

## Effects of Additives on Swelling Properties of Modified Bentonites

H.Y. Jeon. Division of Nano-Systems Engineering, Inha University, Korea. [hyjeon@inha.ac.kr](mailto:hyjeon@inha.ac.kr)  
W.S. Lyoo. School of Textiles, Yeungnam University, Korea. [wsllyoo@yu.ac.kr](mailto:wsllyoo@yu.ac.kr)

### ABSTRACT

Swelling of bentonite decreases with increasing ion valence. It was seen that increasing hydrated cation size for mono-valent cation(; +1 ion) gives swelling to bentonite structure and no difference results for bi-valent cation(; +2 ions) regardless of hydrated cation size. The cases of pH<3 and pH>12 showed a greater influence on swelling of bentonite. In this study, we analyzed the swelling behavior of sodium bentonites in mono-valent and bi-valent cation solutions, distilled water and also HCl and NaOH solutions with different pH values. The test temperatures are ambient temperature, 30°C, 40°C, 50°C and 60°C, respectively. Finally, we examined the hydraulic properties of bentonite composites which were made of the addition of swelling agents. The hydraulic mechanism of bentonite composites was interpreted through the experimental data to be based on the difference of swelling agent addition behaviour.

### 1. INTRODUCTION

Swelling of montmorillonite particles is generally attributed to the volume of water molecules that are bound to the clay surface, size and valence of cations, concentration of the solution and pH vales of permeate solution (Koerner 2005, Egloffstein 2001, Bouazza 2002). Swelling of bentonite decreases with increasing valence thus, it was reported that increasing hydrated cation size for mono-valent cations gives swelling to bentonite structure and no difference results for bi-valent cations regardless of hydrated cation size (Gleason et al. 1997, Jo et al. 2001, Shan et al. 2002). In this study, we investigated the swelling of bentonite material in mono-valent cation solutions such as NaCl and KCl, bi-valent cations such as MgCl<sub>2</sub> and CaCl<sub>2</sub>, tri-valent cations such as AlCl<sub>3</sub>, distilled water and also in HCl and NaOH solutions (with different pH values) under different temperatures such as room temperature (16°C), 30°C, 40°C, 50°C and 60 °C.

### 2. EXPERIMENTAL WORK

Bentonites in powder and granular forms have been used in this study and their chemical composition is shown in Table 1. NaCl, KCl, CaCl<sub>2</sub>water were used as permeate mediums. Two kinds of PVA with molecule weight of 22,000 (PVA-I ) and 66,000 (PVA-II ) were selected. Concentration of PVA solution was maintained at 0.1 mol/L and PH values were recorded as 5.44 and 5.75 in PVA-I and PVA-II solutions respectively. Free swell tests were carried out according to ASTM D5890.

Table 1. Chemical composition of used bentonite

Chemical components	Chemical composition [%]
SiO <sub>2</sub>	61.59
Al <sub>2</sub> O <sub>3</sub>	20.43
Fe <sub>2</sub> O <sub>3</sub>	2.78
Na <sub>2</sub> O	3.05
TiO <sub>2</sub>	0.22
CaO	0.66
MgO	2.03
K <sub>2</sub> O	0.31
L.O.I	2.38

