, but CRR samples were wet at the onset of the solution exposure. There were two cycles each of exposure to Na-exchange (NaCl-saturated) and to 1.5-pH solutions (HCl), respectively, for each of the two sample sets. Samples were at rest during these experiments, except that they were gently agitated manually before each pH measurement.

Set 1.—The first experiment was with raw CRR in a 1.5-pH (HCl) solution. The three SD (South Dakota) samples increased the pH of the solution much more than the other three samples. This increase may have been due to minor calcite in the SD samples, whereas the other three CRR samples had no detectable calcite (fig. 1A). In the second experiment, for the first Na-exchange (after the first pH = 1.5 solution exposure), the SD samples showed much lower H^+ loss to the Na-saturated solution than did the other three CRR samples (fig. 1B). During the third experiment, the second pH = 1.5 solution exposure, two of the SD samples showed slightly more pH increase than the other samples (fig. 1C). In the fourth experiment, the second Na-exchange, all samples performed essentially the same with regard to H^+ release, bringing the Na-saturated solution pH from 7 to about 2.2-2.4 (fig. 1D).

Table 5 shows changes in the amounts of Ca, K, Sr, and Ba in six CRR samples during the alternate pH = 1.5 and Na-exchange, as well as the associated change in the mean XRD intensities of clinoptilolite for the raw material and both the first and second Na-exchanges. These experiments showed significant losses of Ca from the Tilden, Ft. LaClede, and Buckhorn CRR during the first Na-exchange (table 5). In contrast, the Ca- and K-rich South Dakota samples were more resistant to Ca loss during the first Na-exchange following exposure to acidic solution (pH = 1.5). This resistance to Na-exchange is reflected in figure 1B in which less H^+ was lost by the South Dakota CRR samples than by the other CRR samples.

During the second pH = 1.5 exposure, the South Dakota (SD) samples captured less H^+ than the Buckhorn, N. Mex., and Ft. LaClede, Wyo., CRR samples. This was because the SD samples released fewer H^+ ions during the prior Na-exchange.

The second Na-exchange resulted in significant Ca losses (63-89 percent) from all six CRR samples. Losses of K were 9-32 percent. The K:Ca ratios of all CRR samples after the second Na-exchange were about 3-5. In contrast, the initial K:Ca values were in the range of about 0.4 to 2. Thus, it seems that Ca displacement enhances the ability of CRR to capture H^+.

Set 2.—In the first experiment with raw CRR in NaCl-saturated pH = 7 solution, the calcite-bearing CRR produced solution pH values above 7, whereas the other three samples gave solution pH values slightly below 7 (fig. 2A). In the second experiment at pH = 1.5, the SD samples again showed solution pH values higher than the other three samples (fig. 2B). The third experiment, and the second Na-exchange, showed higher solution pH values for the SD samples, indicating lower amounts of H^+ released, as compared to the other three samples (fig. 2C). The fourth experiment was the second pH = 1.5 solution exposure. Solution pH values had a range of only about 0.4, and ranged from about 2.2 to 2.6 units for all six samples (fig. 2D).

The relationships of alternate acidic solution (pH = 1.5) exposure and Na-displacement of H^+, respectively, show that about two cycles of each of these treatments at 38°C render the H^+ capacity—as measured by Na^+ displacement of H^+—essentially identical for all six CRR samples. This was not an expected result because these six samples differ significantly in both the chemical compositions of the clinoptilolites and in the amounts of clinoptilolite in each sample. The mean XRD intensities after the first Na-exchange are about 10 percent greater than those after the second Na-exchange. This is consistent with displacement of Ca and K by Na (table 5).

Table 5.—*Effects of two cycles of acidulation (pH = 1.5) and Na-exchange on nonmetallic cations and structural stability of clinoptilolite—Set 1*

[Water:rock = 4, T = 38°C, sat. NaCl solution for Na-exchange at pH = 7, grain size = 1.7-4.7 mm]

	Ca	**K**	**Sr**	**Ba**	Ca	K	Mean XRD
	ppm × 10^3		ppm		(% lost)	(% lost)	intensities
					from raw		
		Tilden, Texas					
Raw	1.6	1.9	780	1,450			
First Na-exchange	0.7	1.7	610	1,210	56	10	10.6
Second Na-exchange	0.3	1.3	260	1,040	81	32	8.4
		Ft. LaClede, Wyoming					
Raw	1.3	1.4	360	1,185			
First Na-exchange	0.6	1.2	345	1,135	54	14	16
Second Na-exchange	0.4	1.2	250	1,135	69	14	14.6
		Buckhorn, New Mexico					
Raw	2.7	1.1	575	2,450			
First Na-exchange	1.1	0.9	475	2,385	59	18	12.7
Second Na-exchange	0.3	1.0	250	2,270	89	9	11.7
		South Dakota, 1					
Raw	3.3	3.7	325	1,150			
First Na-exchange	3.3	3.1	320	1,150	0	16	9
Second Na-exchange	1.0	2.8	255	780	70	24	7.5
		South Dakota, A					
Raw	2.8	3.7	355	835			
First Na-exchange	2.6	3.3	310	835	7	11	10
Second Na-exchange	0.6	2.9	215	835	78	22	9.6
		South Dakota, C					
Raw	1.9	3.7	355	1,020			
First Na-exchange	1.6	3.7	325	1,020	16	0	9
Second Na-exchange	0.7	3.2	325	1,020	63	14	8.1

