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# Thermal Effects on the Physicochemical Properties of Domestic Bentonite as a Buffer Material of Spent Fuel Repository

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# 사용후핵연료 처분장 완충재로서 국산벤토나이트의 물리화학적 특성에 대한 열적효과

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## Abstracts

To investigate the thermal effects on functional properties of domestic bentonite, XRD patterns, TG/DSC curves, swelling rates and distribution coefficients of heat-treated Dong-Hae A bentonite were studied. In the XRD patterns, (001) peak disappeared at above 200℃ and Dong-Hae A was identified as Ca-bentonite through the DSC curve. The loss of swelling capacity and CEC began at 100℃. The distribution coefficients of Am-241, Co-60 and Cs-137 onto heat-treated Dong-Hae A showed negligible variance as temperature was raised and that of Sr-85 decreased at about 150℃. Reviewing these data, it was evaluated that Dong-Hae A colud be used as a buffer material at below 100℃.

## 요 약

국산벤토나이트의 완충기능에 대한 열적 효과를 고찰하기 위하여 동해 A 시료의 X-선 회절 양상, TG/DSC 곡선, 팽윤도 및 분배계수를 각 온도에 따라 분석하였다. X-선 회절 분석결과 약 200℃의 온도에서 몬모릴로나이트의 특성 피크인 (001)이 완전히 붕괴되는 양상을 나타냈으며 DSC 곡선상에서 동해 A 시료가 Ca-벤토나이트임을 확인하였다. 시료의 팽윤도와 양이온 교환능은 약 100℃ 정도에서 감소하기 시작하였다. Am-241, Co-60 및 Cs-137등의 핵종에 대한 분배계수는 온도변화에 따라 큰 변화를 보이지는 않았으나 Sr-85의 경우는 약 150℃에서 감소하는 경향을 나타내었다. 지금까지 얻어진 데이타만을 놓고 볼때, 100℃ 이하의 온도에서는 동해 A가 완충재로서 사용될 수 있을 것으로 평가되었다.

### I. Introduction.

In addition to the properties such as low permeability and high sorptionability, the stability of bentonite is also an important factor for use as a buffer material in an underground repository for

high–heat generating radioactive wastes including spent fuel. A material with good swelling and sorption properties becomes worthless unless it retains its functional properties under the expected repository conditions for the required period of time.

In the case of spent fuel or radioactive high–level–waste (HLW) repository, the bentonite buffer will experience high temperature and high radiation exposure for long time. Tarandi's calculation of temperature distribution in spent fuel repository showed that the maximum temperature of disposal canister was peaked at about 30 years after spent fuel disposition [1]. If the peak temperature exceeds 100℃, the adjacent bentonite buffer would be heated and then dehydrated. Many other experimental results showed that the dehydration resulted in a decrease in cation exchange capacity (CEC) and a loss of swelling ability of montmorillonite [2, 3]. As the reasons, some researchers have suggested the charge reduction accompanying the loss of interlayer water at elevated temperatures and the conversion of major component from montmorillonite to illite [4, 5]. The montmorillonite illitization would occur easily by heating to at temperature less than 100℃ and be accelerated by adding appropriate pressure. The above two suggestions mean that the increasing temperature influences the functional properties of the buffer to prevent the groundwater intrusion and the movement of released radionuclides.

Most radiation fields to be experienced by the buffer will be the gamma radiation emitted by the decay of fission products. The principal effects of gamma radiation are the direct radiation damage and the pH change of aqueous phase due to the radiolysis of groundwater. Krumhansl [3]. and Heremans et al. [6], studied the radiation stability of bentonite exposed at about $10^{10}$ rads, equivalent to the absorbed dose of the buffer at the central surface of a 10–year–old PWR spent fuel for 500~700 years [7], and they found no mineralogic alteration.

