

TYPE OF WATER ASSOCIATED WITH COAL

K. Norinaga, H. Kumagai, J.-i. Hayashi and T. Chiba
Center for Advanced Research of Energy Technology (CARET), Hokkaido University
N13, W8, Kita-ku, Sapporo 060, Japan

M. Sasaki
Hokkaido National Industrial Research Institute (H-NIRI)
2-17, Tsukisamu-Higashi, Toyohira-ku, Sapporo 062, Japan

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INTRODUCTION

The authors¹ have evaluated changes in physical structure of a lignite induced by drying by means of swelling in water and proton NMR relaxation measurements. They have found that the water removal reduces considerably and irreversibly the swelling ratio and the relaxation time of protons in the macromolecular phase meaning that it makes the macromolecular network more rigid, as has been observed for solvent loading and removal processes.² It has been also found that the dryings carried out at different temperatures of 303K and 380 K give rise to difference in the above properties even at the same extents of water removal. This result reveals that physical structure of macromolecules in the lignite is not determined only by the water content but also other factors such as properties of water in its matrix. The systematic analysis of water sorbed on coal should be therefore established for understanding its roles in physical structure of coal.

Differential scanning calorimetry (DSC) has been applied to evaluate the crystallization property of water sorbed on polymers carrying polar functional groups. Nakamura et al.³ investigated the property of water in polyhydroxystyrene employing this technique. When the water content reached a certain level, they observed two exothermic peaks due to the crystallization of water centering at 273 K and 235 K respectively arisen from bulk (or free) water and freezable bound water. They also found another type of water, called as non-freezing water, no crystallization of which was observed. An advantage of this technique is that water can be quantitatively classified by assuming its crystallization heat and it can be also applied for characterization of water sorbed on coal.⁴ The freezing-point temperature depends on the size of space where water is condensed and it is not observed when the size is smaller than a critical value. The distribution of water elucidated by DSC may give informations on the size distribution of assemblies of water molecules. The non-freezing water has been recognized to be directly hydrogen-bonded to polymer functionalities and would be the most important type of water relevant to properties of the macromolecular network of coal. However, the non-freezing water is not directly observed by DSC.

The crystallization of free and bound waters is also expected to be observed in proton NMR relaxation measurements as the conversion of 'mobile proton' giving Lorentzian magnetization decays into 'immobile proton' doing Gaussian ones. Furthermore, the non-freezing water would be observed and its abundance and mobility would be also evaluated. Recently the NMR measurements have been adopted for determination of water content in coal^{5,7}. Lynch et al.⁷ observed a Lorentzian-Gaussian transition in a brown coal around 273 K and thereby estimated the content of free water contained in the coal.

The present study aims first to quantify the amounts of free, bound and non-freezing waters sorbed in coals ranging from lignite to bituminous ranks on the basis the crystallization characteristics measured by DSC. The second objective is to observe the non-freezing water and to evaluate changes in its mobility in the course of cooling as well as the other types of water and coal hydrogen.

EXPERIMENTAL

Coal samples

Table 1 presents the moisture and ash contents as well as the elemental compositions of coal samples so far used. Experiments were conducted with four Argonne PCSP coals and four brown coals supplied from the Nippon Brown Coal Liquefaction Co. Ltd.. The particle sizes were smaller than 150 μm for all samples. The samples other than the PCSP ones were stored in a gas tight vessel which was filled with atmospheric nitrogen saturated by water vapor at 293 K for a week prior to analyses. The moisture contents in the brown coals were determined from fractional mass release from them by a drying under nitrogen flow at 380 K for 2 h, while for the PCSP coals the literature values were used⁸. The PCSP samples were subjected to analyses immediately after opening the ampules.

Drying

Among the coal samples BZ coal was partially or completely dried at 303 K under dried or humidified nitrogen atmosphere. The extent of water removal was controlled by varying the relative humidity in a drying vessel from zero to 84% using conc. H_2SO_4 and aqueous solutions

saturated by selected salts.¹

DSC

DSC measurements were made employing a calorimeter (DSC 200, Seiko Co. Ltd.) equipped with a liquid nitrogen cooling accessory. The coal sample was cooled from 293 K to 123 K at a rate of 2 K/min and then heated up to 293 K at 2 K/min under atmospheric nitrogen gas flow of 80 ml/min.

