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HIGH TEMPERATURE ADSORPTION MEASUREMENTS

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ABSTRACT

Adsorption phenomena are a rich and rather new field of study in geothermal research, in particular at very high temperature. ENEL is interested in the exploitation of geothermal regions with super-heated steam, and it is important to understand the behavior of water-rock interaction. We have analyzed in the 170-200 °C temperature range four samples of Monteverdi cuttings; the next experimental effort will be at 220 °C and over in 1996. The first results of the 1995 runs are collected in this paper. We can highlight four main items:

1. At relative pressures over 0.6 the capillarity forces are very important.
2. There is no significant temperature effect.
3. Adsorbed water can be present, and it is able to multiply by a factor of 15 the estimated reserve of super-heated steam only.
4. Pores smaller than 15 Å do not contribute to the adsorbed mass.

INTRODUCTION

A porous solid can take up a large volume of condensable gas inside its structure. The term *adsorption* was introduced to describe the condensation of gases on free surfaces in opposition to gas *absorption*, where the molecules of gas penetrate into the mass of the absorbing solid. The relevant theory is well described in reference [1]. According to the standard model there are five different shapes of the *adsorption isotherm*, depending on the pore size distribution of the solid, the physical properties of the fluid and the strength of the solid-fluid interaction.

We performed a determination on one geothermal rock sample as adsorbing solid, measured at the University of Pisa with a commercial nitrogen adsorption device [2], in order to measure the pore size distribution.

The data are obtained from a well Monteverdi 7 cutting sample which will be characterized later in the paper. The average of the distribution is at 15 Å, in the micropore range; 50% of the volume is represented by pores with a radius greater than 100 Å, and only 15% is made up by very small pores (with radius < 15 Å). The surface area is 4 m^2/g. This value is in good agreement with other geothermal samples measured at Stanford University as shown in the following table:

Sample	Surface Area m^2/g
Geyser NEGU-17	0.3
Coldwater Creek Core	1.4
Coldwater Creek Cutting	1.7
Prati 29 ST1	0.3
Calpine Co.'s MLM-3	1.1
Monteverdi 1	0.8
Monteverdi 2	0.2
Monteverdi 2B	1.3
Monteverdi 5A	8.2
Monteverdi 7	1.4

BET EQUATION

The standard BET equation for the amount of adsorbed moles at a fixed temperature (without the pore size effect, related to the capillarity forces) has the following well known form (type II isotherms):

$$\frac{n}{n_m} = \frac{C\left(\frac{p}{p_0}\right)}{\left(1-\left(\frac{p}{p_0}\right)\right)\left(1-\left(\frac{p}{p_0}\right)+C\left(\frac{p}{p_0}\right)\right)}$$

where p_0 is the saturation pressure at the given temperature and n_m is the "monolayer capacity" related to the surface area.

For convenience of data analysis the above equation can be rewritten as

$$\frac{\left(\frac{p}{p_0}\right)}{n\left(1-\left(\frac{p}{p_0}\right)\right)} = \frac{1}{Cn_m} + \frac{(C-1)\left(\frac{p}{p_0}\right)}{Cn_m}$$

Thus, the plot of $(p/p_o)/(n(1-p/p_0))$ (called in this paper "BET plot") versus p/p_o should be a straight line with slope [s] and intercept [i], related to n_m and C by

$$n_m = \frac{1}{[s]+[i]}$$

$$C = \frac{[s]}{[i]} + 1$$

THE EFFECT OF PORE STRUCTURE

When the effect of pore structure is important, in the mesopore range (20-500 Å), the capillarity forces will have an important effect on the adsorption isotherm and will produce a hysteresis loop (type IV isotherms). Let us picture a small element of a curved interface between a liquid and a vapor having a mean radius r_m. By combining the Young-Laplace equation (p_l and p_v are the pressure in the liquid and in the vapor):

$$p_v - p_l = \frac{2\gamma}{r_m}$$

and the physicochemical equilibrium, characterized by the constant of the "chemical potential" during the condensation, we get:

$$d\left(\frac{2\gamma}{r_m}\right) = \frac{V_l - V_v}{V_l} d(p_v)$$

If it is possible to apply the gas law, and assuming $V_l << V_v$, we have

$$d\left(\frac{2\gamma}{r_m}\right) = \frac{-RT}{p_v V_l} d(p_v)$$

With an integration from infinite to r_m and from saturation pressure (p_0) to the actual value of p, we have the conclusive Kelvin equation:

$$\frac{2\gamma}{r_m} = \frac{-RT}{V_l} \ln\left(\frac{p}{p_0}\right)$$

with V_l the molar volume of the liquid at temperature T. Consequently, from this equation it follows that the vapor pressure over a concave meniscus is *less* than the saturation pressure (this is called VPL in literature: Vapor Pressure Lowering [3]), so condensation can start even at a pressure less than the saturation pressure, according to the value of the mean pore radius.

