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A Field Test for Molecular Sieve Zeolites

ALI CULFAZ[1], CHARLES A. KEISLING, AND LEONARD B. SAND

Department of Chemical Engineering,
Worcester Polytechnic Institute,
Worcester, Massachusetts 01609

Abstract

A simple field test for molecular sieve zeolites is described. The test utilizes the temperature rise (12°C to 23°C for natural zeolites) from the heat of immersion in water of an activated sample. A rugged, portable kit was designed for practical field use and maintenance.

Introduction

Since the discovery in the 1950's of large deposits of zeolites occurring as small (<25 μm) crystals in altered siliceous pyroclastics and flows, it has been recognized that a simple field test for determining the presence and percent of zeolite content would be useful for exploration and mining. It has been difficult in the field to differentiate diatomite, vitric ash, or bentonite-bearing beds from zeolitized pyroclastics in some deposits. A test to detect the presence of zeolite was reported by Helfferich (1964) using a combination of ion exchange and pH measurement, but the test is qualitative and high-exchange-capacity bentonites interfere.

Molecular sieve zeolites have several unique properties which make it possible to distinguish them from other fine-grained minerals and even other zeolites such as analcime. The molecular sieve zeolites contain intracrystalline pores which are interconnected to the crystal surfaces by ports of 8-, 10-, or 12-membered rings of oxygens. Their porous crystal structure gives them high sorptive capacities to 50 percent pore volume or to 30 wt percent water sorbed (with accompanying high heats of sorption or immersion up to 100 cal/gm) and selective sorption of smaller molecules, such as water and CO_2, with exclusion of larger molecules. Being network aluminosilicates, the Al^{3+} for Si^{4+} substitutions provide active sites for exchangeable cations located in the crystal pores. As with other minerals the zeolites are best identified by X-ray diffraction analysis, but the instrument is too expensive and bulky for general field use. The optical properties of the very small zeolite crystals are not readily distinguishable with the polarizing microscope.

In arid regions the presence of zeolite in an ash bed or flow often can be determined by the heat generated when touching a sample to the tip of the tongue or on a wet spot in the palm of the hand. If the climate is humid or the deposit wet, a small sample can be heated over a lighter, cooled in a closed container, and then tested for the heat generated on the tongue or hand. To ascertain the quality of the deposit by quantitative methods, it has been necessary to rely completely on laboratory tests such as X-ray diffraction, sorption capacity, and ion exchange determinations. Such tests may not be available to some and in any case cause lag time in the field, even if liaison with the laboratory is arranged, because additional field trips must be made after collection and laboratory evaluations.

The diagnostic property of high heat of immersion, as used qualitatively to detect the presence of zeolite, was selected as most suitable for a quantitative field test.

On the above basis a rugged field kit was designed. It is inexpensive and easy to carry, operate, and maintain under field conditions, and provides semiquantitative data in the field but also quantitative information if the zeolites can be identified by X-ray diffraction.

The Field Kit

The field kit designed weighs 9 kg and is shown in Figure 1. To use the working data given in this article, the unit would have to be duplicated. However, a different design can be used and other working data determined with zeolite reference standards.

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[1] Present address: Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey.

The kit is composed of (1) a mortar and pestle to disaggregate the sample, (2) a rugged easily constructed balance utilizing a phosphor bronze flat spring to weigh 5 grams of sample to ±0.02 gm, (3) a 35 mm film canister to contain the sample, (4) an alcohol burner to dehydrate the sample, (5) a 10 ml volumetric pipette to measure the given volume of water, (6) a thermometer with 0.2°C divisions to measure the temperature rise due to heat of immersion, (7) a pair of tongs for handling the sample container when hot, and (8) polyethylene bottles of alcohol and water. A can of alcohol must be carried separately because one test uses 30 ml of alcohol. Vials of reference zeolite samples, a 5 gm weight, coin envelopes used for weighing, and extra canisters are carried in the drawers. The thermometer and pipette with spares are cushion-mounted in the vertical drawer. The side wind-breakers attach to keep the opened door at right angles to the rest of the unit. A spring-tensioned sleeve is used to position the thermometer during the tests. The dimensions of the heater assembly are such that the bottom of the sample canister resting on an asbestos-covered wire screen is 6 cm above the metal tip of the alcohol burner when fully opened.

Test Procedure

The sample is ground in the mortar to below 14 mesh or 1 mm size. After zeroing the balance with the coin envelope suspended on the hook, 5 gm of ground sample are added into the envelope. The weighed sample is placed in the thin-walled aluminum container and heated to 350°C over the burner with the mounted thermometer inserted midway into the sample (Fig. 1). When this temperature is reached, the sample container is removed with gloves or tongs from the burner, capped, and set aside to cool. For rapid cooling the sample container can be set in water. The cover is removed, and the temperature (T_s) of the sample is measured to within 0.2°C. Ten ml of water at a temperature (T_w), preferably atmospheric temperature, are poured on the sample and the mixture is stirred quickly with the thermometer. The temperature of the mixture rises rapidly, reaching a maximum value (T_{max}) within 30 seconds, and then slowly drops to atmospheric temperature. A high temperature rise upon the addition of water is characteristic of the presence of zeolitic material in the sample, and the amount of temperature rise (ΔT) is directly propor-

FIG. 1. Photograph of zeolite test kit.

