

**Supporting Information**

# Characterization of Micro and Mesoporous Materials Using Accelerated Dynamics Adsorption

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### Models for the evaluation of pore size distribution:

Horvath-Kavazoe (HK), Saito-Foley (SF) and Barrett-Joyner-Halenda (BJH) models were evaluated for the adsorption data collected by MeCl adsorption. The parameters used to evaluate the models are reported in equations A1 and A2. HK model was assigned for slitpores of carbon adsorbents and SF model was applied to the oxide surfaces. At 303 K, the temperature at which micropore characterization was conducted with MeCl, the HK model takes the following form

$$RT \ln \left( \frac{P}{P_0} \right) = \frac{58060}{L-0.758} \left[ \frac{3.73 \times 10^{-3}}{(L-0.379)^3} - \frac{1.47 \times 10^{-6}}{(L-0.379)^9} - 0.0594 \right] \quad (A1)$$

where  $L$  is the poresize in Å,  $P$  is the pressure of the gas,  $P_0$  is the saturation pressure at the measurement temperature,  $T$ , and  $R$  is the gas constant.

Due to the curvature of the cylindrical pores, determination of pore size distribution using SF model requires the assumption of line average or area average of the interactive forces inside a pore. Here we chose area average as it is more common to use. The equation takes the form of an infinite series as follows

$$RT \ln \left( \frac{P}{P_0} \right) = 18167 \sum_{k=0}^{\infty} \left[ \frac{1}{k+1} \left( 1 - \frac{0.758}{D} \right)^{2k} \times \left\{ \frac{21}{35} \alpha_k \left( \frac{0.758}{D} \right)^{10} - \beta_k \left( \frac{0.758}{D} \right)^4 \right\} \right] \quad (A2-a)$$

$D$  is the pore diameter in Å. The expansion coefficients are expressed as

$$\alpha_k = \left( \frac{-4.5-k}{k} \right)^2 \alpha_{k-1} \quad (A2-b)$$

$$\beta_k = \left( \frac{-1.5-k}{k} \right)^2 \beta_{k-1} \quad (A2-c)$$

with  $\alpha_0$  and  $\beta_0$  equal to 1. By evaluating equation A-2 at different pressures, we found that the first 12 terms of the expansion were more than enough to have the calculations with the accuracy of 0.001%.

Modified Kelvin models, like BJH, are the common methods to evaluate mesopore size distribution. The Kelvin equation was defined as [1-3]

$$r_c = \frac{-2\gamma V \cos \theta}{RT \ln(P/P_0)} \quad (A3)$$

$r_c$  is core radius of pore,  $\gamma$  is surface tension,  $V$  is specific volume and  $\theta$  is contact angle. In mesopores it is common to assume the contact angle,  $\theta$ , as zero. The pore radius can be calculated from core radius as

$$r_p = r_c + t \quad (A4)$$

with  $t$  as the thickness of the multilayer adsorbed on the pore wall. Harkins and Jura proposed an empirical equation to estimate thickness of the adsorbed layer for  $N_2$  adsorption at 77 K. By using the adsorption energetics data reported for the adsorption of MeCl and comparing them with  $N_2$  adsorption data, we used Harkins-Jura correlations to calculate the thickness of MeCl adsorbed layer

$$t = \sqrt{\frac{13.99}{0.034 - \log(P/P_0)}} \quad (A5)$$

Also the following correlation was recently proposed as a simple but accurate method to calculate pore size from core size [4]

$$r_p = r_c/0.72 + 7.2 \quad (A6)$$

The given correlations were derived for N<sub>2</sub> adsorption data at 77 K. Here, we used them for MeCl adsorption. To estimate how much the assumption was valid, we evaluated the Kelvin model in the following form

$$r_c = \frac{-K}{\ln(P/P_0)} \quad (A7)$$

where **K** is a parameter which for a single molecule only varies by temperature. Evolution of the model for N<sub>2</sub> at 77 K and MeCl at 249 K by using corresponding molar volume and surface tensions resulted in K=9.62 for both molecules. Based on that, we assumed that the bulk behavior of both molecules should be fairly similar. Therefore, the correlations derived for N<sub>2</sub> should be applicable to MeCl as well. Comparing the pore size distributions measured in this work and the corresponding data reported in the literature confirms the accuracy of the assumption.

