J. Chem. Eng. Data **2010,** *55,* 5729–5732

Equilibrium and Do−Do Model Fitting of Water Adsorption on Four Commercial Activated Carbons with Different Surface Chemistry and Pore Structure

Xin Li[†,‡] and Zhong Li*[,†]

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China, and Institute of Biomaterials, College of Science, South China Agricultural University, Guangzhou, 510642, China

---

The textural properties and the surface acidities of four commercial activated carbons (ACs) were determined separately by nitrogen adsorption and Boehm titration. The adsorption isotherms of water vapor on the ACs were measured by the gravimetric method and fitted by the simplified version of the Do−Do (DD) model. The results indicated that all isotherms of water vapor on the ACs can be well-fitted by the simplified version of the DD model. The value of parameter n in the model increases with the pore size of the AC and is very close to 5 when the average pore diameter is between (1.96 and 2.8) nm. The order of parameter N_0 is in good agreement with that of the total surface group concentrations. The parameter $C_{\mu S}$ is almost equal to the amount adsorbed of water on the AC at a relative humidity of 100 % or to the value of its total pore volume. The parameter K_μ depends on the pore size and decreases with increasing pore size. The value of parameter b depends on the combined contribution of the pore size and total surface group concentration of the AC and increases with the total surface group concentration and pore size.

Introduction

The presence of water vapor can severely reduce the adsorption capacity of activated carbons (ACs) toward volatile organic compounds (VOCs) and change the kinetics of sorption processes, especially at high relative humidity (RH),[1−4] because of the competitive adsorption between VOCs and water vapor on the surface activity sites of the ACs. Thus, numerous investigations concerning the isotherms,[5−9] kinetics,[2,10,11] and mechanisms[12−15] of water vapor adsorption on the ACs have been carried out in recent years. The mechanisms of water vapor adsorption on the ACs are more complex than those of water vapor adsorption on other porous materials such as silica gel,[16−18] alumina,[5,19] zeolite,[5,6,18] and mesoporous materials[20] and also more complex than those of nonassociating simple fluids, such as nitrogen, carbon dioxide, or hydrocarbons on the ACs, because of the combined contributions of dispersion interactions, hydrogen-bond interactions, and pore structure.[12]

It is noteworthy that adsorption equilibrium is a simple method to study the water adsorption mechanism on ACs[7,14,15,21] because an isotherm of water is a function of the surface chemistry and pore structure of ACs.[10] Among these theories, the water adsorption mechanism proposed by Dubinin[21] is a commonly accepted one, which is based on the hydrogen-bond interactions and form of water molecule clusters, and the Dubinin and Serpinsky (DS)[6,22] and Dubinin−Astakhov (DA) equations[17,23] were developed. However, the DS equation cannot describe adsorption of water molecules on ACs with a high concentration of surface functional groups, and the DA equation cannot explain the specific mechanism of water adsorption[7] and does not follow Henry's law at low loadings,[9] although it can describe some data.

A very interesting approach was proposed by Do and Do 10 years ago.[7] They proposed a new model to describe both type IV and type V isotherms of water on different ACs[7] using the assumption that water molecules form clusters around functional groups, and if the number of molecules is equal to six, a cluster of five molecules can tear away from the cluster and penetrate into the micropores. Thus, the Do−Do (DD) model can be considered as a so-called "hybrid" in which one term describes the Brunauer−Emmett−Teller (BET) type adsorption on the primary sites and the other term describes the micropore filling. Neitsch et al.[24] generalized the DD model and carried on the optimization for the number of water molecules forming a cluster.

All parameters in the DD model have explicit physical significance, and moreover, the DD model seems to satisfy most of the experimental and theoretical conditions. However, there are still rare data and a comparison of the simplified version of the DD model and experiments on ACs with different surface chemistry and pore structure. The present study attempts to investigate thoroughly water adsorption equilibrium using the simplified version of the DD model. The isotherms of water vapor on the ACs were measured by means of a gravimetric adsorption experiment. The textural properties and the surface acidities of four commercial ACs studied were determined separately by nitrogen adsorption and Boehm titration. The isotherms of water vapor on four ACs were fitted by the simplified version of the DD model. Finally, the water adsorption mechanism on ACs is further discussed.

