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Efficacy of heavy-metal capture by clinoptilolite-rich rocks from heavy-metal-polluted water in five drainages in Colorado

by

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ABSTRACT

Crushed and sized samples of zeolitic clinoptilolite-rich rock (CRR) from several localities were immersed in five heavy-metal-polluted drainages (HMPD's) to determine which CRR's perform best for ion-exchange capture of copper, zinc, lead, and cadmium. The pH of the HMPD's was about 3-9, and the temperature was 3-20°C. The ranges in concentrations (in mg/L) of heavy metals in HMPD waters were: Cu = <0.01-37, Zn = 10.3-230, Pb = 0.03-0.3, and Cd = 0.02-0.36. The concentrations of Zn and Cd in all five of the HMPD's exceeded the "Class 1 Aquatic Life" standards of the Colorado Department of Health, Cu exceeded the standards for four of the five drainages, and Pb exceeded the standards in three.

For the best-performing CRR's, Cu was captured at concentrations as low as 0.3 mg/L; Cd was captured at concentrations as low as 0.07 mg/L; and Pb was captured at concentrations as low as 0.03 mg/L.

Most of the CRR's captured Pb effectively, and the range in the amounts captured by CRR's generally varied less than a factor of two. For Cu, the amounts captured varied as much as a factor of eight among the CRR's. The variations in the amounts of Zn captured by CRR's ranged as much as a factor of 10 in a single test of multiple samples.

In the pH range of about 3 to 6, the Na-rich Ft. LaClede, Wyo. (FLW) CRR was best for the capture of Zn, but it also consistently captured as much (or more) Ca than the other CRR's. In the pH range of about 6 and above, the K-rich South Dakota (SDA) CRR was best for capture of combined Cu and Zn, and best for capture of Cu. Only the FLW and SD CRR's captured Cd from HMPD's at concentrations below 0.3 mg/L. Major factors affecting metal capture of the best-performing CRR's were pH and Ca concentrations in the five HMPD's tested between 5/28/93 and 12/10/93.

The present study shows that if natural zeolites are to be considered for use in potential commercial applications, they must be tested for that application in the environment of the considered use. Specifically, the efficacy of the zeolite for the intended use **cannot** be predicted from characteristics such as bulk chemistry, mineralogy, zeolite content, or cation-exchange capacity (CEC).

INTRODUCTION

This investigation was done to compare the ability of clinoptilolite-rich rocks (CRR) from different deposits to capture heavy metals by ion exchange from water that is high in dissolved copper, zinc, lead, and cadmium. The amounts of these dissolved metals allowed by the Environmental Protection Agency (EPA) drinking water standard are approximately 10-fold greater than the "Class 1 Aquatic Life" standards of the Colorado Department of Health because salmonids (trout) cannot tolerate even low concentrations of several heavy metals or low pH (<6.5). The upper limits for heavy metals allowed by the "Class 1 Aquatic Life" standards vary as a function of alkalinity ($CaCO_3$); the higher the alkalinity, the more dissolved metals are allowed (Colorado Department of Health, 1984). For this reason, it is important to be aware of the Ca capture of CRR's in drainages with low or moderate Ca. The Colorado Department of Health (1989) Colorado Nonpoint Source Assessment Report shows about 20 drainages with high heavy-metal contents. Some of these are shown on figure 1 along with the location, pH, and temperature of the five HMPD's studied for this report. The term heavy-metal-polluted drainage (HMPD) is preferred usage here because several HMPD'S are not acidic (fig. 1), and some acidic drainages are not polluted by heavy metals.

Twenty samples from 17 CRR deposits were studied. Fifteen of these deposits are in eight western states of the U.S.; two deposits are in southern British Columbia, Canada. Only deposits containing about 3 million tons, or more, of CRR were of interest.

Many of the samples studied were not available prior to mid-summer; thus, several samples were not tested in all drainages. A list of those tested in each drainage is provided in the Appendix.

CHARACTERISTICS OF CLINOPTILOLITE-RICH ROCKS

Large pieces (>5 cm) of CRR from each deposit were crushed in a jaw crusher and sized by screening. A 4- to 10-mesh (1.7-4.7 mm) fraction was used for all HMPD immersion studies. A portion of this 4- to 10-mesh fraction was pulverized to 95 percent minus 100 mesh, and this fine fraction was used for X-ray diffraction and chemical analysis. Samples were analyzed for K, Ca, Fe, Cu, Zn, Rb, Sr, Ba, and Pb (table 1). X-ray diffractometer traces were used to determine that all samples have clinoptilolite as the most abundant mineral (table 2). Sheppard and Gude (1982) reported chemical, mineralogical, and NH_4^+-exchange capacity data for samples from seven of the 17 deposits listed in table 1.

Some of the samples from the CRR deposits studied here consist of more than 80 to 95 percent clinoptilolite, but others have only 50 to 70 percent clinoptilolite, according to Sheppard and Gude (1982, table 2) and the present X-ray diffraction studies. The dilutant minerals detected by X-ray diffraction study of the raw CRR samples used in the present study are given in table 2. In addition, the dilutant minerals given by Sheppard and Gude (1982, table 2) are also listed in table 2.

METHODS OF STUDY

Twenty-gram samples of sized CRR (1.7-4.7 mm) in 2×3-mm mesh nylon bags were immersed in each HMPD with a maximum of eight side-by-side tested simultaneously for the widest drainages. For narrower drainages (e.g., Argo tunnel), only six side-by-side tests were run simultaneously. Test periods were from 19 hours to 78 days, but most were from 6 to 12 days. After testing, samples were dried, sieved to remove sand-size particles and adhering Fe-hydroxide precipitates, pulverized, and analyzed for K, Ca, Fe, Cu, Zn, Rb, Sr, Cd, Ba, and Pb using three radioisotope sources and a Li-drifted Si detector. The HMPD water samples were analyzed for Na, K, Ca, Fe, Cu, Zn, Cd, Ba, and Pb by a commercial laboratory (Skyline Laboratories, Inc., Wheat Ridge, Colo.). All pH measurements were made in the field using a digital temperature-corrected pH meter.

ARGO TUNNEL, IDAHO SPRINGS

According to Wildeman (1983), the Argo Tunnel drain has one of the largest flows from draining mines in the Front Range part of the Colorado mineral belt; it varies from 160 to 225 gal/min (10-14 L/s). The amounts of Cu (4.5-6 mg/L), Zn (40-50 mg/L), and Cd (0.10-0.15

Table 1. Concentrations of certain elements in raw clinoptilolite-rich rocks from 17 deposits in the Western U.S. and British Columbia, Canada.

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

Locality and abbreviation	Na	K	Ca	Fe	Cu	Zn	Rb	Sr	Ba	Pb
	ppm × 10^3				parts per million					
British Columbia										
Princeton-PBC	n.a.	2.5	1.1	1.0	40	150	110	645	2,310	<40
Ranchlands-Z1BC	n.a.	2.6	1.8	1.1	20	70	80	1,350	3,760	<40
Ranchlands-Z2BC	n.a.	1.5	0.5	1.5	30	40	40	200	235	<40
Colorado										
Creede-CCO	n.a.	3.2	1.7	0.9	20	80	190	485	590	<40
Idaho										
Castle Creek-CCI	n.a.	1.4	2.5	1.5	20	110	85	135	735	<40
Castle Creek-XYI	n.a.	1.2	1.9	1.3	20	80	60	300	810	<40
Corp. reports	1.2	1.6	2.3	1.8	n.r.					
Crisman Hill-CHI	n.a.	4.1	1.0	1.6	60	110	200	155	1,440	<40
Corp. reports	0.8	4.0	0.7	2.5	n.r.					
Nevada										
Fish Crk.-FCEN	n.a.	2.6	1.6	0.7	20	90	260	100	230	<40
Fish Crk.-FCWN	n.a.	3.0	1.5	0.9	20	80	190	250	670	<40
New Mexico										
Buckhorn-BNM	n.a.	1.1	2.7	1.0	20	60	40	575	2,450	<40
St. Cloud-SNM	n.a.	1.9	2.7	0.9	20	70	40	1,700	1,030	<40
Corp. reports	0.6	3.2	0.5	0.5	n.r.					
Oregon										
Harney Lake-HLO	n.a.	2.4	1.8	0.9	20	80	75	45	200	<40
Sheaville-SVO	n.a.	4.1	1.0	1.8	20	90	160	190	1,190	<40
Succor Crk.-SCO	n.a.	1.6	2.0	1.6	20	135	100	335	1,065	<40
Corp. reports	0.3	2.2	1.9	3.1	n.r.					
South Dakota										
SD1	n.a.	3.7	3.3	2.0	20	100	120	325	1,150	<40
SDA	n.a.	3.7	2.8	1.7	20	100	110	355	835	<40
SDC	n.a.	3.7	1.9	2.0	20	60	120	355	1,020	<40
Texas										
Alamito Crk.-ACT	n.a.	1.9	2.0	1.1	20	70	170	290	820	<40
Tilden-TT	n.a.	1.9	1.6	0.6	20	60	70	780	1,450	<40
Corp. reports	n.r.	1.4	1.7	0.6	n.r.					
Wyoming										
Ft. LaClede-FLW	n.a.	1.4	1.3	0.8	20	75	85	360	1,185	<40
Corp. reports	3.5	1.6	1.1	1.4	n.r.			300	n.r.	n.r.

Table 2. Dilutant minerals in raw clinoptilolite-rich rocks from 17 deposits in the Western U.S. and British Columbia, Canada.

[Minerals are listed in order of decreasing abundance; "clay" refers to layer silicates with a 10-angstrom spacing; SG82 refers to data of Sheppard and Gude (1982, table 2); tr. = trace]

Locality and abbreviation	Dilutant minerals
British Columbia	
Princeton-PBC	opal, potassium feldspar (K-feldspar), plagioclase
Ranchlands-Z1BC	K-feldspar, plagioclase, clay, quartz
Ranchlands-Z2BC	quartz, K-feldspar, tr. pyrite
Colorado	
Creede-CCO	opal, K-feldspar, plagioclase, quartz, clay, SG82-opal, K-feldspar, tr. clay
Idaho	
Castle Creek-CCI	tr. clay; SG82-tr. clay
Castle Creek-XYI	opal, plagioclase
Crisman Hill-CHI	opal, K-feldspar
Nevada	
Fish Crk.-FCEN	K-feldspar, quartz, plagioclase; SG82-plagioclase
Fish Crk.-FCWN	quartz, K-feldspar, plagioclase
New Mexico	
Buckhorn-BNM	K-feldspar, quartz; SG82-tr. clay
St. Cloud-SNM	opal, quartz, plagioclase, clay
Oregon	
Harney Lake-HLO	K-feldspar, plagioclase
Sheaville-SVO	tr. clay, opal(?); SG82-tr. clay
Succor Crk.-SCO	opal, quartz, plagioclase
South Dakota	
SD1	plagioclase, calcite, quartz, opal, K-feldspar, clay
SDA	quartz, calcite, plagioclase, K-feldspar, opal(?)
SDC	quartz, opal, calcite, K-feldspar, plagioclase, tr. clay
Texas	
Alamito Crk.-ACT	opal, plagioclase, clay; SG82-opal, K-feldspar, clay
Tilden-TT	opal, quartz; SG82-opal, clay
Wyoming	
Ft. LaClede-FLW	plagioclase

mg/L) exceed the "Class 1 Aquatic Life" standard. It has the consistently lowest pH (3) of any drainage studied in 1993. This water also has a high concentration of Ca, which interferes with metal capture by CRR (Zamzow and others, 1989).