Set 3.—Sequential experiments were done at 27°C, water:rock ratios of 4, and CRR grain size of 4.7-12.7 mm. After each 24-hour test, CRR was rinsed in 100 ml of water (pH = 7, 27°C) for 20-30 minutes. Five experiments were done for each of seven CRR samples that had weights of 25 g each. For all of the experiments after the first one (Na-exchange), all liquid was drained from the rinse, but CRR samples were wet at the onset of the next solution exposure. There were three cycles of Na-exchange (NaCl-saturated) and two cycles of exposure to 3.0-pH solutions (HCl) for the seven samples. Samples were at rest during the experiment, except they were gently agitated manually before each measurement.

The first experiment was Na-exchange at pH = 7 with raw CRR. Final pH of solutions ranged from about 7 to 8 (fig. 2A).

The second experiment was exposure of Na-exchanged CRR to solutions of pH = 3. The three South Dakota (SD) samples gave a solution pH in the range of 8 to 9; the other samples resulted in a solution pH between 4 to 5 (fig. 2B).

The third experiment was the second Na-exchange (pH = 7). The three SD samples produced solution pH values of about 7.5; the others produced pH values of about 4-4.5 (fig. 2C).

The fourth experiment was the second pH = 3 treatment (after the second Na-exchange). Relationships shown on figure 2D show a final solution pH of about 8 for the SD samples, but the others have final solution pH values of about 4-4.5.

The fifth experiment was the third Na-exchange. The SD samples produced solution pH values of 6.5-7.5, whereas the others produced solution pH values of 3.5-4 (fig. 2E).

The results of the set 3 experiments, if interpreted simplistically, indicate that the South Dakota CRR has a stronger affinity for H^+ in the acidic solution and less affinity for Na^+ (during Na-exchange at pH = 7). The other samples have a greater affinity for Na^+ during exposure to acidic solution and capture less H^+; however, during Na-exchange, their preference for Na^+ is so great that more H^+ is exchanged to the solution.

The results of the set 3 experiments are quite different from the results of sets 1 and 2, where all of the treated zeolites responded in the same manner with regard to the final solution pH. Quantitative analysis of Ca, K, Sr, and Ba for these three sets of experiments did not show trends that would explain the differences in results (table 6), although set 3 was done in a much higher pH solution and at a lower temperature than sets 1 and 2. The mean XRD intensities after the last Na-exchange are consistent with Na displacement of Ca and K.

Exposure of Cycled Na-Exchanged and Acidulated Set 3 to Argo ARD

The results of exposure of set 3 samples to Argo ARD are given in table 7. Net metal gains and gains and losses in Ca, K, Sr, and Ba are listed. The metal gains of the Buckhorn, St. Cloud mine, and Castle Creek CRR are improved between 270 and 550 percent, compared to raw CRR (table 2). There was no significant improvement of the zinc capture for the other four CRR samples. In addition, all of the Na-exchanged samples, except Buckhorn, captured minor amounts of lead that ranged from 10 to 60 ppm, even though the lead content of the Argo water was reported by Ficklin and others (1992) to be only 0.040 mg/l. Capture of lead for raw CRR was not reported in table 2 because it was less than 10 ppm. Ca capture was significant for all samples and ranged from 0.4 to 2.1 weight percent. All of the South Dakota samples and the samples from the St. Cloud mine captured some K, even though the concentration of K in Argo drain was only 3.4 mg/l (Williams, 1988). All but one sample captured 15-105 ppm of Sr, even though the Sr content of the water was only 1.6 ppm (Williams, 1988). Five of the samples captured Ba, and two lost Ba (table 7).

Table 6.—*Effects of two cycles of acidulation (pH = 3) and three cycles of Na-exchange on nonmetallic cations and structural stability of clinoptilolite—Set 3*

[Water:rock = 4, T = 27°C, sat. NaCl solution for Na-exchange at pH = 7, grain size = 4.7-12.7 mm]

	Ca	K	Sr	Ba	Ca (% lost)	K (%lost)	Mean XRD intensities
	ppm × 10^3		ppm		from raw		
			Ft. LaClede, Wyoming				
Raw	1.3	1.4	360	1,185			
Last Na-exchange	0.6	1.3	340	1,050	54	7	13.6
			Buckhorn, New Mexico				
Raw	2.7	1.1	575	2,450			
Last Na-exchange	1.0	1.0	415	2,450	60	9	12.9
			South Dakota, 1				
Raw	3.3	3.7	325	1,150			
Last Na-exchange	1.3	3.2	315	890	61	14	8.3
			St. Cloud mine, New Mexico				
Raw	2.7	1.9	1,700	1,030			
Last Na-exchange	1.1	1.5	1,200	1,030	59	21	12.3
			South Dakota, A				
Raw	2.8	3.7	355	835			
Last Na-exchange	1.2	2.9	310	835	57	23	10.2
			South Dakota, C				
Raw	1.9	3.7	355	1,020			
Last Na-exchange	1.2	3.4	320	870	37	8	9.2
			Castle Creek, Idaho				
Raw	2.5	1.4	135	735			
Last Na-exchange	1.2	1.2	110	735	52	14	13.6

