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MEASUREMENTS OF WATER VAPOR ADSORPTION ON THE GEYSERS ROCKS

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ABSTRACT

The ORNL high temperature isopiestic apparatus was adapted for adsorption measurements. The quantity of water retained by rock samples taken from three different wells of The Geysers was measured at 150 °C and at 200 °C as a function of pressure in the range $0.00 \leq p/p_0 \leq 0.98$, where p_0 is the saturated water vapor pressure. The rocks were crushed and sieved into three fractions of different grain sizes (with different specific surface areas). Both adsorption (increasing pressure) and desorption (decreasing pressure) runs were made in order to investigate the nature and extent of the hysteresis.

Additionally, BET surface area analyses were performed by Porous Materials Inc. on the same rock samples using nitrogen or krypton adsorption measurements at 77 K. Specific surface areas and pore volumes were determined. These parameters are important in estimating water retention capability of a porous material. The same laboratory also determined the densities of the samples by helium pycnometry. Their results were then compared with our own density values obtained by measuring the effect of buoyancy in compressed argon.

One of the goals of this project is to determine the dependence of the water retention capacity of the rocks as a function of temperature. The results show a significant dependence of the adsorption and desorption isotherms on the grain size of the sample. The increase in the amount of water retained with temperature observed previously (Shang *et al.*, 1994a, 1994b, 1995) between 90 and 130 °C for various reservoir rocks from The Geysers may be due to the contribution of slow chemical adsorption and may be dependent on the time allowed for equilibration. In contrast with the results of Shang *et al.* (1994a, 1994b, 1995), some closed and nearly closed hysteresis loops on the water adsorption/desorption isotherms (with closing points at $p/p_0 \approx 0.6$) were obtained in this study. In these cases the effects of activated processes were not present, and no increase in water adsorption with temperature was observed

INTRODUCTION

This project has been undertaken in order to expand our understanding of the adsorption/desorption processes occurring in rocks, which can be used in improving the efficiency of the recovery of geothermal energy. It seems reasonable to assume that any reliable model of the behavior of vapor-dominated geothermal reservoirs has to use information about the amount of water present in the pores and adsorbed on open surfaces. To estimate the size of the available resource and to predict pressure changes during operation it is important to know how much water is present as adsorbed layers and capillary condensate with an equilibrium vapor pressure lower than the saturated vapor pressure over a flat water surface. As the density of the adsorbate and capillary condensate is close to that of bulk liquid water, and not to the superheated vapor which is obtained as the product, it is assumed that the contribution of the water retained inside the porous structure of the rocks to the total reservoir fluid storage is considerable (Horne *et al.*, 1995). Operating experience suggests that adsorbed and capillary condensate water may act as either a source or a potential sink directly influencing the response of the reservoir production to injection projects. This response may be difficult to predict if the hysteresis phenomena inherent in condensation/evaporation of water in mesoporous systems, as well as the kinetics of the vapor-rock interactions, are not taken into account. The physicochemical complexity of interactions between strongly polar molecules and the surface of various compounds forming a

heterogeneous capillary system of pores with unknown shapes and size distributions makes it difficult to predict with a reasonable certainty the water retention by the rocks at different temperatures and pressures. The most useful information could be then expected from experimental measurements carried out at temperatures in the vicinity of the actual reservoir temperatures. The 'normal' temperature of The Geysers reservoir is 240 °C and it is even higher in the 'high temperature reservoir'. However, the results published in the literature until now have been limited to about 150 °C, with most of the experiments conducted at 120 °C and below (Shang *et al.*, 1994a, 1994b, 1995).

EXPERIMENTAL

Apparatus

The ORNL high-temperature isopiestic apparatus is a unique facility capable of accurate measurements of the change in mass of twenty 2-18 g samples simultaneously under high temperature and high pressure conditions (Holmes *et al.*, 1978). This ability makes it an instrument of choice for measurements of adsorption by materials characterized by relatively small surface areas like The Geysers rocks. The samples are placed inside a high-pressure, high-temperature autoclave in pans fitting in holes in a steel disk which can be rotated by the operator. The pans are placed in turn on the torsion suspension electromagnetic balance and weighed *in situ* by adjusting the electric current through the balance coil. The null point is detected by an optoelectronic system using a collimated light source, a dual photoresistor and a servoamplifier. The voltage across the coil at the null point is recorded. Figure 1 shows a schematic diagram of the experimental setup.

