



# Thermal and water storage characteristics of super-absorbent polymer gel which absorbed aqueous solution of calcium chloride

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## Abstract

This paper describes the thermal and water storage characteristics of a super-absorbent polymer gel which has absorbed an aqueous solution of calcium chloride. It is expected that the gel could be used as a heat absorbent material in a fire protection material during the course of the fire. Gels which absorbed calcium chloride solutions of 10 – 40 mass% were tested. The maximum absorbency of polymer and latent heat of the gel were measured using a thermal analyzer of TG/DTA. The water storage characteristics of the gel were obtained leaving the gel in a room whose temperature was controlled and measuring changes in weight of the gel. Also, an equilibrium concentration of the calcium chloride solution in gel and the latent heat of the gel were obtained. © 2000 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

It is empirically well known that a moist fire protection material shows good fire resistant characteristics. Based on this fact, a fire protection material has been developed which consists of a mixture of cement mortar in which a water storage material such as silica gels or humid perlites are mixed. In this case, the latent heat of the water plays an important role in the resistance to heat propagation through the wall. Therefore, a wall of high water content is expected to have good fire resistant characteristics. To confirm this fact, Jin et al. [1] developed a simple one-dimensional numerical model which predicts the thermal response of such

walls subject to fires. Using the proposed model, Jin et al. [2] conducted a parametric study to investigate the effect of the water content on the thermal response of the wall. Consequently, it was analytically confirmed that a wall of high water content has good fire resistant characteristics.

Silica gel and zeolite are desiccating materials but they are widely used as water storage materials for fire protection materials. However, the water content of the silica gel or zeolite itself is generally less than 30 mass %. Therefore, the water content of such a fire protection material in which these desiccating materials are mixed is less than 10 mass %. In case of the humid perlite, it is quite difficult to contain the water for a long period. A super-absorbent polymer can absorb water of 200–1000 times of its weight. However, the water in the super-absorbent polymer gel evaporates and the gel dries within 1 or 2 days depending on the temperature and humidity. To realize a fire protection

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**Nomenclature**

<i>A</i>	absorbency, (kg-solution /kg-polymer)	cr	crystalline water
<i>C</i>	concentration, mass%, (kg-CaCl <sub>2</sub> /kg-solution)	Ca	calcium chloride
<i>M</i>	mass, kg	dp	dry polymer
<i>W</i>	water content (dry basis), (kg-water/kg-dry material)	dry	dry basis
		gel	gel
		max	maximum
		moist	moist basis
		mp	moist polymer
		sol	calcium chloride solution
		w	water
<i>Subscripts</i>			
0	value at the start of heating or value at the time of the sample preparation		

material of high water content, the development of a high water storage material is required.

An aqueous solution of calcium chloride has a characteristic of deliquescence. Namely, the aqueous solution of calcium chloride absorbs water vapor or releases it into the atmosphere here until it reaches an equilibrium state when the humidity of the atmosphere changes. Therefore, it is expected that a super absorbent polymer gel which absorbed the aqueous solution of calcium chloride, can retain much water in it for a long period. Then, the super absorbent polymer gel which absorbed the aqueous solution of calcium chloride could be used for the water storage material of the fire protection material.

This paper describes thermal and water storage characteristics of an alcoxy-polyalkylen glycol group bridged super-absorbent polymer (Nihon Shokubai, CN-80M) gel which absorbed the aqueous solution of calcium chloride. Gels which absorbed calcium chloride solutions of 10 to 40 mass% were tested. The maximum absorbency of the polymer and latent heat of the gel were measured using a thermal analyzer of TG/DTA. The gel was left in a room whose temperature was controlled and the change in weight of the gel was measured to obtain the water content. Also, an equilibrium concentration of calcium chloride solution in the gel was obtained.

## 2. Absorbency

A photograph of the gel particle which absorbed calcium chloride solution of  $C_0 = 20$  mass% is presented in Fig. 1. The largest gel particle diameter is about 0.8 mm. The absorbency of the gels in calcium chloride solutions of  $C_0 = 20$  and 40 mass% at 25°C were measured using a so-called tea-bag method and the results are plotted in Fig. 2 as a function of the soaking time. In the tea-bag method, 1 g of the polymer was put into a tea-bag

and hung in the aqueous solution of calcium chloride, and the weight of the tea-bag was measured. The vertical axis of the figure represents the absorbency based on the moist polymer,  $A_{\text{moist}} = M_{\text{sol}}/M_{\text{mp}}$ , where  $M_{\text{sol}}$  represents the mass of calcium chloride solution which was absorbed in the polymer. The super-absorbent polymer, CN-80M, used for the experiment is highly hygroscopic. Therefore, the polymer is moist before it absorbs calcium chloride solution. The  $M_{\text{mp}}$  which appears in the definition of the absorbency based on the moist polymer, represents the mass of the moist polymer. This will be discussed later. As seen from the figure, the soaking speed of the polymer depends on the concentration of calcium chloride solution. In the case of higher concentration, the soaking speed is slow, however, the absorption is almost completed within the first period of 24 h.

