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Cu, Zn, AND Pb EXCHANGE CAPACITIES OF CLINOPTILOLITE-RICH ROCKS IN LOW Ca AND LOW K ACIDIC WATER

by

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ABSTRACT

Laboratory testing of Cu-, Zn-, and Pb-exchange capacities of three zeolite-rich rocks was done in low K and Ca surrogate solutions. The three zeolite samples tested are clinoptilolite-rich rocks (CRRs); one is a Ca-rich CRR, a second is a Na-rich CRR, and a third is a K-rich CRR. The first test was done to evaluate the potential use of CRRs in remediation of Cu, Zn, and Pb pollution of a mine adit drainage water near Silverton, Colorado that contains less than about 2 mg/L of K and Ca. The second test was done to evaluate the potential use of CRRs in remediation of Cu, Zn, and Pb pollution of Reynolds tunnel drainage water at Summitville, Colorado which contains less than about 4 mg/L of K and Ca.

Prior studies of heavy-metal capture by CRRs in Colorado were done in heavy-metal polluted draninage waters that contained high Ca concentrations which significantly interfered with the ion-exchange capture of Cu, Zn, and Pb.

The present study shows that the Na-rich CRR can remove more than 65 percent of the Zn, 55 percent of the Cu, and 95 percent of the Pb from a synthetic solution of pH = 2.1 containing, in mg/L; 15 Zn, 1.2 Cu, and 1.3 Pb, 2 Ca during a single 46 hour exposure of 3 g of CRR to 1.5 L of solution. Multiple exposures of this CRR to fresh surrogate (synthetic) solutions exchanged about 800 ppm of Cu, 9,900 ppm of Zn, and 3,000 ppm of Pb into the Na-rich CRR. The Ca-rich CRR and the K-rich CRR captured much less Cu and Zn, but captured as much Pb as the Na-rich CRR in side-by-side experiments. These results show that in a CRR to water ratio of 1:500, the Na-rich CRR will remove most of the Cu, Zn, and Pb from the surrogate solution after multiple exposures.

In a second experiment using a surrogate solution of pH = 2.6 and containing, in mg/L; 100 Cu, 19 Zn, 0.31 Pb, 3.1 Ca, 3.3 K, and 15 Na, the Na-rich zeolite captured about 19,000 ppm Cu, 9,000 ppm Zn, and 900 ppm of Pb during a 46 hour exposure of 3 g of CRR to 5.9 L of solution. It is shown that the Ca-rich CRR and the K-rich CRR captured much less Cu and Zn, but captured about the same amounts of Pb as the Na-rich CRR.

INTRODUCTION

There have been many laboratory studies of heavy-metal capture in aqueous systems by cation exchange using natural zeolites during the last two decades (Semmens and Seyfarth, 1978; Schultz and Zamzow, 1993; Vos and O'Hearn, 1993). Most of these studies used clinoptilolite-rich rocks (CRRs). Many of the laboratory studies of cation exchange examined heavy metal capacity of the CRRs in the absence of common competing cations found in both natural drainage waters and metal-mine related drainage waters that are commonly acidic. Schultz and Zamzow (1993) and Vos and O'Hearn (1993) provided significant results for zeolites use in removal of heavy metals from metal-polluted drainage water in the presence of common cations (Na, K, and Ca) that compete with heavy metals for cation-exchange sites in zeolites.

Field studies of heavy-metal capture by CRRs in heavy-metal-polluted drainages (HMPDs) have been done in side-by-side tests in order to understand the influence of CRR exchange capacity, heavy metal concentrations, and the effects of competing non-metallic cations (K and Ca) on heavy metal uptake by CRRs (Desborough, 1994). Field studies at five HMPD sites in Colorado showed these drainage waters contained, in mg/L: <0.01-37 Cu, 10-230 Zn, 0.03-0.3 Pb, <0.1-3.8 K, and 64-308 Ca. CRRs from 16 deposits in the western U.S. and southern B.C. Canada were also tested. For the 141 tests, the Na-rich Wyoming Fort LaClede (FLW) CRR generally captured the most Cu, Zn, and Pb from the HMPD waters tested. However, if dissolved K concentrations were 1.5-3.8 mg/L, between 1,000 and 4,000 parts per million (ppm) of K was exchanged into the FLW CRR, in addition to the heavy metals. When dissolved Ca concentrations were about 65 to 310 mg/L, FLW captured between 2,000 and 12,000 ppm of Ca, in addition to the heavy metals. Thus the strong affinities of this CRR for K and Ca interfered significantly with heavy metal capture, regardless of pH or other known factors.