During the winter of 1992-93, several tests of Cu and Zn capture and nonmetal exchange were done using CRR from six deposits (BNM, CCI, FLW, SDA, SNM, and TT); Ft. LaClede, Wyo. (FLW) CRR performed best for capture of Cu and Zn (Desborough, 1993). In addition, FLW CRR captured about 1 weight percent Ca.

Testing of CRR samples was completed in the fall of 1993, and data for the 8-day tests are given in table 3. As control samples, both FLW and SDA were tested with the samples not previously tested in the Argo tunnel drain. Figure 2 shows that, for all tests, FLW performed best for capture of Cu plus Zn.

Table 3. Concentrations of elements in the water and elements gained or lost (-) by clinoptilolite-rich rock (1.7-4.7 mm) at the Argo tunnel drain, Idaho Springs, Colo.

[n.d. = not determined]

	K	Ca	Cu	Zn	Rb	Sr	Cd	Ba	Pb
	ppm × 10^3		parts per million						
Set 1. 10/27/93 - 11/4/93 (8 d) pH = 2.9-3.0, T = 14.5°C									
water (10/27/93) (mg/L)	2.9	292	4.8	41	n.d.	n.d.	0.11	<0.01	<0.1
ACT	-0.1	0.7	130	730	0	170	<1	-35	10
CCI	-0.5	-0.5	0	35	0	15	<1	-555	0
CCO	-0.6	0.3	40	250	0	115	<1	165	15
CHI	-1.8	0.8	120	755	-35	135	<1	265	15
FLW	0.1	1.5	160	970	20	180	<1	-135	10
SDA	-0.8	-0.2	130	640	0	90	<1	420	0
Set 2. 11/4/93 - 11/12/93 (8 d) pH = 3.0-3.1, T = 14.5°C									
FCEN	-0.2	0.2	20	245	0	95	<1	-25	0
FCWN	-0.1	0.1	15	115	-15	75	<1	-10	10
FLW	0	1.3	85	850	15	270	<1	-105	0
HLO	-0.6	0.2	0	115	65	60	<1	60	0
PBC	0	0.2	0	240	10	105	<1	85	0
SDA	-0.5	-0.7	105	625	0	120	<1	75	0
Set 3. 12/2/93 - 12/10/93 (8 d) pH = 3.1-3.2, T = 15-15.5°C									
FLW	0.2	1.2	150	900	25	175	<1	-105	0
PBC	-0.1	0.2	10	210	0	75	<1	-555	0
SCO	0	-0.2	0	210	0	50	<1	95	0
SDA	-0.4	-0.7	95	635	10	25	<1	-60	10
SVO	-1.3	0.2	110	420	25	140	<1	115	0
Z1BC	-0.1	0	10	230	0	50	<1	-835	20

CALIFORNIA GULCH, LEADVILLE

This drainage is south of Leadville and flows westward into the Arkansas River (fig. 1). The flow rate near the test site is about 150-525 gal/min (9-33 L/s), according to Wetherbee and others (1991) who measured discharge rates and determined chemical parameters during 1986, 1987, and 1988. The data of Wetherbee and others (1991) showed a pH range of 3.5-5.4 for 1986, 3.2-6.3 for 1987, and 3.7-7.3 for 1988. The range of concentrations for dissolved metals of interest were (in mg/L): Cu = <0.001-3.4, Zn = 0.06-110, Cd = 0.06-0.55, and Pb = <0.05-5.2 during 1986, 1987, and 1988 (Wetherbee and others, 1991). These data were obtained prior to the commencement of operations at the ASARCO, Inc., Yak tunnel water-treatment facility in 1992 (located upstream from the sites studied here); thus, some water upstream from the sites studied has been treated to remove heavy metals and raise the pH.

Two sampling sites about 4 km apart were studied. The lower California Gulch site is about 1.5 km west of Stringtown at the junction of California Gulch and State Highway 24. The upper California Gulch site is at the intersection of California Gulch and Spruce Street, on the south side of Leadville, and about 1.5 km downstream from the ASARCO, Inc., Yak tunnel-treatment facility.

Table 4 shows the concentrations of elements in the water and elements gained or lost by CRR during five test periods in 1993. In spite of the Yak tunnel water-remediation operation, the water in California Gulch exceeds the "Class 1 Aquatic Life" standards for both Zn and Cd, and concentrations of Cu, Zn, Cd, and Pb are highest during spring runoff (tables 4, 5). FLW captured the most Zn at low pH but much smaller amounts at high pH (fig. 3). At the highest pH, SDA and SVO captured significantly more Zn than the other samples (fig. 3). At near-neutral pH, the ACT, FLW, and SDA captured about the same amounts of Zn. Using the ratios of Zn/Cu in the water and the amount of Zn and Cu captured by CRR, for those that captured Cu at low pH, FLW preferred Zn over Cu, whereas SDA preferred Cu over Zn. In the same manner, the Zn/Pb values show that all of the CRR samples preferred Pb over Zn. FLW captured up to 2.1 weight percent Ca, and of the seven tests in California Gulch, FLW captured as much or more Ca than any other CRR (tables 4, 5).

The change of pH to the very high values of 8.2 and 9.2 at both test sites in late July and early August might be related to the influence of the ASARCO, Inc., water-treatment facility, because the highest value reported by Wetherbee and others (1991) for 1986, 1987, and 1988 was only 7.3. Figure 4 shows the influence of pH on the capture of Zn by FLW and SDA.

MINERAL CREEK, SAN JUAN COUNTY

This drainage was studied because of the relatively high contents of Cu (27-37 mg/L) and Zn (89-115 mg/L). Only one very short and two very long tests were done. The flow rate is about 150 gal/min (9 L/sec.). Data in table 6 show that FLW captured more Cu and Zn than any other CRR tested; it also captured more Ca than any other CRR. In examining the ratio of Zn/Cu in the water, and that of the CRR samples, all of them had a preference for Cu over Zn. At California Gulch, FLW had a preference for Zn over Cu at a similar pH.

Figure 5 shows the amounts of Cu plus Zn plus Pb captured by CRR for two long-term tests.

Table 4. Concentrations of elements in the water and elements gained or lost (-) by clinoptilolite-rich rock (1.7-4.7 mm) at the lower California Gulch test site, west of Stringtown, Colo.

[n.d. = not determined]

	K	Ca	Cu	Zn	Rb	Sr	Cd	Ba	Pb
	ppm × 10^3		parts per million						
5/29/93 - 6/4/93 (6 d) pH = 4.3-4.9, T = 12-14°C									
water (6/4/93)									
(mg/L)	2.6	145	0.4	21.0	n.d.	n.d.	0.11	0.40	0.30
FLW	0.2	1.1	10	1,625	0	55	1	-230	640
SD1	-0.2	-1.1	30	680	85	60	1	-285	790
SDA	-0.3	-0.1	55	1,180	0	45	<1	-55	525
SDC	-0.1	0.4	50	995	-10	35	1	25	660
TT	-0.3	1.2	50	810	0	20	1	-335	790
6/4/93 - 6/13/93 (9 d) pH = 4.9-6.1, T = 14.5-17°C									
water (6/13/93)									
(mg/L)	2.5	144	0.3	18.1	n.d.	n.d.	0.10	0.40	0.22
FLW	0.3	1.5	0	1,335	0	70	<1	-105	570
SD1	-0.2	-0.5	40	790	75	50	<1	-200	530
SDA	-0.3	0.6	30	1,095	-10	45	<1	-50	810
SDC	-0.2	0.3	40	910	-10	60	<1	-20	785
TT	-0.6	-0.1	0	565	-10	-15	<1	-155	535
6/13/93 - 7/2/93 (19 d) pH = 6.1-7.4, T = 15-17°C									
FLW	0.3	1.9	0	1,300	-10	115	<1	-160	210
SD1	-0.3	0.1	55	1,360	-10	85	<1	-400	165
SDA	-0.2	-0.3	0	1,020	0	65	<1	-315	155
SDC	-0.4	0.7	0	1,190	-15	80	1	-155	175
TT	-1.3	0.4	0	485	-10	70	<1	-160	200
7/20/93 - 8/3/93 (14 d) pH = 8.2-9.2, T = 15-17°C									
water (8/3/93)									
(mg/L)	2.5	218	<0.01	10.3	n.d.	n.d.	0.02	0.04	0.11
CCO	-0.2	0.4	0	1,400	-45	10	<1	160	40
FCEN	0	0.6	0	1,320	-45	55	<1	45	45
FLW	0.4	2.1	0	1,185	-10	80	<1	-255	0
HLO	0	0.5	0	915	15	45	<1	75	35
PBC	0.2	0.5	0	645	-20	-65	<1	-80	50
SDA	-0.7	0.9	0	2,130	0	45	<1	55	50
SVO	-0.8	0.6	0	1,945	-20	60	<1	65	110
10/16/93 - 10/28/93 (12 d) pH = 7.3-7.8, T = 5-10°C									
water (10/16/93)									
(mg/L)	1.5	86	<0.01	14.3	n.d.	n.d.	0.03	0.05	<0.1
ACT	0.2	0.8	0	995	-15	80	<1	25	30
CCI	0.2	-0.5	0	540	0	-10	<1	-375	25
CHI	-1.1	0.8	0	850	-45	45	<1	405	0
FLW	0.2	1.8	0	1,095	0	85	1	0	20
SCO	0.2	0	0	455	0	10	<1	165	0
SDA	-0.3	1.1	0	1,165	0	45	<1	70	65
XYI	0.6	0.3	0	795	0	30	<1	240	40
Z1BC	0.4	0.7	0	525	0	95	<1	625	0

Table 5. Concentrations of elements in the water and elements gained or lost (-) by clinoptilolite-rich rock (1.7-4.7 mm) at upper California Gulch at Spruce Street, south of Leadville, Colo.

[n.d. = not determined]

	K	Ca	Cu	Zn	Rb	Sr	Cd	Ba	Pb
	ppm × 10^3		parts per million						
water (6/4/93)									
(mg/L)	1.9	183	0.6	18.8	n.d.	n.d.	0.11	0.03	0.27
5/29/93 - 6/4/93 (7 d)	**pH = 4.3-4.9, T = 10-11°C**								
BNM	0.2	-0.5	0	215	0	0	< 1	-505	365
CCI	0.3	-0.4	0	145	0	20	< 1	30	460
FLW	0.2	1.0	25	1,295	0	40	2	-20	415
SD1	-0.1	-1.0	20	575	0	35	< 1	-215	425
SDA	-0.3	-0.4	60	950	-10	25	< 1	-50	460
SDC	0	-0.3	10	795	0	20	< 1	320	435
SNM	-0.2	-0.6	0	115	-25	-200	< 1	-245	140
TT	-0.3	0	15	620	0	0	< 1	-225	435
water (6/13/93)									
(mg/L)	2.0	197	0.4	13.2	n.d.	n.d.	0.07	0.05	0.18
6/4/93 - 6/13/93 (9 d)	**pH = 4.9-5.8, T = 11-14.5°C**								
FLW	0	0.2	0	975	85	80	< 1	-65	515
SD1	-0.3	-0.7	0	500	115	70	1	-315	445
SDA	-0.8	-0.1	55	755	120	40	1	40	445
SDC	-0.5	0.2	35	600	120	35	< 1	-80	485
TT	-0.7	0.2	0	340	70	90	< 1	-635	385

Table 6. Concentrations of elements in the water and elements gained or lost (-) by clinoptilolite-rich rock (1.7-4.7 mm) at the headwaters of Mineral Creek, 0.6 km south of Red Mountain Pass in San Juan County, Colo.