Up to now, most of the experimental results related with the thermal stability of bentonite have been focused on sodium bentonite [3, 9, 10]. Summarizing their results, the temperature limit of sodium bentonite to preserve physical and chemical integrity of buffer material appeared to differ from researcher to researcher, however, falling in the range of 100°~300℃. This wide range of temperature limit is due to the different evaluation criteria of bentonite stability reflecting their own conditions. That is, the temperature limit may be set up differently depending upon the priority and the combination of functional properties such as mineralogical integrity, swelling pressure, permeability, CEC and others. Anderson [8] and Couture [9, 10] reported the proper data to show that the thermal stabilities for sodium bentonite is assured in the range of approximately 300℃. However, they left questions over the long–term stability, especially if there exist impurities such as potassium, etc., which exerts an influence on the structural changes of montmorillonite.

When spent fuel is disposed of at a depth of 1000 m in granitic rock mass in which domestic bentonite is used as a buffer material, the safety or evaluation criteria to assure that the domestic bentonite could act as a functional buffer form under the expected repository condition have to be established. Also, in order to assess the real applicability of domestic bentointe as a buffer material and the safety of spent fuel disposition and to design the spent fuel disposal system, being adaptable to domestic actual circumstances, it is important that the thermal effects on the physical and chemical properties of bentonite must be known over the temperature range expected within the repository. Therefore, in this study, as one of the efforts for preparing the evaluation criteria of buffer material, the thermal effects on the properties of Dong–Hae A, which

was selected as a representative domestic bentonite in previous study [11], were investigated to suggest the maximum temperature with reasonable assurance of mineralogical stability, swelling capacity, CEC and sorption capacity. For this purpose, the X-ray diffraction (XRD) patterns, the thermogravimetry (TG) and differential scanning calorimetry (DSC) curves were analysed. For the effects on the chemical properties of heated samples, CECs, swelling rates and distribution coefficients of radionuclides onto domestic bentonite were measured and analysed.

## II. Experimental

Bentonite sample used was Dong-Hae A collected from Yun-Il mining area as in the previous study [11]. The air-dried sample was ground to pass 60 mesh-sieve and its water content was measured as about 12.5 %. And then it was heat-treated in an oven at specific temperatures within 100℃~300℃ for 24 hours and then exposed to atmosphere for 24 hours. Here, the degradation of bentonite, being the function of temperature and water content, was known to be more effective in the case of moisture in limited amounts than excess water or dry [10, 12]. Couture et al. [10] and Allen et al [12]. showed that when the bentonite with water content of about 10 % was heated at 150~250℃, its swelling property, composition and structure changed extensively. In this study, to obtain the conservative data the air-dried samples with water content of about 12.5 % were used in all tests.

XRD measurements were carried out by means of Rigaku D/MAX-3C powder diffractometer with a CuK$\alpha$ X-ray source, operated at 30KV and 15mA. The XRD patterns were recorded over a 2$\theta$ range of 2°~50° and compared with the JCPDS (Joint Committee on Powder Diffraction Standards) mineral powder diffraction file [13]. TG analysis was carried out by means of NETZ STA 5409 thermal analyzer at a heating rate of 10℃/min in air. And then DSC analysis was carried out by means of Perkin-Elmer DSC 7. CECs, free swelling rates and batch experiments to determine the distribution coefficients of heat-treated samples were carried out by the similar method as those applied in the previous work [11]. And all the tests were then conducted at ambient temperature.

## III. Results and discussion

### 1. Mineralogy and swelling properties.

The color of Dong-Hae A bentonite was changed form dark-green to reddish brown as the heat-treatment temperature increased. This change of color might be due to the oxidation of iron elements contained in raw bentonite. A considerable amount of iron elements was identified from the chemical analysis data of Dong-Hae A sample [11].