The formation of a liquid phase from a vapor cannot occur in the absence of a solid surface, which serves to nucleate the process. Inside a pore, the adsorbed film can act as a nucleus upon which condensation can take place when the pressure reaches the value given by the Kelvin equation. Vice versa, in evaporation, the problem of nucleation does not arise: evaporation of the liquid can start at any value of the pressure, if it is low enough. For this reason evaporation and condensation do not start at the exact reverse of each other.

RANGE OF VALIDITY

In the very small pores, with a width of the order of a few molecular diameters, the Kelvin equation is not strictly valid because:

1. the gas law is not valid for this range of volume;
2. the concept of "surface" is meaningless;
3. the value of γ is not constant for small values of the radius, but slowly increases below 100 Å with the law [4]:

$$\gamma = \gamma_0 \left(1 - \frac{3}{r}\right)$$

[r in Å and γ_0 is the value for infinite radius]

Nevertheless, it is possible to identify a "critical radius" through mechanical considerations. The pressure difference across a meniscus separating condensed liquid and its vapor is given by the Young-Laplace equation; since we have $p_v << p_l$, the liquid experiences a tension τ given by

$$\tau = \frac{2\gamma}{r_m}$$

and this tension is related to the pressure by the Kelvin equation; we have

$$\tau = \frac{-RT}{V_l} \ln\left(\frac{p}{p_0}\right)$$

However there is a maximum value for the tension that a liquid can experience, without losing its integrity: it is called "tensile strength" τ_0.

$$\ln\left(\frac{p_{critic}}{p_0}\right) = -\frac{V_l}{RT}\tau_0$$

where p_{critic} is the lower limit of the pressure, below which the tension is greater then the "tensile strength" τ_0. This limit in pressure is related, with the Kelvin equation, to a limit in radius: in other words, there is a lower limit of the pore width below which there is no liquid phase at all: all the liquid in the smaller pores will evaporate, due to the high value of the tension on it.

The limit is given by the following relation:

$$r_{critic} = \frac{-2\gamma V_1}{RT} \cdot 1/\ln\left(\frac{p_{critic}}{p0}\right)$$

A typical value for water for r_{critic} is in the range 11 - 16 Å [5].

We can conclude that in the micropores range the capillarity forces are so strong that the liquid phase cannot be present. From this consideration, we can exclude from the reservoir 15% of all the pore volume, as seen from the data measured on the Monteverdi 7 sample.

WATER-ROCK INTERACTION

The effect of a weak interaction between solid and gas is a convexity in the adsorption isotherm (type III for non-porous and type V for mesopores solid) : it is typical in geothermal systems, where the solid is the reservoir rock and the fluid is the water, in the super-heated thermodynamic region. In that condition, adsorption can be responsible for the existence of liquid water inside the pore network of the rocks, and can explain the "long" exploitation life of reservoirs like Larderello or The Geysers.

From a mathematical point of view, if the value of parameter C in the BET equation is greater than 2, we have a straight line in the BET plot (type II or IV); but if parameter C is close to 1, the BET line is parallel to the p/p_0 axis, at a value of the reciprocal of the monolayer capacity. According to the method studied in ref. [6], from the n_m value it is possible to determine the surface area of the sample.

$$A = N_a * n_m * a_m$$

where a_m is the molecular area of the water, and N_a. is the Avogadro number. Using the estimation for water molecules packed together in a monolayer film on the rock, we have:

$$a_m = 1.091 * \left(\frac{18}{\rho_{water} 6.2E23}\right)^{2/3} = 11Å^2$$

The values of the surface area (A) will be presented in this paper.

