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Zeolites in the Pine Ridge Indian Reservation, South Dakota

By

William H. Raymond, Alfred L. Bush,

and Arthur J. Gude, 3d

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Abstract

Zeolites of possible commercial value occur in the Brule Formation of Oligocene age and the Sharps Formation (Harksen, 1961) of Miocene age which crop out in a wide area in the northern part of the Pine Ridge Indian Reservation. The thickness of the zeolite-bearing interval and the extent of areas within the interval which contain significant amounts of zeolites are far greater than was expected prior to this investigation. The shape of the zeolite-bearing interval is tabular and the dimensions of its exposure are roughly 10 mi x 100 mi x 150 ft (16 km x 160 km x 45 m) thick. Within the study area, there are tracts in which the zeolite resource potential is significant (see pl. 1).

This report is intended to inform the Oglala Sioux Tribe of some of the most promising zeolite occurrences. Initial steps can then be taken by the Tribe toward possible development of the resources, should they wish to do so.

The data contained herein identify areas of high zeolite potential, but are not adequate to establish economic value for the deposits. If development is recommended by the tribal government, we suggest that the tribal government contact companies involved in research and production of natural zeolites and provide them with the data in this report.

Geologic setting

The oldest rocks containing significant zeolites in the Pine Ridge Reservation are tuffs in the upper part of the Brule Formation in the White River Group of Oligocene age. These tuffs are generally thin (a foot (0.3 m) or so thick) and are interbedded with mudstone and siltstone of similar thickness. The upper tuffs of the Brule Formation are commonly overlain by 30-50 ft (9-15 m) of buff mudstone that weathers to form steep slopes. Locally, this mudstone interval is zeolitic, but generally it does not contain more than 20 percent zeolite except in thin beds near the top.

Overlying the Brule Formation is the Sharps Formation of Miocene age. The Sharps Formation is the basal unit of what is mapped as Arikaree Formation on plate 1; and it is composed largely of altered volcanic ash, siltstone, and less commonly, mudstone. The maximum thickness of the formation is 390 ft (118 m), measured by the South Dakota Geological Survey (Harksen and others, 1961). The basal unit of the Sharps Formation, the Rockyford Member, attains a maximum thickness of 55 ft (17 m) at Sheep Mountain Table where it is well developed. The member is a conspicuous white tuff layer or layers which contain vertical "potato-like" concretions as long as a foot or more. Generally, this member contains the largest amounts of zeolite. Above the Rockyford Member is a bright-gray nodular tuff having a variable thickness as much as several meters, which is overlain by several layers of buff or gray tuff. The maximum thickness of zeolitic tuff sampled in the Sharps Formation is 197 ft (60 m). Where the uppermost Sharps Formation has been sampled, the zeolites are minor or absent.

Overlying the Sharps Formation is the Monroe Creek Formation, also of Miocene age, which is mainly silty tuff, siltstone, and fine sandstone. Little or no zeolite was found in this formation or in the overlying formations.

The major occurrences of zeolites are in the lower half of the Sharps Formation which occurs in a band across the northern and western parts of the reservation (see pl. 1). The band of outcrop is about 10 mi (16 km) wide and extends discontinuously from the Slim Butte area to the Chimney Butte area and thence eastward to the Rosebud Reservation boundary. Large areas within the outcrop band contain significant amounts of zeolite; and other areas contain little or no zeolite, depending on the depositional environment of the volcanic ash.

Field investigations

Geologic field investigations concentrating on potential zeolite resources in the Pine Ridge Indian Reservation commenced in the spring of 1977 and resumed in the spring of 1978. Two U.S. Geological Survey geologists and three men from Kyle conducted field studies at many sites across the reservation and collected several hundred samples from late April through June of 1977. Four geologists and several local men worked with helicopter support to complete field studies during the spring of 1978.

During both field seasons extensive collections of samples were made from sites chosen as having resource significance. Sample sites were selected along a general east-west zone across the reservation where the basal part of the Sharps Formation (the Rockyford Member), of Miocene age, crops out in the canyons and hillsides. Most samples were collected at 1 m intervals vertically throughout the extent of the rock, especially where the section appeared to be rich in volcanic ash. At most sites tuff units also extend for several meters down into the underlying Brule Formation (Oligocene). These Brule and Sharps intervals were generally sampled without regard to the stratigraphic contact between them. At many sites the tuff-bearing sequence was present through most of the exposed Sharps Formation. The total thicknesses of tuff were commonly several tens of meters.