Adsorption uptakes in STP cc/g:

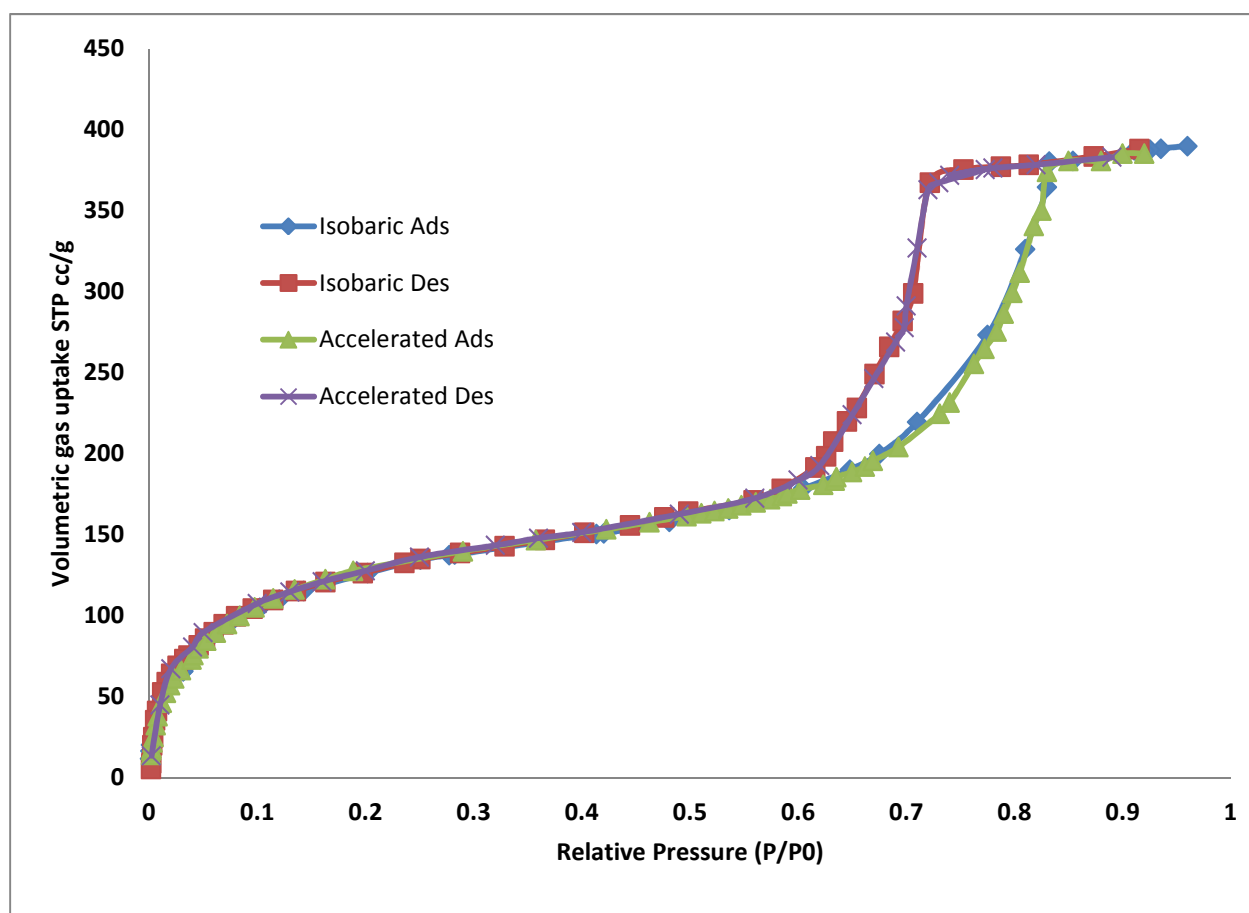


Figure S1: Adsorption-desorption profiles of MSC-Ox measured by MeCl adsorption via isobaric and accelerated methods.