Experimental Section

AC and Reagents. The four kinds of virgin ACs used in this study were purchased separately from the JiangXi HuaiYu AC Group Co. Ltd., Fujian, P. R. China, the NingDe XinSen AC Co. Ltd., P. R. China, and the Liaoning Chaoyang AC Co. Ltd., P. R. China. The particle sizes of these samples ranged from (0.45 to 0.9) mm. Prior to use, they were all dried for 4 h in a

---

* Corresponding author. Fax: +86-20-87110608. E-mail address: cezhli@scut.edu.cn (Zhong Li).

[†] South China University of Technology.

[‡] South China Agricultural University.

10.1021/je1006778

vacuum at 413 K. These ACs have been designated as AC1, AC2, AC3, and AC4, respectively, in the text.

Nitrogen Adsorption Experiments. The specific surface area, pore volume, and average pore diameter of the samples were measured by nitrogen adsorption at the liquid nitrogen temperature of 77 K with the help of a Micromeritics gas adsorption analyzer ASAP 2010 machine. The AC sample was degassed at 573 K for 3 h in a vacuum before the nitrogen adsorption measurements. The BET surface area was calculated from the adsorption isotherms using the standard BET equation. Pore sizes and pore size distribution curves were calculated by the Barrett−Joyner−Halenda (BJH) method from the desorption branch. The total pore volume was estimated from the amount adsorbed at a relative pressure of 0.99.[25]

Determination of the Isotherms of Water Vapor on the ACs. Adsorption equilibrium experiments were performed at atmospheric pressure using the experimental setup shown previously.[26−29] This apparatus consisted of an adiabatic sorption chamber and a system for controlling the temperature and humidity. A microelectronic balance with an accuracy of 0.0001 g was located within the adsorption chamber whose temperature and humidity could be adjusted and maintained at a constant value via the gas cycle employed. The RH was controlled to a precision of ± 3 % through the use of a dehumidifier and humidifier, while the temperature could be controlled to an accuracy of ± 0.5 K.

Experiments were conducted by first introducing 0.2 g of a sample of fresh AC into an airtight flask fitted with a cover, and the flask was then placed on the electronic microbalance located within the sorption chamber. Second, after the temperature and RH within the sorption chamber had been adjusted to a predetermined value via the temperature and humidity controllers, the flask was opened using an internal mechanism thereby allowing the adsorption of water vapor onto the ACs to commence. The weight of the sample increased gradually as the adsorption proceeded up to an equilibrium position which was adjudged to correspond to the situation when the weight of the sample hardly varied with time. At this point, the AC sample was considered to have been equilibrated with water vapor, and hence the equilibrium amount adsorbed of the water vapor on a unit mass of the AC corresponding to a given RH could be obtained. After a series of adsorption equilibrium experiments under different RH conditions were obtained, a plot of the equilibrium amounts adsorbed of water vapor on a unit mass of AC can be plotted against the corresponding RH, and thus the isotherm of water vapor on the AC sample concerned was obtained.

Boehm Titration. The Boehm titration method was used to determine the number of oxygen-containing groups on a sample surface.[29] A portion of 1 g of carbon sample was placed into a vial containing 50 mL of a 0.05 mol·L^{-1} solution of hydrochloric acid, sodium hydroxide, sodium carbonate, and sodium bicarbonate, respectively. These vials were then sealed, stirred by shaking for 24 h, and filtered. A portion of 5 mL of each filtrate was titrated with HCl and NaOH depending on the original titrant. The numbers of different acidic sites were calculated using the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic, and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites was calculated from the amount of HCl that reacted with the basic groups of the carbon surfaces.

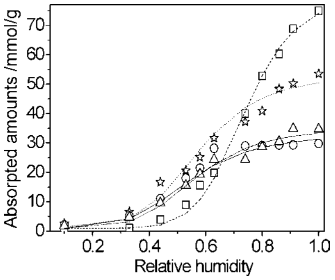

Figure 1. Fitting of the water adsorption model to ACs. Experimental data: □, AC1; ☆, AC2; ○, AC3; △, AC4. Model fitting: lineation.