The Na-exchange improved zinc capture for all of the originally Ca-rich CRR. It also improved lead capture for all but the Buckhorn CRR. Na-exchange did not improve zinc or copper capture for the Na-rich Ft. LaClede or the K- and Ca-rich South Dakota samples.

Table 8 gives the percentages of Cu, Zn, and Pb remaining after the set 3 Argo-exposed samples were exposed to NaCl-saturated solutions of pH = 2.9 in the laboratory. Values of the final pH of the exchange solution are also given (table 8). The Ft. LaClede and the South

Dakota A samples had the highest efficiency of metal exchange, whereas South Dakota C had the lowest percentage of metal exchange. However, South Dakota C increased the solution pH from 2.9 to 8, which is inferred to indicate a remarkably high capture of H^+ from the acidic solution, as compared to the other CRR samples (table 8).

Table 7.—*Net gains and losses of certain elements for last Na-exchanged set 3 samples exposed to Argo ARD for 168 hours*

[Numbers in parentheses are gains (+) or losses (-) of nonmetals. Grain size = coarse (4.7-12.7 mm), 20 g contained in nylon mesh (2x3-mm openings) bags]

Locality	Ca	K	Cu	Zn	Pb	Sr	Ba
	ppm × 10^3		ppm				
Ft. LaClede, Wyo.	1.6	1.3	110	885	10	360	1,120
	(+1.0)	(0)				(+20)	(+70)
Buckhorn, N. Mex.	1.8	1.0	75	525	0	460	2,200
	(+0.8)	(0)				(+45)	(-250)
South Dakota, 1	1.8	3.5	85	460	10	335	800
	(+0.5)	(+0.3)				(+20)	(+90)
St. Cloud mine, N. Mex.	1.6	1.8	15	190	55	1,115	1,060
	(+0.5)	(+0.3)				(-85)	(+30)
South Dakota, A	1.6	3.1	75	555	15	325	855
	(+0.4)	(+0.2)				(+15)	(+15)
South Dakota, C	3.3	3.3	110	595	20	340	750
	(+2.1)	(+0.1)				(+20)	(-120)
Castle Creek, Idaho	1.9	1.2	30	445	60	215	710
	(+0.7)	(0)				(+105)	(+25)

Table 8.—*Metal extraction from set 3 Argo-exposed CRR by Na-saturated solution with pH = 2.9*

[Five grams of powdered sample in 50 ml of solution at 38°C for 25 h, **water:rock** = 5]

Locality	Percent of metals remaining after Na-exchange			Final pH of exchange solution
	Cu	Zn	Pb	
Ft. LaClede, Wyo.	0	7	0	3.9
Buckhorn, N. Mex.	0	20	0	3.9
South Dakota, 1	47	11	0	4.2
St. Cloud mine, N. Mex.	0	38	0	3.9
South Dakota, A	0	3	0	4.1
South Dakota, C	49	71	0	8.0
Castle Creek, Idaho	60	22	0	4.1

Exposure of South Dakota CRR to ARD in Colorado and Southwestern Spain

Since the report of Desborough (1992), 24 samples exposed to ARD at eight localities in Colorado have been analyzed for Ca and K. Losses in Ca and K and gains in Zn, Cu, and Pb for these samples are given in table 9. The mean XRD intensities of half of these samples were measured and compared with those of raw CRR (table 9).

Because of the very acidic and metal-rich nature of two major drainages (Rio Tinto and Odiel River) in southwestern Spain, South Dakota samples were taken to Spain for exposure to ARD at two localities each in these two drainages. Ca and K losses and metal gains are given at the end of table 9, along with mean XRD intensities of three ARD-exposed samples relative to raw CRR. The samples analyzed for table 8 were selected independently of water-flow rates, water temperatures, pH, metal content, and exposure times. Thus, a wide range of physical and chemical conditions is represented by the samples in table 9.

Examination reveals Ca losses from all samples except two at Chalk Creek, which has the highest pH of all the drainages (table 9). Although Empire Creek is not metal rich, the low pH of 3.5 apparently resulted in the loss of Ca but not K. K losses occurred in half of the samples and was greatest in the Upper Rio Tinto during a long (68 days) exposure. Only small K losses occurred in about one-third of the samples exposed to ARD in Colorado. It is significant that losses of either Ca or K or both occurred in all of the ARD-exposed samples (table 9). A plot of Ca + K losses versus Zn + Cu + Pb for all the samples in table 9 shows some correlation between Ca + K loss and metal gain (fig. 3), except for Empire Creek which has no significant amounts of Zn, Cu, or Pb. The mean ratio of Ca + K loss to net Zn + Cu + Pb gain is about 10. It is not demonstrated that the metals substitute on either Ca or K sites or both. The mean XRD intensity ARD/raw is about 80 percent and is probably the result of H^+ substitution as shown previously. The greatest decrease in XRD intensities occurred in Empire Creek which has smaller amounts of Cu, Zn, and Pb than any of the other drainages tested.