The maximum absorbency of calcium chloride solution in the gel at 25°C was measured by a thermogravimeter (Seiko Densi, TG/DTA 300). Details of the method will be discussed later. The water content in the gel was evaluated first from the change in weight measured by the thermo-gravimeter and the maximum absorbency was evaluated from the water content. The correlation between the maximum absorbency and the concentration of calcium chloride solution is plotted in Fig. 3. The water content of the polymer before it absorbs calcium chloride solution was also evaluated using the thermo-gravimeter. It was found that the water content of CN-80M before it absorbed calcium chloride solution was about 6.7 mass% of the dry polymer. Note that the absorbency based on the moist polymer,  $A_{\text{moist}}$ , is defined by  $A_{\text{moist}} = M_{\text{sol}}/M_{\text{mp}}$ , and the absorbency based on the dry polymer,  $A_{\text{dry}}$ , is defined by  $A_{\text{dry}} = M_{\text{sol}}/M_{\text{dp}}$ . The absorbency in this paper is the absorbency based on the dry polymer unless otherwise stated. Also, the concentration of calcium chloride solution in the gel could be diluted by the water contained in the moist polymer. In case of the gel which absorbed calcium chloride solution of 10

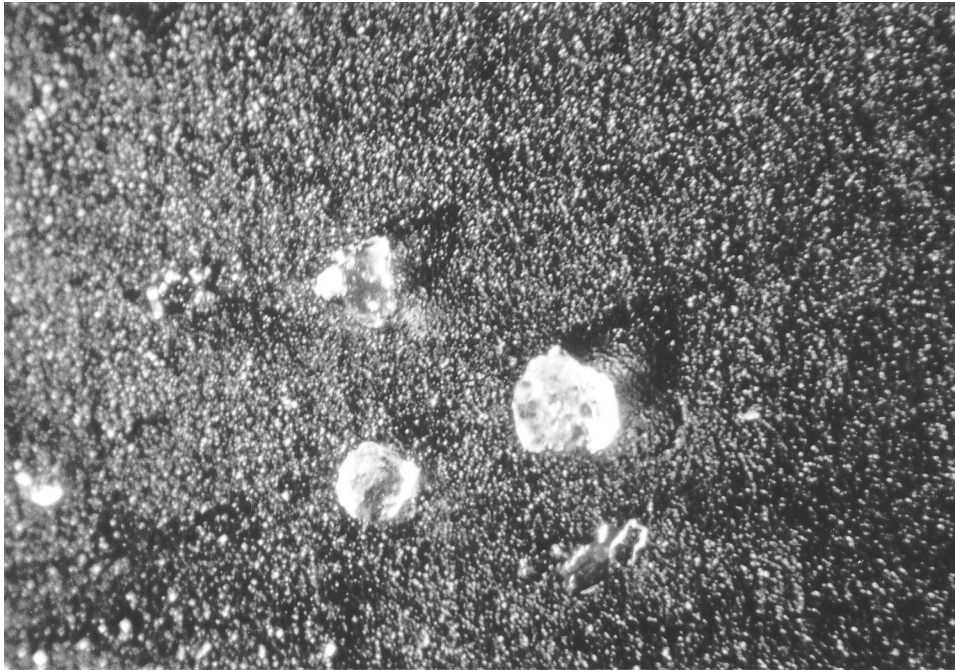


Fig. 1. A photograph of CN-80M gel particles.

mass%, the dilution of the concentration was only 0.03%, however, in case of the gel which absorbed calcium chloride solution of 40 mass%, the dilution of the concentration was 0.23%.

The effect of temperature on the maximum absorbency of CN-80M was investigated. Namely, the maximum absorbency was measured by the tea-bag method for different temperatures. The maximum absorbency based on the moist polymer,  $A_{\text{moist, max}}$ , is plotted in Fig. 4 as a function of temperature. It can be seen from the figure that the maximum absorbency also

depends on temperature. The maximum absorbency decreases as temperature increases. This tendency is accentuated for the case of the solution of low concentration.

### 3. Water storage characteristics

#### 3.1. Equilibrium concentration

To investigate the water storage characteristics of

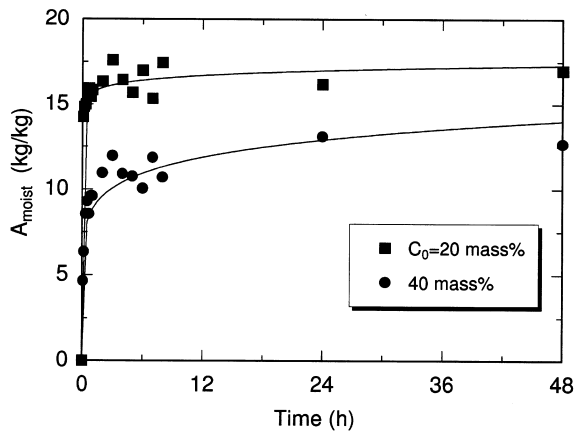


Fig. 2. Absorbency of moist polymer as a function of soaking time.