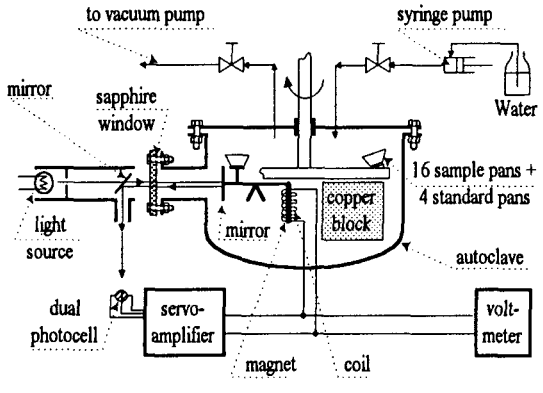

Figure 1. Schematic of the isopiestic apparatus with torsion suspension balance and optoelectronic null detector for in situ weighing.

In contrast to the sorptometers used by other investigators for measuring adsorption on geothermal reservoir rocks, the quantity measured using this apparatus is the change in the mass of the solid instead of the change in the vapor pressure caused by adsorption or desorption. In the sorptometers relying on monitoring vapor pressure in vessels of known volumes, a small leak, temperature variation, or an inaccuracy in calibrating the internal volumes of the sample chamber and the vapor chamber of the apparatus may result in significant errors. To make the relative change in pressure larger, the total volume of the instrument should be kept small, but then the errors due to leaks, volume of the sample, and possibly changing internal volumes of valves increase. In the isopiestic apparatus the mass is measured by comparison with a set of standard weights placed inside the pressure vessel together with the samples. This method makes the results particularly reliable and free of large systematic errors. The densities of the samples, which have to be known in order to correct the results for the effect of buoyancy, are conveniently measured inside the isopiestic apparatus by weighing the samples in vacuum and then in the atmosphere of a compressed gas of known density (e.g. Ar). The free volume of the autoclave is large (about 28 L), so that vapor pressure does not change significantly because of adsorption and minor leaks have no effect on the results. These characteristics of the isopiestic apparatus make it relatively easy to evaluate the time needed for reaching equilibrium, as the samples may be left under the same vapor pressure for many days and the change of mass with time can be monitored.

The temperature inside the air thermostat which encases the autoclave was controlled to better than ±0.01 °C and the temperature gradients inside the steel vessel containing the samples were expected to be smaller than 0.1 °C. The pressures were measured using a thermocouple vacuum gauge, a Heise gauge from 0 to 5 bar, and an Ashcroft Digigauge (Dresser Industries) from 0 to 30 bar. The pressure was known with an accuracy better than ±0.1 % or ±5 mbar, whichever is greater. The vacuum maintained at $p/p_0 = 0$ was better than 0.5 mbar. Overall accuracy of the amounts of water retained by the rocks is estimated to be better than 0.1 mg/g. The isopiestic apparatus is capable of and has been previously used for measurements at t = 250 °C and p = 40 bar.

Samples

The measurements were performed on core samples taken from the producing steam reservoir. Well numbers and approximate footages are as follows (after Jeff Hulen of the University of Utah Research Institute who supplied the samples):

- NEGU-17, 8530-8530.5 ft (rubble)
- PRATI-STATE 12, 6261.7-6261.8 ft
- MLM-3, 4336-4336.3 ft.

The rocks were crushed and sieved. Three fractions were prepared of each sample with the following grain sizes: 2.00 - 4.25 mm ('coarse'), 0.355 - 2.00 mm ('medium'), and 0 - 0.355 mm ('fine'). The surface areas as determined by PMI ranged from 0.64 to 3.52 m^2/g.

Rocks / Fractions	PRATI-STATE 12	NEGU-17	MLM-3
COARSE	0.641	1.825	1.814
MEDIUM	1.151	3.524	0.898
FINE	2.623	2.496	2.859

Table 1. Specific surface areas (m^2/g) as determined by PMI laboratories using nitrogen or krypton adsorption at 77 K and BET isotherm surface area analysis.