Table 1. Surface Areas and Pore Structure of AC

	S_{BET}	V_{total}	d_{ave}	V_{meso}	d_{meso}	V_{micro}	d_{micro}
AC	m^2·g^{-1}	cm^3·g^{-1}	nm	cm^3·g^{-1}	nm	cm^3·g^{-1}	nm
AC1	1700	1.429	3.362	1.363	3.856		0.528
AC2	1519	1.062	2.797	0.6953	4.453	0.2881	0.506
AC3	1299	0.6364	1.960	0.1611	2.053	0.3810	0.498
AC4	1071	0.6915	2.540	0.3469	4.830	0.3084	0.487

Results and Discussion

The isotherms of water vapor on the four ACs at 303 K are shown in Figure 1. It can be seen from Figure 1 that all of the ACs gave type V isotherms according to the International Union of Pure and Applied Chemistry (IUPAC) classification.[30] A steep increase in the amount adsorbed of water vapor at higher RH for AC1 suggested that the mesoporous volume of AC1 is larger than those of the other three ACs. The data in Table 1 also indicate that AC1 has the largest specific surface area and total pore volume, and the average pore diameters of AC1, AC2, and AC4 are all larger than 2.0 nm, which shows that these three samples belong to the mesoporous carbons according to the IUPAC classification.[30]

These isotherms are complex and cannot be fitted by the DA or DS equation. Therefore, the DD isotherm equation was used to fit the isotherms of water vapor in this study.

Do and Do first proposed the DD isotherm equation[7] on the assumption that five water molecules form one cluster called a pentamer, as shown in eq 1 and then educed a simplified version of the DD model[10,31] by replacing the BET type equation in the DD model using a so-called Langmuir type function as in eq 2:

$$C = C_{\mu S}\frac{K_\mu \sum\limits_{n=6} x^n}{K_\mu \sum\limits_{n=6} x^n + \sum\limits_{n=6} x^{n-5}} + N_o \frac{K_f \sum\limits_{n=1} x^n}{1 + K_f \sum\limits_{n=1} x^n} \tag{1}$$

$$C = C_{\mu S}\frac{1}{1 + (x^{-n}/K_\mu)} + N_0 \frac{bx}{1 + bx} \tag{2}$$

where C is the total concentration of water adsorbed (mmol·g^{-1}), x is the relative pressure or the RH, n represents the average number of water molecules entering into the pore, K_μ is the micropore equilibrium constant, K_f is the chemisorption equilibrium constant, $C_{\mu S}$ is the saturation concentration in the micropores (mmol·g^{-1}), N_0 represents the amount adsorbed of water on acidic and basic sites (mmol·g^{-1}), and b is a constant ratio.

The equation was solved by the software of Matlab using a numerical method, and the fitting parameters resulting from the simplified version of the DD model are given in Table 2. It is

Table 2. Isotherm Fitting Parameters of Water Adsorption on ACs

absorbent	$C_{\mu S}$ mmol·g^{-1}	n	K_μ	N_0 mmol·g^{-1}	b	mean absolute error %
AC1	79.54	8.100	11.52	0.935	219.4	3.799
AC2	51.89	5.360	17.05	1.431	338.0	7.319
AC3	32.05	4.531	50.00	1.135	49.03	4.141
AC4	34.13	5.013	17.60	1.013	196.0	8.733

Table 3. Surface Group Concentration of AC by Boehm Titration

	group acidities/ mmol·g^{-1}			total basicity	total acidity	total
AC	carboxylic	lactonic	phenolic	mmol·g^{-1}	mmol·g^{-1}	mmol·g^{-1}
AC1	0.147	0.109	0.134	0.361	0.39	0.751
AC2	0.257	0.145	0.176	0.401	0.578	0.979
AC3	0.177	0.123	0.136	0.419	0.436	0.855
AC4	0.152	0.095	0.136	0.435	0.383	0.818

seen from Table 2 that all mean absolute errors are smaller than 10 %, which means the model fitting is in good agreement with the experimental data. At the same time, Figure 1 gives a comparison of the experimental isotherms and the isotherm fitting by using the simplified version of the DD model. It is also seen from Figure 1 that the simplified version of the DD model can fit these complex isotherms of water vapor on the ACs well.