[n.d. = not determined]

	K	Ca	Cu	Zn	Rb	Sr	Cd	Ba	Pb	Cu+Zn+Pb
	ppm × 10^3		parts per million							
7/13/93 - 7/14/93 (19 h)			**pH = 4.1-4.2,**	**T = 16-20°C**						
water (7/14/93)										
(mg/L)	0.3	63.8	27	89	n.d.	n.d.	0.3	0.02	<0.1	
FLW	-0.1	0.2	490	1,185	0	100	<1	-160	0	1,675
SD1	-0.3	-0.9	330	615	0	90	<1	-265	0	945
SDA	-0.3	-0.4	370	750	0	75	<1	35	0	1,120
SDC	-0.3	-0.3	330	720	0	70	<1	-50	0	1,050
TT	-0.7	-0.1	175	585	0	140	<1	-160	0	760
7/14/93 - 8/10/93 (27 d)			**pH = 4.1-4.4,**	**T = 16°C**						
water (8/10/93)										
(mg/L)	0.5	79	31	100	n.d.	n.d.	0.33	0.02	0.03	
FLW	0	0.8	2,420	6,040	-15	410	1	-300	145	8,605
SD1	-0.5	-2.0	1,205	1,975	-30	230	1	-335	210	3,390
SDA	-0.8	-1.3	1,725	3,395	-20	225	1	-160	130	5,250
SDC	-0.4	-0.5	1,485	2,930	-35	315	1	-260	215	4,630
TT	-0.7	-0.3	815	1,940	-25	265	1	-330	135	2,890
8/10/93 - 10/27/93 (78 d)			**pH = 3.0-4.4,**	**T = 3-10°C**						
water (10/27/93)										
(mg/L)	<0.1	88	37	115	n.d.	n.d	0.36	0.02	<0.1	
CCO	-0.6	-0.1	680	1,720	-25	395	1	85	160	2,560
FCEN	-0.4	0.4	895	1,740	-40	430	<1	25	170	2,805
FLW	-0.1	0.7	2,550	5,880	-25	630	1	-265	220	8,650
HLO	-0.5	0.2	515	830	20	275	1	75	120	1,465
PBC	-0.1	0.1	705	1,210	-15	215	<1	0	160	2,075
SDA	-0.5	-1.1	1,755	3,530	0	205	<1	305	175	5,460
SVO	-1.3	0.3	2,000	2,670	-25	500	<1	85	280	4,950

RAWLEY TUNNEL, BONANZA

This tunnel drain is estimated to flow at a rate of at least 200 gal/min (12.5 L/s). Throughout testing, the water temperature was 10°C. For the water, Cu varied from 2.5 to 4.8 mg/L, and Zn varied from 44 to 59 mg/L; Cd and Pb were essentially invariant (table 7). Copper, Zn, and Cd concentrations exceed the "Class 1 Aquatic Life" standards.

FLW captured more Zn than any other CRR, whereas the SD group (SD1, SDA, SDC) captured the most Cu. Combined Cu + Zn in SDA is similar to combined Cu + Zn in FLW for all tests. FLW and the SD group captured only trace amounts of Cd, but the other CRR samples captured no detectable Cd. The ratios of Zn/Cu and Zn/Pb are shown in table 7 for the water and the CRR samples. Copper was preferred over Zn, and Pb was preferred over Zn in all tests. For those CRR that captured Cd, the Zn/Cd ratios of the water and the CRR (not shown) revealed that Zn was preferred over Cd. The metal selectivity of all CRR samples was Pb > Cu > Zn. For the five longest tests, capture of Pb varied by less than a factor of two among samples; capture of Zn varied by a factor of two to five; and capture of Cu varied by a factor of four to five. FLW captured more Ca than the other samples in all tests.

Figure 6 shows the amounts of Cu plus Zn plus Pb captured during the first two tests. Figure 7 shows the combined amounts of Cu plus Zn plus Pb captured during the last two tests at Rawley tunnel.

WELLINGTON MINE DRAIN, BRECKENRIDGE

This HMPD has an estimated flow rate of about 100 gal/min (6 L/s), the pH is 5.7-8.2, and the Ca content is high. The Zn concentration of 180-230 mg/L is apparently higher than that for any HMPD in the Western U.S., and the Zn and Cd exceed the "Class 1 Aquatic Life" standards (table 8). Both FLW and SDA captured 30 to 50 percent more Zn than the other CRR's, and FLW performed about 10 to 20 percent better than SDA. All CRR's captured significant amounts of Pb. Cadmium was not detected by the chemical analyses and apparently was not captured in significant amounts. FLW showed a preference for Ca over Zn. Figure 8 shows the capture of Zn plus Pb by CRR during three tests of the Wellington drain.

Table 7. Concentrations of elements in the water and elements gained or lost (-) by clinoptilolite-rich rock (1.7-4.7 mm) at the Rawley mine tunnel drain at Bonanza, Colo.

[n.d. = not determined]

	K	Ca	Cu	Zn	Rb	Sr	Cd	Ba	Pb	Zn/Cu	Zn/Pb
	ppm × 10^3		parts per million								
Water (6-12-93 & 6-17-93)											
(mg/L)	1.3	170	4.85	58	n.d.	n.d.	0.25	0.2	0.06	12	967
6/12/93–6/17/93 (5 d)			**pH = 7.1, T = 10°C**								
FLW	0	1.3	370	2,415	0	190	<1	-145	190	6.5	12.7
SD1	0.1	-0.8	960	1,265	0	110	<1	-165	150	1.3	8.4
SDA	-0.2	-0.6	720	2,315	10	110	1	270	115	3.2	20.1
SDC	-0.2	0	765	1,475	0	125	1	0	135	1.9	10.9
TT	-0.6	0.3	235	1,250	0	170	<1	-195	180	5.3	6.9

Table 7. Concentrations of elements in the water and elements gained or lost (-) by clinoptilolite-rich rock (1.7-4.7 mm) at the Rawley mine tunnel drain at Bonanza, Colo.--Continued

	K	Ca	Cu	Zn	Rb	Sr	Cd	Ba	Pb	Zn/Cu	Zn/Pb
	ppm × 10^3		---------parts per million---------								
6/17/93–7/15/93 (28 d)			**pH = 7.1, T = 10°C**								
FLW	0.2	1.4	455	2,770	0	270	2	-180	250	6.1	11.1
SD1	-0.5	-1.2	1,100	1,625	0	225	1	-235	350	1.5	4.6
SDA	-0.6	-0.3	940	2,180	0	245	< 1	310	275	2.3	7.9
SDC	-0.5	-0.1	675	1,835	0	225	2	-130	255	2.7	7.2
TT	-0.7	0.2	265	1,415	-25	170	< 1	-345	270	5.3	5.2
7/15/93–8/11/93 (27 d)			**pH = 7.1-7.4, T = 10°C**								
Water (8-11-93)											
(mg/L)	1.2	166	4.3	59	n.d.	n.d.	0.26	0.01	0.10	13.7	590
FLW	0.1	1.8	355	2,560	0	270	2	-145	345	7.2	7.4
SD1	-0.3	-0.3	775	1,290	0	140	< 1	-455	265	1.7	4.8
SDA	-0.7	0.3	775	1,955	0	200	1	-160	280	2.5	7.0
SDC	-0.5	0.4	825	1,840	0	210	1	-215	285	2.2	6.4
TT	-0.7	0.2	215	1,250	-20	105	< 1	-270	320	5.8	3.9
8/11/93–8/12/93, (27 h)			**pH = 7.4-7.6, T = 10°C**								
CCO	-0.1	0.1	35	515	0	50	< 1	95	80	14.7	6.4
FLW	0.2	0.9	120	1,425	-15	50	1	-340	50	12.0	28.5
FCEN	0.2	0.4	35	450	0	25	< 1	-55	40	13.0	11.2
HLO	-0.1	0.2	85	325	20	35	< 1	0	0	3.8	
PBC	-0.1	0.1	0	435	0	30	< 1	-240	0		
SDA	-0.3	0.6	250	970	0	10	1	-75	70	4.0	13.8
SVO	0	0.1	150	545	0	40	< 1	-80	35	3.6	15.5
8/12/93–10/16/93 (65 d)			**pH = 7.4-6.6, T = 10°C**								
Water (10-16-93)											
(mg/L)	1.2	154	2.5	45	n.d.	n.d.	0.2	0.01	0.1	18.2	445
CCO	-0.6	0.4	280	1,005	-25	220	< 1	155	220	3.6	4.6
FLW	0.2	2.1	490	3,140	15	430	1	-70	390	6.4	8.1
SD1	-0.7	-0.8	1,105	1,740	10	285	1	-185	320	1.6	5.4
SDA	-1.0	0	1,050	2,630	10	355	1	380	335	2.5	7.9
SDC	-0.8	0.4	790	2,020	0	265	< 1	-45	310	2.6	6.5
10/16/93–10/28/93 (12 d)			**pH = 5.7-6.6, T = 10°C**								
Water (10/28/93)											
(mg/L)	1.2	152	2.5	44	n.d.	n.d.	0.2	0.01	0.1	18.2	440
ACT	-0.1	1.0	400	1,545	0	230	< 1	-60	95	3.9	16.2
CCI	-0.2	-0.6	245	415	0	20	< 1	-445	85	1.7	4.9
CHI	-1.2	0.7	205	1,940	-40	200	< 1	250	145	9.5	13.4
FLW	0.2	1.7	295	2,305	0	265	3	-175	145	7.8	15.9
SCO	0.4	0.3	125	680	0	75	< 1	165	85	5.4	8.0
SDA	-0.2	0.3	660	1,900	0	185	2	675	130	2.9	14.6
XYI	0.2	0.4	545	885	25	115	< 1	160	145	1.6	6.1
Z1BC	0.2	0.3	100	795	0	170	< 1	621	110	8.0	7.2

Table 8. Concentrations of elements in the water and elements gained or lost (-) by clinoptilolite-rich rock (1.7-4.7 mm) at the Wellington mine drain, French Creek, near Breckenridge, Colo.

[n.d. = not determined]

	K	Ca	Cu	Zn	Rb	Sr	Cd	Ba	Pb
	ppm × 10^3		---parts per million---						
5/28/93–6/4/93 (7 d)	**pH = 6.8-7.1, T = 9-11°C**								
water (6/4/93)									
(mg/L)	3.6	292	0.01	220	n.d.	n.d.	0.09	0.01	0.09
BNM	0.2	-0.3	0	1,900	10	90	<1	-495	205
CCI	0.1	-0.4	0	1,915	0	50	<1	-180	250
FLW	0.3	1.1	0	3,315	0	220	<1	-275	215
SD1	-0.1	-0.2	0	2,540	10	140	<1	-340	155
SDA	-0.3	-0.4	0	3,030	0	175	<1	30	190
SDC	0	0.3	0	2,700	0	165	<1	-255	195
SNM	-0.1	-0.6	0	1,010	-20	-120	<1	-135	165
TT	-0.3	0.1	0	2,400	0	150	<1	30	150
6/4/93–6/13/93 (9 d)	**pH = 7.1-7.4, T = 11-12°C**								
water (6/13/93)									
(mg/L)	3.8	308	0.01	230	n.d.	n.d.	0.10	0.03	0.13
FLW	0.2	1.2	0	3,505	0	225	<1	-185	125
SD1	-0.1	-0.6	0	2,620	0	140	<1	-670	160
SDA	-0.2	-0.5	0	3,160	0	150	<1	-30	170
SDC	-0.1	0.1	0	1,760	-15	145	1	-150	105
TT	-0.5	1.0	0	1,940	0	110	<1	-100	85
7/20/93–8/13/93 (24 d)	**pH = 7.9-8.2, T = 11-12°C**								
CCO	-0.3	0.2	0	1,630	-30	35	<1	-40	210
FCEN	-0.1	0.3	0	1,470	-35	75	1	-65	120
FCWN	0.3	0.2	0	1,510	-20	100	<1	-155	195
FLW	0.4	1.1	0	3,900	-20	155	<1	-385	240
HLO	-0.1	0.1	0	1,870	15	60	<1	-25	305
SDA	-0.5	-0.5	0	3,720	-25	135	<1	-135	335
SVO	-0.8	0.2	0	2,505	-20	100	<1	-255	345
PBC	-0.1	0.1	0	1,560	-15	0	<1	-505	220
10/16/93–10/28/93 (12 d)	**pH = 5.7-6.5, T = 3.5-7°C**								
water (10/16/93)									
(mg/L)	3.7	301	<0.1	180	n.d.	n.d.	0.11	0.08	0.2
ACT	0.3	0.5	0	2,230	-15	170	<1	-70	180
CHI	-1.1	0.5	0	2,585	0	20	<1	230	180
FLW	0.4	1.2	0	3,260	0	255	<1	-100	225
SCO	0.1	-0.1	0	1,500	0	25	<1	0	165
SDA	-0.3	0.6	0	2,640	0	140	<1	0	145
XYI	0.4	0.3	0	2,135	0	60	<1	85	275
Z1BC	0	0.3	0	1,230	0	110	<1	590	130

RELATED FIELD STUDIES AND SIGNIFICANCE OF CALCIUM IN STREAM WATER

Cobalt

Water analysis for Co in the five HMPD's studied above showed a range of <0.1-0.2 mg/L in the present study. Wetherbee and others (1991) found a maximum of of 0.53 mg/L in one of many water samples from California Gulch. Ficklin and others (1992) reported 0.53 mg/L for the Reynolds Tunnel at Summitville and 17 mg/L for the Blackstrap drain at Summitville. These sites were not considered appropriate for study due to heavy-metal and cyanide pollution remediation measures being undertaken in 1993 which significantly altered dissolved metal content and pH.

