U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

SOME CHEMICAL AND PHYSICAL PROPERTIES OF CLINOPTILOLITE-RICH ROCKS

by

George A. Desborough[1]

Open-File Report 96-265

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards or with the North American Stratigraphic Code. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government

[1]Denver, Colorado

1996

CONTENTS

TABLES

ABSTRACT

Laboratory tests on 12 samples of clinoptilolite-rich rocks (CRRs) from nine deposits in Colorado, Idaho, Montana, Nevada, New Mexico, South Dakota, Texas, and British Columbia used mostly K plus Ca-rich (>4 wt. %) CRRs from deposits larger than a few to several million tons. The prinipal interest was to test high K plus Ca CRRs for agricultural uses, particularly ion-exchange and water capacity. Water capacity tests of CRRs show that 2.0-4.7 mm granules can hold 52-60 weight percent water in the pore space.

Tests of powdered CRRs in acidic (pH = 2.5, HCl) solutions, having a CRR:solution ratio of 1:100, gave highly varied results. Alteration of solution pH by the CRRs varied nearly three-fold. Release of K and Ca to the acidic solutions also was highly variable and K and Ca releases ranged from 0 to 0.7 weight percent among the CRRs. No significant amounts of Ba were exchanged out of CRRs by the acidic solution.

INTRODUCTION

Clinoptilolite-rich rocks (CRRs) from several deposits were studied to determine some of their chemical and physical properties. This was done to assist CRR producers and potential CRR producers. Although CRR characteristics have been studied for more than three decades, there have been very few standardized tests that are accepted as satisfactory concerning their widely variable chemical and physical properties. CRRs from nine deposits were studied; six of the CRR samples are from deposits known for more than a decade, but three samples are from CRR deposits recognized or explored during the past few years. One of these deposits, near Preston, Idaho was only recognized and sampled in 1995. Most of the CRRs contain more than four weight percent of K plus Ca, but one sample from a deposit in British Columbia has only about 3.7 weight percent of K plus Ca. The reason for emphasis of high K plus Ca, and low Na CRRs is that these CRRs are being studied for their potential use as agricultural soil amendments, plant fertilizer, and additives to livestock and poultry feeds. Na-rich CRRs have the potential of releasing excess sodium to either plants or animals which could have adverse effects. The K plus Ca-rich CRRs, however, will release cation-exchangable K and/or Ca to soil or animal digestive systems. The tests done in acidic solutions were to determine the potential mobility of Ba from CRRs; if significant amounts of Ba were released from CRRs in the digestive tract of animals, it could have adverse affects.

Table 1. Locality data, abbreviations, and dilutant minerals in clinoptilolite-rich rocks (CRRs) used in the present study. Minerals determined by X-ray diffraction by G.A. Desborough and Richard Sheppard (U.S. Geological Survey)
[Minerals listed in decreasing order of abundance; "clay" refers to layer silicates with a 10-angstrom spacing; tr. = trace]

Locality and abbreviation	Diluent minerals
British Columbia	
Princeton-PBC	Opal, feldspar, mordenite, quartz (tr.)
Colorado	
Creede-CCO	Opal K-feldspar, plagioclase, quartz, clay
Idaho	
Crisman Hill-CHI	Opal, K-feldspar
Preston-PMLI	Opal, plagioclase
PMUI	Opal
POLI	Opal (tr.)
POMI	Opal
Montana	
Grasshopper Creek-GCM	Opal, K-feldspar, plagioclase
Nevada	
Fish Creek-FCWN	K-feldspar, quartz, plagioclase
New Mexico	
Winston-SNM	Opal, clay (tr.)
South Dakota	
Rocky Ford-SDH	Plagioclase, calcite, quartz, opal, K-feldspar, clay (tr.)
Texas	
Tilden-ZBT	Opal, clay, calcite

Table 2. Chemical composition of selected elements in clinoptilolite-rich rocks (CRRs) determined by X-ray fluorescence analysis. (Analyst: G.A. Desborough)