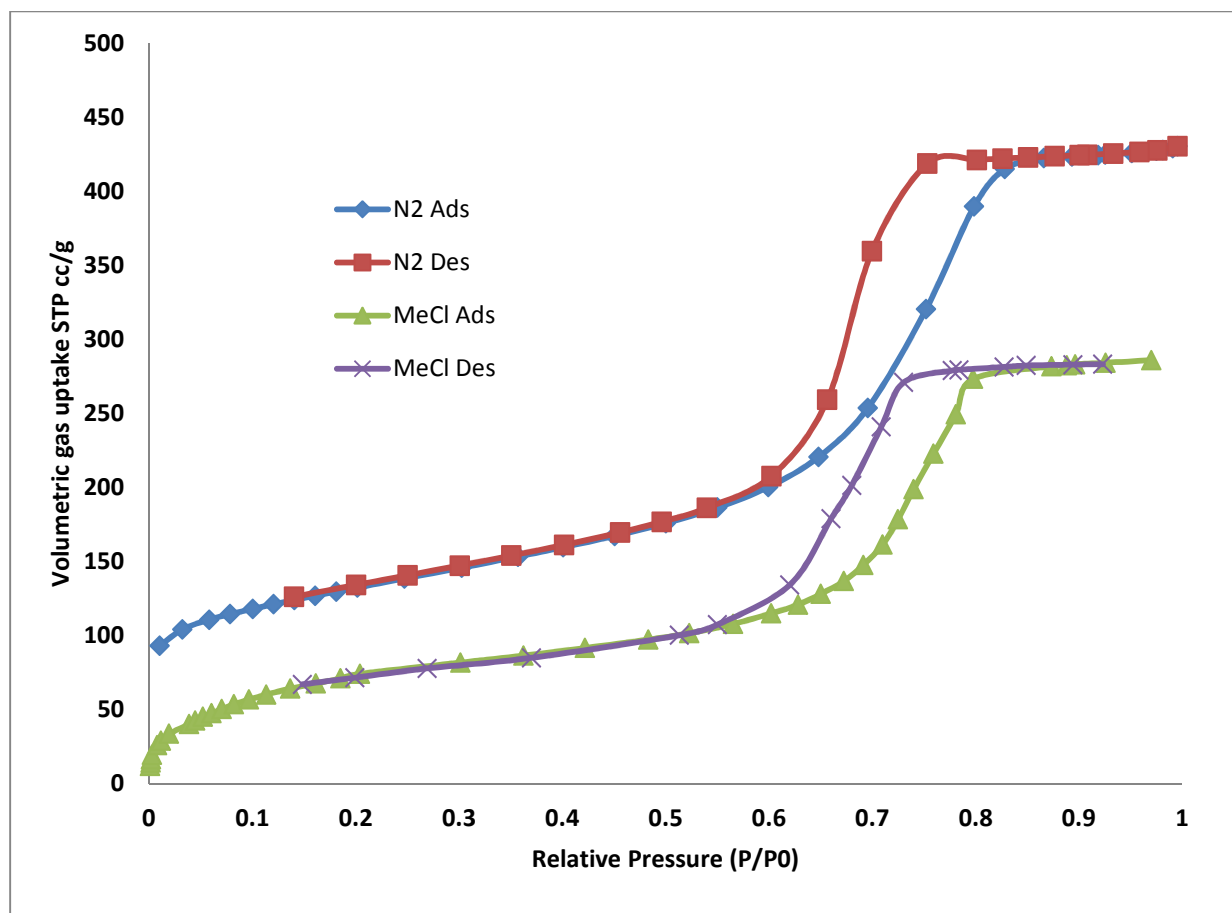


Figure S2: Adsorption-desorption profiles of MSC measured by MeCl via accelerated method and N<sub>2</sub> adsorption at 77 K.