Sampling for zeolite-bearing rock was undertaken at about 70 sites in the zone crossing the reservation as described earlier. A total of about 1,300 samples was collected, with an average of about 20 samples per site. All samples were taken to the U.S. Geological Survey laboratories in Denver, Colo., for analysis.

Analytical work

Of the 1,300 samples studied, a representative number were analyzed by semiquantitative spectrographic methods to deteremine their elemental content, by scintillometer to check radioactivity, and by microscopic examination of rock thin sections to determine the mode of occurrence of the minerals contained. Selected samples were examined by using a scanning electron microscope to identify minerals occurring in small grains and to determine the manner in which zeolite minerals occur with other components in the rocks. All samples were crushed and a portion of each was examined by X-ray diffraction. All analytical data are tabulated in the final report (Raymond and others, 1980).

X-ray diffraction is the most useful way of identifying minerals that are present in amounts greater than several percent of a rock. This method of study was used to determine the minerals present in the rock samples from the Pine Ridge Indian Reservation. The mineralogic compositions (with the exception of zeolites) of samples from the reservation are fairly consistent in both vertical and horizontal intervals. The major zeolite mineral is clinoptilolite, a common zeolite mineral formed by alteration of volcanic ash. In some samples and in much smaller amounts, the presence of erionite, another zeolite mineral, has been determined by X-ray diffraction and confirmed by using a scanning electron microscope. Clinoptilolite is in the rocks over wide areas, but erionite has been identified in only a few areas. Clinoptilolite may make up as much as 60–70 percent of certain layers of rock at the most favorable localities.

In addition to zeolites, all samples contain variable amounts of clay minerals, quartz, feldspars, opaline silica, and amorphous materials. Many samples contain calcite in varying amounts, and many contain minor amounts of barite, micas, and/or amphiboles.

Estimated zeolite contents

Unfortunately, X-ray diffraction cannot be used to accurately determine the amount of a mineral contained in a rock, nor can it be used to determine the range of physical properties that make zeolite minerals useful. Estimates of the relative proportions of zeolite in the whole rock have been made considering the whole rock as 10. The numbers must be regarded only as estimates and may differ by as much as ±25 percent of the amount reported.

Included here are the available field and analytical data pertaining to estimated zeolite content at four sample localities in zeolite-bearing strata on tribal land. The localities are shown on plate 1. The four localities were selected as representative of areas of high zeolite content on or very near tribal land. Many other sample sites were studied, some on tribal land and some on privately held land. Analytical results from all sample sites have been included in the final report to the tribe (Raymond and others, 1980).

Locality 1045, at the north end of Cedar Butte (south of Sheep Mountain Table), encompasses a vertical interval of 89 ft (27 m). The lower 34 ft (10.5 m) of the vertical section is in the Brule Formation, and the zeolite content of the samples from the Brule Formation varies from a few percent to about 50 percent. About 52 ft (16 m) of the Sharps Formation is present between the top of the Brule Formation and the Quaternary gravel and eolian sands capping Cedar Butte. The 16 samples from the Sharps Formation part of the section have the highest zeolite content (by X-ray diffraction analysis) of any locality studied for this report. The average estimated zeolite content of this interval (K through Z on fig. 1*A*) is more than 50 percent, but the range is 25-100 percent.

The zeolite content at locality 1093 (fig. 1*B*), about 2.5 mi (4 km) northwest of Wanblee, is somewhat lower than at Cedar Butte, ranging from a few percent to about 75 percent over a vertical interval of about 59 ft (18 m). This interval includes about 6 ft (2 m) of the Brule Formation, but it does not include about 98 ft (30 m) of overlying strata of the same type which is thought to be of similar quality. About 16 ft (5 m) of the basal unit of the Sharps Formation (the Rockyford Member, Tsr on fig. 1B) has an average zeolite content of about 40-50 percent. This zeolite-rich part of the section is at or near the grass level over many acres near this locality.

At locality 1049, 3.75 mi (6 km) north of Wanblee, 59 ft (18 m) of rock were sampled below the tabletop, of which 6 ft (2 m) are in the Brule Formation (fig. 1C). Of the 16 samples taken in the Sharps Formation, those from the lower 30 ft (9 m) (mainly in the Rockyford Member) are estimated to average about 40 percent zeolite. The top of the sampled section is essentially the butte top at the locality and is overlain by thin eolian sand.