EXPERIMENTAL DETERMINATIONS

Due to the economic importance of adsorption phenomena in the exploitation of vapor dominated geothermal reservoirs, the Stanford Geothermal Program at Stanford University has developed an automatic system for determining the adsorption isotherm on different rock samples. The measurement is made at constant temperature by performing vapor expansion in and from a rock sample and recording the pressure variation in a known volume; the deviation from the gas law is given by the amount of adsorbed/desorbed moles of water. Due to the limitations of the electronic device, the upper limit of the operating temperature is 120 °C [7]. The description of the recent results, as well as of the experimental set-up, is in [8].

In the Italian situation, there are very high temperature systems, with values up to 350 °C. For this reason, we have performed an experimental determination at higher temperature values, with a new manually operated apparatus. Our upper experimental limit is 220 °C [9].

Due to the volumes and the precision of the pressure transducer, the minimum desorbed water which is possible to measure is roughly **0.05** mg/g. We performed two different series of runs during this year, with slight modifications in the set-up of the apparatus and of the procedure in order to eliminate a number of experimental problems. For this reason we have two different values for the error bars.

THE SAMPLES

Four samples from Monteverdi geothermal field were analyzed in the 1995 experimental schedule.

1. Monteverdi 7 is a sample made up of cuttings collected between 2700 and 2960 m, where the reservoir pressure is 75 bar and the temperature is 315 °C; the productive zone is at 2690 m, with a flow rate of 20 t/h; the main lithologic formation in the sample is in the gneiss. The trasmissivity is 0.3 Dm.
2. Monteverdi 2B is representative for the 2000-2850 m depth interval, in the same lithofacies as MV7; the fracture is at 2700 m, and hk has a value of 0.5 Dm and a negative skin of -1.6. In the production test the flow rate was 23 t/h, but with a clear indication of storage effect.
3. The Monteverdi 5 sample is formed of the cuttings from 2000 and 3000 m; it is a sterile well; the lithologic distribution is a mix of micaschists and gneiss.
4. Monteverdi 1 is a poor producer from a fracture at 2100 m; the sample is taken from 1780 and 1960 m, in the micaschists region, where the reservoir pressure is 70 Bar and the temperature is 300 °C.

The results from the measurements will be presented in two groups: first, each individual sample and then the data are grouped according to the temperature.

MV7

This sample was the first examined; in order to verify the repeatability of the measurements, we have two determinations at low temperature, 170 and 180 °C, and one at 200 °C.

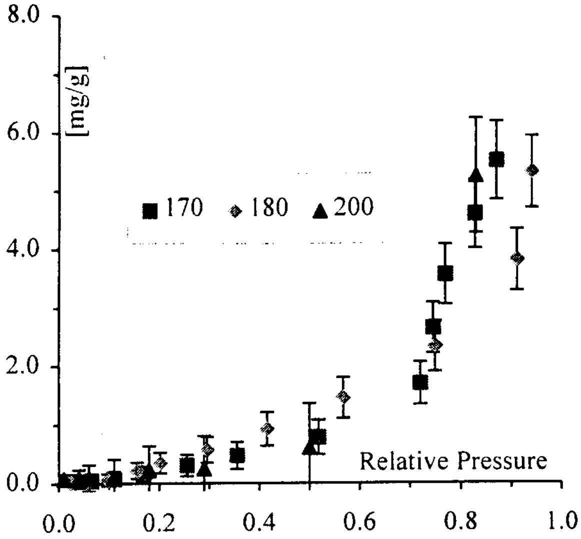

Fig. 1: MV7 isotherms.

The capillarity phenomena are predominant above the relative pressure of 0.7. The BET plot is shown in the next figure.

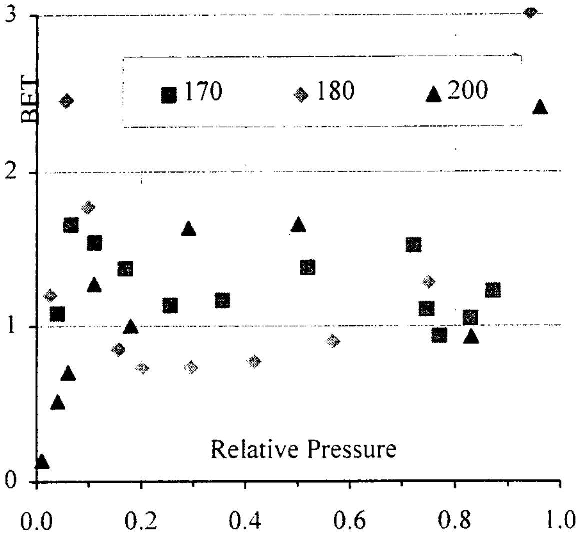

Fig. 2: MV7 BET plot.