H <sub>2</sub> O	5.50
Others	1.05

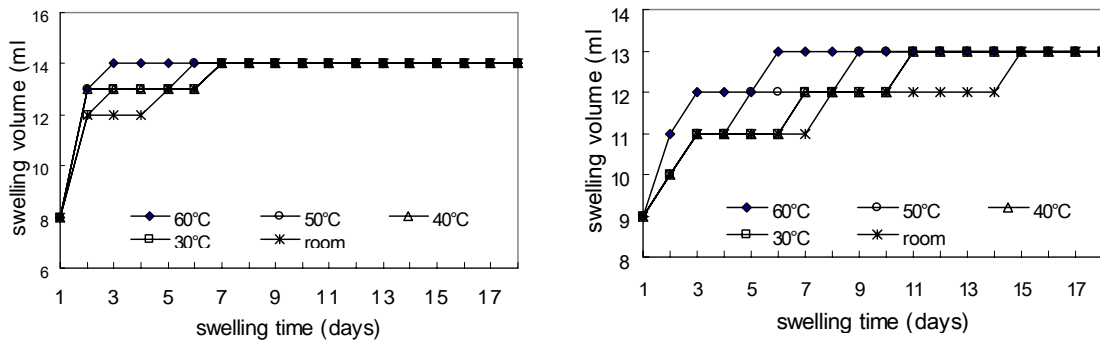
Table 2. pH values of permeate solutions

Solution	NaCl	KCl	CaCl <sub>2</sub>	MgCl <sub>2</sub>
pH	6.94	6.70	6.54	8.28

### 3. RESULTS AND ANALYSIS

#### 3.1 Free swell index in NaCl solution

Figure 1 shows the swelling behaviour of bentonite in powder and granular form in NaCl solutions under different temperatures. In here, it is clearly indicated that swelling volume is dependent on the bath temperature till the 7<sup>th</sup> day. After that, swelling of bentonite lies at a constant level of 14 ml. Thus, higher temperatures rapidly bring the bentonite to a stable swelling volume. According to Figure 1, dependency of granular bentonite swelling on temperature exists till 15<sup>th</sup> day, which is longer than powder bentonite. After that, swelling volume does not change and stays at 13ml, which is lesser than powder form of bentonite. Thus, as in Figure 1, powder bentonite rapidly comes to a stable swelling volume at higher temperatures. During swelling, bentonite stays at constant level/s for certain period before coming to a stable volume, but powder bentonite at 60°C is an exceptional case.



(a) Powder bentonite in 0.1mol/l NaCl solution

(b) Granular bentonite in 0.1mol/l NaCl solution

Figure 1. Swelling behaviour of bentonites in NaCl (0.1mol/L) solution under different temperatures

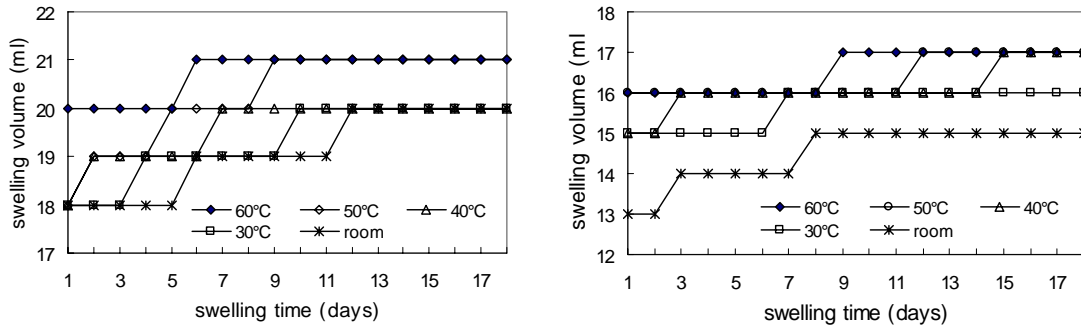
#### 3.2 Free swell index in KCl solution

Figure 2 shows the swelling behaviour of granular and powder bentonite in KCl solution under different temperatures. In both cases, swelling volume is higher than the bentonite in NaCl solution. The pH value doesn't have any effect on this, because, both solutions had approximately equal pH values. The only possible reason is that higher reactivity of K<sup>+</sup> ions raises the chemical reaction to give higher swell volume. Thus, powder bentonite gives higher swell volume than their granular form in all experimented temperatures. Hence, powder form shows a shorter period of temperature dependency to achieve a constant level of swelling than granular form. In addition, two stage of swelling behaviour was observed in all cases of powder and granular bentonite as in NaCl solution.