Figure 1 shows the XRD patterns of Dong-Hae A samples heat-treated at room temperature to 300℃, where the black points mean the characteristic peaks of montmorillonite contained in the bentonite. It is found that only (001) peak decreases at elevated temperatures but other peaks do not vary. That is, the intensity of (001) peak decreases gradually up to 150℃. Then (001) peak changes to a poorly defined peak at 200℃ and it is not even detected at 300℃. From these data, (001) peak of montmorillonite is found to be collapsed fully above 200℃, which is due to the fact that the disordering or the structural change of (001) might increase as the temperature increases. These patterns agreed well with Krumhansl's results [3]. Thus, the changes of (001) suggest the possibility that the swelling property of bentonite may decrease with increasing the temperature since the characteristic peaks of montmorillonite, the swelling properties are known to be attributed

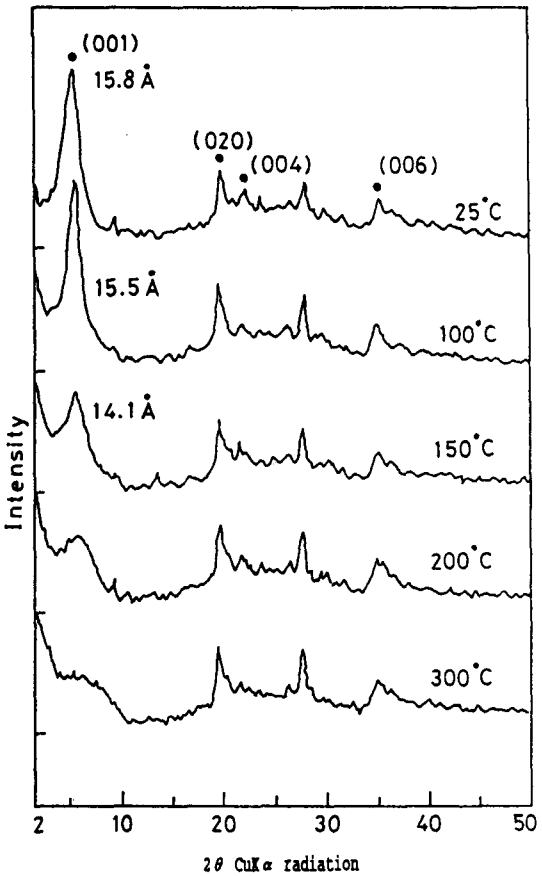


**Fig 1. X-ray diffraction patterns of Dong-Hae A samples heat-treated at given temperatures for 24 hours.**

to only the (001) properties.

In figure 1, the (001) peak is found to shift slightly to the right at elevated temperatures. Considering Bragg s law of X-ray diffraction, this gradual shift of (001) peak might be due to the decrease of basal spacing of interlayers which constitute (001) of montmorillonite. The decrease of basal spacing could be explained by the process of interlayer water loss. Slightly above the boiling point of water, most of the water sorbed losely on the interlayer surfaces is lost first and then the loss of hydration water of cations (cation coordinated water) existing in interlayers follows. The process of hydration water loss is known to differ in hydration energy from cation to cation. That is, because the divalent ions such as calcium and magnesium have higher hydration energies, they retain water longer than monovalent ion, sodium, at the same temperature. Krumhansl [3] showed that a sodium montmorillonite heat-treated at 105℃ had an interlayer spacing characteristic of a fully collapsed structure and Berkheiser et al. [14] also showed that after heating calcium bentonite to 105℃ the partially hydrated calcium ions were still existing in the interlayers. This means that sodium ion may be driven off or migrate into other cavities existing in lattice faster than calcium, which results in a reduction of interlayer charge.

Figure 2(a) shows the heat capacity and the weight loss of Dong-Hae A bentonite with iccreasing the temperatures. The TG curve shows three distinct regions : In first region, it is thought that as the temperature is raised to about 100℃, the water adsorbed losely on the clay's surface begins to be driven off. Next, the rapid weight loss takes place in the range of 100~200℃, which is due to the loss of most water sorbed on the interlayer surface and some parts of the hydration water of cations. And above 200℃ follows a gently sloped plateau. It was reported that the plateau region indicated the overlapped losses of the hydration water of cations and the lattice water, consisting of structural OH groups, and that it is difficult to separate cation-coodinated water from lattice water up to now[15].