An examination of the BET surface analysis data shows, however, that the accuracy of these determinations may be too low to draw conclusions about the differences in surface area between the three rocks and between their size fractions. Additionally, these differences may be of the same magnitude as those caused by heterogeneity of the samples. Despite appropriate precautions during sample preparation, the heterogeneity of the samples may be significant, as indicated by our water retention results on the 'identical' pairs of samples of the medium fraction rocks.

The PMI helium pycnometry density results showed densities of the fine fraction smaller by up to 0.79 g/cm^3 compared to the two larger fractions. Our measurements yielded fine fraction densities larger by up to 0.34 g/cm^3 than those of the two larger fractions. The precision of our density measurements was better than that of PMI (better than 1% versus better than 3 %). We used our density values to correct for the buoyancy effect in water vapor as their accuracy was probably higher.

Rocks / Fractions	PRATI-STATE 12	NEGU-17	MLM-3
COARSE	2.739	2.772	2.736
MEDIUM	2.751	2.779	2.745
FINE	2.889	2.977	3.078

Table 2. Densities (g/cm^3) of the samples as determined by measuring the effect of buoyancy in argon at 25 bar.

Procedures

Prior to the measurements the samples were dehydrated *in vacuo* at 200 °C overnight. Four samples of each rock were loaded in the titanium cups of the isopiestic apparatus. The medium fraction of each of the rocks was loaded in two cups (samples 'medium a' and 'medium b'), so that the repeatability of the measurements could be verified. Four of the remaining cups contained pure minerals (silica gel, chlorite, magnetite, and anatase). The results obtained on these pure mineral samples, which have surface areas and water retaining capacities significantly higher than The Geysers rocks, can be compared with literature data. The last four cups contained standard weights made of titanium.

The time needed to reach equilibrium was estimated during the adsorption/desorption runs at 150 °C. The samples were weighed repeatedly after 0 - 4 days of equilibration. It was determined that the sample mass change between weighings repeated every 24 hours was smaller than the experimental error after about 10 hours following a vapor pressure adjustment for The Geysers rocks. This time was longer (up to 24 hours) for the pure minerals due simply to their greater water retention capacities. The weighings were made usually with a frequency of one a day (for all 12 rock samples, four pure minerals and four standard weights). For some measurements 3 days of equilibration time were allowed, and several were made at an interval of about 7 hours.

RESULTS

The Amount of Water Adsorbed And Hysteresis

The rocks may vary in their specific surface areas and water retention capacities in a manner not simply correlated with the depth from which they were taken (Shang *et al.*, 1994a). Additionally, when directly comparing the results with literature data, a significant heterogeneity of the rocks and of the samples has to be taken into account. Quantitative comparisons can only be valid for samples taken from exactly the same well and depth. Nevertheless, Figure 2 shows a comparison of the adsorption and desorption isotherms obtained in this study at 150 °C for the MLM-3 rock, with the 120 °C isotherms obtained by Satik and Horne (1995) on a sample taken from the same well at the depth of 4335.1 ft, close to that of our MLM-3 core. The agreement is better than expected for the adsorption isotherm, taking into account the above considerations.

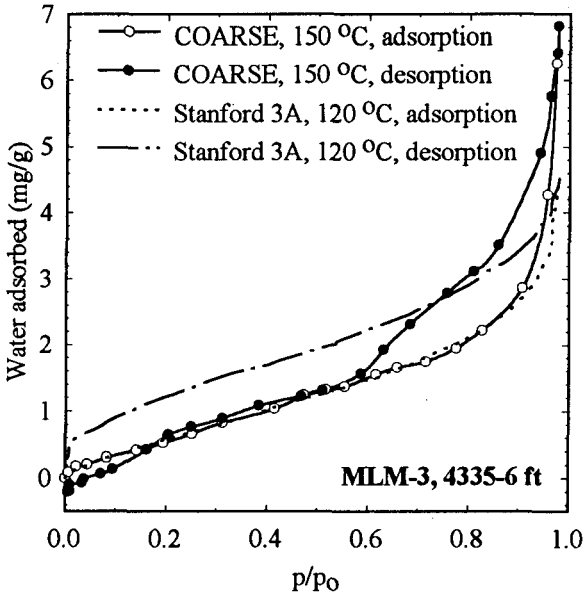

Figure 2. Comparison of the adsorption/desorption isotherms for MLM-3 rocks obtained in this study and corresponding isotherms reported by the Stanford researchers.