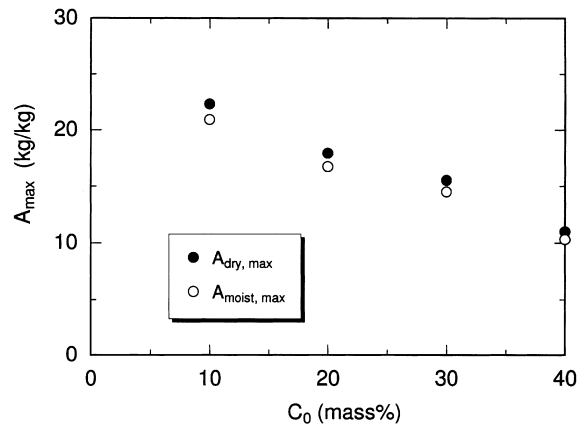


Fig. 3. Maximum absorbency as a function of concentration of calcium chloride solution.

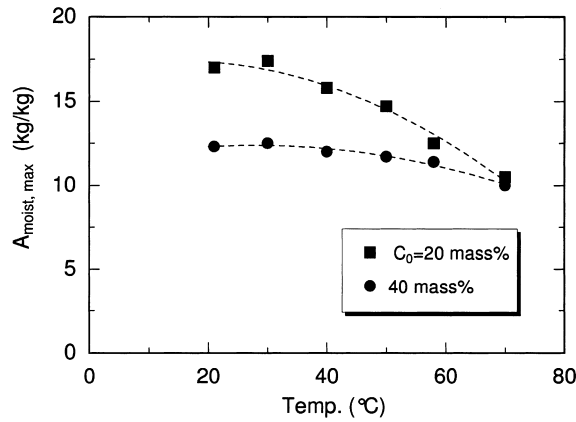


Fig. 4. Maximum absorbency as a function of temperature.

the gel, the effective moisture diffusivity of the gels was measured using the method of slopes [3]. Namely, the gels which absorbed calcium chloride solution of 20 mass% resulting in  $A_{dry, 0} = 17.9$ , were squeezed into petri-dishes of 5.1 mm depth and 50 mm diameter, and were put in a hygrostat (Shimadzu Physical & Chemical Appliances, HT30W), operated at temperature of 25°C and relative humidity of 60%. The change in weight of the gel was measured by an electric balance (A&D, ER-185A, minimum scale: 0.1 mg). The effective moisture diffusivity of the gel evaluated from data, was  $1.9(\pm 0.3) \times 10^{-9} \text{ m}^2/\text{s}$ .

An aqueous solution of calcium chloride has a characteristic of deliquescence. It is expected that the super-absorbent polymer gel which absorbed the aqueous solution of calcium chloride, absorbs water vapor in an atmosphere or releases water vapor until it reaches an equilibrium state when the humidity of a room changes. To confirm this, 14 different sample gels which absorbed calcium chloride solutions of  $C_0 = 10, 20, 30$  and 40 mass%, were prepared. The absorbencies of the sample gels are tabulated in Table 1. The sample gels were put in the hygrostat, operated at 25°C and relative humidity of 50% for 42 h. The equilibrium concentration of the solution in the gel was evaluated from the change in weight during 42

Table 1  
Absorbency of samples

	$C_0$ (mass%)			
	10	20	30	40
$A_{dry}$ (kg-solution/kg-polymer)	23.1	17.9	16.1	11.6
	19.3	16.1	15.0	10.7
	15.0	15.0	12.9	8.6
		12.9	10.7	

h. The Fourier number of the sample gels of 2 mm thickness was about 72 after 42 h referring to the above mentioned effective moisture diffusivity. Also the Biot number took a value of 14,000 under the condition that the average wind velocity in the hygrostat was about 0.72 m/s, when a forced convection mass transfer coefficient on a flat plate was used for that on the surface of the sample. Thus, it can be assumed that the gel reaches the equilibrium state after 42 h. Similar experiments were done for relative humidities of 60, 70, and 80%. The experimental results are presented in Fig. 5. The horizontal axis of the figure represents the average concentration of calcium chloride solution in the gel,  $C$ , and the vertical axis represents the absorbency of the gel,  $A_{dry}$ . Here, we consider a situation that the super-absorbent polymer gel which absorbed calcium chloride solution of  $C_0$  mass% and whose absorbency is  $A_{dry, 0}$ , releases water vapor until it reaches an equilibrium state. Consequently, the average concentration of the solution in the gel becomes  $C$  mass% and the absorbency becomes  $A_{dry}$ . Here, the effect of water which is contained in the polymer before it absorbs the solution on concentration will be neglected. The mass of the calcium chloride in calcium chloride solution in the gel is denoted by  $M_{Ca}$ , and the mass of the solution absorbed in the gel is denoted by  $M_{sol}$ . Then, the concentration of the solution in the gel,  $C$ , can be expressed as