The parameter n represents the average number of water molecules entering into the pore. The data in Table 2 indicate that n was the biggest for AC1 and smallest for AC3, which shows that n increases with the average pore diameters of the ACs, as shown in Table 1. This may be because the larger the average pore diameters of the ACs are, the larger the water molecule clusters formed in the pore may be. It was also found that the values of n for AC2, AC3, and AC4 are all almost equal to 5, which was the value in the original DD model. The results suggest that the value of n was close to 5 when the average pore diameter was between (1.96 and 2.8) nm. Therefore, it indicates that the original DD model is most suitable for the AC with an average pore diameter between (1.96 and 2.8) nm.

The parameter $C_{\mu S}$ represents the saturation concentration in the micropores and mesopores (mmol·g^{-1}). Table 2 lists the isotherm fitting parameters of water adsorption on the ACs, which were obtained by fitting the adsorption isotherm data of water vapor on the ACs to the simplified version of the DD model. As compared with the results in Figure 1 and Table 2, it can be seen that the values of the parameters $C_{\mu S}$ for four samples were very close to the amounts adsorbed of water on the ACs at an RH of 100 % or to the value of its total pore volume of micropores and mesopores. This shows that the water has filled the entire passageway of the ACs at 100 % RH. Therefore, in a sense the parameter $C_{\mu S}$ can be used to estimate and analyze the total pore volume of the AC.

The parameter N_0 represents the amount adsorbed of water on acidic and basic sites of the AC (mmol·g^{-1}), which can also represent the total concentration of surface acidic and basic groups because the second term described in eq 2 describes the Langmuir type adsorption on the primary sites. Compared with the results in Tables 1 and 2, it can be seen that Langmuir type adsorption equation could still well describe the water adsorption on the AC at low RH when N_0 increases from (0.9350 to 1.4311) mmol·g^{-1}. It is also seen that the amounts adsorbed of water increase with the total concentration of surface functional groups, which further indicates that every site of the functional groups is available for acting as primary sites for water adsorption to form clusters by hydrogen bonding.

Table 3 lists the surface acidity and basicity strengths of AC1, AC2, AC3, and AC4 as obtained via the Boehm titration method. It indicates that the total acidity and basicity value on the surface of AC2 was highest, while that on the surface of AC4 was the lowest. The values of total surface groups on these ACs studied follow the order: AC2 > AC3 > AC4 > AC1, which is in good agreement with that of N_0. This indicates that the parameter N_0 can be used to characterize the total concentration of groups on the surface of AC. It is also observed that the total concentration of surface groups by Boehm titration is obviously smaller than that of N_0. This is due to the fact that the principle of Boehm titration is the neutralization reaction of acid and alkali; therefore, the weak acidic or basic position cannot be served by this method.

The parameter K_μ is the micropore equilibrium constant. It is seen from Table 2 that AC1 has the smallest value of K_μ, but AC3 has the largest value of K_μ. The possible reason is that AC1 has the largest pore size, but AC3 has the smallest pore size. It is also observed that the K_μ of AC2 is very close to that of AC4, which is due to the pore size of AC2 being almost equal to that of AC4. This suggests that the parameter K_μ is an affinity parameter and the affinity forces increase with decreasing pore size. In other words, the adsorption force fields increase with decreasing pore size.[28] Therefore, the value of K_μ mainly depends on the pore size and decreases with increasing pore size.

The parameter b is a constant ratio. Table 2 shows that the value of the parameter b on AC3 was the smallest, whereas that on AC2 was the largest. Comparing the values of the parameter b with the average pore sizes for four ACs listed in Table 1 and the total surface group concentration listed in Table 3, it is found that the values of the parameter b depend on the combined contribution of the average pore diameters and the total surface group concentrations of the ACs and increase with increasing the total group concentrations and the average pore diameters. This was because the larger the average pore diameter was, the larger the adsorption rate constant was.[28] At the same time, the larger the total group concentration on the AC was, the larger the adsorption force fields were, and the larger the rate constant was. Although the total group concentration on AC3 was slightly larger than those of AC1 and AC4, the average pore diameter of AC3 was much smaller than those of AC1 and AC4. As a result, AC3 has the smallest value of b. Also, the average pore diameter of AC2 was slightly smaller than that of AC1, but the total concentration of AC2 was larger than that of AC1, so the value of b on AC2 was the largest.