The data are in good agreement with the type V isotherm; a BET analysis is able to determine the monolayer capacity (in mg/g), and it is possible to estimate the surface area with an assumption on the water molecular dimension:

Temperature [°C]	Monolayer Capacity [µmoles/g]	Surface Area [m²/g]
170	50	3.6
180	61	4.2
200	28	2.1

MV2B

Below the capillarity threshold at 0.6 the value of the adsorption for this sample is very low. For the moment, there are two determinations at 180 °C.

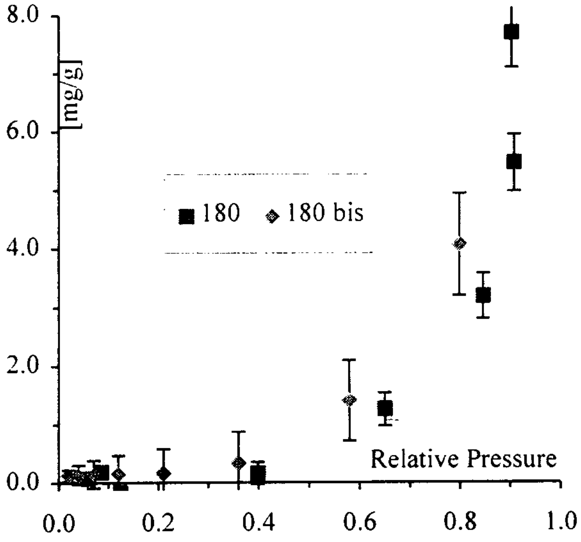

Fig. 3: MV2B isotherms.

The BET analysis has a high degree of scattering around the high values of p/p_0, and it is poor in data on the left edge of the pressure scale:

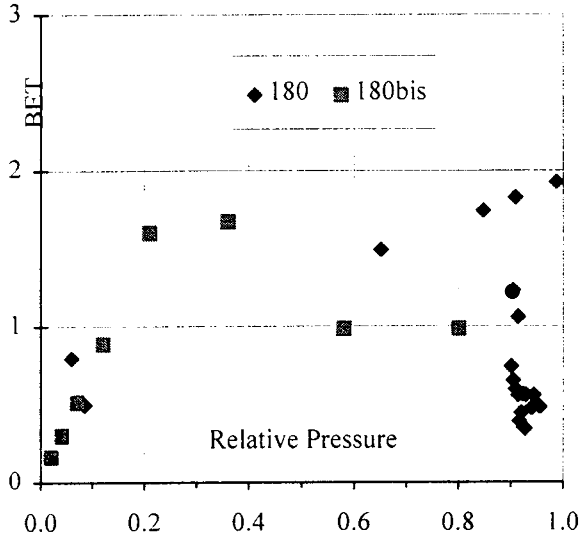

Fig. 4: MV2B BET plot.

The monolayer capacity and the surface area are given in the following table.

Temperature [°C]	Monolayer Capacity [µmoles/g]	Surface Area [m²/g]
180	67	4.6
180 bis	39	2.6

MV5

For this sample we have two measurements, at 180 and 200 °C. The trend is similar to MV7, but the 180 °C data are so scattered that it is impossible to calculate the monolayer parameter. However, the same limit of 0.6-0.7 for the capillarity domination is evident from the data. The monolayer capacity from the 200 °C data is 28 μmoles/g and the surface area is 1.9 m^2/g.

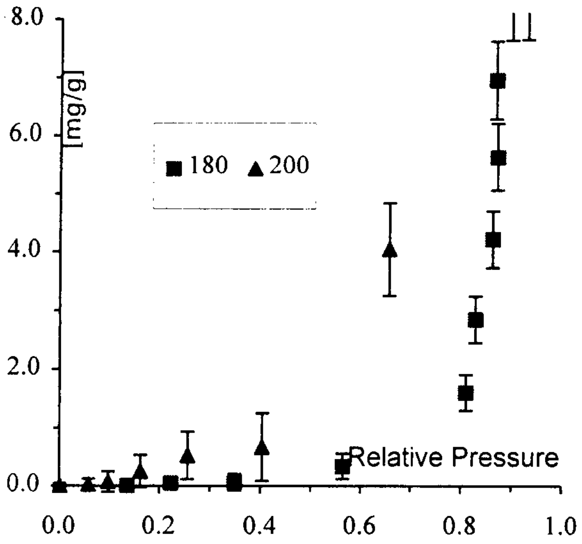

Fig. 5: MV5 isotherms.