The present study examines CRRs from three deposits to determine their Cu, Zn, and Pb affinities in acidic water conmtaining relatively low concentrations of K and Ca such as those at a mine adit drainage (Joe and John) in Prospect Gulch, near Silverton, Colorado, and the water of the Reynolds tunnel at Summitville, Colorado. Of the three CRRs used, one is Ca-rich, a second is Na-rich, and a third K-rich. The concentrations of certain elements in the raw, or untreated CRRs are given in Table 1, along with the dilutant minerals in each.

Table 1. Concentrations of certain elements in raw clinoptilolite-rich rocks used in the present study and the dilutant minerals in them. [n.a., not analyzed; n.r., not reported]

Locality and abbreviation (dilutant minerals)	Na	K	Ca	Fe	Cu	Zn	Rb	Sr	Ba	Pb
	weight percent				-----parts per million----					
Alamito Creek, Texas-**ACT** (quartz, opal)	n.a.	1.9	3.1	1.4	<20	70	125	345	730	<40
Fort LaClede, Wyoming-**FLW**	n.a.	1.5	1.3	0.7	<20	45	85	370	870	<40
Corp. reports (plagioclase)	3.5	1.6	1.1	1.4	----n.r.---			300	n.r.	n.r.
Preston, Idaho-**PWI** (opal)	n.a.	3.2	1.6	1.0	<20	45	155	115	820	<40

OBJECTIVES AND METHODS

The main objective of this study was to conduct laboratory tests on the three CRRs in surrogate solutions that simulate two acidic drainages with known concentrations of metallic and nonmetallic cations. This should provide a basis for selecting the best CRR for maximum metal capture for field tests.

Surrogate metal-bearing solutions were prepared with 18 liters of deionized water which was acidified with reagent grade H_2SO_4 prior to adding appropriate amounts of reagent grade metal and non-metal salts (e.g. $ZnSO_4.5H_2O$, $CuSO_4.5H_2O$, $Pb(NO_3)_2$, $CaCO_3$, KCl, or Na_2CO_3). Each of the CRRs was sieved to obtain a 1-2 mm fraction which was washed to remove adhereing CRR powder.

For the first set of experiments, three grams of each of the CRRs was placed in 3.5 L glass beakers with 1.5 L of the surrogate solution with a very small plastic aquarium water pump to circulate the liquid continuously for 46 hours. After the first three exposures, each liquid was sampled (0.45 um nitrocellulose filtered) for analysis, and each of the three CRR samples was dried at 40°C and nondestructively analyzed by energy dispersive X-ray fluorescence for Cu, Zn, and Pb using a Li-drifted detector, a ^{109}Cd radioisotope source, and the program of Yager and Quick (1992) for quantitative analysis. After each analysis each CRR was placed in another 1.5 L of the surrogate liquid. The original three grams of each CRR was serially exposed to 1.5 L of the fresh surrogate solution four times, each 46 hours in duration. A fifth exposure of the three CRR samples to the remaining surrogate solution was done to determine equilibrium saturation of the CRRS at rest for 96 hours. This was done in a CRR:solution ratio of 1:487, instead of 1:500 used for the prior four tests because this consumed the remainder of the original surrogate solution. All experiments were conducted side-by-side except the quantitative analyses which were done serially. The first surrogate liquid contained, in mg/L: 1.2 Cu, 15 Zn, 1.3 Pb, and 2 Ca.