Conclusions

The adsorption isotherms of water vapor on four ACs with different surface chemistry and pore structure can be well-fitted by the simplified version of the DD model. Therofore, the mechanisms of water adsorption can be proposed according to the assumption of the DD model as follows: (i) the adsorption of water on functional surface groups, (ii) the coalescence of water clusters at low relative pressure (< 0.3) and in a final stage, and (iii) micropore filling by water. The value of n, a parameter of the simplified version of the DD model, increases with increasing average pore diameter of the AC and is very close to 5 when the average pore diameter was between (1.96 and 2.8) nm. The value of N_0 in the model is in direct proportion to the total concentration of surface groups on the ACs. The value of parameter $C_{\mu S}$ in the model was almost equal to the amount adsorbed of water on the AC when RH is 100 % or to the value of its total pore volume. The value of parameter K_μ mainly depends on the pore size of the AC and decreases with increasing pore size. The value of parameter b depends on the combined contribution of the average pore diameter and the total group concentration of the AC and increases with the average pore diameter and the total group concentration.

Literature Cited

(1) Li, J.; Li, Z.; Liu, B.; Xia, Q. B.; Xi, H. X. Effect of Relative Humidity on Adsorption of Formaldehyde on Modified Activated Carbons. *Chin. J. Chem. Eng.* **2008**, *16*, 871–875.

(2) Narayan, S.; Harrison, B.; Liang, S.; Evans, M.; Croll, L.; Smith, S. Sorption kinetic studies of water vapour on activated carbon beds. *Carbon* **2008**, *46*, 397–404.

(3) Kaplan, D.; Nir, I.; Shmueli, L. Effects of high relative humidity on the dynamic adsorption of dimethyl methylphosphonate (DMMP) on activated carbon. *Carbon* **2006**, *44*, 3247–3254.

(4) Rodriguez-Mirasol, J.; Bedia, J.; Cordero, T.; Rodriguez, J. J. Influence of water vapor on the adsorption of VOCs on lignin-based activated carbons. *Sep. Sci. Technol.* **2005**, *40*, 3113–3135.

(5) Kim, J. H.; Lee, C. H.; Kim, W. S.; Lee, J. S.; Kim, J. T.; Suh, J. K.; Lee, J. M. Adsorption equilibria of water vapor on alumina, zeolite 13X, and a zeolite X/activated carbon composite. *J. Chem. Eng. Data* **2003**, *48*, 137–141.

(6) Kim, M. B.; Ryu, Y. K.; Lee, C. H. Adsorption equilibria of water vapor on activated carbon and DAY zeolite. *J. Chem. Eng. Data* **2005**, *50*, 951–955.

(7) Do, D.; Do, H. A model for water adsorption in activated carbon. *Carbon* **2000**, *38*, 767–773.

(8) Do, D. D.; Junpirom, S.; Do, H. D. A new adsorption-desorption model for water adsorption in activated carbon. *Carbon* **2009**, *47*, 1466–1473.

(9) Qi, N.; LeVan, M. Adsorption equilibrium modeling for water on activated carbons. *Carbon* **2005**, *43*, 2258–2263.

(10) Cossarutto, L.; Zimny, T.; Kaczmarczyk, J.; Siemieniewska, T.; Bimer, J.; Weber, J. Transport and sorption of water vapour in activated carbons. *Carbon* **2001**, *39*, 2339–2346.

(11) Foley, N.; Thomas, K.; Forshaw, P.; Stanton, D.; Norman, P. Kinetics of water vapor adsorption on activated carbon. *Langmuir* **1997**, *13*, 2083–2089.

(12) Brennan, J. K.; Bandosz, T. J.; Thomson, K. T.; Gubbins, K. E. Water in porous carbons. *Colloids Surf., A* **2001**, *187−188*, 539–568.

(13) Brennan, J.; Thomson, K.; Gubbins, K. Adsorption of water in activated carbons: Effects of pore blocking and connectivity. *Langmuir* **2002**, *18*, 5438–5447.

(14) McCallum, C.; Bandosz, T.; McGrother, S.; Müller, E.; Gubbins, K. A molecular model for adsorption of water on activated carbon: comparison of simulation and experiment. *Langmuir* **1999**, *15*, 533–544.