Solid-state proton NMR

A proton magnetic resonance was adopted to elucidate spin-spin relaxation characteristics for the coal samples. The relaxation measurements were carried out on a JEOL Mu-25 spectrometer operated at 25 MHz. A 90°_x - τ - 90°_y solid echo sequence was used to obtain the entire free induction decays (FID). The FID was measured at temperature intervals of 2-5 K in the course of cooling from 293 K to 203 K. At each temperature the signal was recorded after a time period of 15 min since the temperature was reached for confirming homogeneous temperature distribution in the specimen. The FID curves were analyzed by a sequential linear-least-squares fitting method which has been commonly employed to deconvolute the total FID into two Gaussian and a Lorentzian functions with different specific relaxation times, i.e., T_2 . The following equations were used to fit the FID signal.

$$I(t) = I_1(t) + I_2(t) \quad (1)$$

$$I_1(t) = I_1(0) \exp[-t/T_{2L}] \quad (2)$$

$$I_2(t) = I_{G1}(0) \exp[-t^2/2T_{G1}] + I_{G2}(0) \exp[-t^2/2T_{G2}] \quad (3)$$

where $I(t)$ and $I_i(t)$ are the intensity observed and that attributed to the component i at time t . In Figure 1 natural logarithm of the FID intensity of YL, BZ and WY coals at 293 K are shown versus the relaxation time. The long-decaying component observed after 30 μ s for each coal is evidently a Lorentzian function. After fitting the Lorentzian component by Eq. (2) to determine $I_1(0)$ and T_{2L} and subtracting it from the signal, the rest was further fitted by Eq. (3) to obtain $I_{G1}(0)$, $I_{G2}(0)$, T_{G1} and T_{G2} . This procedure was successful for all curves observed. FID curves of dried BZ coal shown in Figure 2 were also analyzed by the same procedure.

RESULTS AND DISCUSSION

DSC results

Figure 3 exhibits the DSC curves for four different coals together with that for pure water. The positive peaks appearing on the curves mean exothermic processes. Though not shown here such peaks were never observed for the coals dried at 380 K. Negligible weight change was confirmed for all samples during the measurements. These peaks are thus arisen from a transition of water sorbed on the coal into ice, i.e., crystallization. For YL coal two peaks centering at 226 K and 258 K are evident. The larger one appears in the same temperature range as that for pure water and is ascribed to the crystallization of water having no specific interactions with the coal. The water can be defined as 'free water' or 'bulk one'. On the other hand, the smaller peak is attributed to 'bound water' being frozen at temperatures lower than that for the free water. Water condensed in capillaries with diameters of less than several microns has been known to be frozen around 220-230 K. Hence the bound water defined here can be also regarded as water condensed in macropores. The curves for the other coals indicate the existence of the bound water, while no free water. The peaks around 226 K are common among the curves for all coals, and in addition, for BZ and SB coals they overlap with the peaks observed at higher temperatures which are also assigned to the bound water.

The amounts of the free and bound waters can be estimated by assuming their crystallization heat. The heat for the free water was calculated as 333 J/g by analyzing the DSC curve for pure water. The value is nearly equivalent to that for the transition of bulk water into ice having Type-I polymorphic form, an only one that can be formed under the present conditions, i.e., 334 J/g.² This literature value was thus employed for estimating the free water content. This was also used to estimate that of the bound water content assuming its crystallization into Type-I ice.

Calculated fractions of the free and bound waters are summarized in Table 2. It should be noted that these types of waters account only for a portion of total for the all coals tested. This means the existence of another type of water that is not frozen at any temperatures examined. This type of water is here defined as 'non-freezing one' according to Nakamura et al.³ as well as the other types of waters.