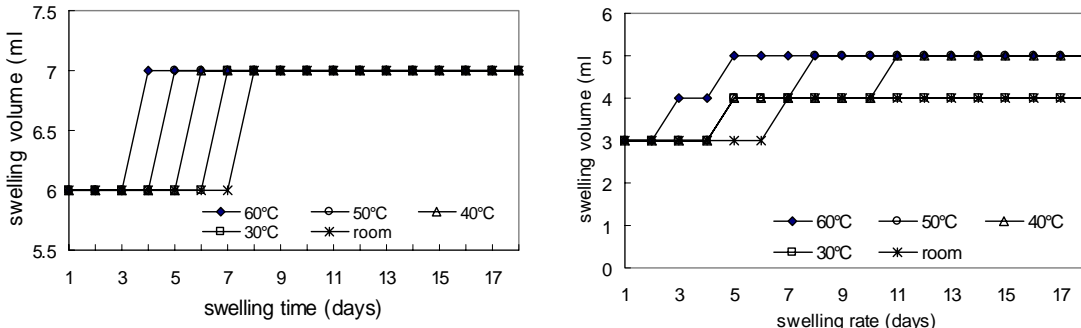
#### 3.3 Free swell index in MgCl<sub>2</sub> solution

Figure 3 illustrates the swelling behaviour of powder and granular bentonite in MgCl<sub>2</sub> (bi-valent) solution under different temperatures. It gives lowest swelling volumes under all temperatures tested. Reason can be the lowest reactivity power of Mg<sup>2+</sup> than Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>. Even though solution pH value is slightly higher than other cases, it is hard to think its significant effect on the lowest swell

volume. Also, Figure 3 clearly demonstrates the temperature dependency of swelling of powder bentonite. However, higher temperatures bring the bentonite rapidly to a constant level. Until 8 days, temperature dependency of powder bentonite can be observed, but that is for granular form is more longer (11 days). This means powder bentonite can swell rapidly to a constant level than their granular form.



(a) Powder bentonite in 0.1 mol/l KCl solution (b) Granular bentonite in 0.1 mol/l KCl solution  
Figure 2. Swelling of bentonites in KCl ( 0.1 mol/L) solution under different temperatures



(a) Powder bentonite in 0.1 mol/l MgCl<sub>2</sub> solution (b) Granular bentonite in 0.1 mol/l MgCl<sub>2</sub> solution  
Figure 3. Swelling of bentonites in MgCl<sub>2</sub> solution. (0.1 mol/L) under different temperatures

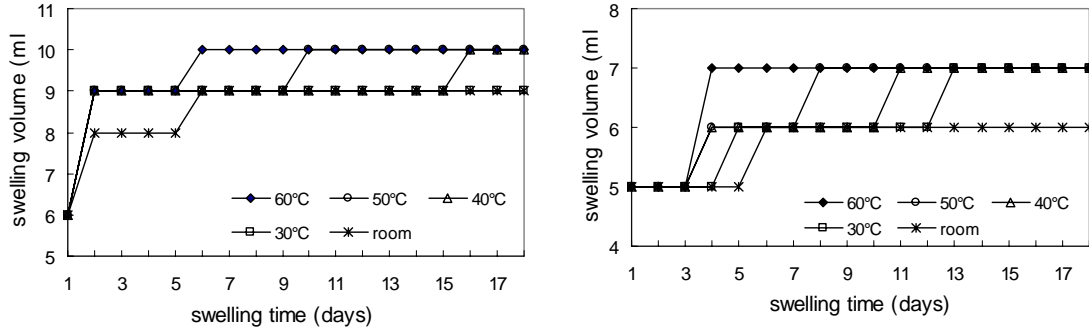
3.4 Free swell index in CaCl<sub>2</sub> solution