Table 9.—*Calcium and potassium loss and heavy-metal gain of South Dakota, 1 CRR in ARD of Colorado and Huelva Province, southwestern Spain, and associated decreases in mean XRD peak intensities of clinoptilolite*

[Colorado localities are those of Desborough, 1992, tables 1 and 2;
i.s., insufficient sample for analysis]

ARD Locality	Ca	K	Zn	Cu	Pb	Mean XRD Intensity ARD/raw
	ppm × 10^3			ppm		
			Colorado			
Upper St. Kevin Gulch, pH = 3.2-3.6 (Smith and others, 1991)						
4B	-1.1	0	750	0	0	
4D	-1.6	0	1,150	20	0	
4I	-1.9	0	1,052	0	0	87
4J	-1.0	0	1,419	45	0	
4K	-2.0	0	1,455	50	0	100
4L	-0.8	0	1,570	15	0	
4N	-1.1	0	570	0	0	

Table 9.—*Calcium and potassium loss and heavy-metal gain of South Dakota, 1 CRR in ARD of Colorado and Huelva Province, southwestern Spain, and associated decreases in mean XRD peak intensities of clinoptilolite*--Continued

ARD Locality	Ca	K	Zn	Cu	Pb	Mean XRD Intensity ARD/raw
	ppm × 10^3			ppm		
			Colorado--Continued			
California Gulch, pH = 4-5						
5B	-0.1	-0.2	840	0	0	
Empire Creek, pH = 3.5						
E6H	-2.6	0	0	15	0	70
E6I	-1.8	0	0	35	0	80
Chalk Creek, pH = 5						
6D	0	-0.5	1,400	0	210	90
6E	0	-0.2	820	0	0	
6F	-0.8	0	1,090	0	40	93
Longfellow and Koehler pond drain (upper), pH = 2						
7-3B	-1.0	0	800	320	120	
7-3E	-1.2	0	700	520	150	
7-3F	-1.8	-0.2	975	595	190	
7-3G	-1.8	0	875	570	35	77
7-3H	-2.9	0	1,080	775	95	85
Lower St. Kevin Gulch, pH = 3.7-4.0 (Smith and others, 1991)						
8C	-2.1	0	1,415	10	0	92
8G	-1.7	0	1,410	10	0	83
Rockford Tunnel Pond, pH = 4						
9C	-0.9	-0.2	230	95	0	
9D	-1.2	-0.2	220	95	0	
Middle Mineral Creek, pH = 4						
12C	-0.8	-0.5	605	225	45	78
12D	-1.4	-0.2	435	175	0	82
			Huelva Province, southwestern Spain			
Lower Rio Tinto at Niebla, pH = 2.5						
H1A (45.8 hours)	-3.0	-0.6	490	665	1,140	77
H1B (1632 hours)	-1.7	-1.6	1,575	1,130	1,455	
Upper Rio Tinto at Berrocal, pH = 3						
H2A (40.5 hours)	i.s.	i.s.	890	630	170	
H2B (1632 hours)	-1.9	-2.1	1,510	1,655	1,340	
Odiel River 9 km west of Valverde, pH = 3						
H3A (40.4 hours)	-2.8	-0.3	575	815	2,270	100
Odiel River at HWY. C421, pH = 3						
H4A (23.7 hours)	-2.2	-0.3	415	725	0	85
H4B (1680 hours)	-0.4	-0.4	1,360	1,555	60	

Copper and Zinc Capture by Several Raw and Na-Exchanged CRR Samples Exposed to Argo ARD, Idaho Springs

The amounts of copper plus zinc captured by raw and Na-exchanged CRR samples in the Argo drain are ranked below. The data for raw CRR samples are largely based on data from table 2. The Na-exchanged CRR samples are those of set 3 that were Na-exchanged twice and acidulated at pH = 3 and listed in table 6. Except for the St. Cloud mine, N. Mex., CRR, test periods for samples ranked below were 168 hours.

	Raw Cu + Zn, ppm 1.4-4.7 mm
Ft. LaClede, Wyo.	1105
South Dakota, A	825*
South Dakota, C	795*
South Dakota, 91-3	680
Tilden, Tex.	600*
South Dakota, 1	550*
South Dakota, D	540
South Dakota, B	515
South Dakota, 91-1	465
Buckhorn, N. Mex.	160
Castle Creek, Idaho	110
St. Cloud mine, N. Mex.	80#

	Na-exchanged Cu + Zn, ppm 4.7-12.7 mm
Ft. LaClede, Wyo.	995
South Dakota, C	705
South Dakota, A	630
Buckhorn, N. Mex.	600
South Dakota, 1	545
Castle Creek, Idaho	475
St. Cloud mine, N. Mex.	205

*, mean for two tests; #, mean for 10 days.