(15) Striolo, A.; Gubbins, K.; Chialvo, A.; Cummings, P. Simulated water adsorption isotherms in carbon nanopores. *Mol. Phys.* **2004**, *102*, 243–251.

(16) Chua, H. T.; Ng, K. C.; Chakraborty, A.; Oo, N. M.; Othman, M. A. Adsorption characteristics of silica gel plus water systems. *J. Chem. Eng. Data* **2002**, *47*, 1177–1181.

(17) Xia, Z. Z.; Chen, C. J.; Kiplagat, J. K.; Wang, R. Z.; Hu, J. Q. Adsorption Equilibrium of Water on Silica Gel. *J. Chem. Eng. Data* **2008**, *53*, 2462–2465.

(18) Wang, Y.; Levan, M. D. Adsorption Equilibrium of Carbon Dioxide and Water Vapor on Zeolites 5A and 13X and Silica Gel: Pure Components. *J. Chem. Eng. Data* **2009**, *54*, 2839–2844.

(19) Serbezov, A. Adsorption equilibrium of water vapor on F-200 activated alumina. *J. Chem. Eng. Data* **2003**, *48*, 421–425.

(20) Oh, J. S.; Shim, W. G.; Lee, J. W.; Kim, J. H.; Moon, H.; Seo, G. Adsorption equilibrium of water vapor on mesoporous materials. *J. Chem. Eng. Data* **2003**, *48*, 1458–1462.

(21) Dubinin, M. Water vapor adsorption and the microporous structures of carbonaceous adsorbents. *Carbon* **1980**, *18*, 355–364.

(22) Dubinin, M.; Serpinsky, V. Isotherm equation for water vapor adsorption by microporous carbonaceous adsorbents. *Carbon* **1981**, *19*, 402–403.

(23) Stoeckli, F.; Jakubov, T.; Lavanchy, A. Water adsorption in active carbons described by the Dubinin?Astakhov equation. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 783–786.

(24) Neitsch, M.; Heschel, W.; Suckow, M. Water vapor adsorption by activated carbon: a modification to the isotherm model of Do and Do. *Carbon* **2001**, *39*, 1437–1437.

(25) Lu, A.; Schmidt, W.; Spliethoff, B.; Schüth, F. Synthesis of ordered mesoporous carbon with bimodal pore system and high pore volume. *Adv. Mater.* **2003**, *15*, 1602–1606.

(26) Li, X.; Chen, X.; Li, Z. Adsorption Equilibrium and Desorption Activation Energy of Water Vapor on Activated Carbon Modified by an Oxidation and Reduction Treatment. *J. Chem. Eng. Data* **2010**, *55*, 3164–3169.

(27) Li, X.; Li, H. L.; Huo, S. Q.; Li, Z. Dynamics and Isotherms of Water Vapor Sorption on Mesoporous Silica Gels Modified by Different Salts. *Kinet. Catal.* **2010**, *51*, 754–761.

(28) Li, X.; Li, Z.; Xia, Q. B.; Xi, H. X. Effects of pore sizes of porous silica gels on desorption activation energy of water vapour. *Appl. Therm. Eng.* **2007**, *27*, 869–876.

(29) Li, X.; Li, Z.; Xia, Q. B.; Xi, H. X.; Zhao, Z. X. Effects of textural properties and surface oxygen content of activated carbons on the desorption activation energy of water. *Adsorpt. Sci. Technol.* **2006**, *24*, 363–374.

(30) Sing, K.; Everett, D.; Haul, R.; Moscou, L.; Pierotti, R.; Rouquerol, J.; Siemieniewska, T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* **1985**, *57*, 603–619.

(31) Vagner, C.; Finqueneisel, G.; Zimny, T.; Weber, J. Water vapour adsorption on activated carbons: comparison and modelling of the isotherms in static and dynamic flow conditions. *Fuel Process. Technol.* **2002**, *77*, 409–414.

Received for review June 22, 2010. Accepted October 23, 2010. The work is supported by the National Natural Science Foundation of China (Grant Nos. 20936001 and 20906034), the Science and Technology Foundation of Guangdong Province, and the State Key Lab of Subtropical Building Science, South China University of Technology (No. x2yjC709028Z).

JE1006778