At 1042, 1.25 mi (2 km) southwest of Bowman Pond in Redstone Basin, 19 samples were taken representing 62 ft (19 m) of rock of which 5 were from the Brule Formation and 14 were from the Sharps Formation (fig. 1D). All samples taken from the Brule Formation and the upper nine taken from the Sharps Formation contain only a few percent zeolite. However, the five samples from the Rockyford Member average about 40 percent zeolite.

Ammonium ion-exchange capacity and oxygen-adsorption capacity

Inasmuch as one of the useful properties of natural zeolites is their ability to adsorb nitrogen, nitrogen-compound gases, water, and other molecules, the most practical method of evaluating zeolites is to measure the amounts of certain gases that can be adsorbed by a particular zeolite-bearing rock. Certain of these results are reported in table 1. Another important measure of the chemical and physical properties of zeolites is the ammonium ion-exchange capacity. Certain of these results are also reported in table 1.

Fourteen samples were sent to the Minerals Research, Inc., laboratory for determination of ammonium ion-exchange and oxygen-adsorption capacities. An additional 12 samples were analyzed in U.S. Geological Survey laboratories for ion-exchange capacity. The samples were selected to represent a range of relative values of samples containing clinoptilolite, but no attempt was made to select samples containing unusually large amounts of clinoptilolite. The analyses of this sample group are shown in table 1.

The headnote of table 1 gives a value for the ion-exchange capacity for clinoptilolite-bearing rock from a deposit at Hector, Calif. Clinoptilolite-bearing rock from Hector is almost pure and thus is widely used as a standard against which other natural clinoptilolites are compared. Sample MS4A, at the bottom of table 1, is a synthetic molecular sieve zeolite which was purchased for use as a standard of comparison. The data presented in table 1 are incomplete at this time; however, it is evident that the ammonium ion-exchange capacities of these samples are considerably less than those for MS4A and somewhat less than those of the Hector clinoptilolite.

Ion-exchange capacities are affected by the presence of montmorillonite (a clay mineral), which also is capable of exchanging ammonium ions; montmorillonite has been identified in many samples collected in the reservation. It occurs in varying amounts and is difficult to identify because it is mixed with other clay minerals. Therefore, ammonium ion-exchange data presented in table 1 are probably a little higher than would be indicated by clinoptilolite alone. The presence of clays, as in most samples taken in the reservation, is likely to be beneficial for most potential commercial uses of zeolite because clays act as binders that allow the material to be ground and sized without overgrinding. For many applications, this is essential.

Explanation of Figure 1

Figure 1 comprises diagrams of vertical sections of the rock units and sample positions of four representative sample sites including a graphic expression of the estimated zeolite content. The locations of the sample sites are as follow:

1045--Stirk Table quadrangle, NE 1/4 SE 1/4 sec. 16, T. 42 N., R. 34 W.
1093--Wanblee quadrangle, SW 1/4 NE 1/4 sec. 23, T. 42 N., R. 37 W.
1049--Wanblee NW quadrangle, NW 1/4 SW 1/4 sec. 7, T. 42 N., R. 36 W.
1042--Pass Creek NW quadrangle, SE 1/4 SE 1/4 sec. 6, T. 42 N., R. 34 W.

These samples were taken either on or very near tribal land.

The letters in the columns at the left of each diagram represent individual rock samples taken from the measured sections at places indicated by the arrows. A bar scale, at the right of each stratigraphic section, indicates the thickness of the sampled section. The vertical sample interval was carefully measured in the field and is generally 1 m.

Following are explanations of the symbols in the stratigraphic sections; units are listed youngest to oldest:

Qe = Eolian (windblown) material, sand or silt, Quaternary age
Qg = Gravel, Quaternary age
Ts = Sharps Formation (undifferentiated), Tertiary age
Tsu = Upper part, Sharps Formation (where distinguishable), Tertiary age
Tsr = Rockyford Member of the Sharps Formtion (basal white tuff), Tertiary age
Tb = Brule Formation, Tertiary age

To the right of each stratigraphic section is a bar graph that shows the estimated zeolite content for each sample throughout each vertical section. The vertical scale of the graph is the same as that of the stratigraphic section, and the horizontal scale is divided into 10 parts. The bars represent estimates of the zeolite content of each sample in tenths, considering 10 as the whole rock. These estimates were made using X-ray diffraction records, as described on page 3. Caution must be used in interpreting these data because they are estimates--not quantitative measurements. The bars should be thought of as estimated percents that may vary by ±25 percent of the amount reported. For example, a bar two units long may actually represent 15-25 percent--a bar showing eight units may have values that vary from 60 to 100 percent.

