

# Study of Inorganic Sorbents as Material for Underground Repositories in China

Wang Zhixiong

*China Institute for Marine Development, Beijing, PRC*

## INTRODUCTION

Since 1983, the construction of nuclear power plants has been carrying out in Zhejiang and Guangdong provinces of China. The project is a part of the radwaste disposal plan of China. The project under the Contract with IAEA (No.4496/RB) aims at studying absorption kinetics and mechanism of backfill material and selecting the proper backfill material for the radwaste disposal of China.

There are varieties of clay minerals as inorganic sorbents in China, such as zeolite, illite montmorillonite, kolinite, and so on. Bentonite is the first selected material for the research project. Bentonite is a common montmorillonite clay with good mechanical properties and chemical stability under certain conditions in a repository capacity. There are many huge bentonite deposits in China. China's LILW disposal will be possibly selected in the bentonite district. The investigation on China's bentonite will include the properties of China's sites, the study on migration of radionuclides and the geochemistry of actinides elements. Various bentonites of China have been studying to select a good-quality bentonite. The project is significant to assess the barrier ability of bentonite.

The project also made the primary work for zeolite as a sorbent which has been using for the disposal of LILW liquid in China. Clinopliotite has been used in China's hydraulic fracture test of the radwaste liquid.

## METHODS

Since August 1986 we have carried out the geological study and comparison on the two bentonites deposits (one, Ca-bentonite deposit; the other one, Na-bentonite deposit) and collected bentonites samples of the two districts from outcrop, surface, core material, subsurface, excavation.

A number of tests and laboratory determination have been conducted as follows: Microscopic identification, X-ray diffraction, Electronic microscopic determination, Differential analysis, Thermo-gravimetric analysis, Infrared absorption spectrometry, Chemical analysis, X-ray fluorescence, Plasma spectrometry, Measurement of effective porosity, Partical analysis, Measurement of pH, Measurement of colloide properties, absorb methyl blue, Expansion power, Exchangeal cation capacity, Measruement of rare-earth elements, Measurement of age, Counting, Batch and Colum tests.

## GEOLOGICAL FEATURE OF TWO BENTONITS DEPOSITS

### 1. Na-bentonite deposit

The studied Na-bentonite deposit occurred in a basin formed at Mesozoic Era. The basin's trend is NE-SW consisting with the direction of the region structure line. The ore body is located in stratum of J<sub>1</sub>g which formed a syncline trending NE.

The ore body was controlled by stratum showing sheet. The host rock are sediment-tuff and so on. The rock consists of quartz, plagioclase, feldspar and minor amount of rock fragments. The crystalline fragments occurred devitrification and formed fine-particle aggregate of feldspar and quartz. The rock shows the alteration phenomena of montmorillonization, chlorination and calcitization.

### 2. Ca-bentonite deposit

The studied Ca-bentonite deposit occurred in a Jurassic formation forming a synclinorium. The ore body is located in vitric tuff of J<sub>1</sub>g with its roof and bottom of tuffite being tuffstone, sandstone grit respectively. The bentonite is at an age of 97.64-103.07 m.y. Its mineralization was determined as the Cretaceous with the K-Ar method.

The study under microscopy indicates that the rock are composed dominantly of hyalocry stalline and minor amount of crystalline clastic, quartz, biotite, feldspar, volcanic ash. The rock has montmorilloization in various degrees.

### 3. Comparison between Na-bentonite deposit and Ca-bentonite deposit

(a) The forming of the two deposits were controlled by volcanic movement and geological structure, for instance, they all occurred in basins controlled by the structures of NEE direction; (b) The forming of the two deposits were controlled by stratum; (c) Their mineralization was determined to be in Jurassic and Cretaceous; (d) The main differences of them are the different pH values of bearing-mineral liquid and different basic degrees as the mineralization was formed.

## STUDY ON MINERAL COMPOSITION OF BENTONITES

### 1. Electronic microscopic observation

The observation indicates that the the bentonite consists mainly of montmorillonite with a content 40-50% (maxim 70%). The bentonite is a kind of clay with silicate arranged in parallel sheets and the cations of K, Na, Ca, Mg filled in interformational sheets. The bentonite contains quartz, feldspar, biotite as well as a small amount of clinoptilote, chlorite, illite, elhuyarite, magnetite, etc. Montmorillonite in bentonite is derived from tuff.

The properties of bentonites depend basically on that of montmorillonite. The electronic microscopic observation shows that Na-bentonite contains mainly sodium montmorillonite which occurs in typical aggregate of scale form, or with crimping margin. Ca-bentonite contains mainly of calcium montmorillonite.

### 2. Differential thermal and thermo-gravimetric analysis

For Na-bentonite, there is an individual endothermal peak at 145 °C representing the loss of water and the peak's high is lower than that of Ca-bentonite. However for Ca-bentonite, there is a double endothermal peak at 140°-165 °C, a small endothermal peak at 224°-230°C and an endothermal at 300°C, indicating loss of water. For Na-bentonite, the thermo-gravimetric analysis shows that water of 9-13% lost at 100°-300°C, water of 30% lost at 500°-700°C. For Ca-bentonite, lost

by 11-15% at 300° and losing of crystalline water at 800°C.