In Figure 4(a) the amount of the non-freezing water per unit mass of coal on a dry basis is plotted against the sum of oxygen and nitrogen molar contents in them, which is a measure for the amount of polar and hydrophilic functional groups. The non-freezing water seem to be more abundant in the coal carrying more oxygen and nitrogen. This tendency can be reasonably explained by that water molecules as the non-freezing water are dispersed in the coal matrix at molecular levels being hydrogen-bonded to polar functional groups, a necessary condition of which is that the water is not frozen at any temperatures scanned in the DSC measurements. It is also noted in Figure 4(b) that the coal having more oxygen and nitrogen functionalities binds the larger number of water molecules as the non-freezing water per that of oxygen and nitrogen atoms. There is a wide variation in the number ranging from 0.3 for IL coal to 1.5-1.8 for the brown coals. Although the values indicated

in the figure are averaged ones, they are small enough to support that water molecules directly interact with oxygen and nitrogen-containing groups.

The above DSC results reveal that the coals contain freezable water which is classified into the free water and bound one based on their crystallization temperature. They also indicate the existence of the non-freezing water, the crystallization of which is not observed. As suggested from the result shown in Figure 4(b), when water molecules are dispersed on a molecular scale, the crystallization as a phase transition should be not observed even if their mobility as liquid is lost by the cooling. The NMR relaxation measurements were therefore made to examine the mobility of molecules as the non-freezing water and its temperature dependence as well as to observe the crystallization of the free and bound waters as the conversion of the Lorentzian component into Gaussian one.

NMR results

In Figure 5 are shown relationships between the amount of proton assigned to the Lorentzian component at 293 K and that as water sorbed on the coals. The former, given as $I_L(0)/I(0)$ multiplied by the total amount of hydrogen in water-containing coal, is larger than the latter without an exception, suggesting that a portion of coal hydrogen has mobilities characteristic to those in a liquid environment. Under an assumption that all protons as water are attributed to the Lorentzian component at 293 K, fractions of coal hydrogen having such mobility to the total are 9-38 % as indicated in the figure. The effect of water content on the amount of mobile coal hydrogen is shown for BZ coal in Figure 6. It is seen that the amount increases with an increase in the water content. This suggests that both non-freezing and bound waters mobilize coal hydrogen. The authors previously reported that water contained in the coal plays a role of solvent as a swelling agent based on volumetric shrinkage due to its removal.¹ Yang et al.,¹⁰ who studied the proton relaxation characteristics of dried and pyridine-swollen high-volatile bituminous coals by means of a spin-echo NMR technique, found that the fraction of the Lorentzian component in the coals increases from zero to 70-80% due to the swelling. The results shown in Figs. 5 and 6 are therefore quite reasonably accepted.

Figure 7 presents the amount of hydrogen giving the Lorentzian decay, H_L , normalized by that as water contained in the coal as a function of temperature ranging from 213 K to 293 K. For MW coal, the reduction of H_L is first observed at 273 K. There seems to be two different temperature dependences of the H_L reduction in the ranges of 263-273 K and 213-263K. Similar profiles were obtained for LY and YL coals. Considering that such sharp decrease in H_L at 263-273 K is not observed for the other coals, it can be mainly attributed to the crystallization of free water which is also observed in the DSC measurements. The liquid-solid transition should be observed as the conversion of the Lorentzian component to the Gaussian one. Moreover, the decrease in H_L in the range of 213-263 K should involve that due to the phase transition of the bound water, while it may also involve other Lorentzian-to-Gaussian transitions for hydrogen as the non-freezing water and/or coal hydrogen. The total decrement of H_L is thus expected to be at least equivalent to the amount of hydrogen as the free and bound waters, or larger if other transitions are also observed. The extents of H_L reduction for MW and YL coals are respectively 52 and 57 % and are in good agreement with the total fractions of the free and bound waters in these coals, i.e., 52 and 58 %. Hence the decrease in H_L can be referred to the crystallization of these types of waters, and hydrogen of the non-freezing water and coal hydrogen being mobile at 293 K both give the Lorentzian decay even at 213 K.

Table 3 summarizes the decrement of H_L in the range of 213-293 K for six different coals. For the coals other than the brown ones, the decrement is evidently larger than the amount of hydrogen as the bound water, while H_L at 213 K also appears to be larger than that as the non-freezing water. The result means that the reduction of H_L involves the transition of a portion of coal hydrogen being mobile at 293 K, that of hydrogen as the non-freezing water or both of them. Although their contributions to the reduction are not clear at present, it can be said that at least most of the non-freezing water is in a liquid environment even at 213 K by postulating higher mobility of water molecules than that of coal macromolecules based on much smaller mass of the former than the latter.