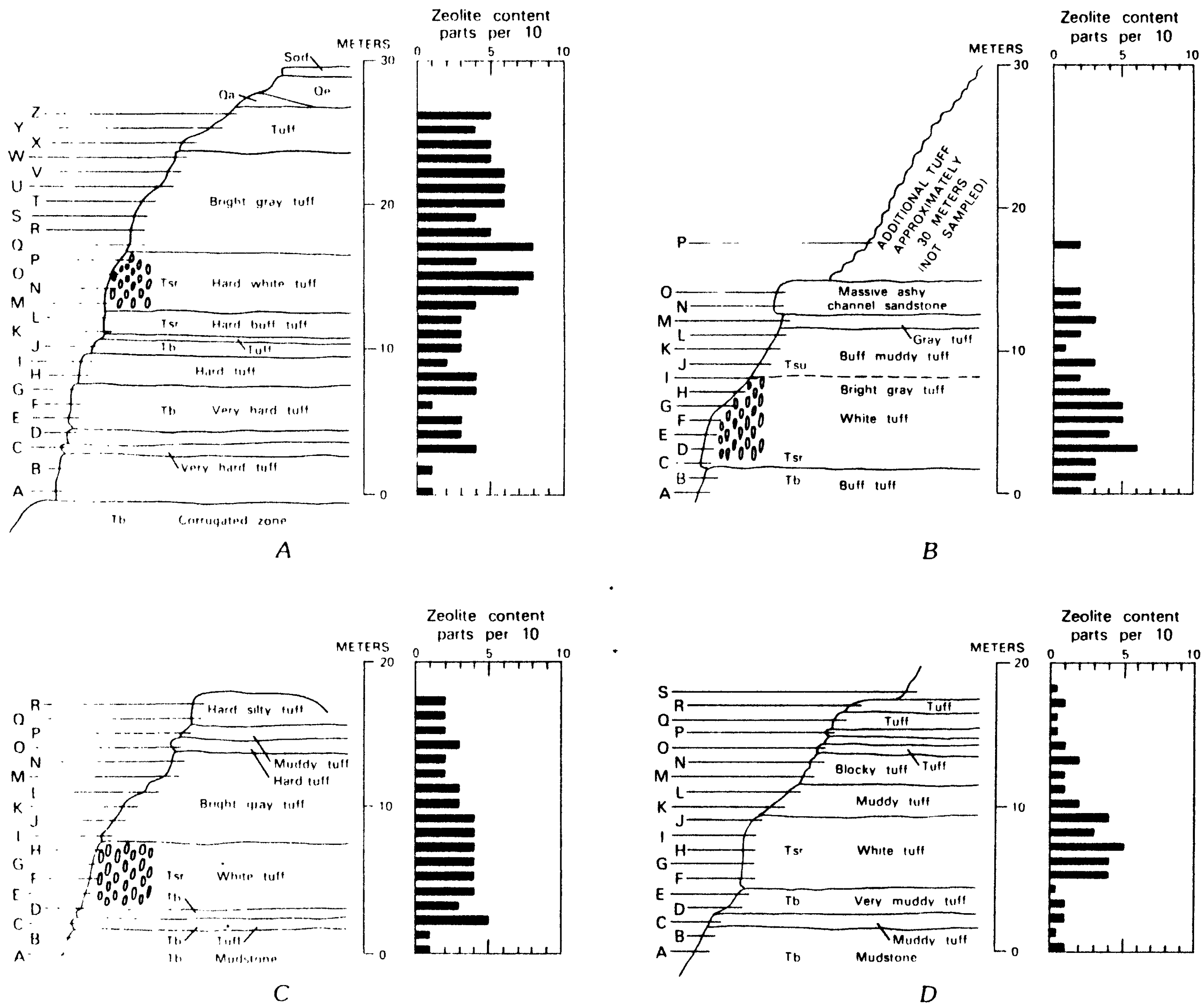

Figure 1.--Diagrams showing the stratigraphic positions of samples and their estimated zeolite contents. A, 1045; B, 1093; C, 1049; D, 1042.

Table 1.--Ammonium ion-exchange capacity and oxygen-adsorption capacity of samples of zeolite-rich rock collected in the Pine Ridge Indian Reservation

[Ammonium ion-exchange capacity (NH_4^+-CEC) analyses by H. C. Starkey, U.S. Geological Survey laboratories, Denver, Colo. Results are reported in milliequivalents per gram (Meq/g). Oxygen (O_2) adsorption capacity analyses by Minerals Research, Inc., Clayton, N.Y. Results are reported in weight percent (wt%). Reference sample of clinoptilolite from Hector, Calif., was evaluated at the same time as the U.S. Geological Survey samples and yielded values of 1.70 Meq/g±0.03 Meq/g. --- indicates sample not tested.]