$$C = \frac{M_{Ca}}{M_{sol}} = \frac{M_{Ca}}{A_{dry} \times M_{dp}} \tag{1}$$

This can be rewritten as

$$C \times A_{dry} = \frac{M_{Ca}}{M_{dp}} \tag{2}$$

The right-hand side of Eq. (2) represents the mass

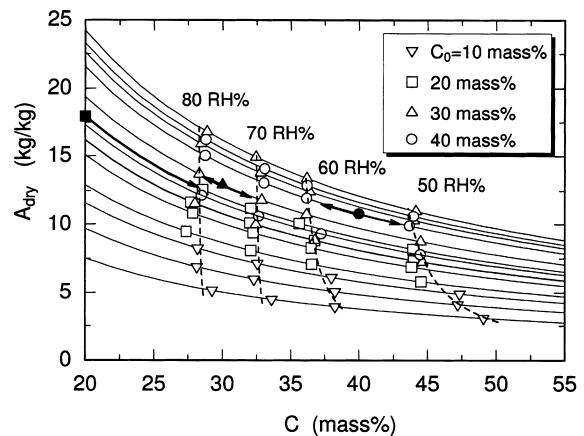


Fig. 5. Equilibrium concentration and absorbency.

ratio of calcium chloride to the dry polymer. This value is unchanged even though the gel absorbs the water vapor in the atmosphere or releases water vapor until it reaches an equilibrium state. Therefore, the value can be calculated from the values at the sample preparation.

$$C \times A_{\text{dry}} = C_0 \times A_{\text{dry}, 0} \quad (3)$$

Eq. (3) indicates that the absorbency of the gel decreases and the concentration of the solution in the gel increases when the gel releases water vapor. The thin lines in Fig. 5 indicate the correlation between the absorbency and the concentration of the solution in the gel. The black square symbol in Fig. 5 represents the absorbency and the concentration of the solution in a gel at the time of the sample preparation. Namely, the gel absorbed calcium chloride solution of 20 mass% for  $A_{\text{dry}, 0} = 17.9$  at the time of the sample preparation. The correlation between the absorbency and the concentration of the solution in the gel, moves on the solid line and reaches the equilibrium state indicated by the white square in the figure, when the gel is put in the hygostat operated at 25°C and the relative humidity of 80%. The white symbols in the figure represent the equilibrium points. And the dashed lines are the approximation obtained by the least square method. The other black symbols, for example, the black triangle and the black circle indicate the absorbency and the concentration of calcium chloride solution at the time of the sample preparation.

The equilibrium concentration of calcium chloride solution at 25°C and the relative humidity of 60% is about 31.7 mass% (e.g. [4]). However, the equilibrium concentration of calcium chloride solution in the gel ranges from 36 to 38 mass%, depending upon the absorbency. The equilibrium concentration of the calcium chloride solution in the gel is several percent higher than that of the solution. The similar tendency can be seen for the relative humidities of 50, 70 and 80%.

In Fig. 5, the different symbols are used to distinguish the concentration of the solution in the gel at the time of the sample preparation. From the figure it can be seen that the equilibrium concentration does not depend on the concentration of the solution in the gel at the time of the sample preparation. And also the equilibrium concentration increases with decreasing absorbency under identical humidity. This tendency is accentuated in the case of low humidity.

### 3.2. Comparisons with other water storage materials

A silica gel or a zeolite is widely used as the desiccating material. These desiccating materials could be used for the water storage material of the fire protec-

tion material since they adsorb water vapor. The correlations between water content of such a desiccating material and relative humidity of the environment at 25°C (e.g. [5]) are presented in Fig. 6. The mass ratio of the adsorbed water to the dry material is widely used for the definition of the water content for such a desiccating material. For the convenience of comparisons, the same definition will be used for water content of the gel. Namely, the mass ratio of water in the adsorbed solution,  $(M_{\text{sol}} - M_{\text{Ca}})$ , to sum of the calcium chloride and the mass of the polymer,  $(M_{\text{Ca}} + M_{\text{dp}})$  is defined as the water content of the gel,  $W$ , as

$$W = \frac{M_{\text{sol}} - M_{\text{Ca}}}{M_{\text{Ca}} + M_{\text{dp}}} = \frac{1 - M_{\text{Ca}}/M_{\text{sol}}}{M_{\text{Ca}}/M_{\text{sol}} + M_{\text{dp}}/M_{\text{sol}}} \\ = \frac{1 - C}{C + 1/A_{\text{dry}}} \quad (4)$$

The water content can be calculated from the equilibrium concentration,  $C$ , and the absorbency,  $A_{\text{dry}}$ . The water contents of the gels are also plotted in Fig. 6. The equilibrium concentrations and the absorbencies of the gels which absorbed calcium chloride solutions of 10, 20 and 40 mass% for  $A_{\text{dry}, 0} = 23.1, 17.9$  and 11.6, respectively, at the time of the sample preparation, were evaluated from Fig. 5 for the relative humidities of 50, 60, 70 and 80%. Substituting the evaluated equilibrium concentration and the absorbency into Eq. (4), the water content of the gel is obtained. The water content of the gel which absorbed the calcium chloride solution, is extremely higher than that of the silica gel or that of the zeolite. The water content of a poly-acrylic acid group super-absorbent polymer, N-100 (e.g. Sumitomo Chemical, [6]), which is widely used as the SAP, is also plotted in the figure for reader's reference.