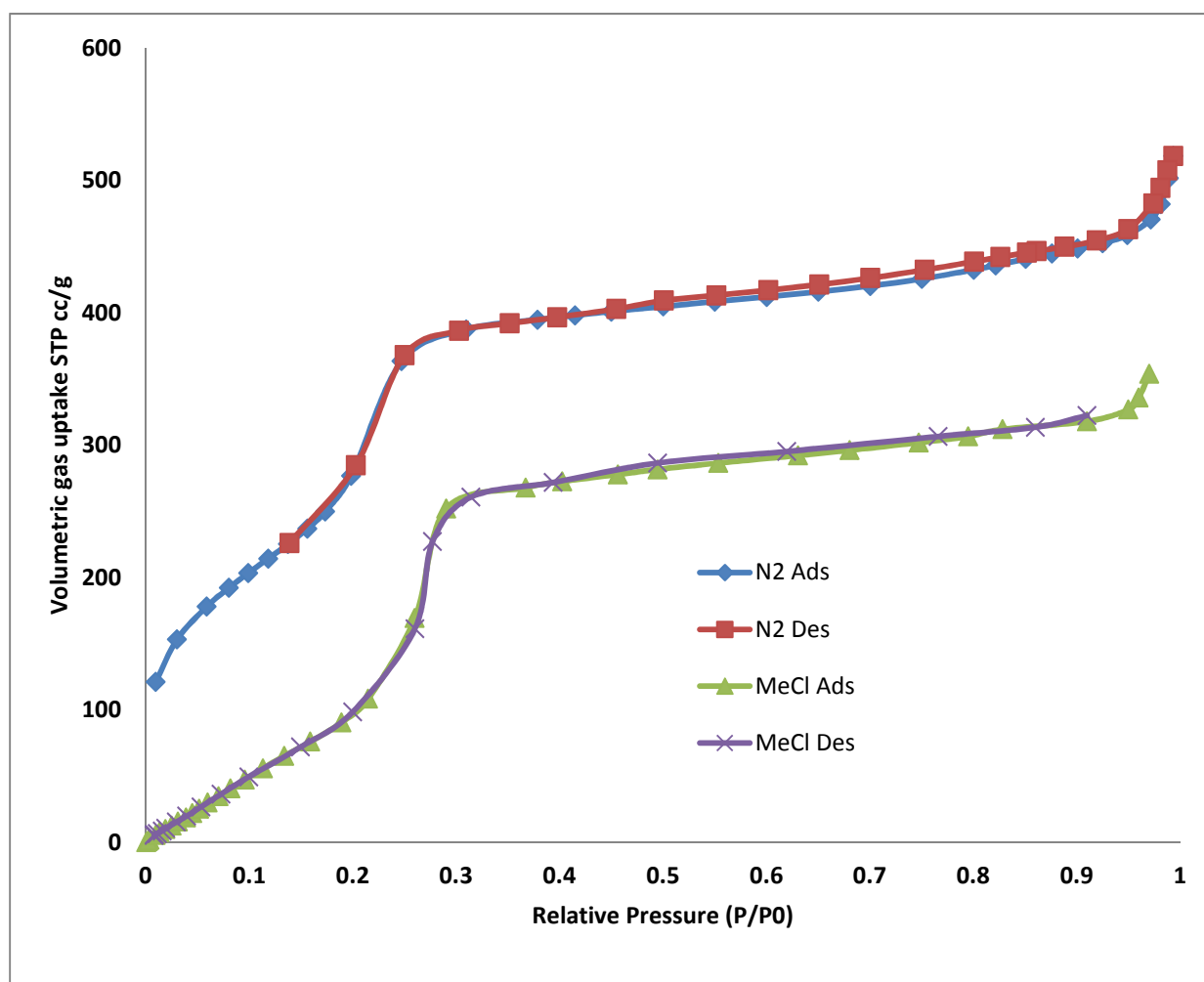