For these reasons, a site in Lemhi County, Idaho, was studied. This site is about 40 km southwest of Salmon, at the toe of a waste pile from a Cu-Co prospect adjacent to the north Fork of Iron Creek. The HMPD is almost ponded; thus, the flow is nearly negligible. Only data for Ca, Co, and Cu are given in table 9 because the concentration of Zn in the water was only 0.1 mg/L, and the concentrations of Cd and Pb were <0.01 mg/L. FLW and SDA captured the most Co and Cu, but CHI captured significant amounts of both elements (fig. 9). The ratios of Ca/Cu for the water and the CRR's show that about half of the CRR's preferred Cu over Ca, and the other half preferred Ca over Cu. The ratios of Cu/Co for the water and the CRR's showed that all preferred Cu over Co.

Table 9. Concentrations of Ca, Co, and Cu in the water and Ca, Co, and Cu gained or lost (-) by clinoptilolite-rich rock (1.7-4.7 mm) at the toe of a waste pile in the North Fork of Iron Creek, Lemhi County, Idaho.

	Ca	Co	Cu	Ca/Cu	Cu/Co
	-----------parts per million-----------				
9/20/93 - 9/24/93	**(4 d)**	**pH = 5.8,**	**T = 9.5°C**		
water (9/24/93) (mg/L)	24	5.7	8.9	2.7	1.6
CCI	-2,000	95	195	-10.3	2.0
CHI	0	135	475	0	3.5
FCEN	3,000	75	160	19	2.1
FLW	1,000	205	525	1.9	2.5
HLO	-2,000	70	305	-6.5	4.4
PBC	2,000	100	180	11	1.8
SCO	1,000	120	215	4.6	1.8
SDA	1,000	215	500	2.0	2.3
SVO	0	85	360	0	4.2
XYI	1,000	140	295	3.4	2.1
Z1BC	2,000	100	315	6.3	3.2
Z2BC	0	25	115	0	4.6

Calcium and the "Class 1 Aquatic Life" Standards

As previously mentioned, the statutory limits for heavy metals for "Class 1 Aquatic Life" standards in Colorado change as a function of $CaCO_3$ content of the water; the higher the $CaCO_3$, the more of certain dissolved metals are allowed. The reason is that salmonids (trout) have a higher tolerance for trace amounts of heavy metals in the presence of high calcium (Phillips and others, 1963). Apparently, higher Ca concentrations ameliorate trout tolerance for traces of heavy metals. Also, according to Love (1970, p. 188), "Calcium ions play an important part in osmoregulation." Even in the absence of heavy metals, brown trout have adverse reactions to osmotic and temperature stress and die from such stresses at Ca concentrations below about 3 mg/L (Podoliak, 1965). A minimum Ca concentration in the range of 15-25 mg/L is required in the water for trout health in the absence of heavy metals (George Ketola, pers. commun., 1993). For these reasons, it is important to be aware of CRR with a very high affinity for Ca in HMPD's. Of course, Ca deficiency in the HMPD-treated water can be remedied by addition of soluble Ca compounds. Many of the HMPD's have relatively high initial Ca concentrations, and many of the HMPD's drain into much larger drainages so that the treated HMPD water is diluted perhaps 10-70 times.

An example of the exacerbation of the HMPD problem by excessive Ca capture by CRR is provided by the upper St. Kevin Gulch site near Leadville. At the time of water sampling and immersion (6/11/93) of five CRR's for 21 days, the water contained (mg/L): Ca = 5.6, Cu = 0.08, Zn = 3, Cd = 0.03, Pb = <0.01, and the pH was 5.2-5.4 in the test period for CRR samples. FLW, SD1, SDA, SDC, and TT were tested, and FLW captured 0.7 weight percent of Ca and 2,600 ppm of Zn; the other CRR's captured 790-1,925 ppm of Zn, but all **lost** Ca to the HMPD. St. Kevin Gulch is not a perennial stream in the lower reaches, but this provides an example of the high affinity for Ca of one of the CRR's that also has the highest affinity for metals in the lower pH range.

SUMMARY

Samples of clinoptilolite-rich rocks (CRR) from 17 deposits, tested in a wide range of pH, temperature, and cation concentrations in heavy-metal-polluted drainages (HMPD'S), vary widely in their ability to capture of copper, zinc, and cadmium. All have a strong affinity for lead. Results show that only a few of these CRR capture copper and zinc much more effectively than most others. The Ft. LaClede, Wyo., CRR is best for capture of copper plus zinc in the pH range of about 3 to 6, but it also captures large amounts of calcium. The South Dakota CRR is best for capture of copper plus zinc in the pH range of about 6 to 9.

The variations in the amounts of heavy metals captured by CRR cannot be explained simply by the amount of clinoptilolite in the rocks or by the chemical composition of the clinoptilolite. Some of the CRR's with the highest contents of clinoptilolite capture far less copper and zinc than some CRR's that contain less than 80 percent clinoptilolite. The metal preferences (e.g., Zn > Cu) of the CRR's differ significantly, and the relations of metal preferences may vary from one HMPD to another for the same CRR.

Large variations in both pH and competing metal and nonmetal ions are observed in the water of some HMPD's; these variations have significant impact on the capture of heavy metals by CRR.

ACKNOWLEDGMENTS

I thank Richard A. Sheppard for advice and discussions regarding clinoptilolite. I also thank those individuals and corporations who provided large samples of some of the CRR's. David Frishman gave helpful advice and prepared two illustrations that are used herein.

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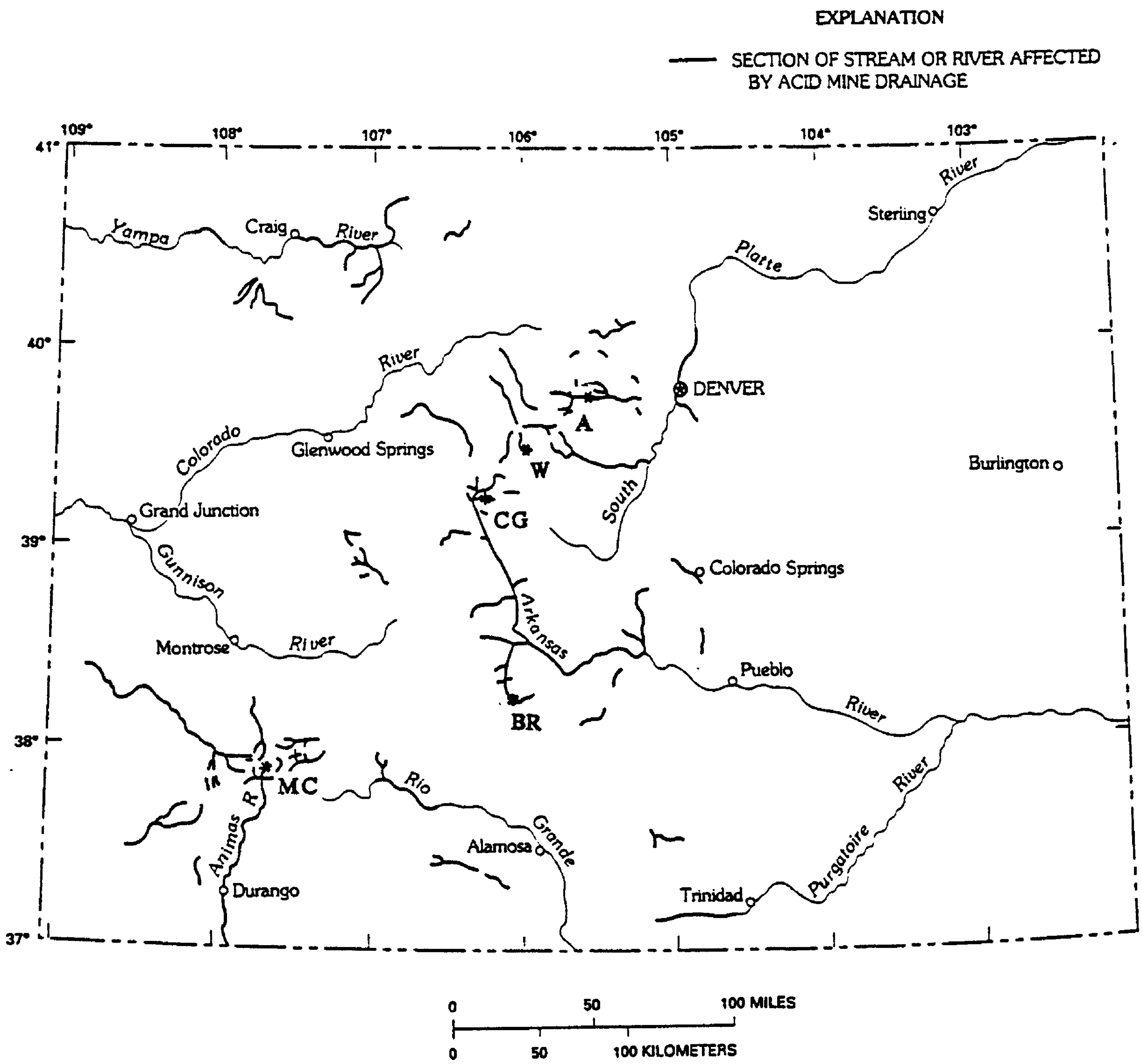
APPENDIX

Testing was done with the following CRR samples during May through mid-December, 1993, for the five Colorado HMPD's.