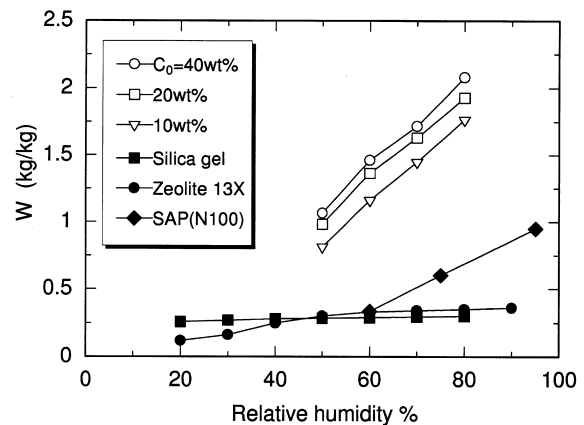


Fig. 6. Water content as a function of relative humidity.

3.3. Water storage characteristics

The gels of 2 mm thickness which absorbed calcium chloride solutions of 10, 20 and 40 mass% for  $A_{dry,0} = 23.1, 17.9$  and  $11.6$ , respectively, were put in a room whose temperature was only controlled. And the weight of the gel was measured for 20 days by an electronic balance (A&D, ER-185A, minimum scale: 0.1 mg). The room temperature and the relative humidity were measured by an asman aspiration psychrometer (Isuzu Seisakusyo, Type S). The accuracies of the temperature and humidity measurements are  $\pm 0.1^\circ\text{C}$  and  $\pm 3$  RH%, respectively. The changes in temperature and humidity of the room are plotted in Fig. 7. In this experiment, the room temperature ranges from 23 to 26°C. It can be considered that the equilibrium concentration of calcium chloride solution only depends on the relative humidity, since the room temperature range is narrow. Then, the equilibrium concentration of the solution in the gel which is estimated from the correlation in Fig. 5, is plotted in Fig. 8. The equilibrium concentration of calcium chloride solution is also plotted in the figure.

The changes in weight of the gel are plotted in Fig. 9. The vertical axis of the figure represents the mass ratio normalized by the mass of the gel at the time of the sample preparation,  $M_{gel}/M_{gel,0}$ . The experimental results are shown by white symbols. In the case of the gels which absorbed calcium chloride solutions of 10 and 20 mass%, the gel released water vapor and its weight decreased rapidly on the first day. On the contrary, in the case of the gel which absorbed calcium chloride solution of 40 mass%, the gel absorbed the water vapor and its weight increased rapidly on the first day. The estimated mass ratio of the gel under the condition that the gel absorbs or releases water vapor until it reaches the equilibrium state shown in Fig. 8, is also plotted in the figure by black symbols. It can be seen that the coincidence

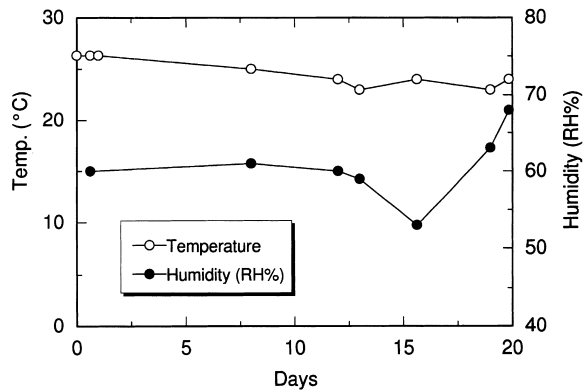


Fig. 7. Temperature and relative humidity.

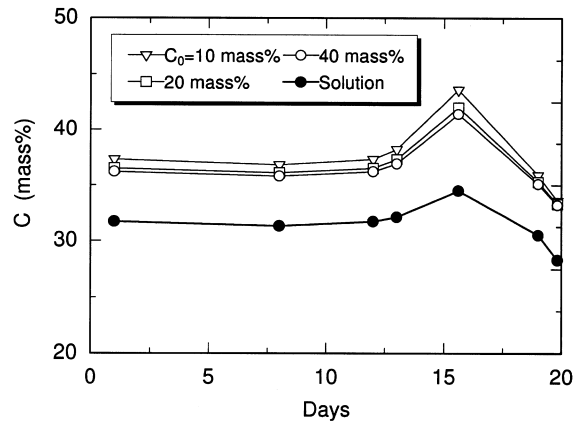


Fig. 8. Equilibrium concentration of gels and  $\text{CaCl}_2$  solution.

between the experimental and estimated results is very good.