METAL CAPTURE IN FIRST TEST

The percentage of Cu, Zn, and Pb, respectively, removed during each of four exposures of the CRRs to fresh surrogate solution are shown on Figures 1A, 1B, and 1C. Relevant data for each of these tests are given in Appendix I. The Na-rich FLW CRR performed best for both Cu and Zn, removing 55 and 67 percent, respectively, in the first exposure. All three CRRs were very good for Pb, removing more than 90 percent during the first three exposures. The overall perfromance for capture of Cu, Zn, and Pb after each of the five exposures is shown on Figures 2A, 2B, and 2C. These experiments were done to simulate what might occur if the CRRs were placed in metal-bearing water for a long period of time such as months or a year. It can be observed that for Cu (Fig. 2A) the ACT CRR lost some of the Cu it captured during the first exposure during subsequent exposures to the surrogate solutions. However, all of the CRRs continued to capture Pb, even during the fifth exposure. These data show the wide variability of CRRs to capture Cu, Zn, and Pb. Field experiments will be conducted on drainage adit water to determine the applicability of these laboratory surrogate water tests.

METAL CAPTURE IN A SECOND TEST

The second test test was done with a surrogate solution containing, in mg/L: 100 Cu, 19 Zn, 0.31 Pb, 3.1 Ca, 3.35 K, and 15.6 Na, with a pH of 2.6. This approximates the composition of the now-plugged Reynolds tunnel at Summitville, Colorado, and the water composition data were provided by a private firm. The first test used 3 g (1-2 mm diameter) of each of the same CRRs used in the first experiment. They were each placed in a plastic bucket with 5.9 L of surrogate solution and the water was agitated gently with small plastic-coated aquarium pumps. After 46 hours the CRRs were removed, dried, and analyzed for Cu, Zn, and Pb. They were subsequently placed in the same liquid from which they were removed and were exposed for an additional 149 hours to see what occurs during the longer exposure. The results are shown for Cu, Zn, and Pb for each exposure on Figure 3A, 3B, and 3C. Data for these tests are given in Appendix II. Assuming an analytical uncertainty of 10 percent, there is no difference in the 46 hour and 195 hour exposures, except for Zn uptake by ACT and PWI which was increased slightly during the longer exposure. Figure 3 also shows the great contrast in the total amount of metals exchanged into each of the CRRs.

SUMMARY

The present study shows that relatively large amounts of Cu, Zn, and Pb can be exchanged into CRRs when the concentrations of competing cations such as Ca and K are present in concentrations less than about 2-4 mg/L. The Na-rich CRR (FLW) captured significanely more Cu and Zn than the Ca-rich and the K-rich CRRs; however, the Ca-rich and K-rich CRRs may be more effective for Pb capture under certain conditions.

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APPENDIX I

Percentage of Cu, Zn, and Pb removed by each clinoptiolololite-rich rock from each fresh surrogate solution during four serial cycles or exposures of 46 hour duration. [Surrogate solution had a pH of 2.1 and contained, in mg/L; 1.38 Cu, 12.13 Zn, 1.46 Pb, and 2.0 Ca]

3 g CRR in 1.5 L

CRR Exposure	ACT	FLW	PWI
	Percent of Cu removed from surrogate solution		
1	9	55	30
2	0	17	8
3	0	0	0
4	0	0	0
	Percent of Zn removed from surrogate solution		
1	20	67	42
2	7	27	20
3	5	7	7
4	0	5	0
	Percent of Pb removed from surrogate solution		
1	96	98	97
2	94	97	94
3	89	95	93
4	33	49	26

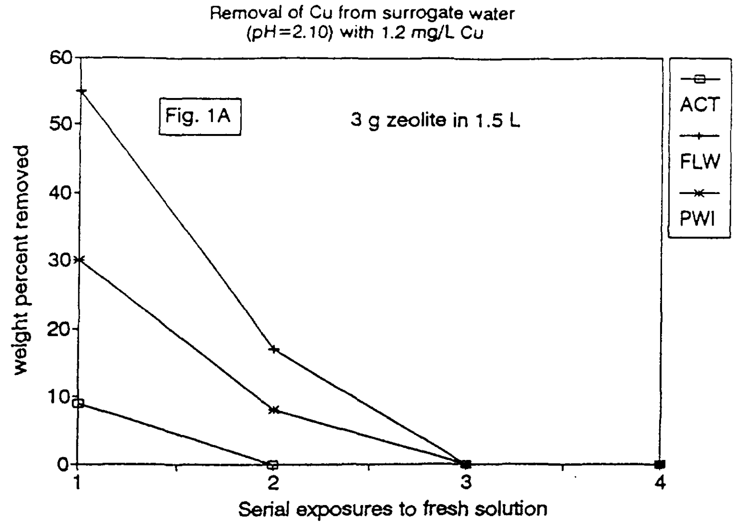
Total Cu, Zn, and Pb in the CRRs after each of five exposures to the surrogate solution.