TABLE 1. Temperature Rises Obtained with Naturally Occurring Zeolites, Associated Minerals, and Synthetic Zeolites

Sample	Purity (%)	Temperature Rise (°C)*		Heat of Immersion****	
		meas.**	calc.***	1	2
Natural Zeolites					
Na,K-Chabazite Bowie, Ariz.	92	20.6	22.4	50	67.2†,52.2†
Na,K-Phillipsite Rome, Ore.	84	16.6	19.8	44	
Na,K-Erionite Pine Valley,Nev.	94	16.2	17.2	38	
Ca,Na,K-Mordenite Itado Tuff, Japan	78	14.7	18.8	42	
Na,K,Ca-Mordenite Rome, Ore.	60	9.6	16.0	36	
Na,K-Ferrierite Lovelock, Nev.	60	8.0	13.3	30	30.7†††
Na,K-Clinoptilolite Sheaville, Ore.	94	11.6	12.3	28	41.0
Analcime Wikieup, Ariz.	90	0.7	0.8	2	
Synthetic Zeolites					
NaA (2 sources)		28.2,28.9		63,64	73.9
CaA (2 sources)		26.2,28.2		58,63	83.0
NaX (2 sources)		32.5,35.5		72,79	84.3
CaX (1 source)		27.6		61	103.4
Na-Mordenite (1 source)		16.3	18.1	40	46.1

*The temperature rise (°C) for associated minerals is: bentonite, Wyoming, 6.0; gypsum, 4.2; rhyolite ash, partially altered, 3.4; and chalk, 1.1.

**measured on as-obtained sample

***calculated for 100% zeolite

****in calories per gram of hydrated zeolite. Col. 1, Field Test, Col. 2, Barrer and Cram (1971).

†Na-exchanged Ca,Na-Chabazite; ††-K-exchanged Ca,Na-Chabazite; †††Na-exchanged Sr-Ferrierite (synthetic).

tional to the amount of zeolite present in the sample.

When the cooled sample and added water are both at atmospheric temperature, the temperature rise is given by

$$\Delta T = T_{\max} - T_s$$

Under field conditions, it might be difficult to bring the dehydrated sample and the water to be added to the same temperature. In this case an equivalent temperature rise, ΔT_{eq}, can be obtained through an energy balance for the contents of the canister after mixing. Thus, assuming an average specific heat of 0.22 cal $g^{-1}{}^{\circ}C^{-1}$ for the solid sample and neglecting the heat loss to the surroundings during the short period between the mixing and measurement of $T_{\max}$, we have:

$$\Delta T_{eq} = \frac{1.1(T_{\max} - T_s) + 10(T_{\max} - T_w)}{11.1}$$

A single test requires one-half hour to complete, but in an 8-hour span thirty to forty tests can be carried out, because while one sample is being activated and cooled another can be tested for temperature rise.

Important natural zeolites and commonly associated minerals were tested, as well as several commercial synthetic zeolites. The ΔT values determined with this test method are given in Table 1 and plotted in Figure 2. The purity of the sample was determined independently by X-ray powder diffraction analysis and adsorption capacity determinations. ΔT was determined to be directly proportional to the purity of the zeolite by testing prepared mixtures of the chabazite and rhyolite volcanic glass, this latter being the usual parent material for zeolite crystallization in continental deposits and therefore the most common impurity in many zeolite deposits. The linear relationship obtained is shown in Figure 3.

When testing an unknown sample from a new deposit, a ΔT value of 4° to 8°C would indicate the presence of zeolite but probably not in sufficient quantity to be of interest. A temperature rise greater than 20°C would indicate a high grade zeolite deposit, probably rich in chabazite, while a rise between 8° and 20°C would suggest an intermediate to high grade deposit, depending on the variety or varieties of zeolite present. If possible to obtain through the mail, identification of the zeolites by X-ray diffraction analysis would be helpful at this point, and the field testing with the kit then could be completed on a quantitative basis.