Figure 4 illustrates the swelling volumes of powder and granular bentonite in CaCl<sub>2</sub> solution under applied temperatures. According to this, CaCl<sub>2</sub> (bi-valent cation) solution gave lower swelling volumes to powder and granular bentonite compared to the swelling volumes given by NaCl and KCl (mono-valent cations) solutions. Reason would be the lower reactivity power of Ca<sup>2+</sup> than K<sup>+</sup> and Na<sup>+</sup>, which effect on ion exchange process in swelling mechanism of bentonite to change the its micro from smaller, finely distributed clay mineral flakes to larger clay mineral crystals. The pH value cannot be affected on this change, because, we maintained the pH values approximately in same range (about 7) in all above mentioned solutions. Thus, they also show the temperature dependency of bentonite swelling. Hence, higher temperature gives higher swell volumes and quickly came to a highest state. Meanwhile, powder bentonite indicate higher swell volumes than with granular bentonite.

3.5 Free swell index in mono-valent and bi-valent cation solutions

Figure 5 shows the swelling behaviour of powder bentonite in NaCl solutions and CaCl<sub>2</sub> solution under different concentration in 50 °C. The lower concentration gives a higher swelling volume, for both the

0.001mol/L solutions, the maximum swelling volume in  $\text{Na}^+$  solution is 24ml, and for  $\text{Ca}^{2+}$  solution is 21ml, this is the result of the influence of electrolytic concentration.



(a) Powder bentonite in 0.1mol/l  $\text{CaCl}_2$  solution (b) Granular bentonite in 0.1mol/l  $\text{CaCl}_2$  solution

Figure 4. Swelling of bentonites in  $\text{CaCl}_2$  solution. (0.1mol/L) under different temperatures

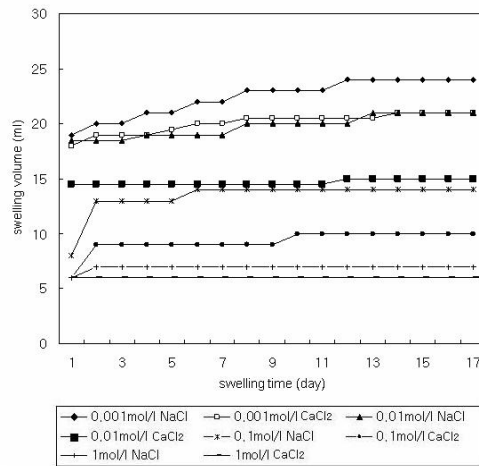
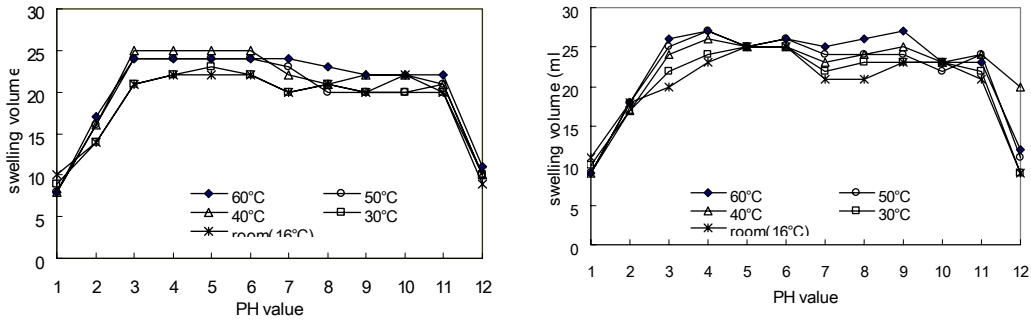


Figure 5. Swelling of powder bentonite in different concentration of mono-valent cation ( $\text{Na}^+$ ) solution and bi-valent cation ( $\text{Ca}^{2+}$ ) solution at 50°C.