In the DSC curve, an endothermic peak is obserbed between 100℃ and 110℃. In this region, heat is absorbed for the dehydration of interlayer water contained in bentonite sample. And then a shoulder on the slope of peak, indicating an incompletely resolved double peaks, appears at about 150℃. It is interpreted as a second peak when the hydration water of exchangable cations is driven off from interlayers. The shoulder is reported to appear in DSC or DT (Differential Ther-

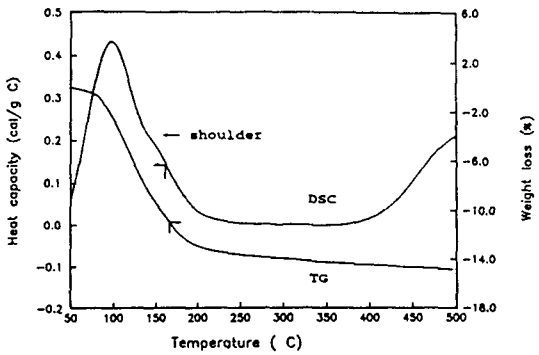


**Fig. 2-1. TG and DSC curve Dong-Hae A sample.**

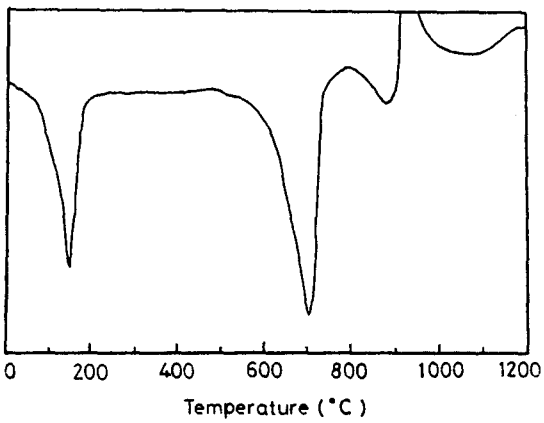


**Fig. 2-2. Differential thermal curves of montmorillonite, Upton, Wyoming[2]**

mal) curve when a part of the water existing in interlayers is more tightly adsorbed than another part [15, 16]. In the case of Ca-montmorillonite, the shoulder is obserbed distinctively since divalent calcium ion has higher hydration energy so that the its hydration water is lost later than that adsorbed on the surface of particle above 100℃ [15]. In the case of Na-montmorillonite, as in Fig. 2-2, only a single peak (downward) is observed in the range of 100℃~200℃ [15, 16]. The reason is thought that the hydration energy of sodium is lower than that of calcium, so that the hydration water of sodium and the water adsorbed losely on the surface of particle are lost simultaneously. Therefore, together with Berkheiser s results[14], it can be said that under the expected thermal condition at underground repository, Ca-montmorillonite retains water longer than Na-montmorillonite.

Figure 3 shows the swelling rates of Dong-Hae A samples heat-treated at various temperatures for 24 hours, where the bars indicate the error range of values actually measured. The swelling rate of sample is found to decrease as the temperature of heat-treatment is raised. Slightly above 100℃ the swelling rate decreases abruptly up to 200℃ and above 200℃ it becomes about half the value of untreated sample. According to the manual of soil testing[17], the clay with swelling values less than 50 % is considered not to have expansive properties. Therefore, Dong-Hae A is evaluated to lose most of its swelling capacity above 200℃. At present, although the reasons for the reduced swelling capacity and the swelling machanisms of bentonite have not been cleared, many researchers reported that van der Waals attraction, the hydration energy, the electrostatic energy between the charged layers and the exchangeable cations, and the double-layer repulsion forces, etc. are interrelated complicately [2, 3].

However, as expected previously, it is thought that the reduced swelling property of heat-treated