Field No.	NH_4^+-CEC (Meq/g)	O_2-Adsorption Capacity (wt.%)
1000A	0.96	---
1000B	0.96	---
1000C	0.59	---
1001	0.82	---
1005A	0.78	---
1011C	1.09	---
1011D	1.04	---
1012B	1.07	---
1012C	0.79	---
1012D	0.93	---
1012E	1.08	---
1012F	1.03	---
1015A	1.29	---
1015B	1.45	---
1015C	1.35	---
1015E	1.22	---
1015F	1.21	---
1015I	1.10	---
1015J	0.83	---
1015K	0.94	---
1015L	0.88	---
1015M	0.78	---
1022K	0.90	---
1022L	0.86	---
1022N	0.90	---
1022Q	1.00	---
1022R	0.94	---
1022T	0.97	---
1024L	1.05	---
1024M	1.05	---

Table 1.--Ammonium ion-exchange capacity and oxygen-adsorption capacity of samples of zeolite-rich rock collected in the Pine Ridge Indian Reservation--Continued

Field No.	NH_4^+-CEC (Meq/g)	O_2-Adsorption Capacity (wt.%)
1024N	1.02	---
1024O	1.05	---
1024P	0.97	---
1025D	1.23	---
1025J	0.93	---
1025K	1.07	---
1025N	0.98	---
1025O	1.01	---
1028H	1.11	---
1028Q	1.02	---
1028R	1.04	---
1028S	0.99	---
1028CCC	1.00	---
1028FFF	0.71	---
1033H	0.63	---
1033I	0.68	---
1033J	0.53	---
1033K	0.99	---
1033L	1.05	---
1033M	0.94	---
1033N	0.94	---
1033O	0.95	---
1033P	1.03	---
1033Q	1.10	---
1042E	0.36	---
1042F	1.01	---
1042G	1.01	---
1042H	0.99	---
1042I	1.03	---
1042J	0.97	---
1044L	0.72	---
1044M	0.78	---
1044Z	0.79	---
1044BB	0.81	---
1045F	0.61	1.4

Table 1.--Ammonium ion-exchange capacity and oxygen-adsorption capacity of samples of zeolite-rich rock collected in the Pine Ridge Indian Reservation--Continued

Field No.	NH_4^+-CEC (Meq/g)	O_2-Adsorption Capacity (wt.%)
1045M	1.17	---
1045N	1.27	---
1045O	1.38	3.4
1045P	0.96	---
1045Q	1.07	---
1045R	1.11	1.6
1045S	0.96	---
1045T	0.96	---
1045U	0.85	---
1045V	0.94	---
1045W	0.82	---
1045X	0.68	---
1045Y	0.67	---
1045Z	0.60	---
1046P	0.67	---
1046Q	0.76	---
1046R	0.83	---
1046S	0.63	---
1046T	0.67	---
1046U	0.64	---
1046V	0.61	---
1048H	1.05	---
1048I	0.49	---
1048J	0.61	---
1048K	0.71	---
1048L	0.75	---
1048M	1.03	---
1048N	1.02	---
1048O	0.99	---
1048P	0.94	---
1048Q	0.90	---
1048R	0.85	---
1048S	0.42	---
1048T	0.43	---
1049C	1.11	2.1

Table 1.--Ammonium ion-exchange capacity and oxygen-adsorption capacity of samples of zeolite-rich rock collected in the Pine Ridge Indian Reservation--Continued

Field No.	NH_4^+-CEC (Meq/g)	O_2-Adsorption Capacity (wt.%)
1049D	0.83	---
1049E	1.02	---
1049F	1.11	---
1049G	1.03	---
1049H	1.07	2.3
1049I	1.12	---
1049J	1.00	---
1050GG	0.81	---
1050HH	0.85	---
1050II	0.78	---
1050JJ	0.61	---
1050KK	0.68	---
1050LL	0.79	---
1070CC	0.25	---
1077Y	0.88	---
1077Z	0.75	---
1077AA	0.97	---
1077BB	0.99	---
1077CC	0.89	---
1077DD	0.81	---
1077EE	0.61	---
1077FF	0.43	---
1087Z	0.97	---
1087AA	1.02	---
1088E	1.08	---
1088F	1.02	---
1088G	0.72	---
1088H	0.89	---
1088I	0.64	---
1088J	0.79	---
1088K	0.65	---
1091D	1.08	---
1091E	0.93	---
1091F	0.99	---
1091G	0.83	---