### 3.6 Free swell index in different pH values solutions

Figure 6 illustrates the swelling behaviour of sodium bentonites in powder and granular forms with different pH values (using  $\text{HCl}$  and  $\text{NaOH}$  solutions) under different temperatures. We changed the pH values from 1 to 12, without considering 13 and 14, because these pH values were not familiar to leachate solution. It is clearly shown that  $\text{pH} < 3$  and  $11 < \text{pH} < 12$  show a greater influence on swelling of bentonite. Specially, with lower pH values increase and higher pH values decrease the swell volume, in concern of active pH ranges. Usually, a higher temperature and powder bentonite (compared to granular form) leads to higher swell volumes. Sodium bentonite swelling behaviour depends on permeate liquids. Solutions with mono-valent cations swell the bentonite highly than bi-valent cation solutions. Thus, swell volume also depends on the reactive power of these cations. Distilled water gave highest swell volumes among all tested solutions. Hence, swell volume depends also on the temperature of solutions as higher the temperature higher the swelling rate. Powder bentonite showed comparatively higher swell

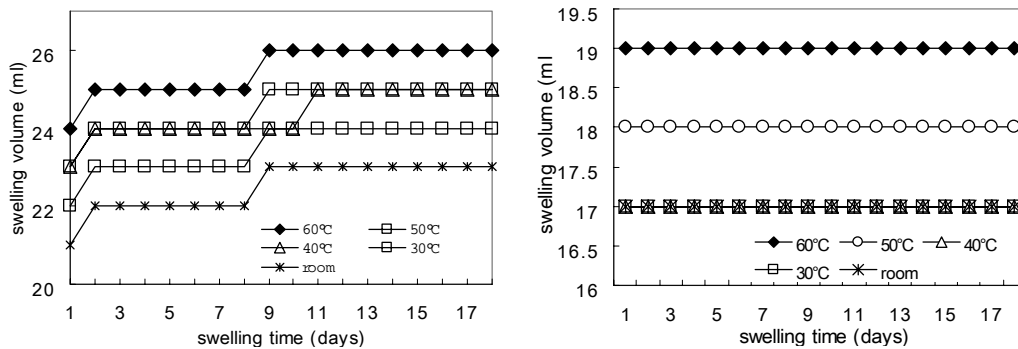


(a) Powder bentonite in different pH values (b) Granular bentonite in different pH values

Figure 6. Swelling volume of bentonites under different pH values.

### 3.7 Free swell index in different PVA solutions

Figure 7 (a) and (b) show variations of swell volume of granular and powder bentonite in PVA-I solution under different temperatures. It is shown that swell volume increases with time and temperature. Figure (a) indicates that swelling behaviour at room temperature and 30°C are almost same and also after 8<sup>th</sup> experimental day, almost same behaviour reported with 40°C, 50°C and 60°C temperatures. However, swell volume of granular has not come to a constant level till the end of experimented period. But, lower temperature such as room temperature and 30°C of powder bentonite has achieved the constant of swell volume later than other three higher temperatures. It implies the effect of temperature on swell behaviour of powder bentonite. By comparing two figures, it is clear that higher swelling volumes have given by granular bentonite, due to its higher structure volume than in bentonite in powder form.



(a) Powder bentonite in PVA solutions (b) Granular bentonite in PVA solutions

Figure 7. Swelling of bentonites in PVA-I solutions

Figure 8 (a) and (b) show the swell volume of granular and powder bentonite of PVA-II solution. Higher (almost double) swell volumes were recorded with granular bentonite than powder form in all experimented temperatures. Thus, after 1 day of experimented, swell volumes of granular and powder bentonite specimens came to a constant levels, which is different behaviour than other experiments done with distilled water and PVA-I solution. In comparing swell volumes in distilled water and PVA-I, PVA-II give higher values. One reason would be that due to higher molecular weight of PVA-II, its lengthy polymer chains can expand bentonite structure volume. In granular bentonite structure, there is higher structure volume than powder structure, therefore, granular bentonite give higher swelling

volume. However, swelling volume depends on temperature as in the cases of distilled water and PVA-I solution.