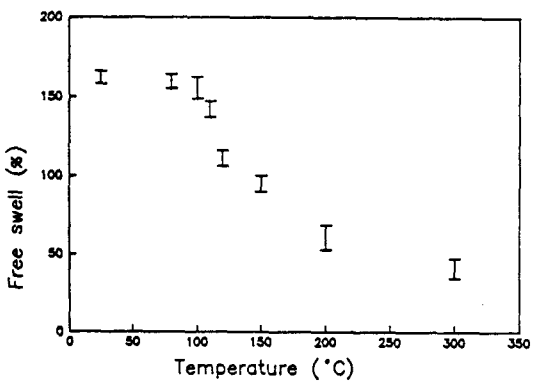


**Fig. 3. Free swelling rates of Dong-Hae samples heat-treated at given temperatures.**

bentonite is due to the reduction of interlayer charge and the structural change of (001) of montmorillonite as the temperature is raised. A relation between the (001) of montmorillonite and its swelling capacity is demonstrated in figure 4 by combining the peak intensity of (001) given in figure 1 and the swelling data given in figure 3. Figure 4 shows the relation between relative swelling ratios and relative peak intensitiy ratios of (001) of the heat-treated samples. The relation is found to be linear, which indicates that the reduced swelling capacity of heat-treated bentonite is related directly with (001) of montmorillonite contained in bentonite samples. And then Table 1 shows the changes in CEC of reference Ca-montmorillonite and Dong-Hae A bentonite sample heat-treated at various temperatures. In this table, although each CEC value at specific temperature is not given completely, the CEC values tend to reduce gradually by heating and reach about the half of starting values. The reason for decrease in CEC has been explained by the interlayer charge reduction due to the heat—treatment [18, 19].

Figure 5 demonstrates the swelling data of samples heat-treated at 100℃ for 42 days, of which the purpose is to investigate its long-term thermal stability under the expected repository condition. Consequently, as in Fig. 5, the swelling rates do not vary. It is an expected result considering the genesis of montmorillonite which is formed by the alteration of volcanic ash under the condition of about 100℃ and relatively high pH.

**Table 1. Effect of heating on the cation-exchange capacity of reference Ca-montmorillonte and Dong-Hae A bentonite sample**

| Temp.(℃) | CEC(meq/100g) | |
|---|---|---|
| | Ca-Mont. [2] | Dong-Hae A |
| Room temp. | | 72.9±4.0 |
| 100 | – | 65.4 |
| 150 | 93 | 63.2±3.2 |
| 200 | – | 63.0±1.3 |
| 300 | 45 [3] | 44.1±1.0 |
| 390 | 12 | – |

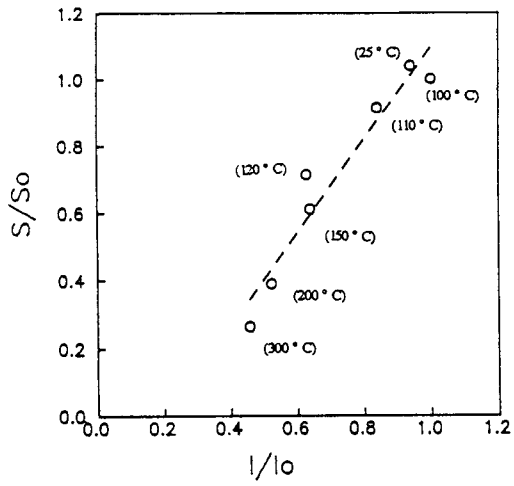


**Fig. 4. Relation between relative swelling ratio and (001) peak intensity ratio of heat-treated to untreated Dong-Hae A samples.**
(S : Swelling rate of samples heat-treated,
So : Swelling rate of unheat-treated sample,
I : (001) peak intensities of samples heat--treated,
Io : (001) peak intensities of unheat-treated sample)