The shape of the desorption isotherm is different, however, as the hysteresis loop closes at $p/p_0 \approx 0.55$ in the isotherm obtained in this study, while it remains open down to very low pressures in the isotherm reported by Satik and Horne (1995). The shapes of most of the adsorption isotherms obtained in this study are generally similar to those found in the literature (Shang *et al.*, 1994a, 1994b, 1995). They are characterized by a nearly linear increase in water retention in a wide range of p/p_0 from less than 0.1 up to 0.8 and a steep upward swing due to condensation in the largest pores starting at $p/p_0 \approx 0.85$-0.90. The shapes of the hysteresis loops are of the type H3 according to the IUPAC recommended classification (Sing *et al.*, 1985). This type has been usually associated with adsorbents having slit-shaped pores.

The amount of water adsorbed by the rock samples at $p/p_0 = 0.8$ varied from 0.8 mg/g on the adsorption branch of the coarse fraction of PRATI-STATE 12 rock at 150 or 200 °C to about 13 mg/g on the desorption branch of the MLM-3 rock at 200 °C. The water retention capability was generally increasing in the sequence PRATI-STATE 12 < NEGU-17 < MLM-3 (Fig. 3) and in the sequence coarse < medium < fine (Fig. 4 - in this case the medium fraction shows slightly less adsorption than the coarse fraction). The differences in adsorption by different grain size fractions of the same rock can not in general be accounted for by the differences in surface areas (resulting from the crushing process) as determined by PMI.

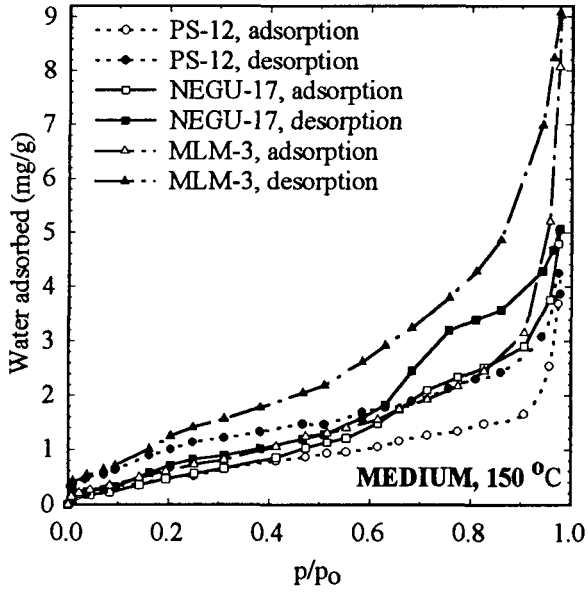

Figure 3. Water retention by the three rocks (averages of MEDIUM fractions) at 150 °C.

Knowing that the rocks have a complex heterogeneous structure, it can not be ruled out that the process of crushing the rocks not only increases the overall surface area, but also makes available for adsorption the components of the rock which might not have been exposed before.

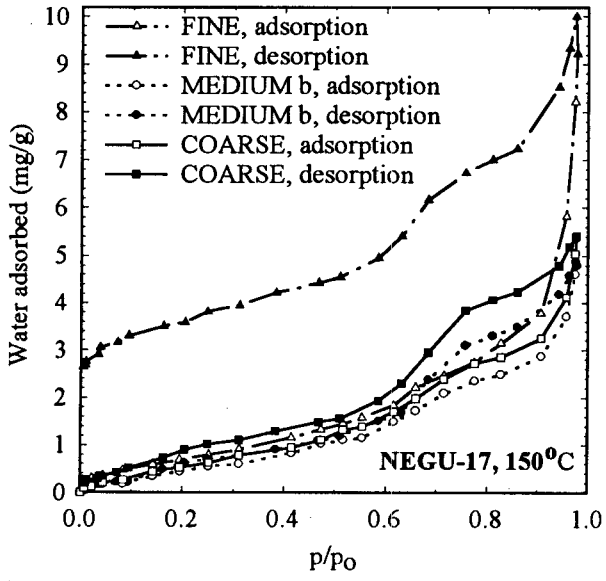

Figure 4. Water retention by the three grain size fractions of the NEGU-17 samples at 150 °C

The amount of water retained on the desorption branches for fine grain size samples is much larger than the corresponding quantity for the medium and coarse grain samples (Figure 4). We assume that this is due to the presence of a large proportion of newly created surface in the crushed rocks. This surface is able to adsorb some amount of water irreversibly at high p/p_0, and as a result the desorption branch is much higher than the adsorption branch at low p/p_0. This causes the hysteresis loops to be widely open down to very low p/p_0. The hysteresis loops for most of the large and medium fraction samples are, however, closed or nearly closed.