CRR	K	Ca	Fe	Cu	Zn	Rb	Sr	Zr	Y	Nb	Ce	Nd	La	Ba	Pb
	Weight percent			------------Parts per million----------------											
CCO	3.6	1.8	0.9	<20	50	205	580	135	15	10	55	20	35	650	50
CHI	4.2	0.9	1.5	30	120	195	150	540	75	40	135	55	90	1650	<30
FCWN	3.4	1.6	0.6	<20	60	190	305	185	30	15	75	25	45	670	35
GCM	2.8	1.9	0.5	20	55	95	530	55	15	15	30	10	30	1475	<30
PMLI	3.2	1.9	1.0	<20	40	130	165	430	60	40	130	45	85	1050	<30
PMUI	3.0	2.0	1.2	20	40	120	270	435	50	40	120	35	70	1000	<30
POLI	3.4	1.9	1.1	<20	60	135	210	400	55	35	125	75	90	950	<30
POMI	2.9	2.4	1.2	<20	50	105	255	425	50	30	115	60	75	1050	<30
SDH	4.0	1.7	1.4	20	60	90	455	170	20	10	65	25	30	700	35
SNM	2.0	2.7	0.9	30	70	70	1720	190	30	20	90	15	40	1030	40
PBC	2.1	1.6	1.8	25	125	50	490	320	45	5	75	30	30	1970	<30
ZBT	1.2	3.1	0.8	<20	45	50	500	165	30	5	60	20	40	800	<30

LABORATORY METHODS

All CRR samples were crushed and sized with the same equipment. The 10-4 mesh (2.0-4.7 mm) fraction was used for most studies; a 20-50 g sample from this sized material was pulverized to powder (95 % < 100 micrometers) for X-ray diffraction, non-destructive chemical analysis, and acid stability experiments.

Table 1 gives the locality data and mineralogy of the CRRs determined by X-ray diffraction. Table 2 gives the concentrations of selected elements in each CRR sample as determined by non-destructive X-ray fluorescence analysis. Chemical composition data for CRRs were obtained by X-ray fluorescence analysis using radioisotope excitation sources (^{55}Fe, ^{109}Cd, and ^{243}Am) with a Li-drifted silicon detector and the computer program of Yager and Quick (1992). Because the clinoptilolite weight varies with relative humidity, all CRR samples were simultaneously dried at 60°C before weighing. Each experiment or testing of the CRRs was done side-by-side, or simultaneously--except for chemical analysis and pH measurements which were done serially.

POROSITY AND PERMEABILITY OF SIZED GRANULES OF CLINOPTILOLITE-RICH ROCKS

A simple test was used to determine "pore space" in the CRRs. After drying the CRR samples at 60°C, 24 grams of 2.0-4.7 mm sized samples of each CRR was placed in 72 ml of water (pH = 7.5) in 100 ml sealed graduated cylinders. Cylinders were inverted once after initial combining to assure wetting of all CRR particles; they were inverted again after 24 hours at rest to remove trapped bubbles of air. The water level in each graduated cylinder was recorded after the second inversion (24 h). Combined volumes of water plus CRRs ranged from 82 to 85.5 ml in the first test of nine CRR samples indicating 44 to 58 weight percent of water capacity of the CRRs for this 2.0-4.7 mm size. Results of a second test of 12 CRRs are given in Table 3. The water capacities of the CRRs ranged from 52 to 60 weight percent.

Interestingly, the range among the 12 CRRs is only 8 weight percent, but their content of clinoptilolite probably ranges from 50 to 80 percent. The relatively large water capacity of CRRs in rather coarse granules is a desirable physical property that will conserve water in agronomic and horticulture applications because water held in the pore space of each granule is not so easily evaporated as is intergranular water.

Table 3. Weight percent water capacity in pore space of 12 clinoptilolite-rich rock (CRR) samples sized to 2.0-4.7 mm, dried at 60°C, and immersed in 72 ml of water for 24 hours in 100 ml graduated cylinders.