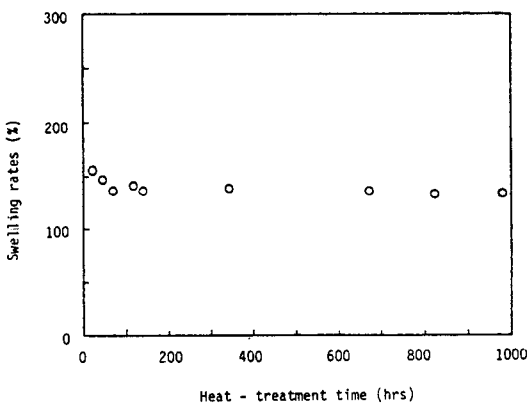


**Fig. 5. Free swelling rates of Dong-Hae A samples heat-treated at 100℃ for 1~42 days.**

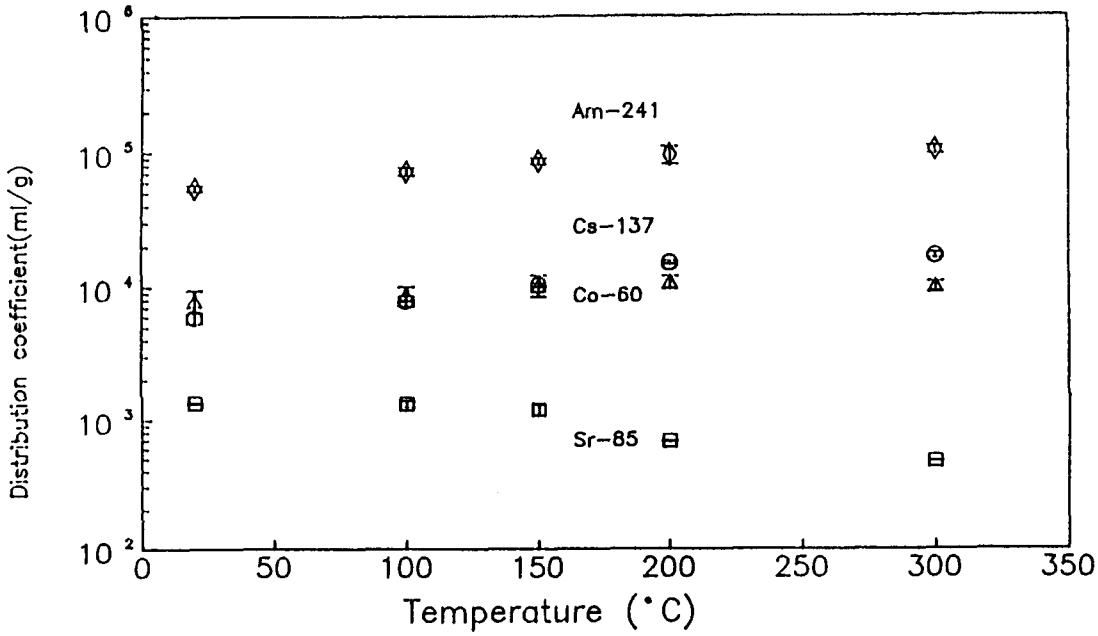


**Fig. 6. Distribution coefficients of Am, Cs, Co and Sr onto Dong-Hae A sample heat-treated at specific temperatures for 24 hr.**

### 2. Sorption property

When the radionuclides concentration was about 0.1 $\mu$Ci/mℓ and the heat-treated bentonite samples were contacted with synthetic groundwater for 10 days, the distribution coefficients of Am-241, Cs-137, Co-60 and Sr-85 measured by batch method are shown in figure 6. As the temperature increases, the values for Am-241, Cs-137 and C0-60 appear to increase slightly. The values for Sr-85 appear to be constant up to about 150℃ and above a slight decrease follows. As the sorption mechanism of strontium has been well known as the ion exchange, it is thought that the decreasing tendency of distribution coefficient for Sr-85 is due to the reduced number of exchangeable cations which may be backed up by the results in Table 1. Comparing the sorption results in figure 6 with the CEC results as listed in Table 1, the sorption behaviors of Co-60, Cs-137 and Am-241 appear not to be affected by the variance of CEC, which indicates that some machanism other than ion exchange is primarily responsible for the sorption of these radionuclides.

## IV. Conclusions

From the XRD analysis, (001) peak of Dong-Hae A was identified to be collapsed fully above 200℃, and in the DSC data, the shoulder on the peak appeared at about 150℃, which is the evidence that Dong-Hae A is predominated by Ca-montmorillonite.

The loss of swelling capacity and CEC of samples started at about 100℃, However, the swelling rate of samples heat-treated at 100℃ for 42 days stayed constant. Coupling the swelling data and the (001) peak intensity, it was found that they are linearly interrelated.

The distribution coefficients of Co-60, Cs-137 and Am-241 onto the samples heat-treated at elevated temperatures did not vary remarkably. But those of Sr-85 decreased at about 150℃.