4. Thermal characteristics

The thermal characteristics of the gel which absorbed calcium chloride solution, were measured using the thermo-gravimeter and the differential thermal analyzer. Note that the correlation between the weight of the sample gel and temperature is obtained by the thermo-gravimeter. And the endothermic or exothermic values are obtained by the differential thermal analyzer. The temperature range of the thermal analysis was from 25 to 300°C, and the heating rate of 5°C/min was selected.

4.1. Thermo-gravimetry (TG) and differential thermal analysis (DTA)

The results of the thermo-gravimetry (TG) and the

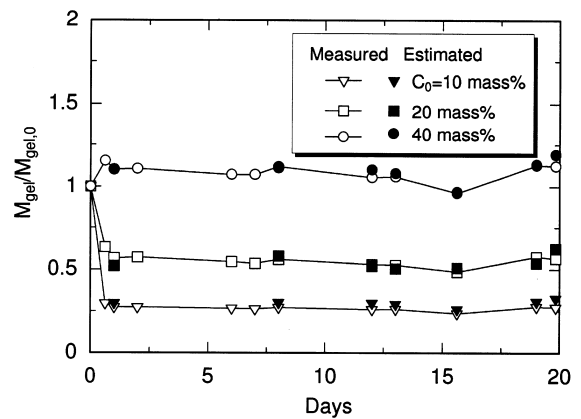


Fig. 9. Change in weight as a function of day.

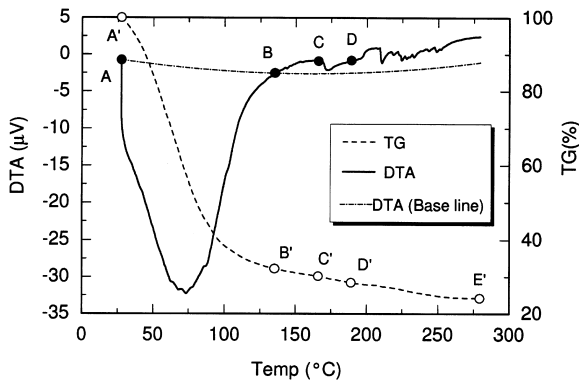


Fig. 10. TG–TDA curves (20 mass%).

differential thermal analysis (DTA) for the gel which absorbed maximum amount of calcium chloride solution of  $C_0 = 20$  mass%, are presented in Fig. 10. The dashed and solid lines in the figure represent the results of TG and DTA, respectively. The water evaporates from the gel when it is heated. The mass of the gel decreases rapidly from the point  $A'$  ( $25^\circ\text{C}$ ) until the point  $B'$  ( $135^\circ\text{C}$ ) with increasing temperature. Then, the mass decreases very slowly until the point  $E'$  ( $279^\circ\text{C}$ ). The results for the gel which absorbed calcium chloride solution of 40 mass%, are presented in Fig. 11. In the case of 40 mass%, the mass decreases in a step fashion. The first decrement of the mass occurs from the point  $A'$  ( $25^\circ\text{C}$ ) to the point  $B'$  ( $107^\circ\text{C}$ ). The second decrement occurs from the point  $B'$  to the point  $D'$  ( $182^\circ\text{C}$ ). After the point  $D'$ , the mass of the gel decreases very slowly until the point  $E'$  ( $247^\circ\text{C}$ ). It can be considered that the evaporation of the water in the gel is completed by the point  $E'$ . Only the polymer and the anhydrous calcium chloride remain at the point  $E'$ . Then, the value of TG at the point  $E'$  can be expressed as

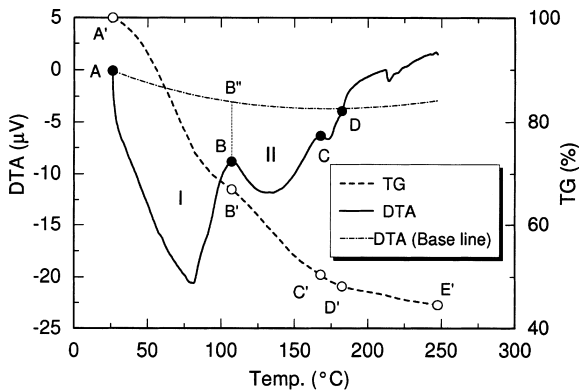


Fig. 11. TG–TDA curves (40 mass%).

$$TG_{(E')} = \frac{M_{Ca} + M_{dp}}{M_{gel, 0}} \quad (5)$$

where  $M_{gel, 0}$  represents the mass of the gel at the start of heating. It can be considered that the decrement of the mass between points  $A'$  and  $E'$  depends only on the evaporation of water. Then, the following correlation can be obtained.