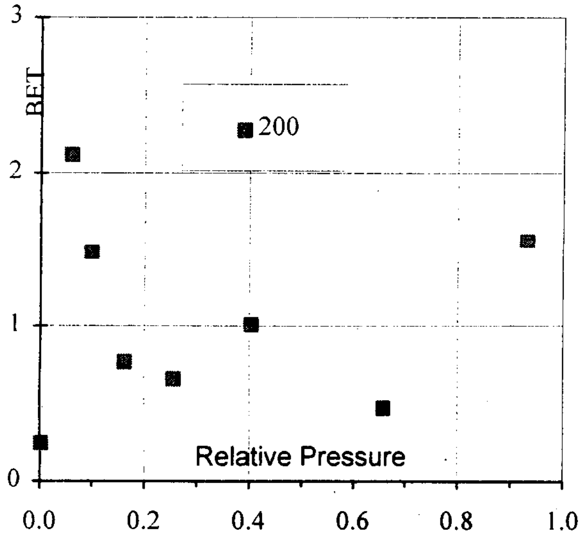

Fig. 6: MV5 BET plot.

MV1

For this sample we have one determination at 180 and two at 200 °C. It is difficult to define where the threshold between capillarity and pure adsorption is because there was a sharp jump from 0.7 to 0.4; nevertheless, there is no appreciable difference for the temperature effect.

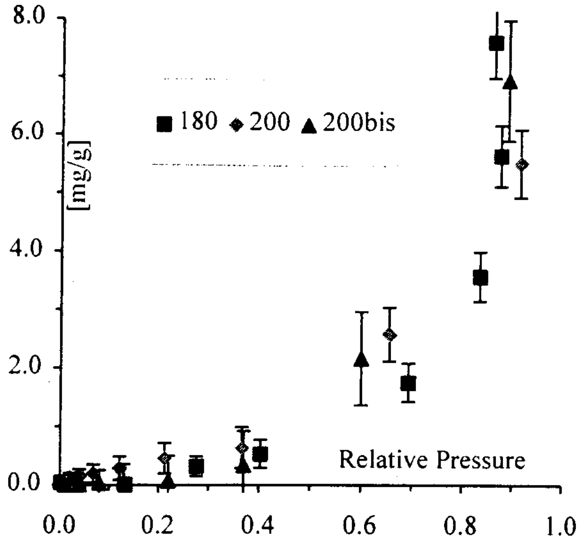

Fig. 7: MV1 isotherms.

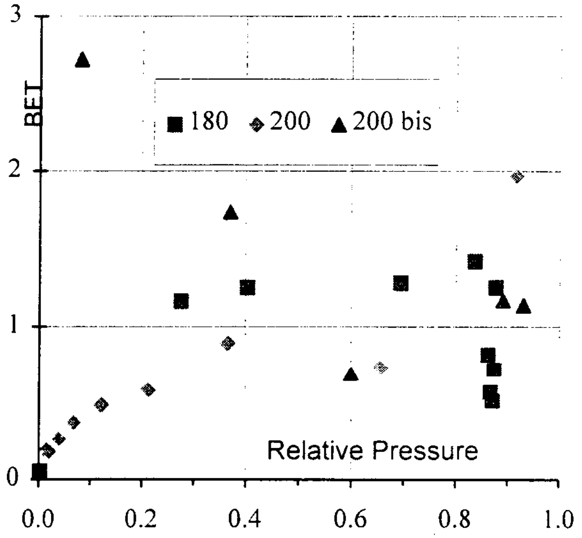

Fig. 8: MV1 BET plot.

The BET analyses for the monolayer capacity determination is rather good for this sample, at both temperatures.

Temperature [°C]	Monolayer Capacity [μmoles/g]	Surface Area [m^2/g]
180	56	4.0
200	28	2.2
200 bis	56	4.1

TEMPERATURE EFFECT

The measured data are collected all together according to the value of the temperature, in two categories: 170-180 and 200. The data are very well distributed without a clear difference among the samples; the general curves for the two temperature classes are in rather good agreement.