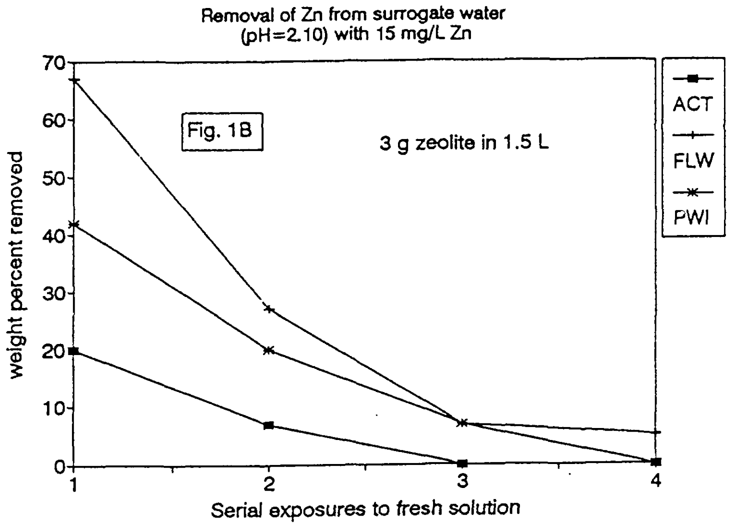
CRR Exposure	ACT	FLW	PWI
	Parts per million of Cu in CRRs		
1	190	590	290
2	160	740	445
3	135	750	480
4	145	760	440
5	120	800	510
	Parts per million of Zn in CRRs		
1	1650	6960	3750
2	2290	9300	5760
3	2620	9500	6920
4	2525	9850	6750
5	2630	9980	7130
	Parts per million of Pb in CRRs		
1	910	640	870
2	1630	1330	1730
3	2520	1940	2630
4	2760	2320	2830
5	3140	3000	3400

APPENDIX II

Concentrations of Cu, Zn, and Pb in CRRs after a 46 hour and 195 hour exposure of 3 grams of CRR to 5.9 L of the second test. [Surrogate solution had a pH of 2.6 and contained, in mg/L; 100 Cu, 19 Zn, 0.31 Pb, 3.1 Ca, 3.35 K, and 15.6 Na]

CRR	ACT	FLW	PWI
	Parts per million of Cu in CRRs		
Exposure time, hr,			
46	6460	20500	10000
195	6360	18600	9600
	Parts per million of Zn in CRRs		
46	2030	8510	3570
195	2600	9100	4690
	Parts per million of Pb in CRRs		
46	670	800	810
195	735	900	880