$$\begin{aligned} 1 - TG_{(E')} &= \frac{M_{w, 0}}{M_{gel, 0}} = \frac{M_{sol, 0} - M_{Ca} + 0.067M_{dp}}{M_{gel, 0}} \\ &= \frac{(1/C_0 - 1)M_{Ca} + 0.067M_{dp}}{M_{gel, 0}} \quad (6) \end{aligned}$$

where  $M_{sol, 0}$  and  $M_{w, 0}$  represent the mass of calcium chloride solution and the mass of water in the gel at the start of heating. The term  $0.067M_{dp}$  in Eq. (6) represents the mass of water which was contained in the moist polymer before it absorbed calcium chloride solution. The concentration of calcium chloride solution in the gel at the start of heating,  $C_0$ , is known. Then, the mass fraction of calcium chloride in the gel,  $M_{Ca}/M_{gel, 0}$  and the mass fraction of the polymer in the gel,  $M_{dp}/M_{gel, 0}$  can be obtained, using Eqs. (5) and (6). From Eq. (1), the mass fraction of the solution in the gel,  $M_{sol, 0}/M_{gel, 0}$ , and the absorbency,  $A_{dry, 0} = M_{sol, 0}/M_{dp}$ , can be obtained. These values are tabulated in Table 2. To investigate the uncertainty of this method, the absorbency of a gel whose absorbency was known, was evaluated by this method. With this method, the absorbency of  $A_{dry, 0} = 10.9$  was obtained for the sample gel which absorbed calcium chloride solution of 40 mass% for  $A_{dry, 0} = 11.6$ .

The chain lines in Figs. 10 and 11 represent the base line of the DTA curve which is obtained from the result for an empty sample pan. Note that the DTA curve locates below the base line when the endothermic reaction occurs. On the contrary, the DTA curve locates over the base line when the exothermic reaction occurs. The area which is surrounded by the base line and DTA curve, corresponds to the endothermic or exothermic values.

As shown in Fig. 11, there are two endothermic peaks. The endothermic peak between the points  $A$  and  $B$ , is due to the evaporation of the free water. The movement of water molecules in the gel is affected by the polymer chains. The movement is more restricted by the polymer chains by decreasing the size of the network structure of polymer chains. It can be considered that in the gel which absorbed calcium chloride solution of 40 mass%, the concentration of calcium ion is high and the physical bridge between the oxygen molecule of the polymer and the calcium ion is formed. Therefore, some of the water molecules in the gel act as bound water. The endothermic peak between the

Table 2  
Mass fraction in CN80-M gel

$C_0$ (mass%)	$M_{W,0}/M_{gel,0}$ (%)	$M_{Ca}/M_{gel,0}$ (%)	$M_{dp}/M_{gel,0}$ (%)	$M_{sol,0}/M_{gel,0}$ (%)	$A_{dry,0} = M_{sol,0}/M_{dp}$
20	75.8	18.9	5.3	94.3	17.9
40	55.5	36.6	7.9	94.6	11.6

points *B* and *C*, is due to the evaporation of the bound water.

#### 4.2. Phase change

The concentration of calcium chloride solution in the gel increases when it is heated by the TG/DTA analyzer since the water in the gel evaporates by heating. The correlation between the concentration of calcium chloride solution, *C*, and the value of TG can be expressed as

$$C = \frac{M_{Ca}}{M_{sol}} = \frac{M_{Ca}/M_{gel,0}}{M_{sol}/M_{gel,0}} = \frac{M_{Ca}/M_{gel,0}}{(M_{gel} - M_{dp})/M_{gel,0}} \quad (7)$$

$$= \frac{M_{Ca}/M_{gel,0}}{TG - M_{dp}/M_{gel,0}}$$

From this correlation, the concentration of calcium chloride solution, *C*, can be evaluated from the value of TG. The change in the concentration of the calcium chloride solution, *C*, and the change in the temperature of the gel when it is heated by the TG/DTA analyzer is traced in Fig. 12. This figure expresses the equilibrium phase diagram of calcium chloride solution (e.g. [7]). The dashed and solid lines in the figure represent the results for the gels which absorbed calcium chloride solutions of  $C_0 = 20$  and 40 mass%, respectively. The points *A*, *B*,... correspond to that in Figs. 10 and 11.

The small endothermic peaks can be seen in both

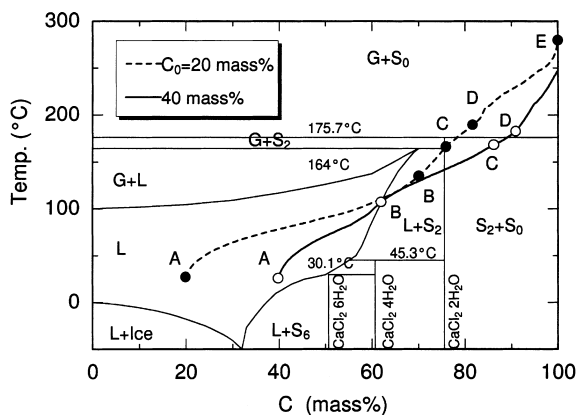


Fig. 12. Phase diagram of  $CaCl_2$  solution.