The above results show that Na-exchange prior to Argo ARD exposure greatly enhances the Cu and Zn capture of the Buckhorn, N. Mex., Castle Creek, Idaho, and St. Cloud mine, N. Mex., CRR samples. However, Na-exchange does not significantly improve the others, although the lack of coarse material from Tilden, Tex., prohibited testing that CRR.

Summary and Future Studies

Based on the heavy-metal capture by CRR at the Argo ARD, the three best raw CRR in this application are from the Ft. LaClede, Wyo., the South Dakota, and the Tilden, Tex., deposits. However, with pretreatment (Na-exchange) of the Ca-rich Buckhorn, N. Mex., and the Castle Creek, Idaho, CRR, there is remarkable improvement in their capture of copper and zinc from the Argo ARD. For all of these raw CRR samples exposed to the Argo ARD, there is no correlation between Ca- and K-exchange and metal capture by CRR. Except for the Ft. LaClede CRR, most samples lost more Ca than K. In the strictest sense, Ca loss from CRR in metal-rich ARD is of benefit because it increases the hardness of the water and thereby allows a higher heavy-metal content (Colorado Department of Health, 1984, table 3) in the "Class 1 Aquatic Life" stream standards. Likewise, capture of H^+ is beneficial because it reduces acidity. Conversely, the release of large amounts of Na to certain drainages may adversely affect salinity. Some CRR would seem to be useful in reducing heavy-metal concentrations in ARD to drinking water standards, if the water volumes are small. However, studies so far do not indicate that raw CRR alone in ARD could reduce all heavy-metal concentrations to meet the Class 1

Aquatic Life standards because they are an order-of-magnitude lower than drinking water standards.

Future studies will evaluate the heavy-metal capture of several CRR in other ARD in Colorado. Ultimately, analysis of untreated and CRR-exposed water in ARD testing will have to be done to determine metal-capture rates and CRR nonmetal ion exchange contributions to the water. Pre-treatment of CRR under certain conditions, not give here, suggests that heavy-metal capture capacity may be enhanced 30 percent greater than raw Ft. LaClede, Wyo., 100 percent greater than raw Tilden, Tex., and 800 percent greater than raw Buckhorn, N. Mex. This aspect will be pursued.

Knowledge of the chemistry of ARD water is essential and critical for understanding potential methods that might be used in remediation.