Site	Samples (see table 1)
Argo tunnel	ACT, CCI, CCO, CHI, FCEN, FCWN, FLW, HLO, PBC, SCO, SD1, SDA, SDC, SVO, Z1BC
California Gulch	ACT, BNM, CCI, CCO, CHI, FCEN, FLW, HLO, PBC, SCO, SD1, SDA, SDC, SNM, SVO, TT, XYI, Z1BC
Mineral Creek	CCO, FCEN, FLW, HLO, PBC, SD1, SDA, SDC, SVO, TT
Rawley tunnel	ACT, CCI, CCO, CHI, FCEN, FLW, HLO, PBC, SCO, SD1, SDA, SDC, TT, XYI, Z1BC
Wellington drain	ACT, BNM, CCI, CCO, CHI, FCEN, FCWN, FLW, HLO, PBC, SCO, SD1, SDA, SDC, SNM, SVO, TT, XYI, Z1BC



Map symbol	Drainage site	pH	Temperature
A	Argo tunnel	2.9-3.2	14-16°C
BR	Rawley tunnel, Bonanza	5.7-7.6	10
CG	California Gulch	4.3-9.2	10-17
MC	Mineral Creek	3.0-4.4	3-20
W	Wellington mine drain	5.7-8.2	8-12

Figure 1. Heavy-metal-polluted drainages studied in Colorado in 1993.

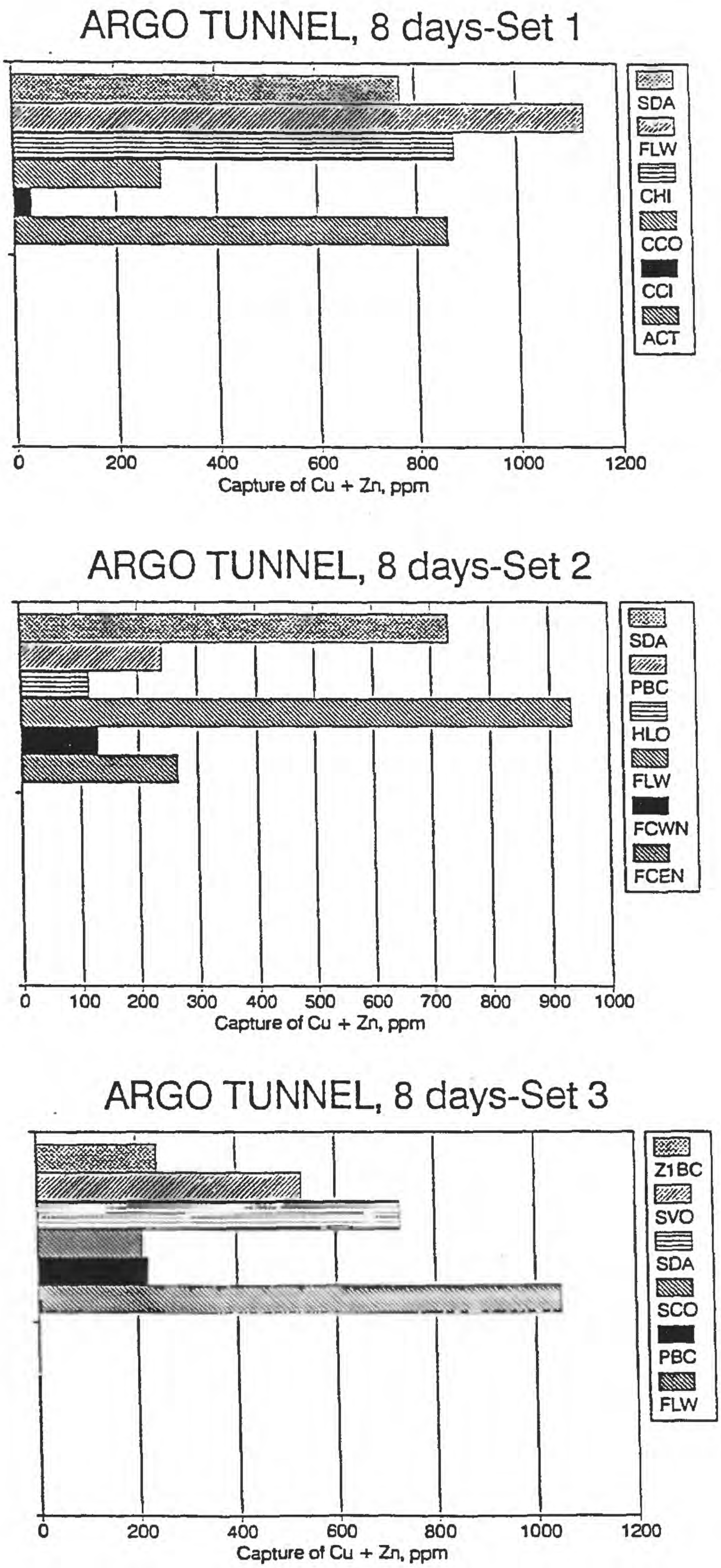


Figure 2. Capture of copper and zinc from water by clinoptilolite-rich rocks during three tests at Argo tunnel, Idaho Springs.

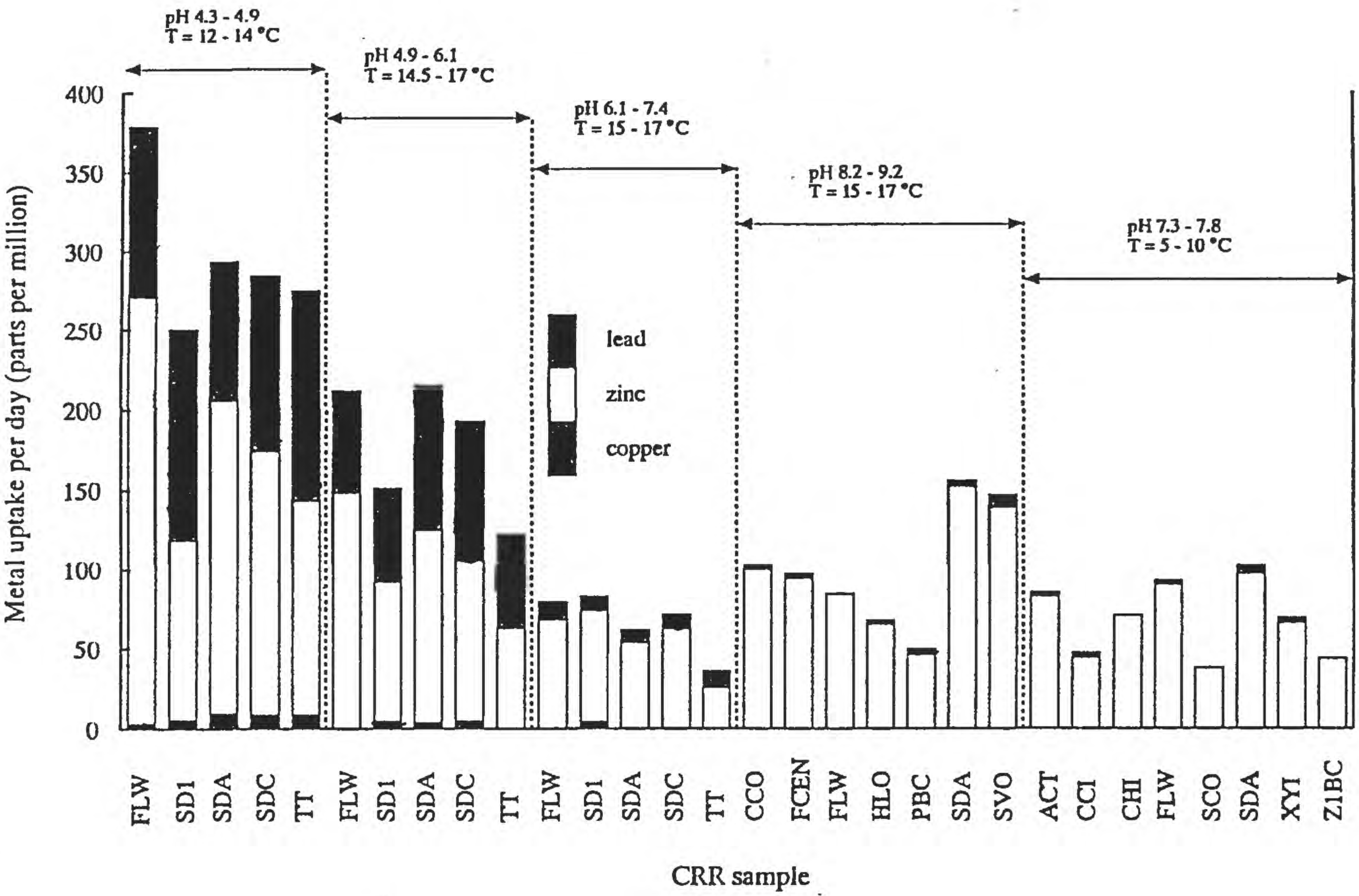


Figure 3. Relations of lead, zinc, and copper capture from water by clinoptilolite-rich rocks with changes in water pH for lower California Gulch, Leadville.