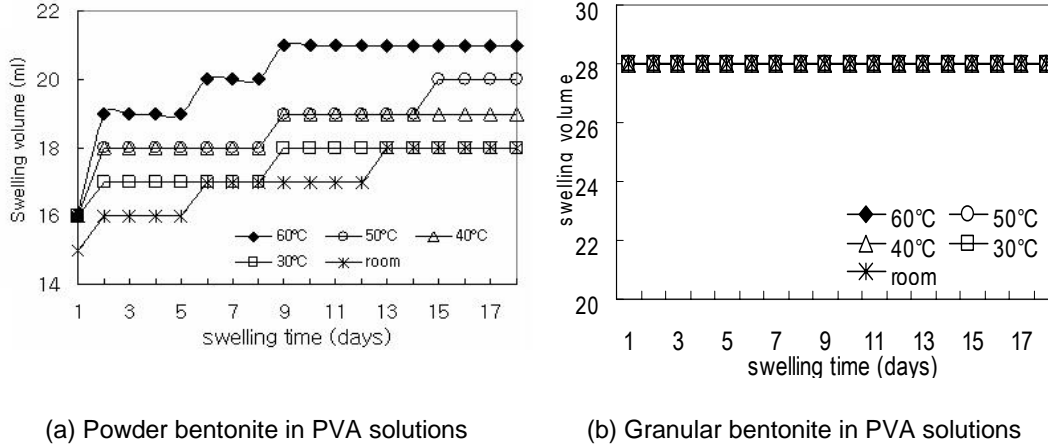


Figure 8. Swelling of bentonites in PVA-II solutions

At solid contents above 3% the dispersions became gel-like with the appearance of a yield value and viscoelastic properties. (Figure 9-11) Increasing salt concentration reduced the thickness of the diffuse ionic layers and the immobilization of the particles. As a consequence, the yield value and the viscosity decreased to a minimum at about 2–20 mmol/l NaCl (depending on the montmorillonite). This behaviour was virtually independent on the type of salt. The cause is the contraction of the network into distinct particles when the attraction between the silicate layers is too strong. Formation and properties of the attractive gel were influenced by the type of salt. Potassium and cesium ions enhanced the elasticity of the gel. Sulphate anions reduced the yield value and storage modulus. This effect was very strong with diphosphate which liquefied the gel to a sol. The different states of sodium montmorillonite dispersions: sol, repulsive and attractive gel, sediment, is represented in phase diagrams which were constructed on the basis of compliance (creeping) measurements.

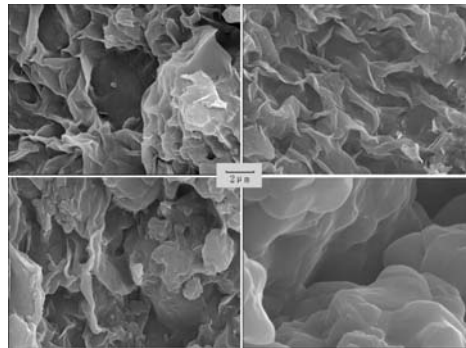


Figure 9 Comparison of the micro structures using electron scan microscope pictures of powder bentonite pre-swelling in different concentration of NaCl solutions at 60°C.  
(a) pre-swelling bentonite in 0.001 mol/l NaCl solution.  
(b) pre-swelling bentonite in 0.01 mol/l NaCl solution.  
(c) pre-swelling bentonite in 0.1 mol/l NaCl solution.  
(d) pre-swelling of bentonite in 1 mol/l NaCl solution.



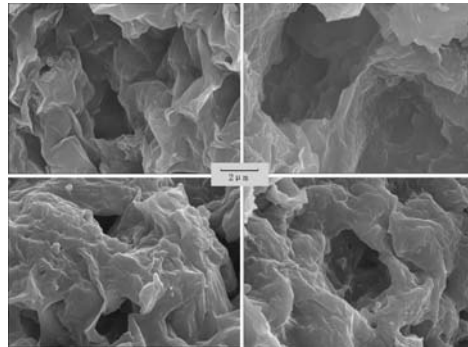


Figure 10 Comparison of the micro structures using electron scan microscope pictures of granular bentonite pre-swelling in same concentration of solutions at 60°C.