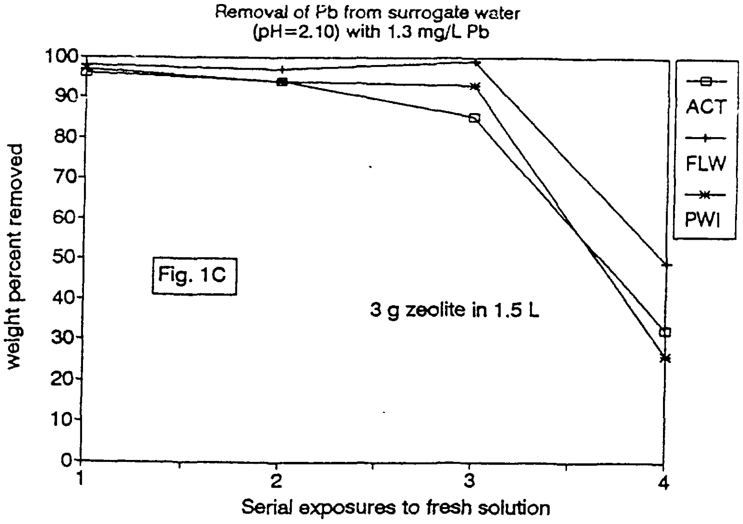
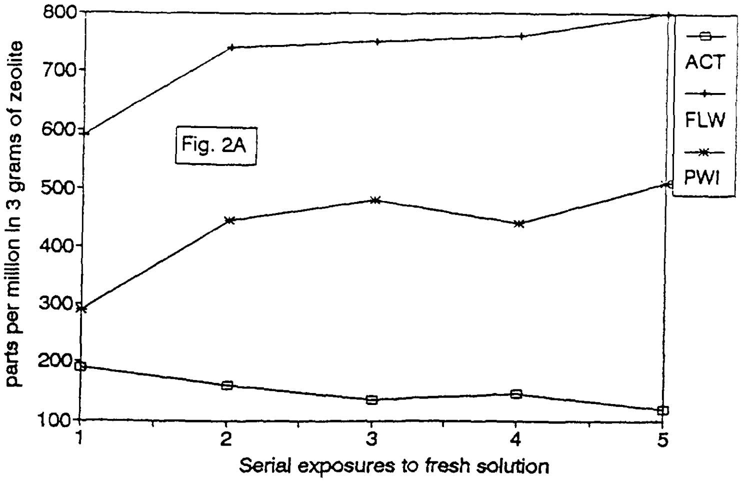
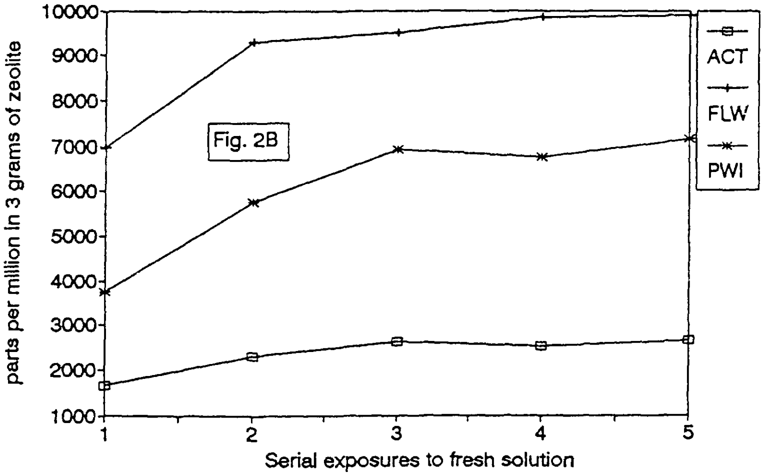


Figure 1. Removal of Cu, Zn, and Pb from surrogate water by clinoptilolite-rich rocks during four serial tests.

Cu concentrations in zeolite after five exposures (pH=2.10) with 1.2 mg/L Cu



Zn concentrations in zeolite after five exposures (pH=2.10) with 15 mg/L Zn



Pb concentrations in zeolite after five exposures (pH=2.10) with 1.3 mg/L Pb

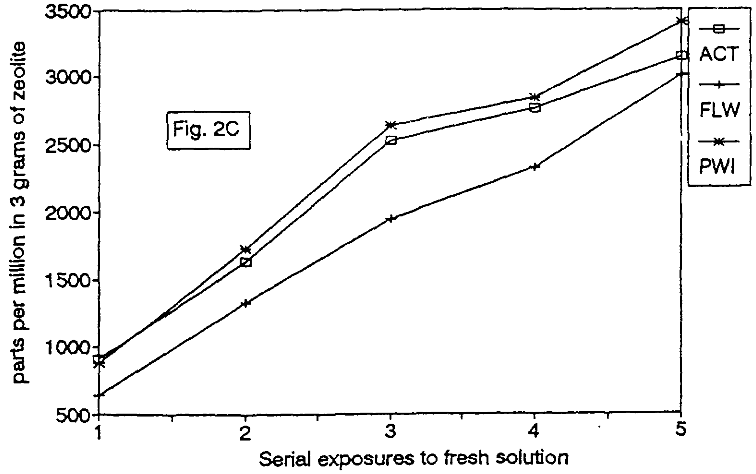


Figure 2. Concentrations of Cu, Zn, and Pb in clinoptilolite-rich rocks after five exposures to surrogate water.