This result differs from the isotherms observed by Shang *et al.*, who obtained open hysteresis loops for water adsorption in all cases, although they obtained closed hysteresis loops for nitrogen adsorption (Shang *et al.*, 1995). The desorption branches of all their isotherms were significantly higher than the corresponding adsorption branches and they remained so down to the lowest p/p_0 values. However, as they used samples that were less finely divided than our samples, the proportion of the 'fresh' surface should have been less.

The Temperature Dependence of Water Retention

Investigations of adsorption on various geothermal reservoir rocks by Shang *et al.* (1994a, 1995) indicated that the amount of water adsorbed increases with temperature between 80 and 130 °C. Moreover, the increase is the most pronounced at high p/p_0, when the water is condensing on the surfaces buried under multiple layers of the adsorbate. This seems to be counter-intuitive in the case of physical adsorption for two reasons. First, any temperature dependence of the amount adsorbed as a function of p/p_0 should converge to zero at the limit $p/p_0 = 1$, i.e. as the process approaches condensation into bulk water. Second, the increase of the amount adsorbed with temperature implies that adsorption/capillary condensation process is slightly less exothermic than the process of ordinary water condensation. This would mean that the presence of the solid surface under the adsorbed layers is energetically disadvantageous for further condensation. In general, such a case is possible, but it is unlikely for such an adsorptive-adsorbent pair as water and the components of rocks (Gregg and Sing, 1982). The results of Shang *et al.* and the present results suggest that chemical bonding between the surface and water molecules has to play a role with a possible significant increase in the reaction rate with increasing temperature. When a relatively short time is allowed for equilibration an apparent increase of the amount adsorbed with temperature might be observed. Such an increase was observed for the fine grain size samples in this study. A comparison of the 150 °C and 200 °C isotherms for the fine fraction of the PS-12 core is shown in Fig. 5.

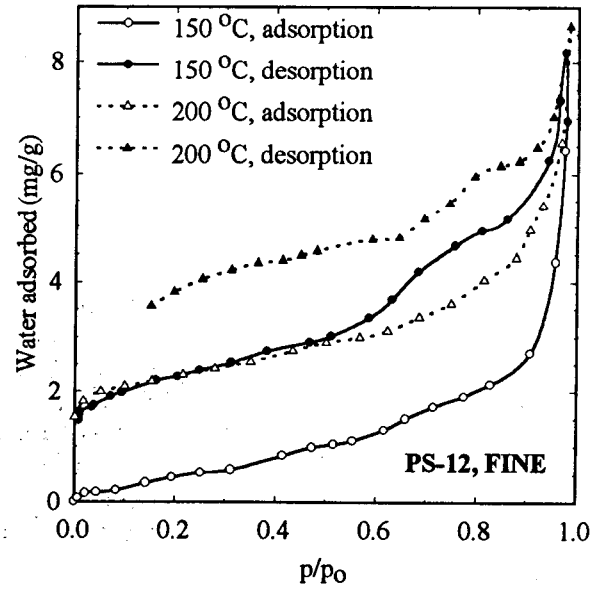

Figure 5. Adsorption/desorption isotherms at 150 °C and at 200 °C for small grain size fraction showing an apparent increase of water retention with temperature.

Both hysteresis loops are widely open, with the amount of water retained significantly higher at 200 °C on both branches. The 200 °C adsorption isotherm follows closely the 150 °C desorption isotherm. This would likely be the case even if the 150 °C run were simply repeated. This observation could be made thanks to the *in situ* weighing method used in this work, which allows for comparing the water content of the samples between consecutive runs. In the sorptometers based on monitoring the vapor pressure changes (Shang *et al.*, 1994a, 1994b, 1995; Satik and Horne, 1995), the reference point for the amount of water retained is the state of the sample before each run, which can be quite different, as apparent from Figure 5. As a result, the adsorption isotherms start always from zero, regardless of the actual water content of the sample. The increase in water retention with temperature in Figure 5 would not be seen if the 200 °C isotherm were forced to start from zero water content.