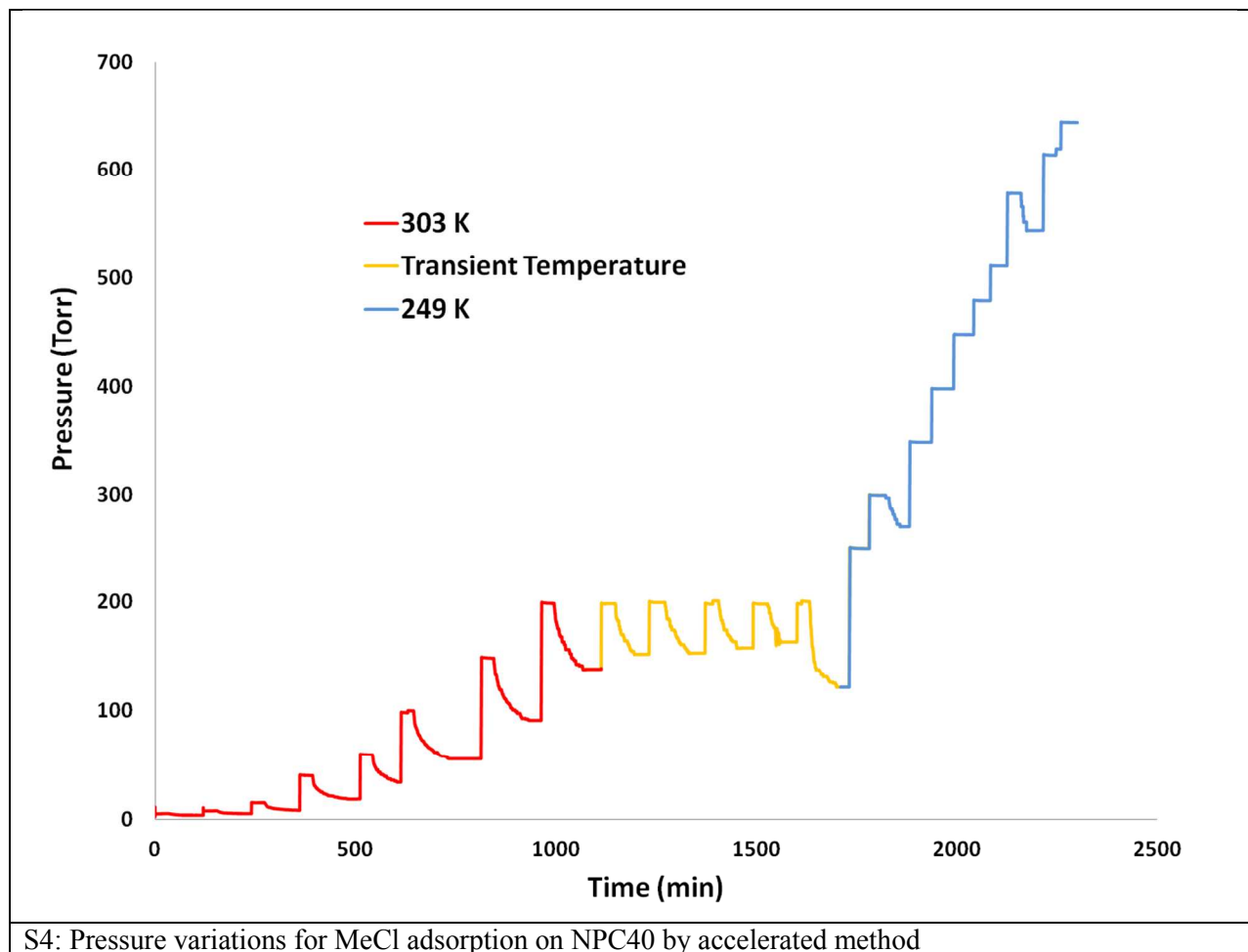


