BEAR RIVER ZEOLITE BRZ™
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QUALITY CONTROL

QUALITY CONTROL IN PLANT

Samples are collected on a daily basis, for each lot and run for a granular particle size and moisture. The CEC is typically run on a monthly basis from a composite sample for the month.

PARTICLE SIZE DISTRIBUTION (PSD)

Particle size distributions are determined by using a Horiba LA-920 laser scattering particle size distribution analyzer. Delta Analytical Instruments, Inc. at 1061 Main Street, North Huntington, PA. 15642 (phone 724-864-9850) does the analyses for different speed settings on the variable frequency drive for the whizzer (the classifier). The speed settings produce uniform particle sizes. The 60-cycle setting is what is used for this product. See the attached particle size distribution chart.

GRANULAR PARTICLE SIZES

Granular particle sizes are determined using a rotap with various sample screens. See letter from Ed Huffman dated 28 August 2009.

CATION EXCHANGE CAPACITY

1. There are many methods that have been used to determine the CEC in natural zeolites. Some tests are more popular than others, but there is no universally accepted method such as an ASTM methods.

2. Quoting Pete Bunger “The BRZ natural zeolite cation exchange (CEC) as measured by typical test methods is much lower than the actual CEC. The higher potassium in BRZ causes the CEC to be lower than zeolites with lower potassium. Accurately determining the CEC is difficult primarily due to clinoptilolite having a greater selectivity for the potassium ion than ammonium ion. The attached research publication discusses the differences in both selectivity and kenetics. The widely used CEC methods have an ammonium acetate solution soak step for typically 30 to 60 minutes. The CEC results from our soaking various zeolites for extended times shows that even after 192 hours (8 days) of soaking the CEC is continuing to increase, and the 30 to 60 minute soak time is too short for an accurate determination of CEC. For a lab test method, a soak time of several days is impractical. Further complications involve the diffusion rate and partitioning. Nearly all of these complicating factors can be mitigated by changing from a timed soak to a column extraction. I suggest a 2.5 cm diameter column with a 15 cm bed depth and a 1 N (5.2%) ammonium chloride solution flow rate of 50 ml per hour. Due to the slightly basic properties of natural zeolites, the more acidic ammonium chloride is recommended over ammonium acetate.”

3. The fast methods, “soak tests”, are good for field quality control, but they do not reflect the accurate CEC. However, they also show comparative results from different clinoptilolite properties. Accordingly, Pete Bunger provides the following soak tests: Here are the single soak results (Idaho USA is BRZ).

Hours	ID USA	NM USA	S. Africa	Australia	Turkey
0.5	0.98	0.35			
24	1.28	0.48			
96	1.32	0.65	0.88	0.66	1.04
192	1.36	0.75	0.93	0.77	1.06

4. For more information the reader is referred to: http://www.sciencedirect.com/science/article/pii/S0304389407007789

APPARATUS AND REAGENTS

1. Ring stands to hold burets and separatory funnels.
2. Burets of approximately 2.5 cm diameter.
3. Separatory funnels with PTFE plug stop cock, a capacity of 500 mls minimum.
4. 500 ml beakers.
5. Ammonium chloride.
6. Drying oven with internal fan and thermostat.

COLUMN METHOD OF DETERMINING CEC

1. Determine the percentage of moisture in the zeolite by drying 100 grams in a drying oven for 2 hours at 105 degrees centigrade.
2. Prepare a 1 N (5.2%) ammonium chloride solution using distilled water in quantities of at least 500 ml.
3. Swirl 100 grams of 14 x 40 sample with 500 ml of water. Pour off the cloudy water. Repeat two more times.
4. Place a bed depth of 15 cm of the sample in the buret partially filled with water.
5. Fill the separatory funnel with a minimum of 500 mls of ammonium chloride solution (10 hors worth) so that it feeds into the top of the buret on the ring stand.
6. Adjust the flow from the separatory funnel to 50 mls/hour.
7. Adjust the discharge from the buret so that the bed stays immersed and the buret discharges 50 mls/hour.
8. After 192 continuous hours of running, allow the ammonium chloride solution to run out.
9. Wash and refill the separatory filter with distilled water. Allow a 5000 ml wash of the bed in the column at a rate that is a fast as possible.
10. Discharge the zeolite and allow it to air dry (increased temperature will volatize the nitrogen as ammonia).
11. The samples are submitted to Huffman Laboratory of 4630 Indiana Street, Golden CO, 80403 (phone 303-278-4455) for the total nitrogen exchanged. The procedure is described by Ed Huffman: “Nitrogen is determined on a Therm Flash EA 1112 analyzer. The technique is based on the classical Dumas method with thermal conductivity detection (TCD). The method is described in ASTM D5373 (coal) and

ASTN D529 (petroleum products). Weighed samples are combusted in oxygen at 950 degrees C. The combustion products (including N2 and NOx) are swept with helium carrier gas through combustion catalysts, scrubbers and through a tube filled with reduced copper. The copper removes excess oxygen and reduces the NOx to N2. The N2 is then separated from other gas on the chromatography column and measured with the TCD. We use relatively large samples so the precision should be better than +/- 0.1% absolute."