### 3. X-ray diffraction analysis

The X-ray diffraction for the studied samples shows that the value of  $d(001)$  of the strongest line is a feature to classify the sort of montmorillonite: Na-montmorillonite  $d(001)=12.5 \times 10^{-10}\text{m}$ , Ca-montmorillonite  $d(001)=14.00 \times 10^{-10}\text{m}$ .

### 4. Infrared absorption spectrum analysis

The infrared absorption spectrum of two bentonites are all similar. As seen from the pattern, the two absorption bands of  $3620\text{ cm}^{-1}$  and  $3410\text{ cm}^{-1}$  are deep and wide, representing the expansion and contraction vibration of water. The absorption band of  $1038\text{ cm}^{-1}$  represents the vibration of Si-O and it shows also the feature of montmorillonite.

## STUDY ON PHYSICO-CHEMICAL PROPERTIES OF BENTONITES

### 1. Chemical composition

Bentonites consist mainly of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{H}_2\text{O}$  and a small amount of  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ . But their chemical compositions are varied due to the difference of locating, medium conditions and geological situation.

Comparing the chemical compositions of Na-bentonite and Ca-bentonite indicates: (a) The content of  $\text{SiO}_2$  is similar in two kinds of bentonites but the content of  $\text{Al}_2\text{O}_3$  in Na-bentonite is a little higher than that in Ca-bentonite; (b) The content of  $\text{Na}_2\text{O}$ ,  $\text{H}_2\text{O}$  are markedly different in the two bentonites. The average content of  $\text{Na}_2\text{O}$  is 19.55% for Na-bentonite but only 0.1% for Ca-bentonite. The average content of  $\text{H}_2\text{O}$  is 16.88% for Ca-bentonite, but 12.68% for Na-bentonite.

The contents of Nd, La, Ce in Ca-bentonite are higher, then the contents of Ho, Er, Yb, Lu in Na-bentonite are higher.

### 2. The contents of cation exchange

Montmorillonite is mineral with negative charge. It must absorb  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  balancing electron charge. Thus measuring the contents of cation exchange and exchanged cation is the important evidences for identifying bentonite.

The bentonites are classified Na-bentonite and Ca-bentonite by using basic coefficient (Basic Coefficient =  $E_{\text{Na}^+} + E_{\text{K}^+}/E_{\text{Ca}^{2+}} + E_{\text{Mg}^{2+}}$ ). Basic Coefficient  $< 1$  for Ca-bentonite, basic coefficient  $> 1$  for Na-bentonite. The contents of cation exchange are determined as follows: Na-bentonite 70.05, Ca-bentonite 59.49.

### 3. pH values, absorb methyl blue, expansion power colloide property

(a) The pH value of Ca-bentonite is 6.15-7.97, Na-bentonite is 10±; (b) The absorb methyl blue is an important parameter to assess the quality of bentonites. The relative content of montmorillonite could be estimated by the parameter. The absorb methyl blue of Na-bentonite is higher than Ca-bentonite; (c) Expansion power of Na-bentonite is 29 ml/g, but expansion power of Ca-bentonite is lower (20ml/g); (d) The colloide property of Ca-bentonite is lower (average 40-50) than Na-bentonite which has better dispersion.

### 4. Surface ratio and porosity volume

Surface ratio of Ca-bentonite are 24.6 mL/g (20-40 mesh) and 26.8 mL/g (100-120

mesh); for Na-bentonite, 23.2 mL/G (20-40 mesh) and 26.6 mL/g (100-120 mesh).

The porosity volume of the two bentonites is approximately 0.06 mL/g. The effective ionic radius is  $20-50 \times 10^{-8}$  m.

## EXPERIMENTS ON STRONTIUM, URANIUM AND CESIUM ADSORPTION IN TWO BENTONITES

### 1. Strontium adsorption on two bentonites

Samples were sieved with the fraction of 80-20 mesh, solid/liquid 1:10, water of  $\text{CaNa}_2(\text{HCO}_3)_2$  type, pH 7.5-8, shaking velocity 120 time/min, centrifuged speed 4,000 n/min.

The equilibrated times of two bentonites were determined by drawing solutions of strontium concentration of 10, 100, 400 ppm respectively. The obtained data show that the absorption equilibrium of strontium in the solutions can be reached immediately after only 10 minutes' shaking, which shows that strontium is very easily captured in the bentonites.

The relation between  $K_d$  and Sr concentration show that for calcium bentonite,  $K_d$  decreases with the increase of Sr concentration at  $c < 30$  ppm. However,  $K_d$  decreases with the increase of Sr concentration at  $c > 30$  ppm. The change trend of  $K_d$  is not obvious after  $c > 400$  ppm. For sodium bentonite,  $K_d$  increases with the increase of Sr concentration at  $c < 400$  ppm,  $K_d$  decreases with the increase of Sr concentration at  $c > 400$  ppm, however, the action of cation exchange is getting obvious at high concentration. The correlation between cation exchange and Sr concentration show that the typical action of cation exchange can produce in bentonites. The mechanism of cation exchange appears as Sr concentration exceeds 1,000 ppm. The degree of cation exchange increases with the increase of Sr concentration.