Figs. 10 and 11 near 170 and 220°C. These peaks were observed for both gels which absorbed the solutions containing 20 and 40 mass% of calcium chloride, and these peaks were observed in the identical temperature ranges even though the different heating rate was selected. Therefore, it is assumed that these endothermic peaks are due to the phase change. The starting temperature of the endothermic peak near 170°C is 164°C. This temperature corresponds to the de-crystallization temperature of calcium chloride hydrate containing two water molecules. The reason for the endothermic peak near 220°C is not clear, however, it can be considered that this temperature corresponds to the de-crystallization temperature of calcium chloride hydrate containing one water molecule. Therefore, calcium chloride hydrate containing two water molecules is crystallized when the gel is heated. After the crystallization, the de-crystallization of the calcium chloride hydrate containing two water molecules occurs and an anhydrous calcium chloride is crystallized when the gel is further heated. It is considered that the de-crystallization of calcium chloride hydrate containing two water molecules starts at the point *C* and ends at the point *D*.

The result of the thermo-gravimetry in Fig. 10 indicates that the gel which absorbed calcium chloride solution of 20 mass% contains water of 75.8 mass%. And water of 68.7 mass% evaporates between points *A'* and *B'*. This amount of water corresponds to 90.6% of water in the gel. Therefore, most of the water in the gel act as free water. The similar tendency can be seen for the gel which absorbed calcium chloride solution of 10 mass%.

The mass of the crystalline water,  $M_{cr}$ , of the calcium chloride hydrate containing two water molecules can be expressed as

$$M_{cr} = \frac{36}{111} M_{Ca} \quad (8)$$

Note that the molecular weights of calcium chloride and the crystalline water, respectively, are 111 and 36. The mass of crystalline water reaches to 6.1% of the mass of gel. However, the decrement of the mass evaluated from Fig. 10 was only 1.8%. Therefore, it can be considered that a part of calcium chloride solution becomes calcium chloride hydrate containing two water molecules.



Table 3  
Latent heat

Mass%	Latent heat I kJ/kg (aq.)	Latent heat II kJ/kg (aq.)	Latent heat I kJ/kg (gel)	Latent heat II kJ/kg (gel)
10	2088	0	1759	0
20	2325	0	1576	0
30	2253	480	1275	19
40	2582	1742	852	317

The result of the thermo-gravimetry in Fig. 11 indicates that the gel which absorbed the calcium chloride solution of 40 mass% contains water of 55.5 mass%. And water of 33.0 mass% evaporates between points  $A'$  and  $B'$ . This amount of water corresponds to 59.5% of the water in the gel. This percentage is lower than that for the gel which absorbed calcium chloride solution of 20 mass%. The mass of the crystalline water reaches to 11.9% of the mass of gel. However, the decrement of the mass evaluated from Fig. 11 was only 2.2%. Therefore, it can be considered that a part of calcium chloride solution becomes calcium chloride hydrate containing two water molecules.

#### 4.3. Latent heat

The latent heat of the gel was evaluated from the area of the endothermic peak in Figs. 10 and 11. The evaluated values, namely, the latent heats per unit mass of water and unit mass of the gel are tabulated in Table 3. The latent heat I in Table 3 represents the latent heat of the endothermic peak between points  $A$  and  $B$ . The latent heat I takes a value very close to that of the ordinary water. Then, this latent heat I can be considered as the latent heat of the free water. Note that the latent heat I was evaluated from the area of  $A-B-B''$  in the case where the endothermic peak by the bounded water exists. The latent heat II was evaluated from the area of  $B-D$ . This value includes the latent heat of the bounded water, heat generation by the crystallization of two water molecules and heat absorption by de-crystallization of the crystalline water.

The measurement of the latent heat was conducted several times for the identical sample. The value which is close to the average value, is tabulated in Table 3. For example, the latent heat was measured for four samples in the case of  $C_0 = 30$  mass%. The average value of the latent heat, I, was 2289 kJ/kg (aq.) and the standard deviation was 89 kJ/kg (aq.).

#### 5. Concluding remarks

This paper deals with thermal and water storage characteristics of a super-absorbent polymer gel which

absorbed the aqueous solution of calcium chloride. The main conclusions are:

1. The super-absorbent polymer gel which absorbed the aqueous solution of calcium chloride, absorbs water vapor from the atmosphere or releases it until it reaches an equilibrium state when the humidity of the room changes.
2. The equilibrium concentration of the solution containing in the gel is several percent higher than that of the ordinary solution and it does not depend on the concentration at the time of the sample preparation.
3. The equilibrium concentration increases by decreasing the absorbency under identical humidity levels. This tendency is accentuated in the case of low humidity.
4. The water content of the gel which absorbed calcium chloride solution is significantly higher than that of the silica gel or that of the zeolite.
5. The most of the water molecules in the gel which absorbed calcium chloride solution of dilute concentration, act as free water, and the latent heat of water in the gel is similar to that of the free water. However, some of the water molecules in the gel which absorbed calcium chloride solution of high concentration, act as bound water.

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