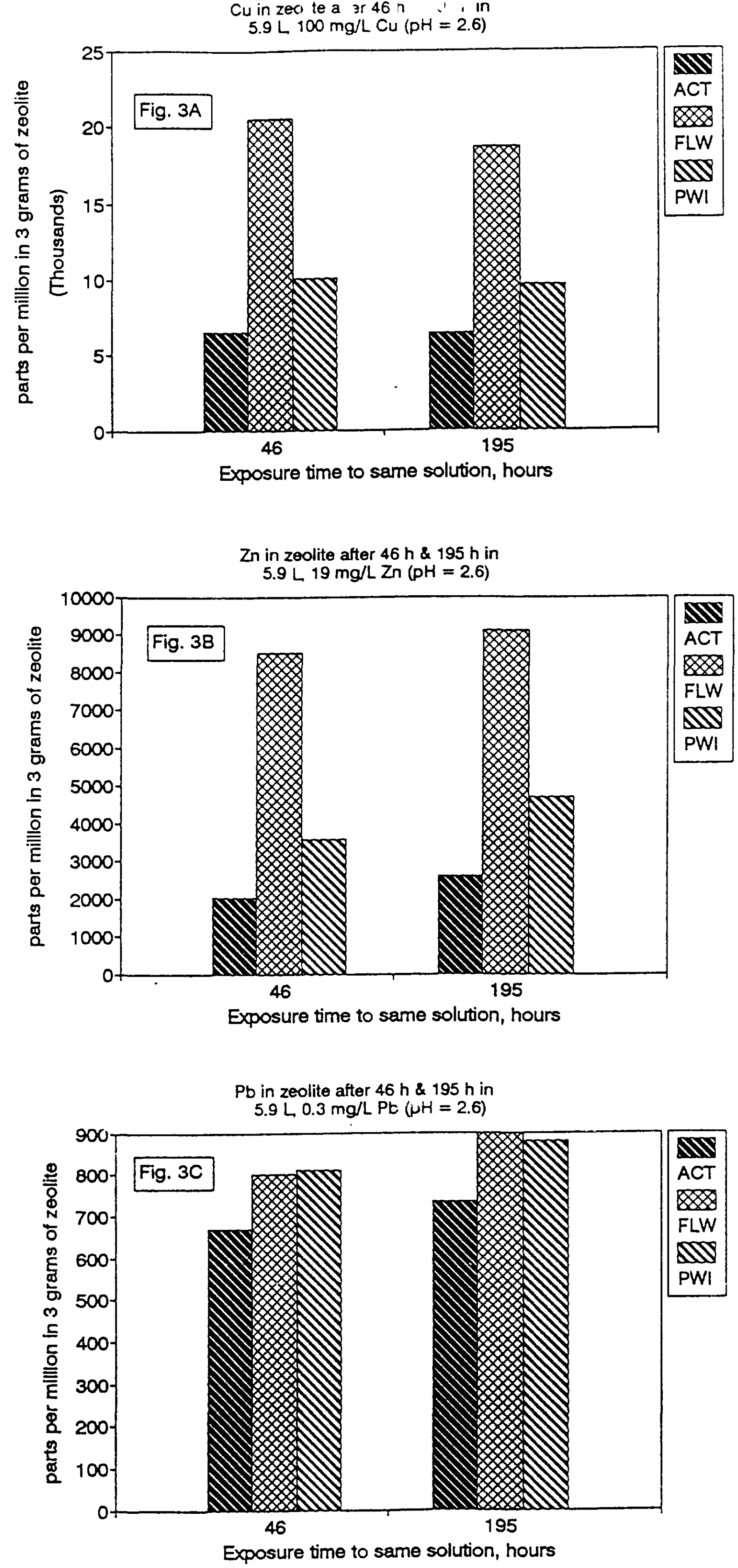


Figure 3. Concentrations of Cu, Zn, and Pb in clinoptilolite-rich rocks exposed to a metal-rich surrogate solution for 46 hours and 195 hours.