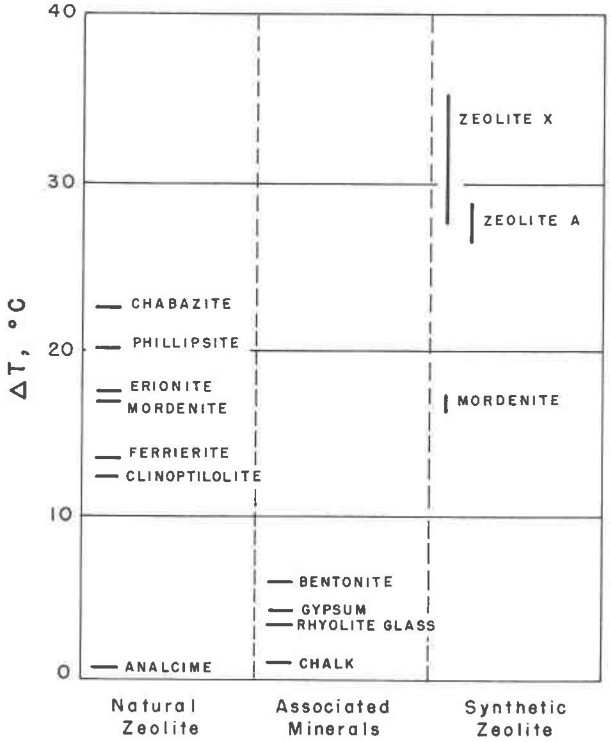

FIG. 2. Temperature data obtained by field kit measurements on natural zeolites, associated minerals, and synthetic zeolites, corrected for impurities.

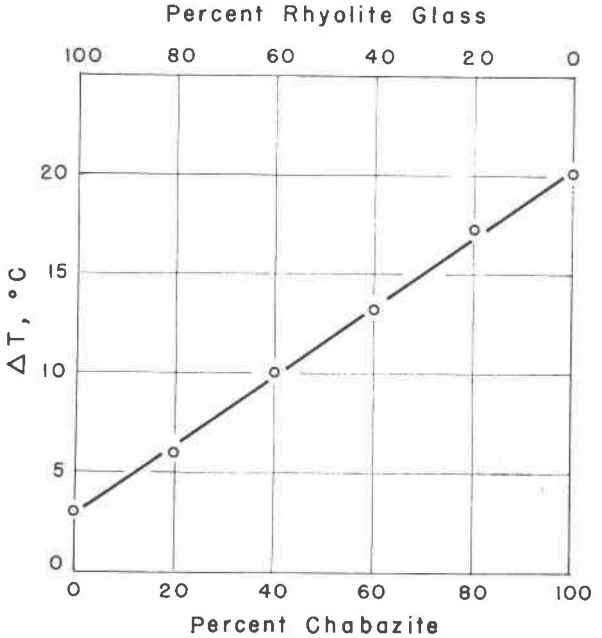

FIG. 3. Temperature data obtained on prepared mixtures of natural Na, K-chabazite and partially altered rhyolite glass.

Discussion

The field kit has been found by the authors to be a practical and quantitative test for zeolite exploration. It is believed to have potential use also in mining operations and in the production of synthetic zeolites as a simple quality control test.

Barrer and Cram (1971) recently have reported on results of laboratory experiments on heats of immersion of outgassed synthetic (with some natural) molecular sieve zeolites in various ion exchanged forms. Even though Barrer and Cram have determined that the variations of heats of immersion for a given zeolite are primarily a function of the exchangeable cation (and the amount of residual presorbed water), synthetic zeolites do not usually vary in the kind and amount of exchange cations. The field test data give results 5 to 30 percent less than the heats of immersion determined by Barrer and Cram. This reflects heat losses unaccounted for in this simplified test, variations in the degree of outgassing, and differences in the exchangeable cation content. Even so, it should be noted that a precision of better than ±0.5°C was obtained on subsamples (See Table 2). On a sample containing a zeolite giving a 30°C temperature rise in the pure form, the zeolite content can be measured to an accuracy of ±3 percent. Such accuracies are often adequate for production quality control, and certainly more than adequate for a field exploration or mining test. For laboratory researchers not equipped with elaborate sorption apparatus, it could easily serve as a diagnostic screening test for zeolite content of raw or treated samples.

TABLE 2. Reproducibility of the Test Results*

Mesh Size of Sample	Temperature Rise (°C)	Mesh Size of Sample	Temperature Rise (°C)
-200	11.0	40/60	11.1
100/200	11.7	20/40	12.0
80/100	11.5	10/20	11.4
60/80	11.2	6/10	12.5

*Sample: Natural Na-K clinoptilolite from Sheaville, Oregon, ground to different size fractions.
Averaged temperature rise, ΔT, for the subsamples = 11.55°C
Standard deviation (95% confidence limits) = ±0.44°C

With the exception of analcime, which presently is not regarded as a molecular sieve, naturally occurring zeolites exhibit temperature rises between 12 and 23°C under the conditions of the test. A deposit containing 60 percent zeolite formed by the alteration of volcanic glass would give a ΔT of 10° to 18°C, depending on the variety of zeolite present. In a deposit partially altered to zeolite, the partially altered glass, even though X-ray amorphous, has been altered sufficiently to contribute to the temperature rise. Other common impurities with significant heats of immersion such as gypsum (ΔT = 4.2°C) and bentonite (ΔT = 6.0°C) can also affect the results, but only when present in major amounts.

References

BARRER, R. M., AND P. J. CRAM (1971) Heats of immersion of outgassed ion-exchanged zeolites. *In*, R. F. Gould, Ed., *Molecular Sieve Zeolites-II. Advances in Chemistry Series*, **102**, Washington, D. C., pp. 105–131.

HELFFERICH, F. D. (1964) A simple identification reaction for zeolites (molecular sieves). *Amer. Mineral.* **49**, 1752–1754.

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