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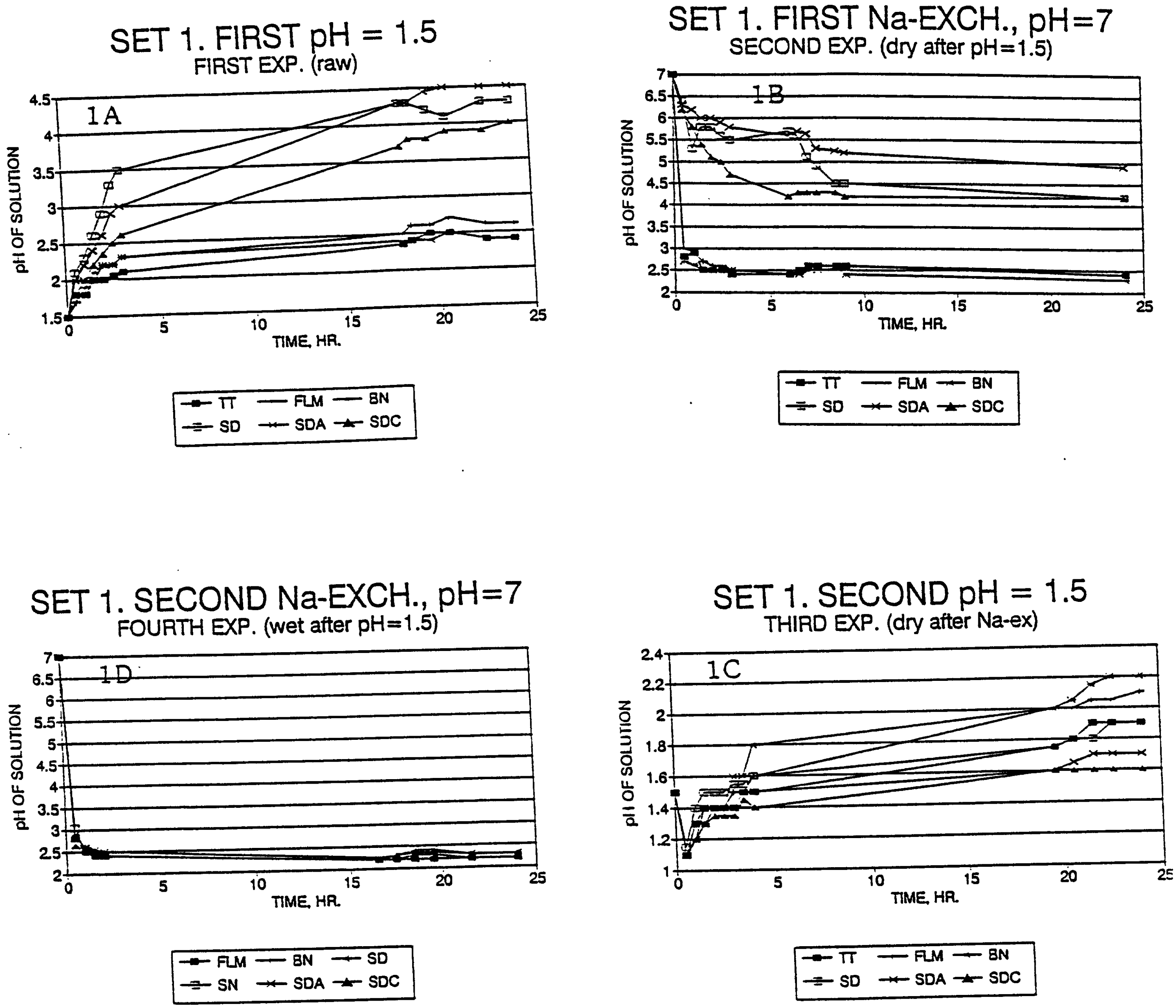
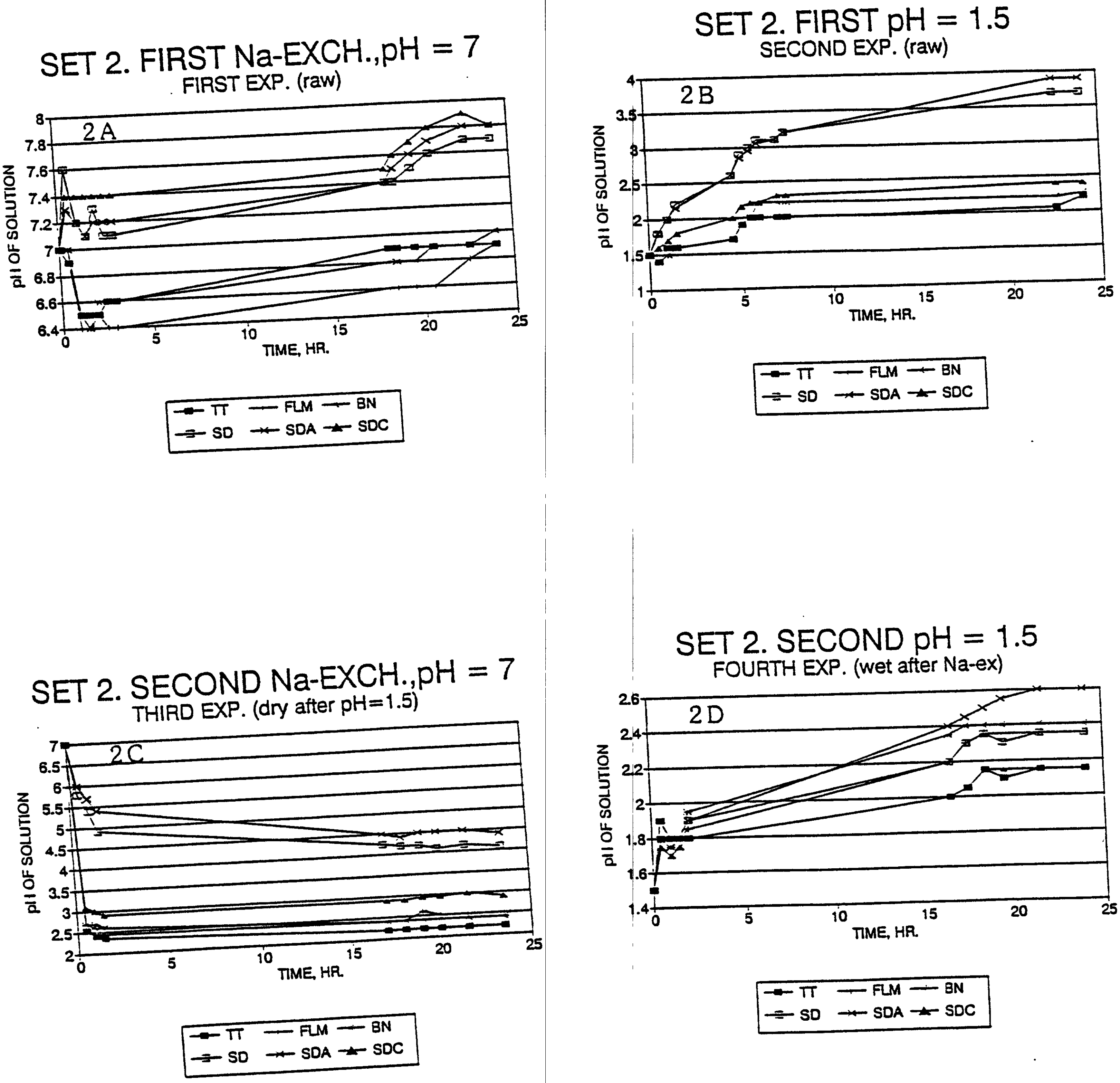


Figure 1.—Set 1 data for pH changes during acidulation and Na-exchange of CRR at 38°C. TT = Tilden, Tex.; FLM = Ft. LaClede, Wyo.; BN = Buckhorn, N. Mex.; Sd = South Dakota 1; SDA = South Dakota 91-4A; SDC = South Dakota 91-4C.