12. Calculate the CEC as follows:

$$\text{CEC (meqs/100gms)} = \frac{\text{Nitrogen exchanged as \%}}{14.0067} \times 1000$$

Divide the CEC by the percentage dry weight determined in Step 1. For instance, if the moisture was 12%, the dry weight should be .88. With a CEC of 160.00, the CEC would be 181.82.

Representative product samples are collected on a daily basis of all BRZ™. A composite sample is prepared for each month and loaded with nitrogen as follows:

BRZ™ FAST PROCEDURE FOR CEC DETERMINATION, 27 AUGUST 2010

PROCEDURE

- Weigh 100 grams of BRZ™. Dry sample in drying oven for exactly 2 hours at 100 degrees centigrade.
- Place in a 400 ml. deep beaker
- Just cover the BRZ™ with an ammonium nitrate solution. Prepare the ammonium nitrate solution by dissolving 20 grams of ammonium nitrate in 15 mls. of boiling distilled water (this solution is known as "AN 20" in the agricultural world).
- Soak the BRZ™ for 24 hours stirring the beaker at least 2 to 3 times.
- Pour off the ammonium nitrate solution, and let it "drip dry" from the beaker placed on its side.
- Fill the beaker three times as full as the beaker will hold with distilled water and each time stir it with a glass rod, let it soak for one hour, and pour it off.
- Dry the BRZ™ in a drying oven at 100 degrees C for one hour.
- Pulverize the sample.
- Send sample to Huffman Laboratories, Inc., 4630 Indiana St., Golden, CO 80403-1849 (303-278-4555). Huffman will report the total nitrogen exchanged.

CATION EXCHANGE CAPACITY (CEC):

$$\text{CEC (meqs/100gms)} = \frac{\text{Nitrogen exchanged as \%}}{14.0067} \times 1000$$

DISCUSSION

- The accepted test for CEC involves 5 immersions of the sample in AN-20. Each immersion involves 1 day. Empirically one immersion corresponds to 80% of the actual CEC. Five immersions have been avoided due to the time requirement.
- Drying the sample is very critical. The clinoptilolite contain free water and water of hydration. At 100 degrees centigrade different moisture contents are a function of time. Further, samples must be packaged immediately after removing an aliquot, because the clinoptilolite is a very effective desiccant.
- The samples are submitted to Huffman Laboratory of 4630 Indiana St., Golden CO., 80403 (phone 303-278-4455) for the total nitrogen exchanged. The procedure is described by Ed Hufffman Jr. as follows:
- "Nitrogen is determined on a Thermo Flash EA 1112 analyzer. The technique is based on the classical Dumas method with thermal conductivity detection (TCD). The method is described in ASTM D5373 (coal) and ASTM D529 (petroleum products).
- Weighed samples are combusted in oxygen at 950 degrees C. The combustion products (including N2 and NOx) are swept with a helium carrier gas through combustion catalysts, scrubbers and through a tube filled with reduced copper. The copper removes excess oxygen and reduces NOx to N2. The N2 is then separated from other gas on a chromatography column and measured with the TCD.
- We use relatively large samples so the precision should be better than +- 0.1% absolute."

MOISTURE DETERMINATION

A composite sample is collected and the free moisture is determined in a drying oven set at 100-105 degrees C for two hours using an initial sample weight of 100 grams.

WEIGHTS

Weights are determined by calibrated scales for packaged product or by certified truck scales.

HEAVY METALS AND MINERALOGIC COMPOSITION

Quoting the late George Desborough:

"This work was done using the modem U. S. Geological Survey (USGS in Denver, CO) XRD equipment using the computerized JADE mineral identification programs to assist in identification of minerals. … More than 20 XRD samples (including composite samples from 3-15 foot thick zones at what is now the main mining pit of BRZ™) were studied. Quartz was never detected. Clinoptilolite was the only zeolite found. Opaline silica commonly referred to as "opal C-T" was the major diluent. Bulk chemical compositions were determined using XRF at USGS to determine concentrations of Na, Ca, K, Al, Si, Fe, Ti, P, etc. Energy dispersive analysis was used to quantitatively determine trace elements such as As, Se, Rb, Pb, Sr, etc."