CRR:	CCO	CHI	FCWN	GCM	PMLI	PMUI	POLI	POMI	SDH	SNM	PBC	ZBT
wt. %	60	60	55	52	58	58	58	58	58	52	60	52

STABILITY IN ACIDIC SOLUTIONS

Powdered (95% < 100 micrometers) and 60°C dried, three-gram CRR samples were immersed in 300 ml of pH = 2.5 HCl solutions. Each of these 12 mixtures of CRR and acidic solutions were at rest for 44 hours, except that each was stirred twice for four seconds after 24 and 40 hours, respectively. The pH of each solution was measured three times after the mixtures were prepared and at the end of the experiment. After 44 hours, the solute was separated from the CRRs using coarse filter paper and the CRRs were dried at 60°C on the pre-weighed filters that retained them; after drying, each CRR was weighed to determine weight loss, if any. Samples of the solute were filtered again with 0.45-micrometer filters to remove suspended material prior to analysis. Each solute was analyzed for Ba using X-ray fluorescense analysis; no Ba was found at or above the 5 mg/L detection limit. Each CRR powder was also analyzed for all elements reported in Table 2 to determine if elements were leached or exchanged from the CRRs. The final pH of the solutions exposed to the CRRs, and the minimum weight loss determined by weighing of each CRR sample after drying at 60°C, and the minimum weight loss determined by elemental analysis are given in Table 4. Most of the weight losses are due to H^+ displacement of Na, K, and/or Ca in the clinoptilolites.

4

Table 4. Final pH of 12 acidic (pH = 2.5) 300 ml solutions exposed to 3 grams of each powdered CRR and the minimum weight loss determined by weighing of each CRR after drying at 60°C, and the minimum weight loss determined by elemental analysis. [w = weight loss determined by weighing; e = weight loss determined by elemental analysis]

CRR:	CCO	CHI	FCWN	GCM	PMLI	PMUI	POLI	POMI	SDH	SNM	PBC	ZBT
Final pH	3.4	3.7	4.3	3.9	3.3	3.3	3.3	3.5	6.7	3.4	3.5	7.2
Wt. % lost-w	1.3	0.9	0.3	1.3	<0.1	<0.1	<0.1	<0.1	3.0	<0.1	2.2	1.7
Wt. % lost-e	0.7	0.7	0.2	1.0	0.2	1.1	1.0	1.4	0.9	0.7	0.2	0.2

Data in Table 5 show the amounts of K and Ca lost from the CRRs during the 44-hour exposure of 3 grams of powders to 300 ml of acidic (pH = 2.5) solutions.

Table 5. Amounts of K and Ca lost (-) in 44-hour, acidic (pH = 2.5), 300-ml solution leaching of 3 grams of each CRR powder. K and Ca determined by elemental analysis of 2.7-3 grams of CRR powders.

CRR:	CCO	CHI	FCWN	GCM	PMLI	PMLU	POLI	POMI	SDH	SNM	PBC	ZBT
					weight	percent						
K	-0.2	-0.5	<0.1	-0.5	<0.1	-0.6	-0.5	-0.7	-0.6	-0.1	<0.1	-0.2
Ca	-0.5	-0.2	-0.2	-0.5	-0.2	-0.5	-0.5	-0.7	-0.3	-0.6	<0.1	<0.1

Except for CRR sample PBC, which lost 0.2 weight per cent of Fe to the acidic solution, the major losses of elements (excluding Na) measured are K and Ca, or both (Table 5). The only measured losses of trace elements were: 10-15 parts per million (ppm) of Zn from six CRP samples, and 10-20 ppm of Cu from three CRR samples. Thus large amounts of minor element such as Ba (650 to 1,970 ppm) and Sr (150 to 1,720 ppm) in the CRRs (Table 2) seem immobile in the acidic solutions. A previous study of the extractability of Pb captured by CRRs from mine drainage water found that Pb could not be extracted in 120 hours by acetic acid solutions (pH = 2.7) in a CRR:acidic solution ratio of 1:10, although the amounts of Pb captured by CRRs was 500 to 800 ppm (Desborough, 1995).