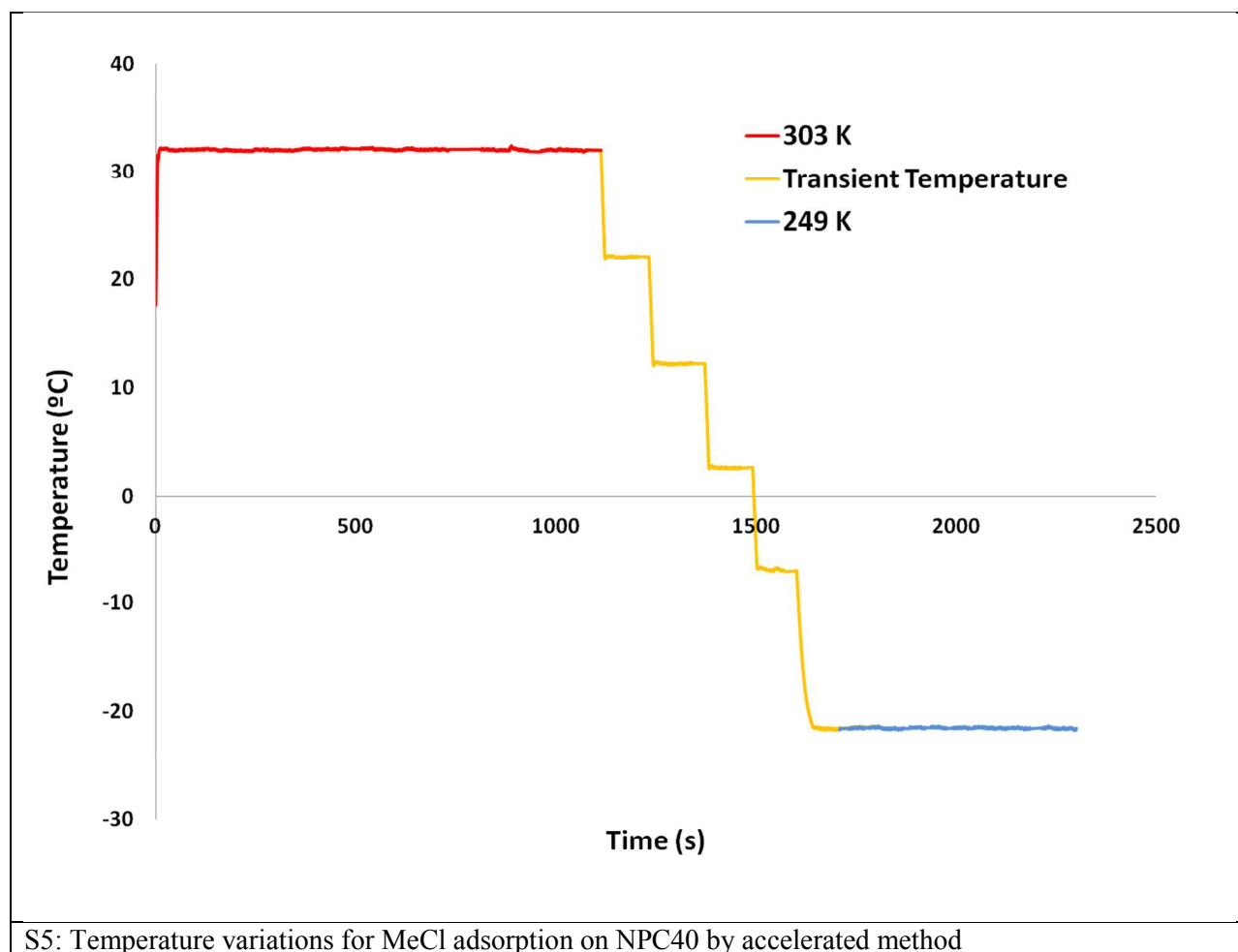
Figure S3: Adsorption-desorption profiles of MCM-48 measured by MeCl via accelerated method and N<sub>2</sub> adsorption at 77 K.