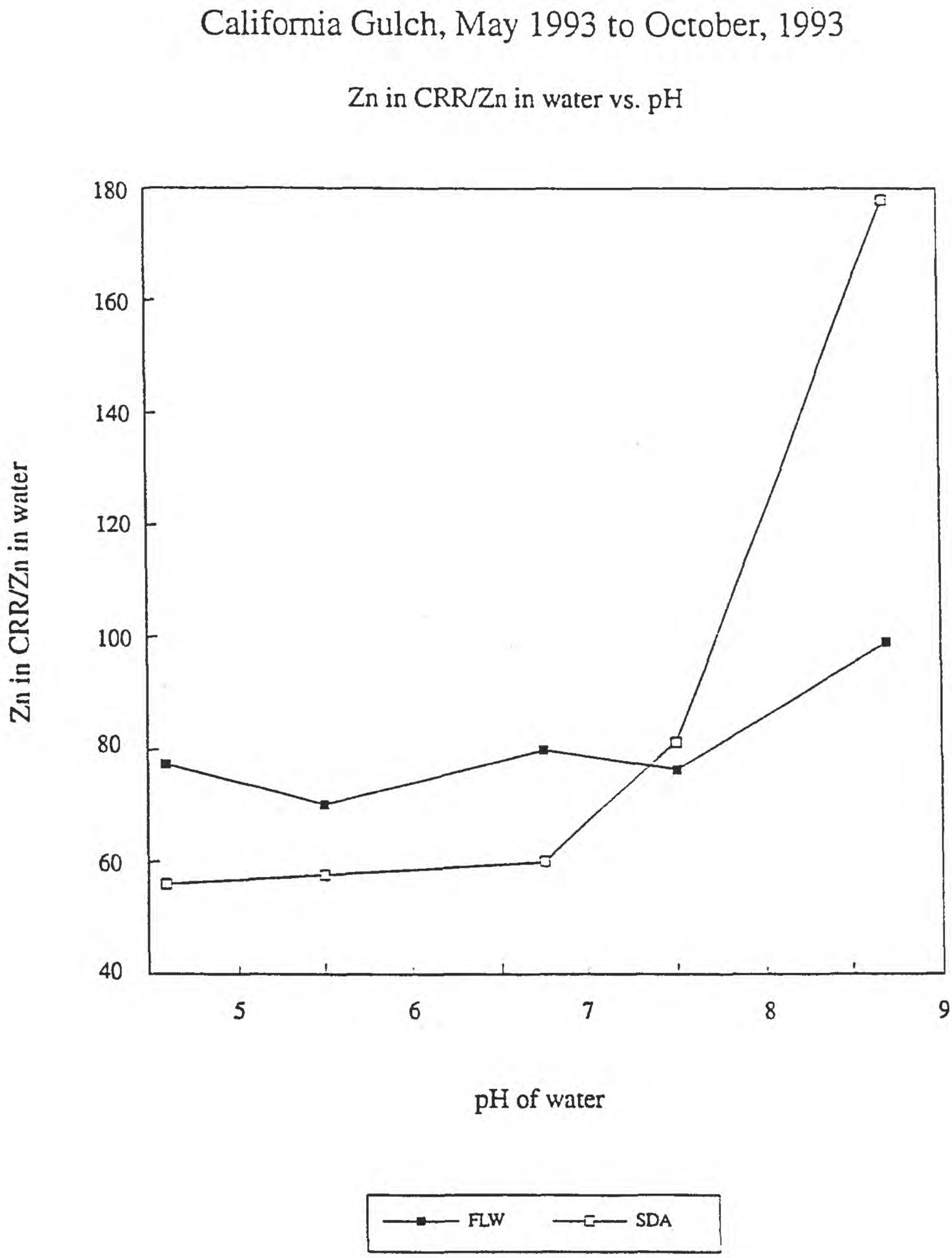
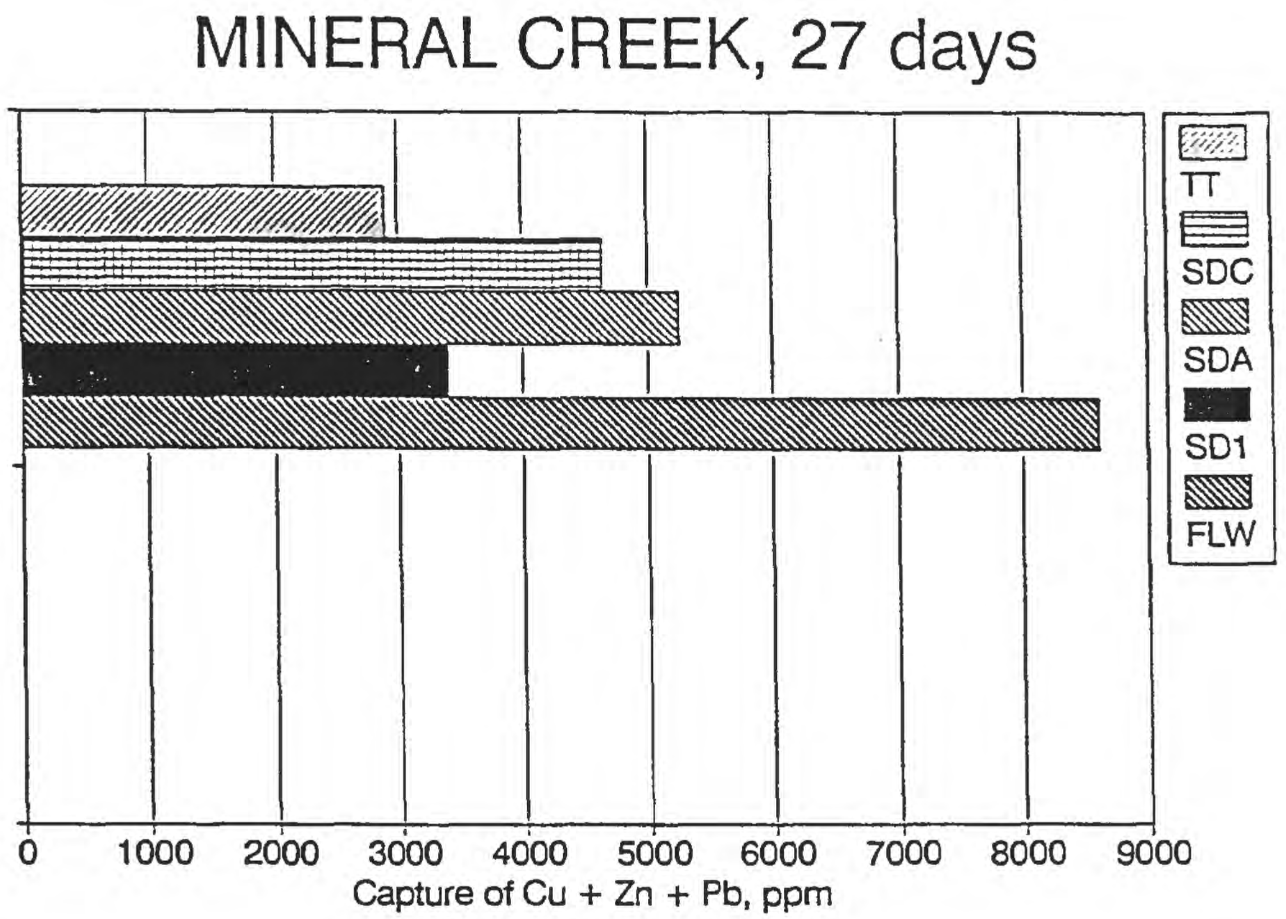


Figure 4. Variations in capture of zinc from water by Ft. LaClede, Wyo., and South Dakota A in relation to zinc concentration in the water and pH.



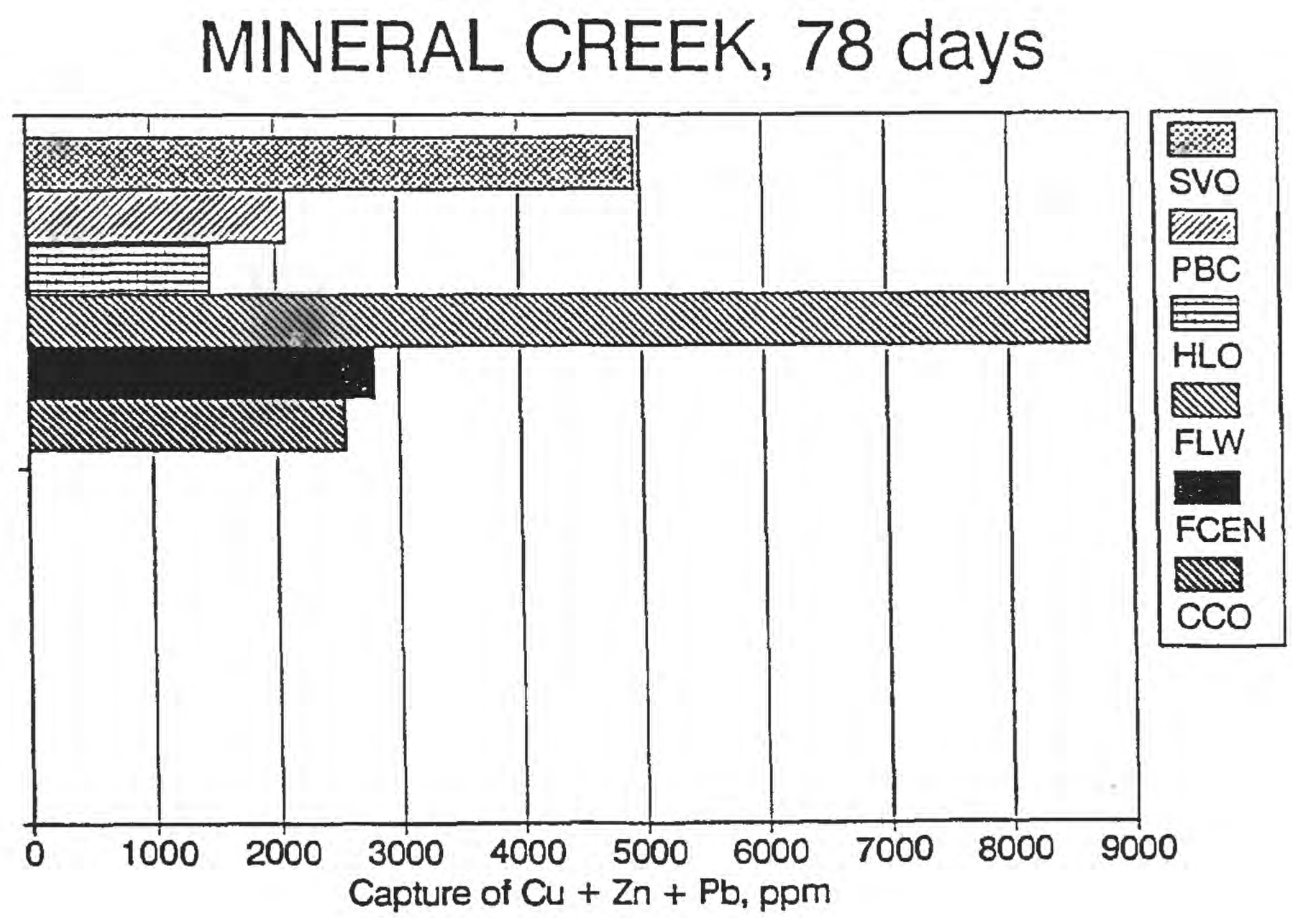
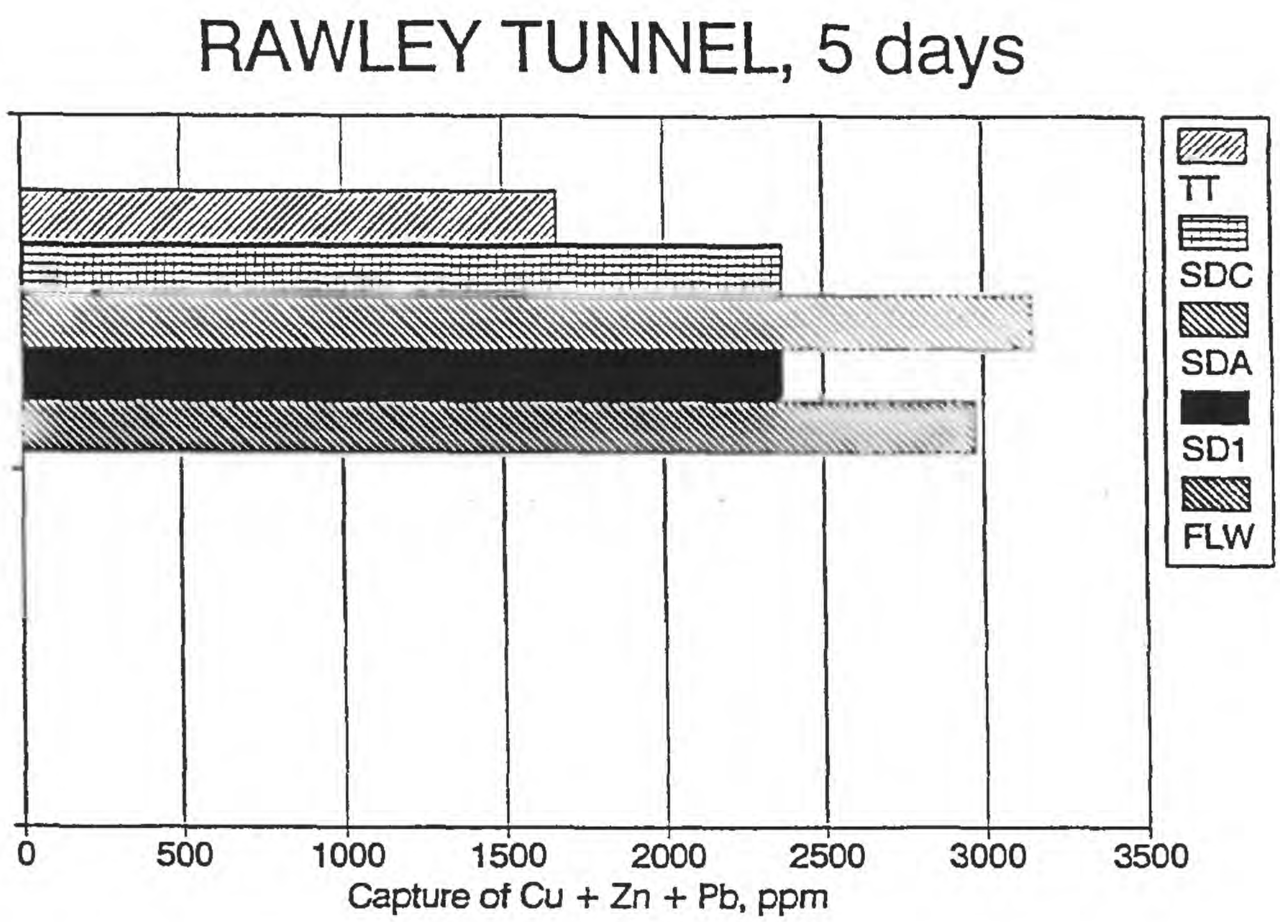


Figure 5. Capture of copper plus zinc plus lead from water by clinoptilolite-rich rocks during two tests at Mineral Creek near Red Mountain Pass.