Figure 5 shows that as the temperature increased, even more water was irreversibly retained at high saturation (p/p_0 close to 1), and the hysteresis loop is still open at low saturation. However, for most of the larger grain size samples no such increase can be seen (Figure 6). A very slight decrease is observed instead.

The observed increase with temperature appears to be proportional to the amount of 'fresh' surface, where chemical adsorption occurs. As chemical adsorption is an activated process, it should be expected that the amount of water retained will depend on the time allowed for equilibration and on temperature. This may explain why Shang *et al.* observed significant hysteresis at low p/p_0 even though their samples were apparently less finely divided (equivalent diameters less than 8 mm) than our 'coarse' fraction. The kinetics of the chemical adsorption may be very slow. In the limiting case of total irreversibility (infinitely slow desorption) the hysteresis loops should be all closed (at an intermediate p/p_0) in a second run made at the same temperature, because hysteresis would be then caused only by the capillary condensation/ evaporation which takes place in the higher half of the p/p_0 range. However, if some amount of water can be chemisorbed at an observable rate (increasing with temperature) only at high p/p_0, and then it can be only very slowly desorbed at $p/p_0 = 0$, then the hysteresis loop will not be completely closed. The difference between the two branches in the region of $p/p_0 < 0.4$ is then the amount of water that is chemically bonded and can in principle be desorbed, but the time required may be extremely long at the temperatures considered here. This type of hysteresis is essentially caused by limited time allowed for equilibration (taking measurements far from the equilibrium associated with chemisorption).

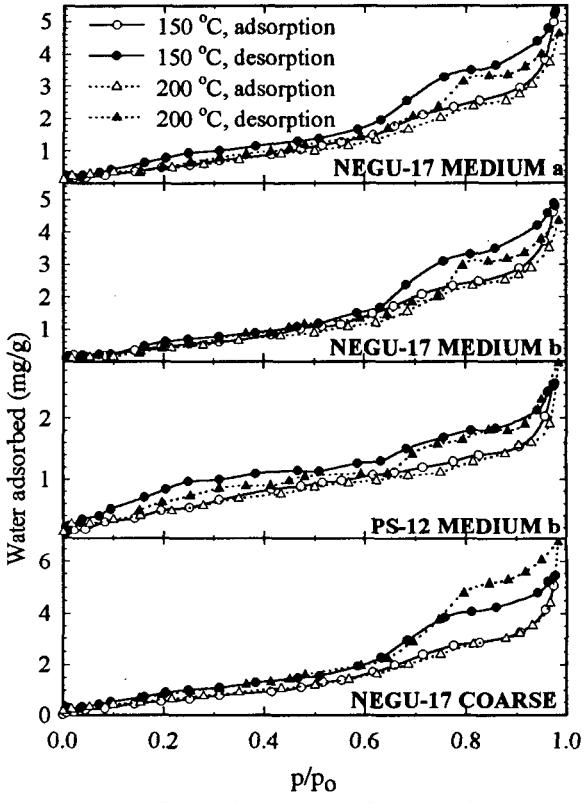

Figure 6. Examples of adsorption/desorption isotherms at 150 °C and at 200 °C which do not show an increase of water retention with temperature.

CONCLUSIONS

The isopiestic apparatus was found suitable for accurate measurements of water adsorption on rock samples. The amount of water adsorbed on The Geysers rocks and the shape of the hysteresis loop varies strongly for different grain size fractions. The results of this study indicate that the chemical interaction of the rocks with water is probably responsible for the observed increases of the amounts of water retained by the rocks with temperature. This might be due to the slow rate (increasing with temperature) of chemical adsorption compared to the time allowed for equilibration during the experiments. However, in the case of the largest grain size fraction of the samples, where it is likely that most of the surface area is already saturated with respect to the chemical adsorption, we did not find an increase of the amount adsorbed between 150 and

200 °C. As the time scale associated with the laboratory experiments and with the operation of geothermal reservoirs may be comparable with that of chemical adsorption, it would be useful to investigate the kinetics of this process. The final conclusions will be formulated after the 200 °C and 250 °C runs are completed and the treatment of all the data (including pore size distribution analysis) is completed.

ACKNOWLEDGMENTS

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