Figure 8 shows T_{2L} of the four different coals as a function of temperature. Although there is a wide variation in the temperature dependence of T_{2L} with the coals, the relaxation time seems to reach a value of 60 μ s at 213 K for the all coals. Such a coal-independent relaxation time implies that the Lorentzian components observed for the different coals at the temperature, which consist mainly of the non-freezing water, have similar mobilities.

CONCLUSIONS

The eight coals were subjected to the DSC and proton solid-state NMR relaxation analyses. Water sorbed on/in their matrices can be classified into three types on the basis of the crystallization characteristics, namely free water, bound water and non-freezing water. The abundances of the free and bound waters can be quantified using the crystallization heat of water, while the non-freezing water by difference. The crystallization of the freezable waters is also observed in the NMR as the conversion of the Lorentzian component into Gaussian one at 213-273 K where the conversion for coal hydrogen is also observed for the coals other than the brown ones. All or at least most of the non-freezing water is in a liquid environment to give Lorentzian decays even at 213 K.

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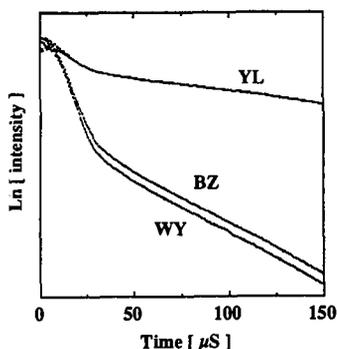


Figure 1. Natural logarithm of FID intensity versus relaxation time at 293 K for LY, BZ and WY coals.

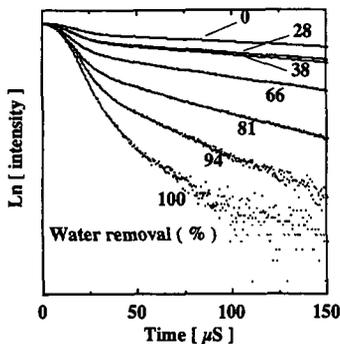


Figure 2. Natural logarithm of FID intensity versus relaxation time at 293 K for BZ coal with different water removal.

Table 1. Properties of coals so far used.

Coal	(Symbol)	Moisture [wt. % -sample]	Ash [wt. % db-coal]	C H N S O(diff.)				
				[wt. % daf-coal]				
Blind Canyon	(BL)	4.6	4.7	80.7	5.8	1.6	0.4	11.6
Illinois #6	(IL)	8.0	15.5	77.7	5.0	1.4	2.4	13.5
Wyodak	(WY)	28.1	8.8	75.0	5.4	1.1	0.5	18.0
Beulah Zap	(BZ)	32.2	9.7	72.9	4.8	1.2	0.7	20.3
South Banko	(SB)	31.5	3.2	70.4	5.8	1.2	0.4	22.2
Yallourn	(YL)	57.5	1.4	62.6	4.6	0.7	0.3	31.9
Loy Yang	(LY)	56.7	1.1	62.7	4.7	0.7	0.3	31.6
Morwell	(MW)	55.5	2.6	64.2	4.7	0.7	0.3	30.1

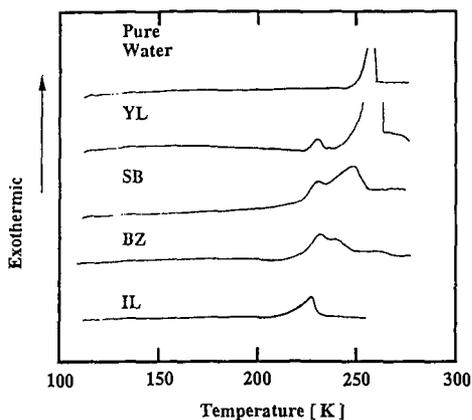


Figure 3. DSC profiles of LY, SB, BZ and IL coals and pure water.