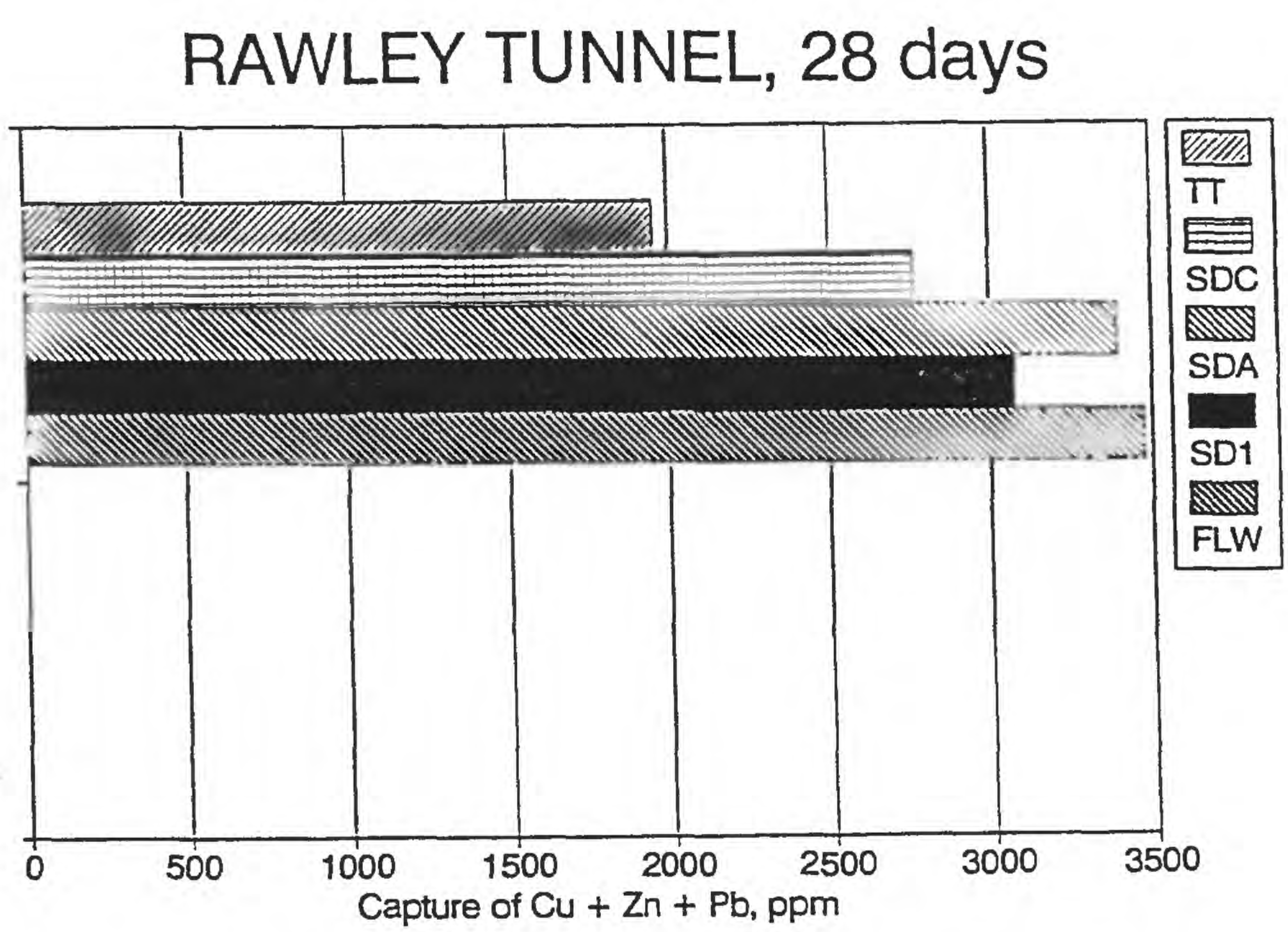
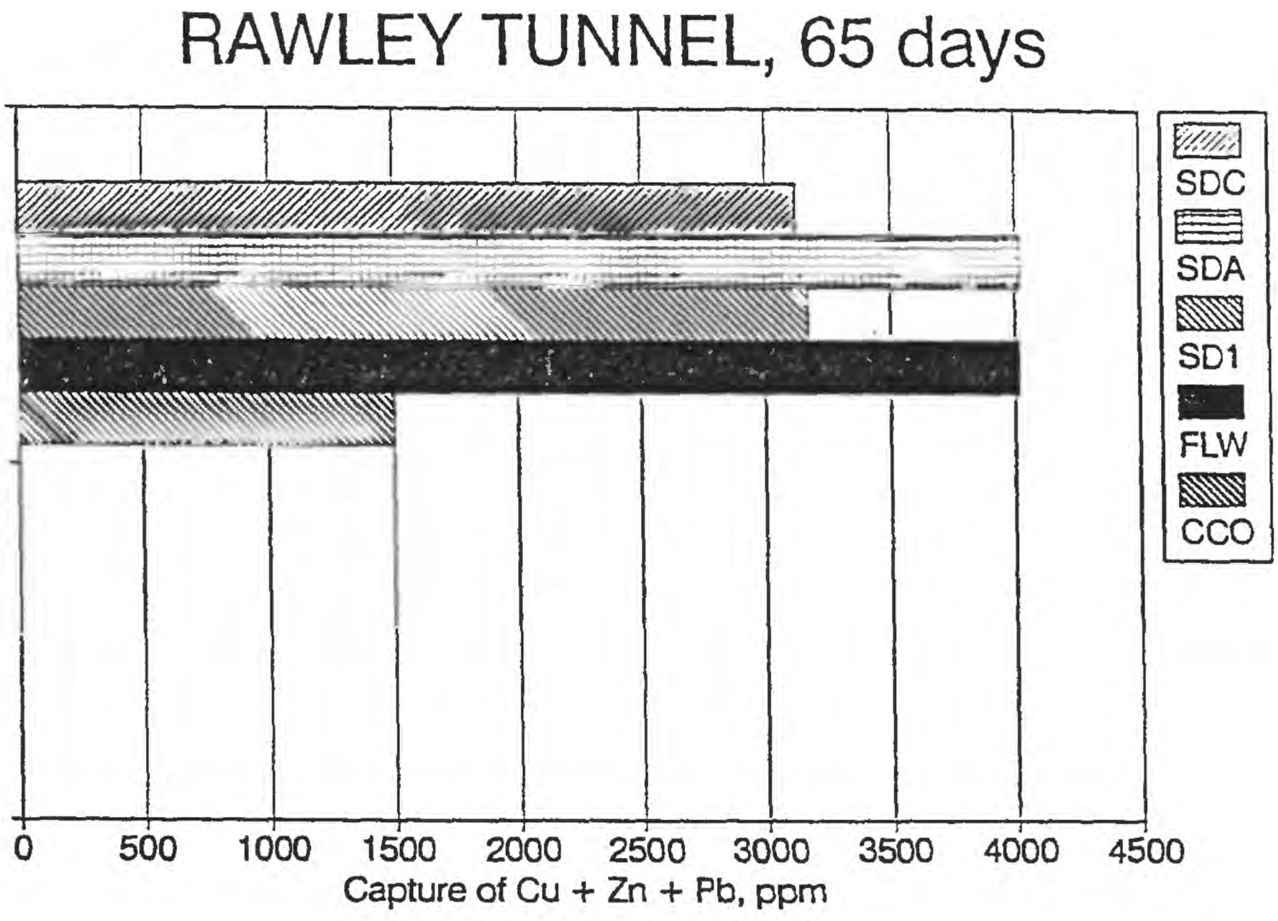


Figure 6. Capture of copper plus zinc plus lead from water by clinoptilolite-rich rocks during the first two tests at Rawley tunnel, Bonanza.



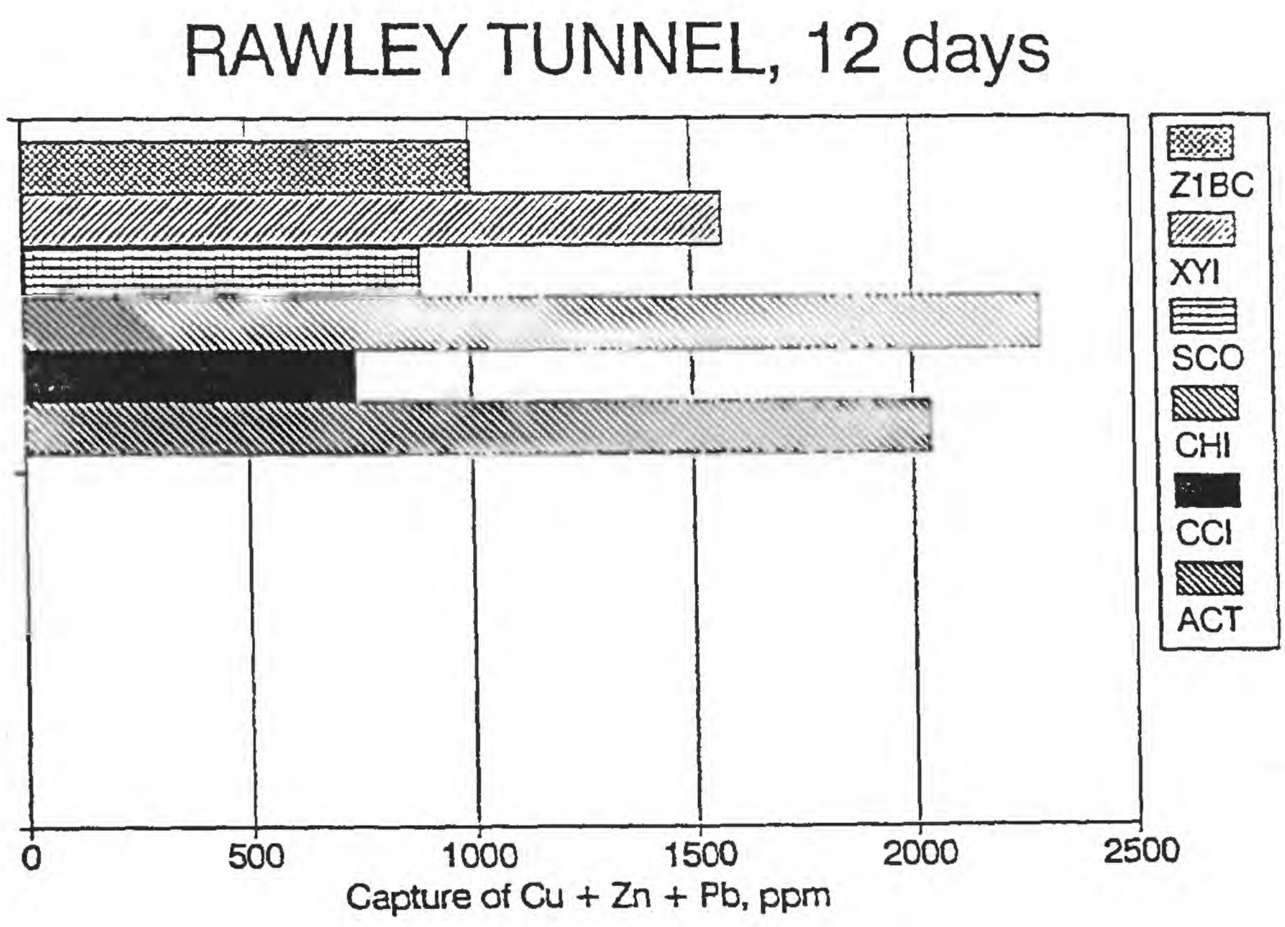


Figure 7. Capture of copper plus zinc plus lead from water by clinoptilolite-rich rocks during the last two tests at Rawley tunnel, Bonanza.