### Variations of temperature, pressure and gas uptake for a typical run for NPC40:

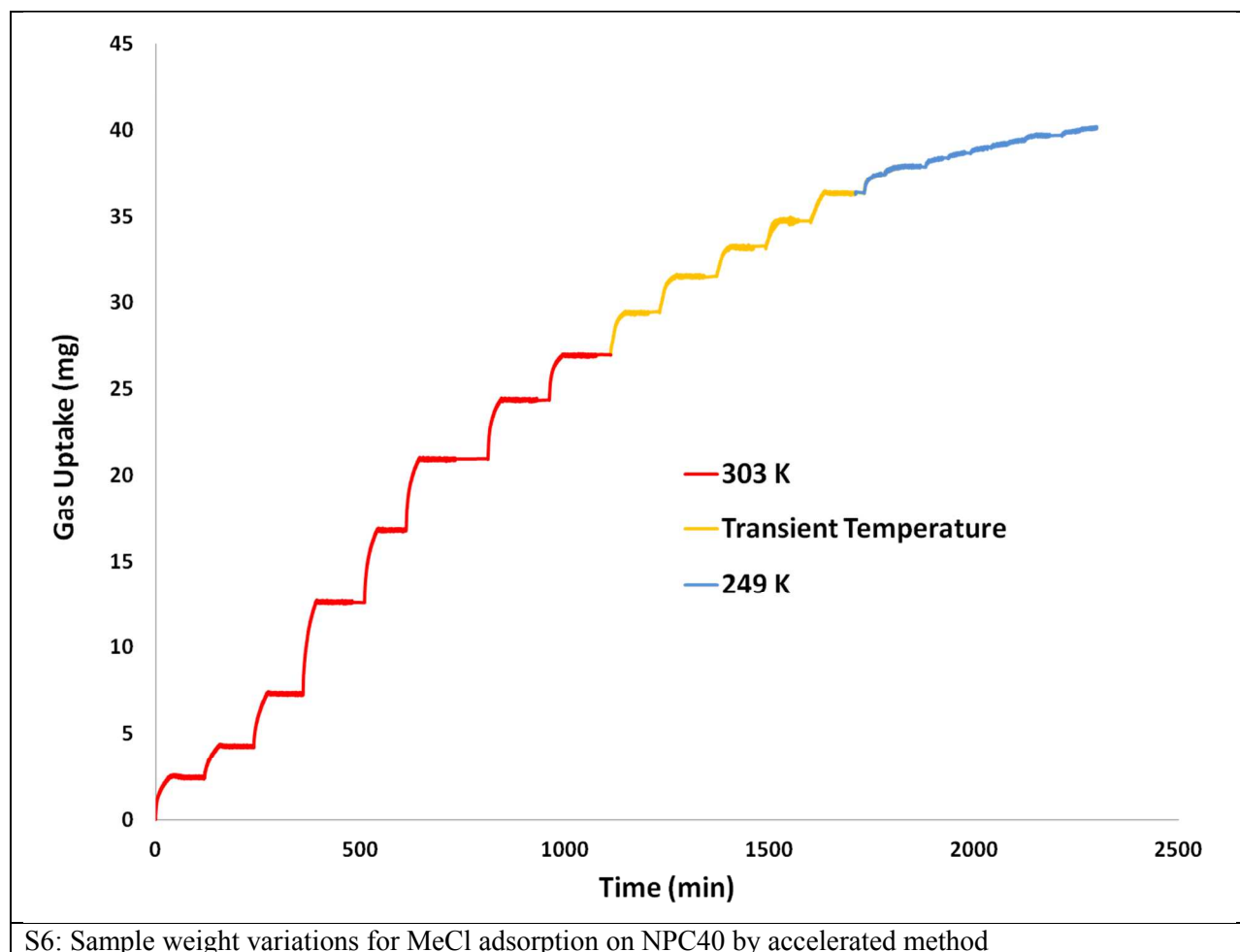
The following figures, S4, S5 and S6, represent pressure, temperature and sample weight variations for accelerated adsorption of MeCl on NPC40. Measurements took less than 2 days and the parameter were chosen 30 min ramp time, 10 min soak time and variations tolerance of  $\pm 0.02$  mg in sample weight. The controller gain was chosen as 3 second on/ 1 second off.







S5: Temperature variations for MeCl adsorption on NPC40 by accelerated method



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(3) Groen J. C.; Peffer L. A. A., Ramirez J. P. Pore size determination in modified micro- and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis. *Microporous and Mesoporous Materials*. 2003, 60, 1–17

(4) Ustinov E. A.; Do D. D.; Jaroniec M. Adsorption of argon and nitrogen in cylindrical pores of MCM-41 materials: application of density functional theory. *Applied Surface Science*, 2005, 252, 1013–1028