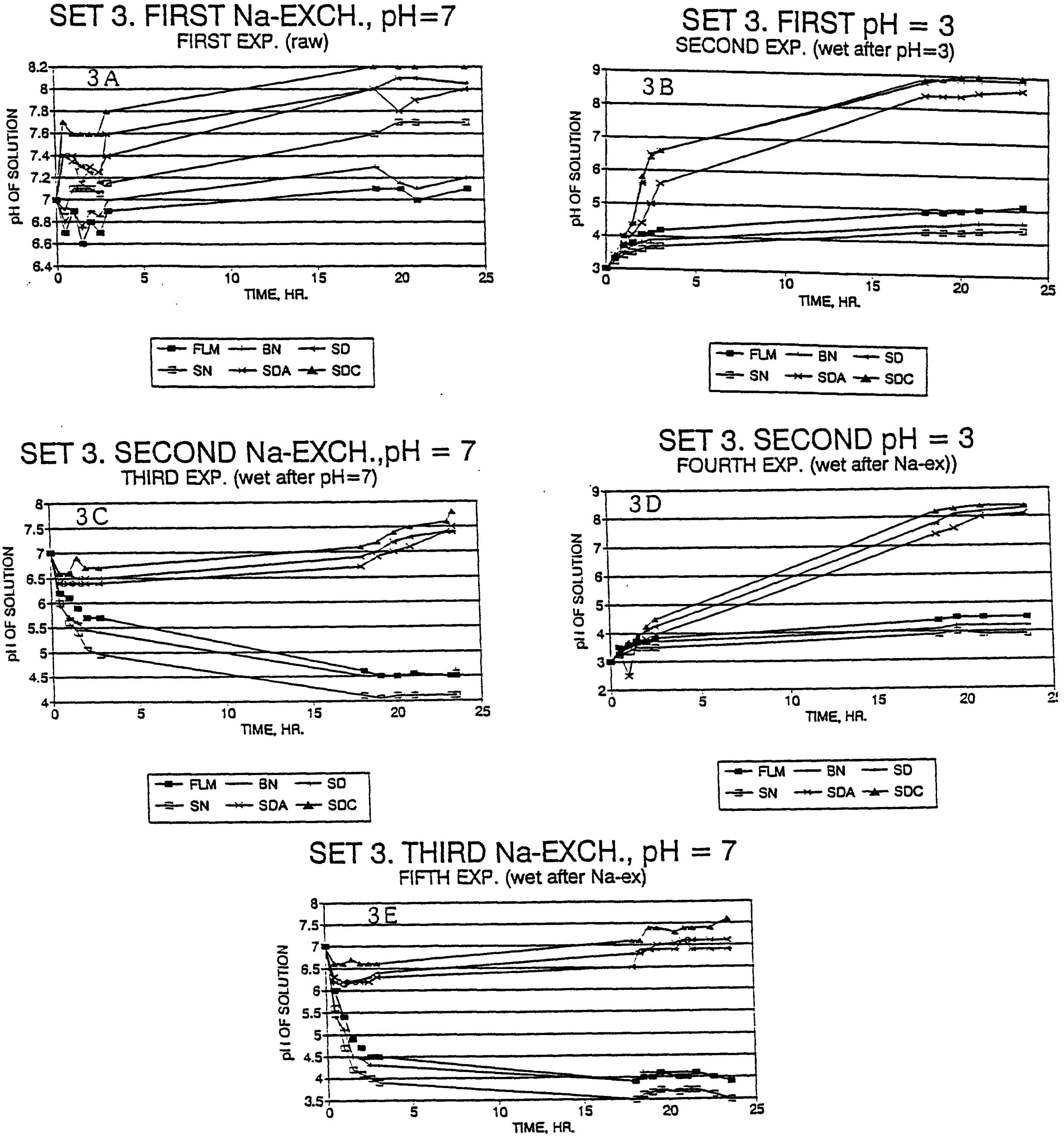
SET 2. FIRST Na-EXCH.,pH = 7
FIRST EXP. (raw)

SET 2. FIRST pH = 1.5
SECOND EXP. (raw)

SET 2. SECOND Na-EXCH.,pH = 7
THIRD EXP. (dry after pH=1.5)

SET 2. SECOND pH = 1.5
FOURTH EXP. (wet after Na-ex)

Figure 2.—Set 2 data for pH changes during acidulation and Na-exchange of CRR at 38°C. TT = Tilden, Tex.; FLM = Ft. LaClede, Wyo.; BN = Buckhorn, N. Mex.; SD = South Dakota 1; SN = St. Cloud mine, N. Mex.; SDA = South Dakota 91-4A; SDC = South Dakota 91-4C.