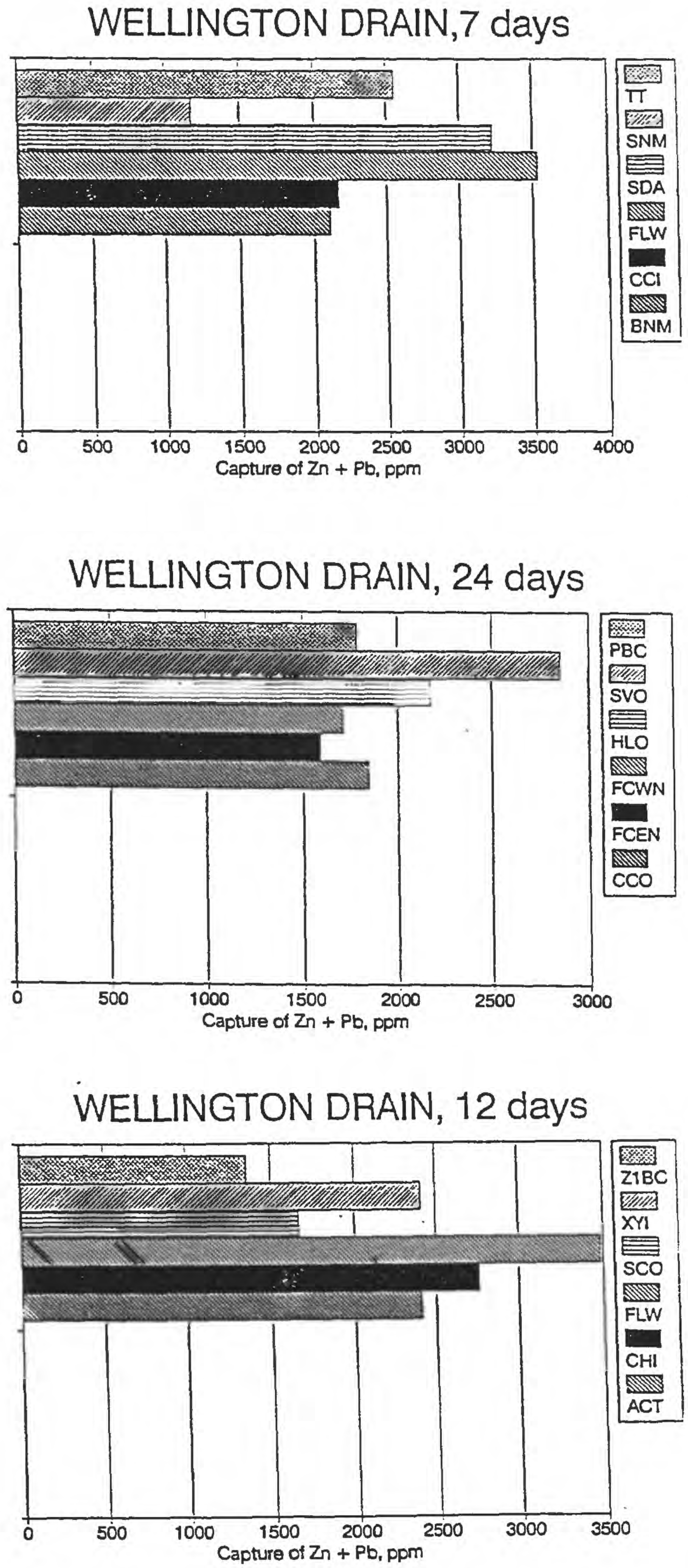
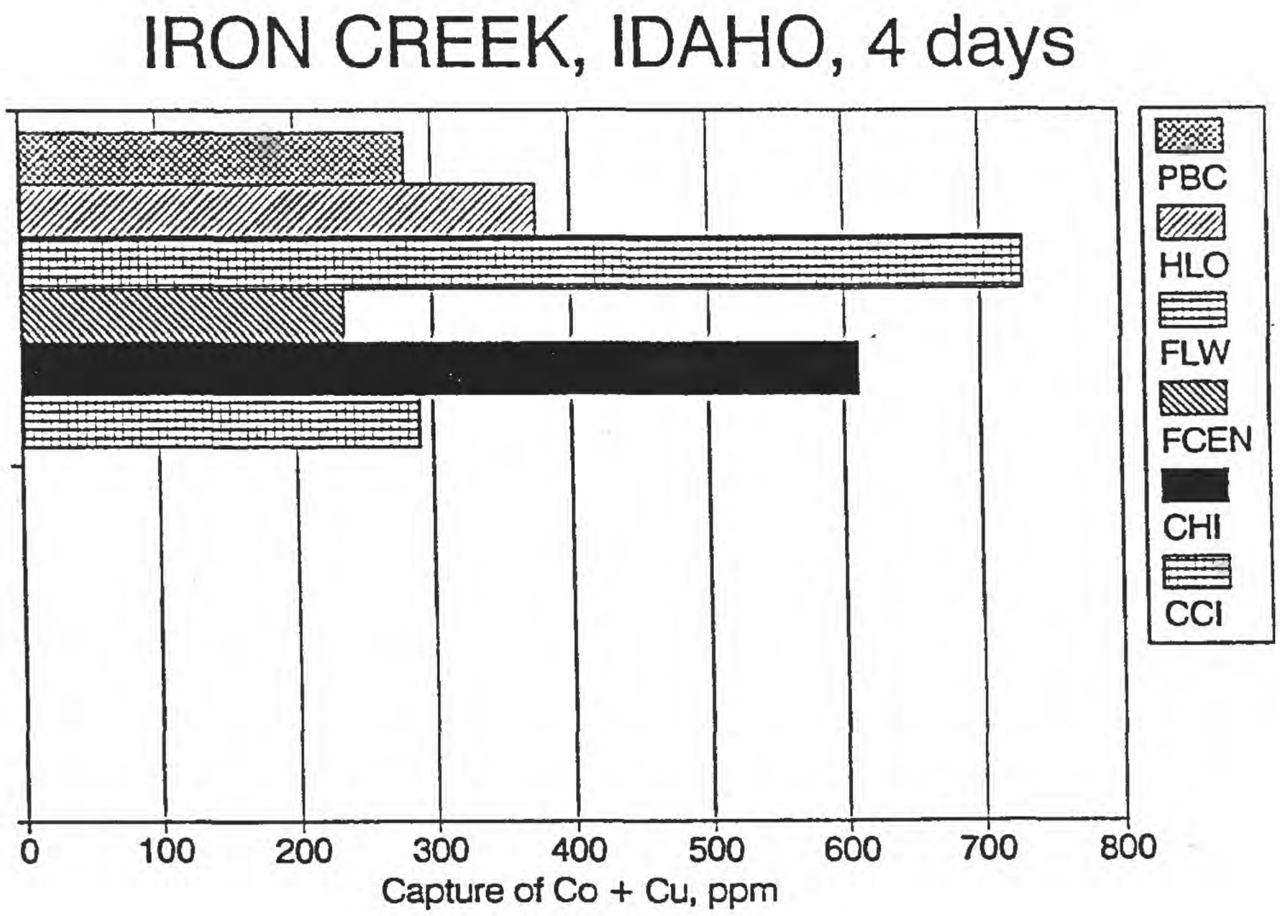


Figure 8. Capture of zinc plus lead from water by clinoptilolite-rich rocks during three tests at the Wellington drain near Breckenridge.



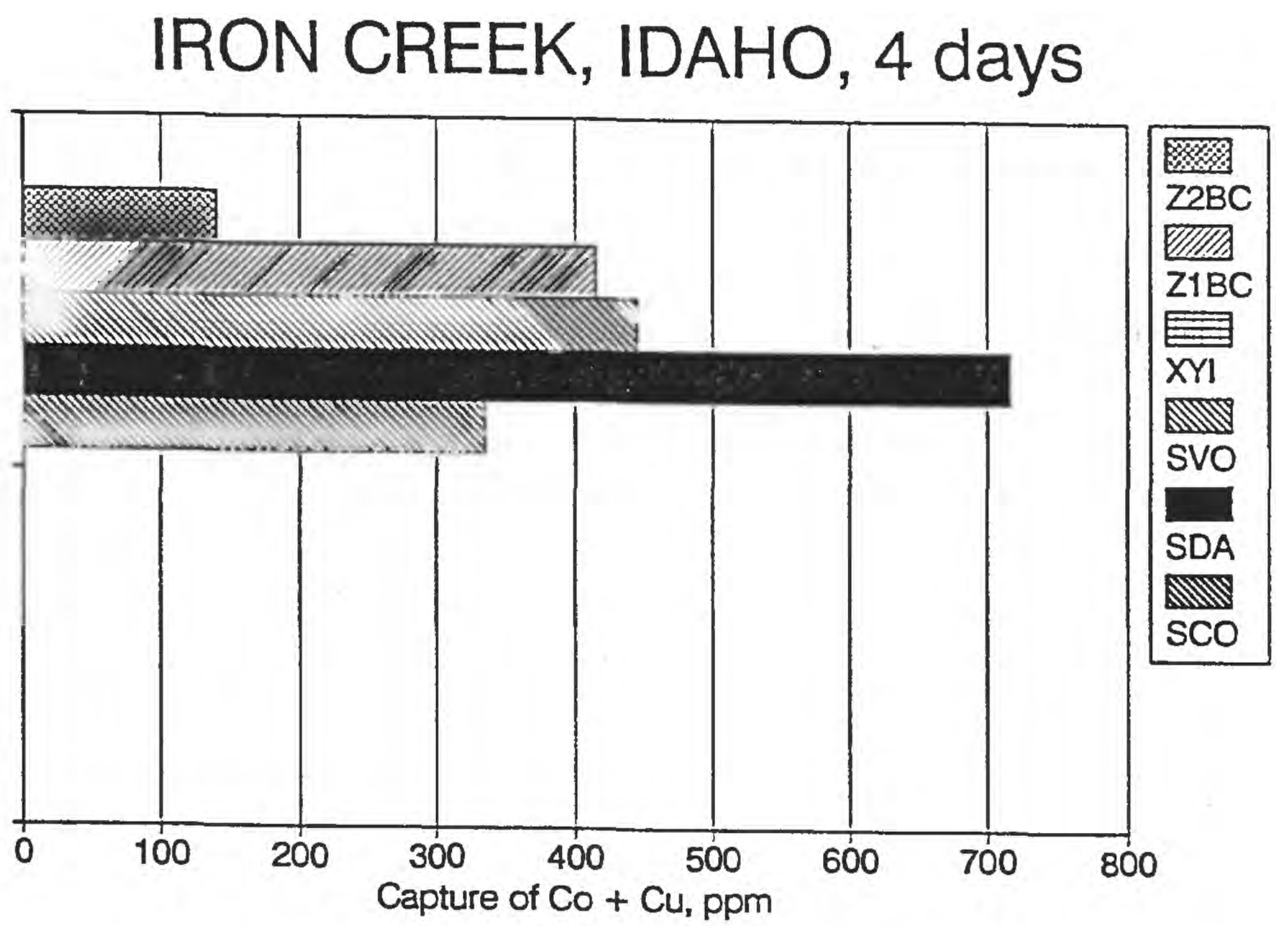


Figure 9. Capture of cobalt plus copper from water by clinoptilolite-rich rocks during testing of 12 samples at Iron Creek, Lemhi County, Idaho.