Table 2 Summary of DSC results

Coal	Peak at higher temp.		Peak at lower temp.		Water type		
	ΔH J/g	Temp. K	ΔH J/g	Temp. K	Free	Bound	Non freezing
					[% to total]		
BL	0	-	1.1	226.2	0	7	93
IL	0	-	5.0	227.0	0	19	81
WY	0	-	25.1	227.6	0	27	73
BZ	0	-	23.0	226.4	0	21	79
SB	0	-	31.0 (248.1, 227.6)	0	0	29	71
YL	86.7	258.5	25.4	226.3	45	13	42
LY	93.6	258.4	18.4	227.1	49	10	41
MW	83.6	257.9	13.9	227.0	45	7	48

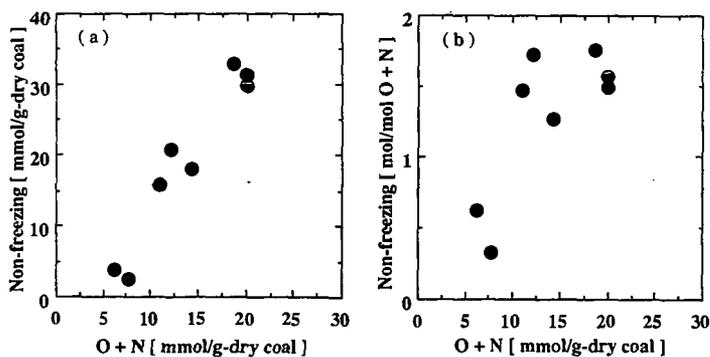


Figure 4. Plots of abundance of non-freezing water against sum of molar oxygen and nitrogen contents (a) and those of number of water molecules as non-freezing water per that of oxygen and nitrogen atoms (b).

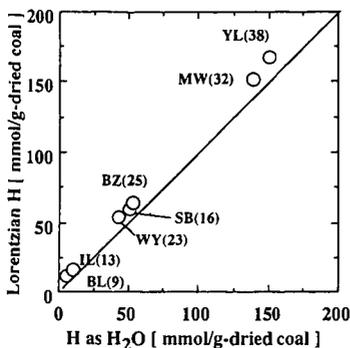


Figure 5. Comparison of amount of proton giving Lorentzian decay with that as water sorbed on coals. Values in (): % fraction of Lorentzian coal hydrogen to total.

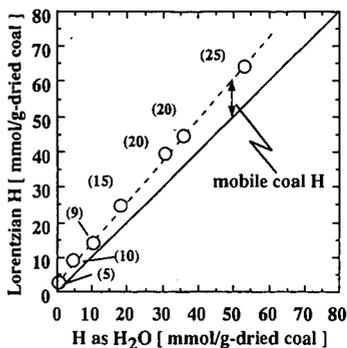


Figure 6. Comparison of amount of proton giving Lorentzian decay with that as water for BZ coal with different water contents. Values in (): % fraction of Lorentzian coal hydrogen to total.

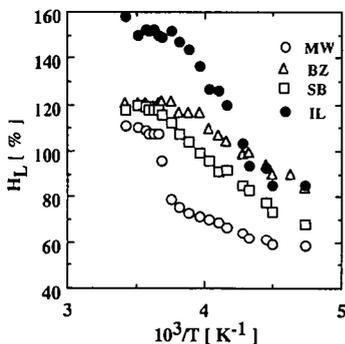


Figure 7. Temperature-dependent changes in H_L being amount of Lorentzian proton normalized by molar amount of proton

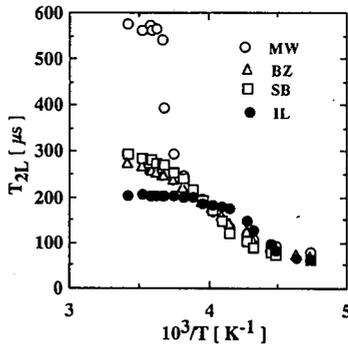


Figure 8. Temperature-dependent changes in relaxation time of Lorentzian component.

Table 3. H_L 's at 293 and 213 K and difference between them.

Coal	H as H ₂ O [mmol/g-dried coal]	H_L [%]		
		293 K (1)	213 K (2)	(1)-(2)
IL	9.6	158	85	73
WY	43.4	126	79	47
BZ	52.9	120	84	36
SB	51.1	118	68	50
YL	150.6	112	55	57
MW	138.7	111	59	52