Reviewing these data, it is sufficient to explain that the domestic bentonite can be used as a buffer material at below 100℃. However, it could not say that the temperature of 100℃ is the maximum temperature to keep the mineralogical integrity and the functional properties of buffer material. The maximum temperature should be determined through analysing the thermal effects on the mechanical properties and the chemical properties comprehensively with their combined functional priority.

In addition to the findings of thermal effects, it is also found, considering the chemical aspects of Ca–bentonite, that because calcium is more difficult to be displaced than sodium, the presense of calcium in bentonite may help to assure long–term stability against deteriorating chemical reactions which may occur within the buffer system of certain conditions. Therefore, when it is considered that calcium is a principal cation in groundwater from granitic rock and Na–bentonite is used as a buffer material in granitic rock mass, the experimental data of Na–bentonite obtained in a short period of time require careful review because the applicability of them may become uncredible partially.

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**References**

1. T. Tarandi, Calculated temperature field in and around a repository for spent nuclear fuel, Sweden, KBS Tech. Report 83–22 (1983).
2. R.E. Grim, 1968, Clay Mineralagy, McGraw–Hill Inc., New York,
3. J.L. Krumhansl, Observations regarding the stability of bentonite backfill in a high–level waste repository in rock salt, SAND 83–1293(1986).
4. R. Push, Use of clays as buffers in radioactive repositories, KBS 83–46 (1983)
5. D. Eberl, The reaction of mont. to mixed–layer clay : The effect of interlayer alkali and alkaline earth cations, Geochim. et Cosmochim. Acta, 42, 1–7 (1978)
6. R. Heremans, A. Bonne and P. Manfroy, Experimentation on the evaluation of near–field phenomena in clay, Proc. of the work shop on near–field phenomena in Geologic Repositories for radioactive waste, OECD/NEA Seattle, USA, 187–204 (1981).
7. A.G. Croff, O.W. Hermann and C.W. Alexander, Calculated two–dimensional dose rates from a PWR fuel assembly, ORNL/TM–6754 (1979).
8. D.M. Anderson, Smectite alteration, Sweden, KBS Tech. Report 83–03 (1983).
9. R.A. Couture and M.G. Seitz, Physical response of backfill materials to mineralogical changes in basalt environment, NUREG/CP–0052 (1984).
10. R.A. Couture and M.G. Seitz, Modification of backfill materials under repository conditions in nuclear technology progress report, ANL–84–57 (1985).
11. J.W. Choi, J.H. Whang, K.S. Chun and B.H. Lee, Applicability of domestic bentonite as a buffer material of spent fuel repository, J. Korean Nucl. Soc., 23(4), 411–420(1991).
12. C.C. Allen, D.L. Lane, R.A. Palmer, and R.G. Johnston, Experimental studies of packing material stability, Materials Res. Soc. Symp. Proc., 26, 105–112 (1984).
13. JCPDS, Powder diffraction data file, Index no. 12–219, 13–135, 13–259, 29–1498, 29–1499, U.S. Joint Committee on Powder Diffraction Standards, Pennsylvania(1972).

14. V.Berkheiser and M.M. Mortland, Variability in exchange ion position in smectite : Dependence on interlayer solvent, Clays and clay Minerals, 23, 401–410 (1975).
15. H.S. Moon, Thermal behavior of some montmorillomites with related their chemical compositions, Jour. Korean Inst. Mining Geol., 18, 253–261 (1985).
16. S.J. Kim, J.H. Noh and J.Y. Yu, Mineralogy and genesis of bentonites from the tertiary formations in Geumgwangdong area, Korea, J. Koream Inst. Mining Geol., 18, 399–409 (1985).
17. K.H. Head, Manual of soil laboratory testing, Vol.1 : Soil classification and compaction tests, Eng. Lab. Equip. Limited (1980).
18. R. Calvet and R. Prost, Cation migration into empty octahedral sites and surface properties of clays, Clays and Clay Minerals, 19, 175–186 (1971).
19. G.W. Brindley and G. Entem, Preparation and solution properties of some variable charge montmorillonites, Clays and Clay Minerals, 19, 399–404 (1971).