The weighing method, versus the elemental analysis method (Tables 4 and 5), of evaluating changes in CRRs due to exposure to acidic solution demonstrated the experimental problems with the laboratory studies of the reactions of CRRs in solutions. The largest problem of determining weight loss by weighing is that the oven-dried CRRs rapidly capture water from the air, partly as a function of ambient relative humidity, between the time they are removed from the oven

and the time of weighing, even though this time is only several minutes. In addition, the potentially different water adsorption rates of each CRR may be a factor. An error of 0.01 gram in moisture uptake by 60°C-dried CRR, or if they are not equilibrated at the 60°C drying conditions, will lead to an error of 0.33 weight percent or more. The variability in data given in Table 4 regarding weight losses is due to both of these factors. The results of the elemental analysis are considered superior to the weighing results because relative humidity is not a consideration.

A significant amount of the weight losses measured by the weighing method, in contrast to elemental analysis, is probably due to displacement of Na and Mg ions by H^+, by cation exchange of Na and Mg from the clinoptilolite. This cation exchange probably accounts for most of the difference in the weight losses measured by weighing, and those determined by elemental analysis. All raw CRRs contain 0.5-2.0 weight percent Na, based on prior studies (Desborough, 1994, table 1).

The significant alteration or increase of the pH = 2.5 HCl solution (Table 4) by some of the CRRs is significant, but the chemical reactions between the CRRs and the solutions are not fully understood. Both SDH and ZBT (Table 1) contain minor amounts of calcite ($CaCO_3$), which would dissolve in acidic solutions and, thereby, raise the pH; the other CRRs contain no X-ray diffraction-detectable calcite. Both of these CRRs (SDH and ZBT) raised the pH nearly three units higher than did the other CRRs.

Similar differences in neutralizing large volumes of acidic irrigation water were found in side-by-side quantitative field and laboratory studies of the South Dakota versus the Creede, Colorado CRRs where the South Dakota CRR raised the final pH at least two units higher than that of the Creede, Colorado CRR (Desborough and Raymond, 1995).

The ability of CRRs to neutralize acidic solutions is very important in several agricultural applications: for example it is important for most crops to have a soil pH near neutral or there is a need for a neutralizing agent near plant roots when nitrification occurs during conversion of NH_4^+ to nitrate, releasing four hydrogen ions. In the absence of a neutralizing agent such as CRR or limestone, the fertilizer industry recommends limeing at a rate of 1.8 pounds of $CaCO_3$ for each pound of N applied in the NH_4^+ form. If a CRR with a stong affinity for H^+ were used as an N-carrier of exchanged NH_4^+; then there would be immediate neutralization of the nitrification-generated acidity.

SUMMARY

This study showed that certain physical and chemical reactions of CRRs cannot generally be predicted until the properties have been measured. The CRRs tested showed a range of only eight weight percent difference in water capacity. The amounts of K plus Ca that were mobilized by acidic solutions varied widely from none to 1.7 weight percent among the CRRs. The CRR with the most Ca (3.1 wt. %) lost no Ca; the CRRs with the most K did not lose as much K as did some with much less K. The ability of CRRs to neutralize acidic (pH = 2.5) solutions varied widely from 3.3 to 7.2.

The differences and similarities among CRRs are best demonstrated in side-by-side simultaneous testing.

ACKNOWLEDGMENTS

REFERENCES CITED

Desborough, G.A., 1994, Efficacy of heavy-metal capture by clinoptilolite-rich rocks from heavy-metal-polluted water in five drainages in Colorado: U.S. Geological Survey Open-File Report 94-140, 25 p.

_____, 1995, Acetic acid leachability of lead from clinoptilolite-rich rocks that extracted heavy metals from polluted drainage water in Colorado: U.S. Geological Survey Open-File Report 95-49, 10 p.

Desborough, G.A., and Raymond, W.H., 1995, Potential remediation measures for acidic irrigation water derived from the Alamosa River in south-central Colorado: U.S. Geological Survey Open-File Report 95-87, 22 p.

Yager, D.B., and Quick, J.E., 1992, SuperXap Manual: U.S. Geological Survey Open-File Report 92-13, 45 p.