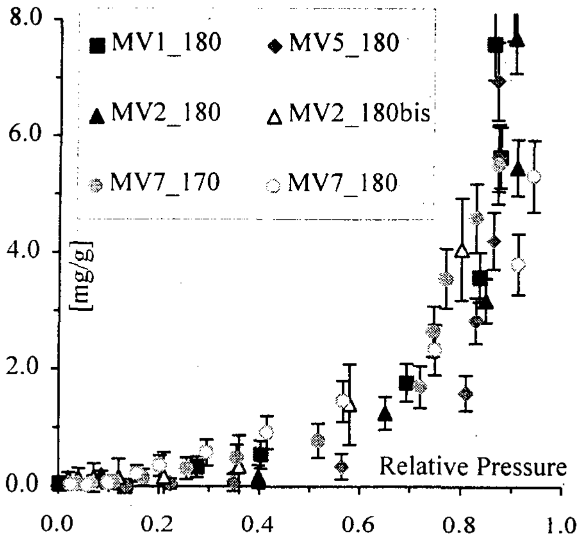

Fig. 9: 180 °C for all the samples

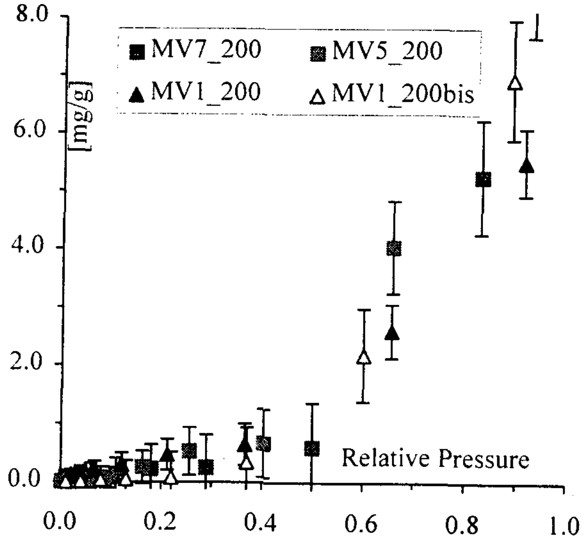

Fig. 10: 200 °C for all the samples

CONCLUSION

The data from the Monteverdi samples clearly show the existence of adsorption phenomena inside the pore network of the rocks. At high temperature, with 80% relative pressure, the amount of adsorbed water could be on the order of 3 mg/g; but below 50% this water is strongly reduced to 1 mg/g. If the pressure inside the pore could be the same pressure as in the fracture system, i.e. the reservoir pressure, the amount of liquid water glued to the rock by the adsorption forces at Monteverdi 7 (where the pressure is 75 bar and the temperature is 315 °C, for a relative pressure of 70%) is on the order of 2 mg/g. Converting this adsorbed water into an equivalent volume of steam, it is possible to calculate an "equivalent porosity" of the system, with:

$$\Phi_{equiv} = ADS \cdot \rho_{rock} \cdot v_{steam}$$

where ρ_{rock} is the rock density, v_{steam} is the specific volume of the steam and ADS is the adsorbed water per grams of rock. Assuming a real porosity of 1%, ADS=2 E-3, ρ_{rock}=2750 kg/m^3 and v_{steam}(315 °C,75 bar)=0.028 m^3/kg, we get Φ_{equiv}=15%. This implies a difference in mass by a factor of 15, from the "full of steam pore" to the actual "liquid adsorbed water+steam".

However it is difficult to know the exact value of the pressure inside the pore: due to the additional resistance between the pore network and the fracture system (the pressure inside the fracture is the so-called "reservoir pressure" because it is in connection with the well and it is possible to measure it), it is possible to have a higher value of the effective pressure on the water inside the pore and a higher adsorbed mass.

The capillarity effects are very important at relative pressures greater than 0.6; below this value the adsorbed mass is roughly linear decreasing. There is no temperature effect in the range 170-200 °C: all the samples exhibit --more or less-- the same behavior, without any noticeable differences.

The value of the surface area is on the order of 3 m^2/g, for all the samples, as determined by the water adsorption. A more precise value from cold nitrogen adsorption is in good agreement.

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