Table 1.--Ammonium ion-exchange capacity and oxygen-adsorption capacity of samples of zeolite-rich rock collected in the Pine Ridge Indian Reservation--Continued

Field No.	NH_4^+-CEC (Meq/g)	O_2-Adsorption Capacity (wt.%)
1091H	0.98	---
1092B	0.91	---
1092C	0.91	---
1092D	1.16	---
1092E	1.05	---
1092F	0.99	---
1092G	1.01	---
1093A	0.54	---
1093B	0.62	---
1093C	0.73	---
1093D	1.09	---
1093E	0.98	---
1093F	1.06	---
1093G	1.05	---
1093H	0.99	---
1093I	0.48	---
1093J	0.66	---
1093K	0.56	---
1093L	0.57	---
1094A	0.93	---
1094B	1.03	---
1094C	1.12	---
1094D	1.07	---
1094E	1.01	---
1096D	1.01	---
1096E	1.05	---
1096F	0.77	---
1096G	1.08	---
1096H	1.04	---
1100D	1.22	---
1100E	1.01	---
1100F	1.16	---
1101E	0.81	---
1101F	0.78	---
1101G	0.77	---

Table 1.--Ammonium ion-exchange capacity and oxygen-adsorption capacity of samples of zeolite-rich rock collected in the Pine Ridge Indian Reservation--Continued

Field No.	NH_4^+-CEC (Meq/g)	O_2-Adsorption Capacity (wt.%)
1101H	0.80	---
1101I	0.93	---
1101J	0.91	---
1101K	0.87	---
1101L	0.91	---
1101M	0.82	---
1101N	0.91	---
MS4A	2.78	20.4

The ammonium ion-exchange and oxygen-adsorption data provide some measure of the physical properties of the clinoptilolite in the samples. Pending further evaluation and comparison with other analytical data for the same samples, these results should be considered neither encouraging nor discouraging.

Additional work

Approximately 70 sample sites have been examined for zeolites. Data on these have been presented in an administrative report (Raymond and others, 1980) in substantially the same format as used here. In addition, other data including eU (equivalent uranium), semiquantitative spectrographic data (elemental content), scanning electron microscope results, and qualitative clay data were reported.

Within the limitations of available information, plate 1 presents a summary showing areas of high and low zeolite potential.

Summary of economic potential of zeolites in the Pine Ridge Indian Reservation

The clinoptilolite contents in many of the samples taken in the reservation are substantial. In many samples, clinoptilolite makes up more than half of the rock, and this occurrence is very unusual in the northern Great Plains. In some areas in the reservation, the rock layer having high contents of clinoptilolite is many meters thick. These thicknesses of zeolitic rock occur in many places having little or no soil cover or overburden.

However, caution should be exercised in considering the value of these deposits. The value of clinoptilolite is generally its ability to adsorb nitrogen and its ammoniuim ion-exchange capacity. To be useful, even as fertilizer or soil conditioner, nitrogen adsorption, and ion-exchange capacities may need to exceed those of clinoptilolite in the reservation.

Clinoptilolite has been used successfully by the Japanese for several purposes. Flooding the minute spaces in the mineral with nitrogen, then tilling the zeolite into fields, produces a fertilizer that holds nitrogen at root level until it can be used by the plants, thereby preventing leaching of the nitrogen downward into the ground-water system. The mineral is also used in carefully determined amounts as a dietary supplement for livestock to accelerate weight gain. In addition, the mineral is useful as a deodorant and collector of ammonia effluent in barnyards and feedlots, and when so used could be converted to an effective low-grade fertilizer and soil conditioner through exchange of the ammonium ion from animal wastes. Clinoptilolite has also been used in the treatment of raw sewage; and it has been suggested that natural gas could be stored in vessels containing zeolite, thereby reducing the storage volume substantially.

The United States is now on the threshold of developing a natural zeolite industry. Several companies are actively involved in developing markets for natural zeolites for a variety of uses. Deposits are being mined in other parts of the nation, but no others of substantial size are known to exist in the northern Great Plains. If the zeolites in the Pine Ridge Reservation have useful physical properties, these deposits will have high commercial potential because of their convenient location to the midwest and their great size.

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