SET 3. FIRST Na-EXCH., pH=7
FIRST EXP. (raw)

SET 3. FIRST pH = 3
SECOND EXP. (wet after pH=3)

SET 3. SECOND Na-EXCH.,pH = 7
THIRD EXP. (wet after pH=7)

SET 3. SECOND pH = 3
FOURTH EXP. (wet after Na-ex))

SET 3. THIRD Na-EXCH., pH = 7
FIFTH EXP. (wet after Na-ex)

Figure 3.—Set 3 data for pH changes during acidulation and Na-exchange of CRR at 27°C. FLM = Ft. LaClede, Wyo.; BN = Buckhorn, N. Mex.; SD = South Dakota 1; SN = St. Cloud mine, N. Mex.; SDA = South Dakota 91-4A; SDC = South Dakota 91-4C. The Castle Creek, Idaho, CRR showed the same response as FLM, BN, and SN.

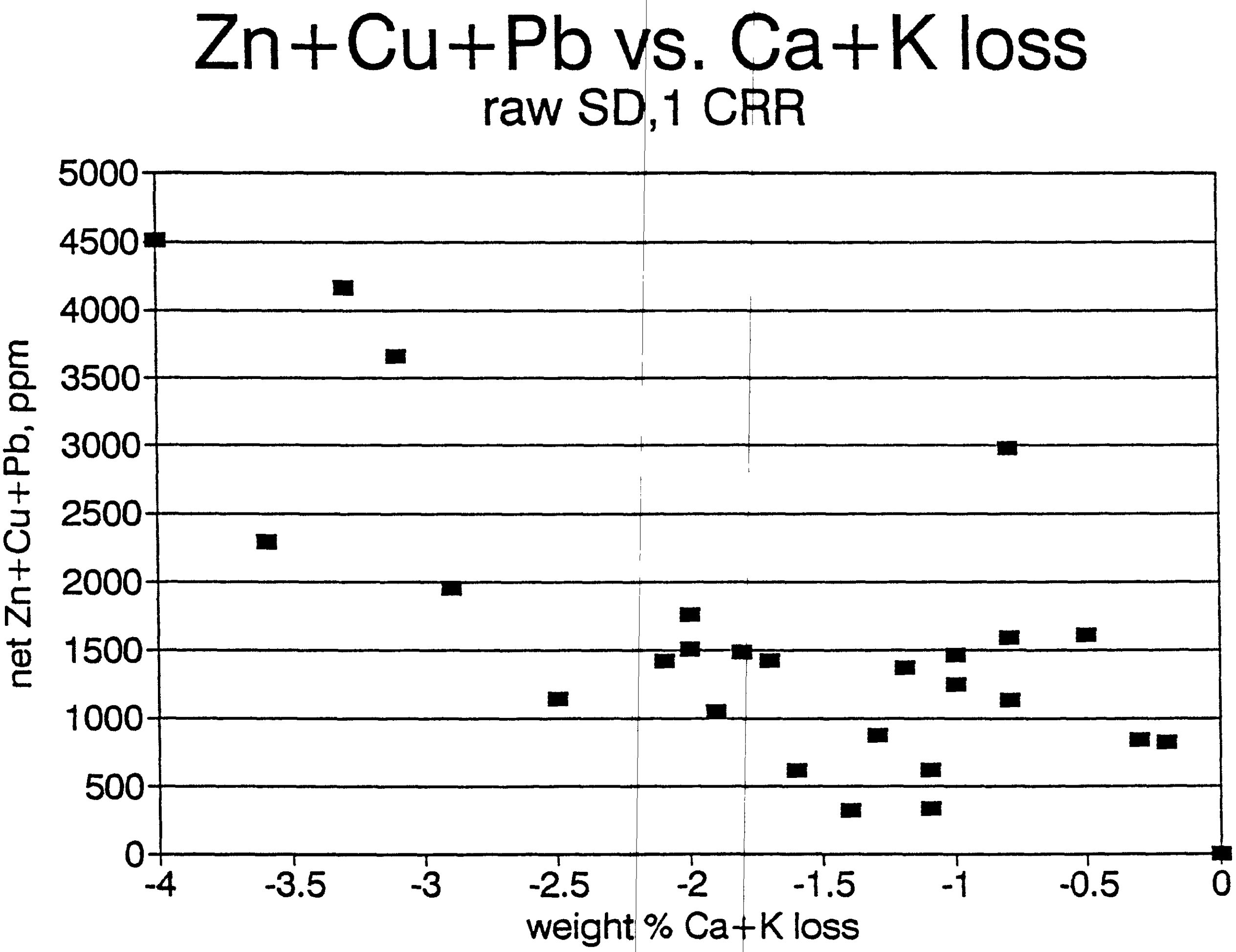


Figure 4.—Relations of Zn + Cu + Pb capture versus Ca + K loss for South Dakota CRR at eight Colorado ARD localities and four ARD localities in Huelva Province, southwestern Spain.