### 2. Uranium adsorption on two bentonites

Samples were sieved with the fraction of 80-120 mesh, solid/liquid ratio 1:10, water of  $\text{CaNa}_2(\text{HCO}_3)_2$  type, pH 6-7.5, shaking time 10 min-6th.

The correlation between uranium adsorption and equilibrated time show the property of uranium adsorption of bentonites is excellent. The adsorption properties of bentonites under the various values of pH show that the bentonites have a good adsorption for uranium. Na-bentonite is especially fit for the treatment of the acid radwaste liquid.

The correlation between adsorption ratio and U concentration and the correlation between  $K_d$  and U concentration show that for Ca-bentonite they are all normal, however for Na-bentonite they appear abnormal which show the mechanism of uranium is more complex in the case of high concentration.

### 3. Cesium adsorption on two bentonites

Test conditions: pH 7.5, 2.5°C, centrifuged speed 12,000n/min, water of  $\text{CaNa}_2(\text{HCO}_3)_2$  type.

The test show that the equilibrated time of cesium adsorption on Ca-bentonite is approximately 5 hours. It is 16-20 hours for Na-bentonite. This indicates that cesium has an extremely low mobility in bentonites.

The experimental results of cesium adsorption on bentonites under various pH values indicate that  $K_d$  of calcium bentonite is maximum at pH 7.0-7.5. There is a higher  $K_d$  value for Na-bentonite at pH 7.

The test was carried out using the cesium solutions of 1.0, 10, 100, 1,000, 2,000 and 5,000 ppm. The obtained results show that the distribution coefficient has a decreasing trend as cesium concentration reach 5,000 ppm.

#### 4. Column tests

In column tests, the saturant adsorption of uranium on Ca-bentonite is 3-10mg at pH=5-6, U concentration 50-200 ppm; for Na-bentonite, 4-22mg. At pH=7, Sr concentration, 50-200 ppm, for Ca-bentonite the saturant adsorption of strontium is 21-38mg/g; for Na-bentonite, 18-29mg/g. Thus the two bentonites have well adsorption capacity for U and Sr.

Dispersion coefficient and dispersion degree are determined in migration experiments of  $^{137}\text{Cs}$ . When rough Ca-bentonites are mixed with sand, its dispersion coefficient and dispersion degree are getting larger. The dispersion coefficient and dispersion degree of Na-bentonite are the medium values between rough grains Ca-bentonite and Ca-bentonite mixed sand.

#### STUDY ON OCCURRENCE, PROPERTIES AND USE OF ZEOLITE

China has also huge natural zeolite deposits. Zeolite has being used for the radwastes treatment in China. Clinoptilolite have being used in hydraulic fracture test for disposal of LILW.

The used clinoptilolite is produced from a zeolite deposit. The deposit is located in volcanic rock of Mesozoic-Cenozoic Era. The studied samples with a value of 4.18-4.9 (Si/Al) are regarded as a kind of clinoptilolite bearing higher sodium comparing with the normal clinoptilolite (Si/Al 4.25-5/7).

The exchanged test between clinoptilolite and  $^{137}\text{Cs}$  has been carried out. The test shows the rate of recovery reaches up 96%. This shows that the clinoptilolite is an excellent inorganic sorbent in the radwastes disposal.

Clinoptilolite has been used in China's hydraulic fracture test of the radwastes liquid. Clinoptilolite was mixed with cement, ash, white clay in drilling mud of radwastes liquid to form the fixed mud. In order to examine the capacity action of the fixed mud the leaching test had been carried out for LILW liquid fixed mud. The results indicate that the activity of the water separated from the radwastes liquid mud approximated 0.45-0.54% of the general activity of origin radwastes liquid.

The study on the use of clinoptilolite and detailed summary have been doing further.

#### CONCLUSIONS

The work mentioned above is the first stage of the project. The obtained results and parameters will provide a basis for the further research work.

Through the obtained results we conclude that the two bentonites have excellent adsorption capacity for radionuclides and the studied Na-bentonite has the advantage of Ca-bentonite at physico-chemical properties. For example, (a) The expansion power of Na-bentonite is higher than Ca-bentonite. This indicates that Na-bentonite has higher recovery capacity for radionuclides; (b) The expansion power of Na-bentonite is also higher. It shows that Na-bentonite has better sorption and retardation for water; (c) The quality of bentonites depends on the content and quality of montmorillonite.

Adsorption kinetics and mechanism of bentonites have the new further

explanation by physic-chemistry, crystallography, mineralogy, geochemistry and radiochemistry.

Clinopliotite was mixed with cement, ash white clay in drilling mud of radwastes liquid to form the fixed mud. The leaching test of the fixed mud shows that the activity of the water separated from the radwastes liquid mud approximated 0.45-0.54% of the general activity of origin radwastes liquid.

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