- (a) pre-swelling of bentonite in 0.1 mol/l NaCl solution.
- (b) pre-swelling of bentonite in 0.1 mol/l KCl solution.
- (c) pre-swelling of bentonite in 0.1 mol/l CaCl<sub>2</sub> solution.
- (d) pre-swelling of bentonite in 0.1 mol/l MgCl<sub>2</sub> solution.

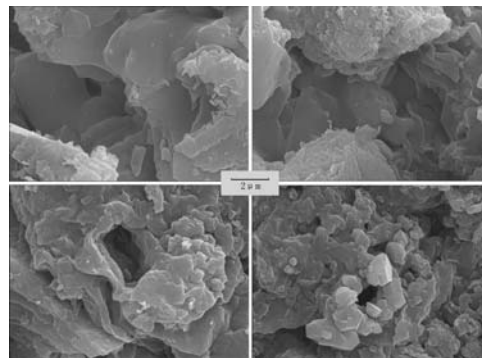


Figure 11. Comparision of the micro structures using electron scan microscope pictures of powder bentonite pre-swelling in same concentration of solutions at 60°C.

- (a) pre-swelling of bentonite in 0.1 mol/l NaCl solution.
- (b) pre-swelling of bentonite in 0.1 mol/l KCl solution.
- (c) pre-swelling of bentonite in 0.1 mol/l CaCl<sub>2</sub> solution.
- (d) pre-swelling of bentonite in 0.1 mol/l MgCl<sub>2</sub> solution.

#### 4. CONCLUSION

Sodium bentonite swelling behaviour depends on permeate liquids. Solutions with mono-valent cations swell the bentonite highly than bi-valent cation solutions. Thus, swell volume also depends on the reactive power of these cations. Powder bentonite showed comparatively higher swell volumes than their granular form. The pH value also effect on swelling volumes of bentonite as lower pH values (pH<3) and higher pH values (11<pH<12) decreased the swell volume of powder and granular sodium bentonite. The swelling index in distilled water shows a lower liquid limit than in the PVA solution, it was caused by the exchange of ions in solution. Powder bentonite maintained a significantly lower swell index than granular bentonite, the grain size of bentonite was also important, which made the powder bentonite more stable than granular bentonite when exposed to chemical constituent in permeate solutions.

#### ACKNOWLEDGEMENTS

This work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Knowledge Economy (MKE).



## REFERENCES

Koerner, R.M. (2005). *Designing with Geosynthetics*, ISBN 0131454153, Pearson Education Inc., New Jersey, USA.

Egloffstein T.A. (2001). Natural bentonites-influence of the ion exchange and partial desiccation on permeability and self-healing capacity of bentonites used in GCLs, *Geotextiles and Geomembranes*, Vol.19, 427-444

Gleason, M.H., Daniel, D.E. and Eykholt, G.R. (1997). Calcium and sodium bentonite for hydraulic containment application. *Journal of Geotechnical and Geoenvironmental Engineering*, ASCE 123(5), 438-445.

Jo, H.Y., Katsiumi, T., Benson, C.H. and Edil, T.B. (2001). Hydraulic conductivity and swelling of nonprehydrated GCLs permeated with single-species salt solutions. *Journal of Geotechnical and Geoenvironmental Engineering*, ASCE 127(7), 557-567.

Bouazza, A. (2002). Geosynthetic clay liners, *Geotextiles and Geomembranes*, 20, 3-17.

Shan, H.-Y., Lai, Y.-J. (2002). Effect of hydrating liquid on the hydraulic properties of geosynthetic clay liners, *Geotextiles and Geomembranes*, 20, 19-38.