Impact of H_2O on the Adsorption of Hg^0 on Activated Carbon

Julian Steinhaus[1], Christoph Pasel[1], Christian Bläker[1], Dieter Bathen[1, 2]

[1] Chair of Thermal Process Engineering, University of Duisburg-Essen, D-47057 Duisburg, Germany
[2] Institute of Energy and Environmental Technology, IUTA e.V., D-47229 Duisburg, Germany

Introduction

For the separation of mercury from fluctuating exhaust air streams, fixed-bed adsorption with activated carbons is suitable in principle. Thermodynamic and kinetic investigations of the adsorption of Hg^0 are very fragmentary in the literature due to the complex experimental conditions. Therefore, the Chair of Thermal Process Engineering at the University of Duisburg-Essen systematically investigates the adsorption of Hg^0 on activated carbons. Physisorptive and chemisorptive mechanisms play a role in the adsorption of mercury. In this poster, the influence of water in the gas phase on the adsorption of Hg^0 is shown. The experimental results are simulated and quantitatively evaluated using an extended transport model. The discussion of the results allows a mechanistic interpretation of the adsorption processes.

Experimental Methods

Experimental Plant:

- Hg^0 concentration: 50 to 1100 µg m^{-3}
- Gas analysis with an atomic absorption spectrometer
- Tempered fixed-bed adsorber (20 to 600 °C)

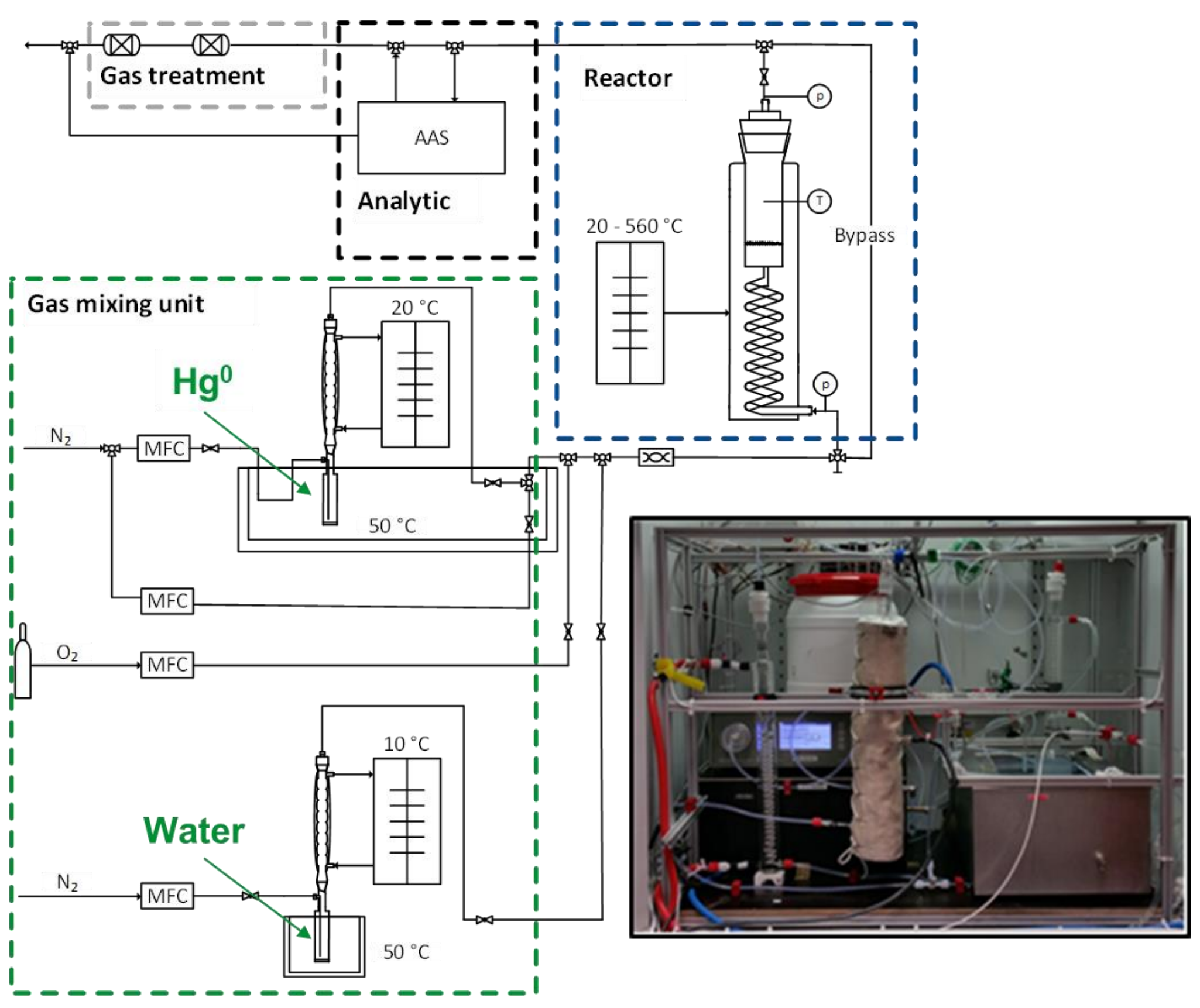

Fig. 1: Flowsheet of the experimental plant

Methods:

- Breakthrough curves for Hg0 adsorption
- Coupled adsorption and desorption experiments with concentration swing desorption (CSA) and temperature-programmed desorption (TPD)
- Determination of reaction parameters by computer-based simulations

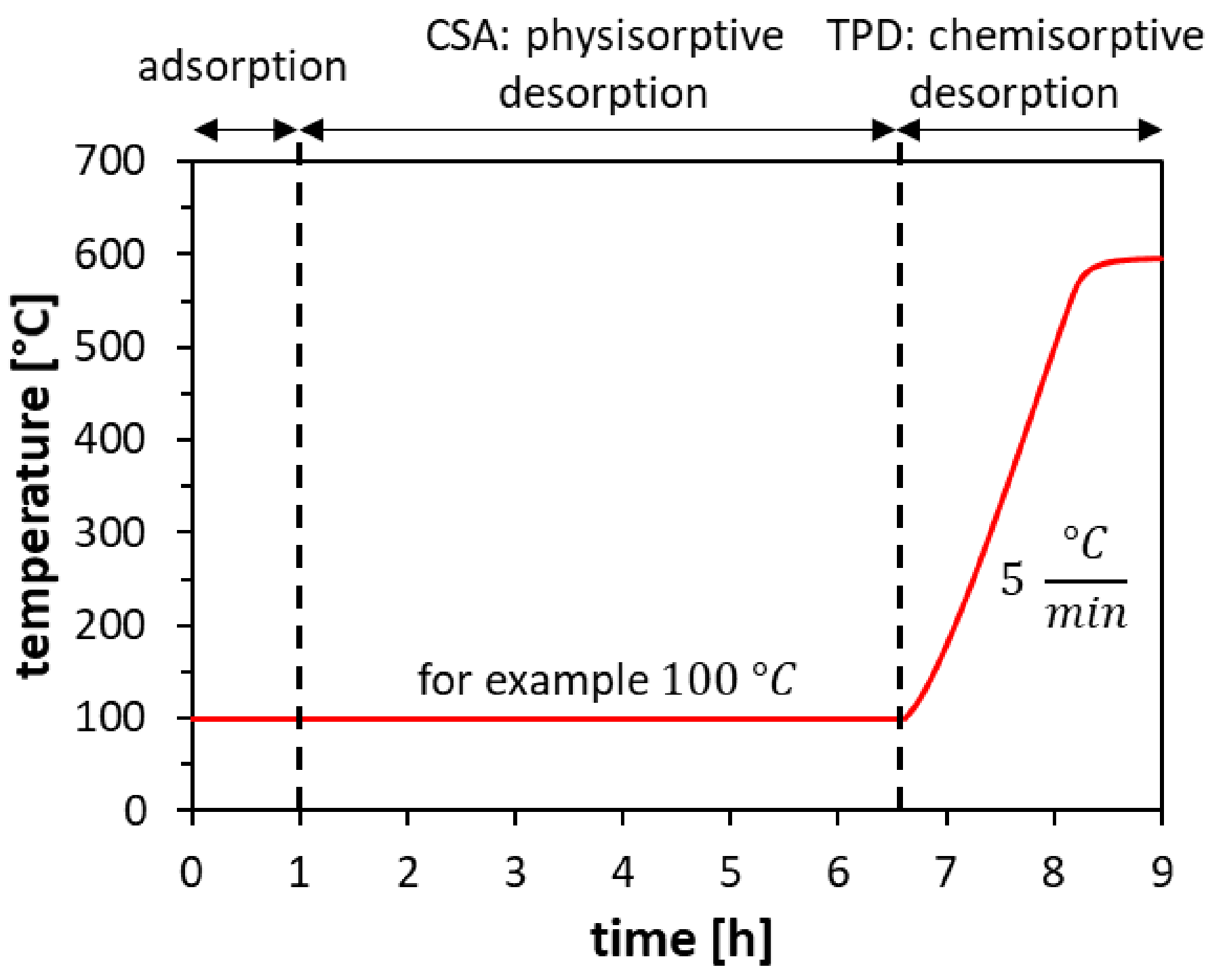

Fig. 2: Principle coupled adsorption and desorption experiment

Model of temperature-dependent gas phase desorption:

- Mass balance solid phase:

$$\frac{\partial X_i}{\partial t} = k_0 \cdot \exp\left[-\frac{E_A}{R \cdot T_G}\right] \cdot X^n$$

$$\frac{\partial X}{\partial t} = \frac{\partial X_1}{\partial t} + \frac{\partial X_2}{\partial t} + \cdots + \frac{\partial X_i}{\partial t}$$

- Mass balance fluid phase

$$\frac{\partial c_A}{\partial t} = D_{ax}\frac{\partial^2 c_a}{\partial z^2} - \frac{\dot{V}_G}{A \cdot \varepsilon_L}\frac{\partial c_a}{\partial z} - \frac{c_a}{A \cdot \varepsilon_L}\frac{\partial \dot{V}_G}{\partial z} - \rho_s \frac{(1-\varepsilon_L)}{\varepsilon_L}\frac{\partial X}{\partial t}$$

- Energy balance solid phase:

$$\frac{\partial T_S}{\partial t} = \frac{-\alpha_p \cdot A_{sp}}{\rho_S \cdot \left(c_{p,S} + X \cdot c_{p,A}\right)} \cdot (T_S - T_G) + \frac{\Delta h_{Ads}}{M_A \cdot \left(c_{p,S} + X \cdot c_{p,A}\right)} \cdot \frac{\partial X}{\partial t}$$

- Energy balance fluid pase:

$$\begin{aligned}\frac{\partial T_G}{\partial t} = &-\frac{\partial \dot{V}_G}{\partial z} \cdot \frac{T_G}{A \cdot \varepsilon_L} - \frac{\partial \rho_G}{\partial z} \cdot \frac{\dot{V}_G \cdot T_G}{A \cdot \varepsilon_L \cdot \rho_G} - \frac{\partial T_G}{\partial z} \cdot \frac{\dot{V}_G}{A \cdot \varepsilon_L} + \frac{\lambda_D}{\rho_G \cdot c_{p,G}} \cdot \frac{\partial^2 T_G}{\partial (z)^2} \\ &+ \frac{\alpha_p \cdot (1-\varepsilon_L) \cdot A_{sp}}{\rho_G \cdot c_{p,G} \cdot \varepsilon_L} \cdot (T_S - T_G) - \frac{\rho_S \cdot (1-\varepsilon_L) \cdot c_{p,A}}{\rho_G \cdot c_{p,G} \cdot \varepsilon_L} \cdot (T_S + T_G) \cdot \frac{\partial X}{\partial t} \\ &- \frac{\alpha_{w,i}}{d_i \cdot \rho_G \cdot c_{p,G} \cdot \varepsilon_L} \cdot (T_G - T_W)\end{aligned}$$

- Energy balance reactor wall:

$$\frac{\partial T_W}{\partial t} = \frac{4}{\left(d_a^2 - d_i^2\right) \cdot c_{p,W} \cdot \rho_W}\ \left(\alpha_{w,i} \cdot d_i \cdot (T_G - T_W) - \ \alpha_{w,a} \cdot d_a \cdot (T_W - T_U)\ \right)$$

Results and Discussion

- Physisorptive and chemisorptive mechanisms are involved in mercury adsorption on activated carbons.
- The systematic study of Hg^0 chemisorption is challenging because equilibrium capacities cannot be determined due to slow adsorption mechanisms.
- Temperature-programmed desorption (TPD) experiments provide information about chemisorptive binding sites on the surface.
- The chemisorptive bonding of Hg^0 on activated carbons increases with increasing H_2O content in the gas phase.
- In contrast, the amount of Hg^0 physisorbed in CSA experiments is independent of water content.
- We assume the formation of complexes of mercury, water, and various oxygen-containing functional groups on the surface of the activated carbon.
- Simulations of the peaks provide the reaction order, frequency factor, and activation energy of the desorption mechanisms.

Peak [-]	k_0 $[g^{1-n} \cdot s^{-1} \cdot µg^{1-n}]$	E_A $[kJ \cdot mol^{-1}]$	**n** [-]
1	$7 \cdot 10^{19}$ – $1.5 \cdot 10^{20}$	155	2
2	$9 \cdot 10^{11}$ – $2.5 \cdot 10^{12}$	117	2
3	$4 \cdot 10^{9}$ – $1 \cdot 10^{10}$	130	2
4	13-17	56	1

Tab. 1: Activation energy of desorption E_A, frequency factor k_0 and reaction order n

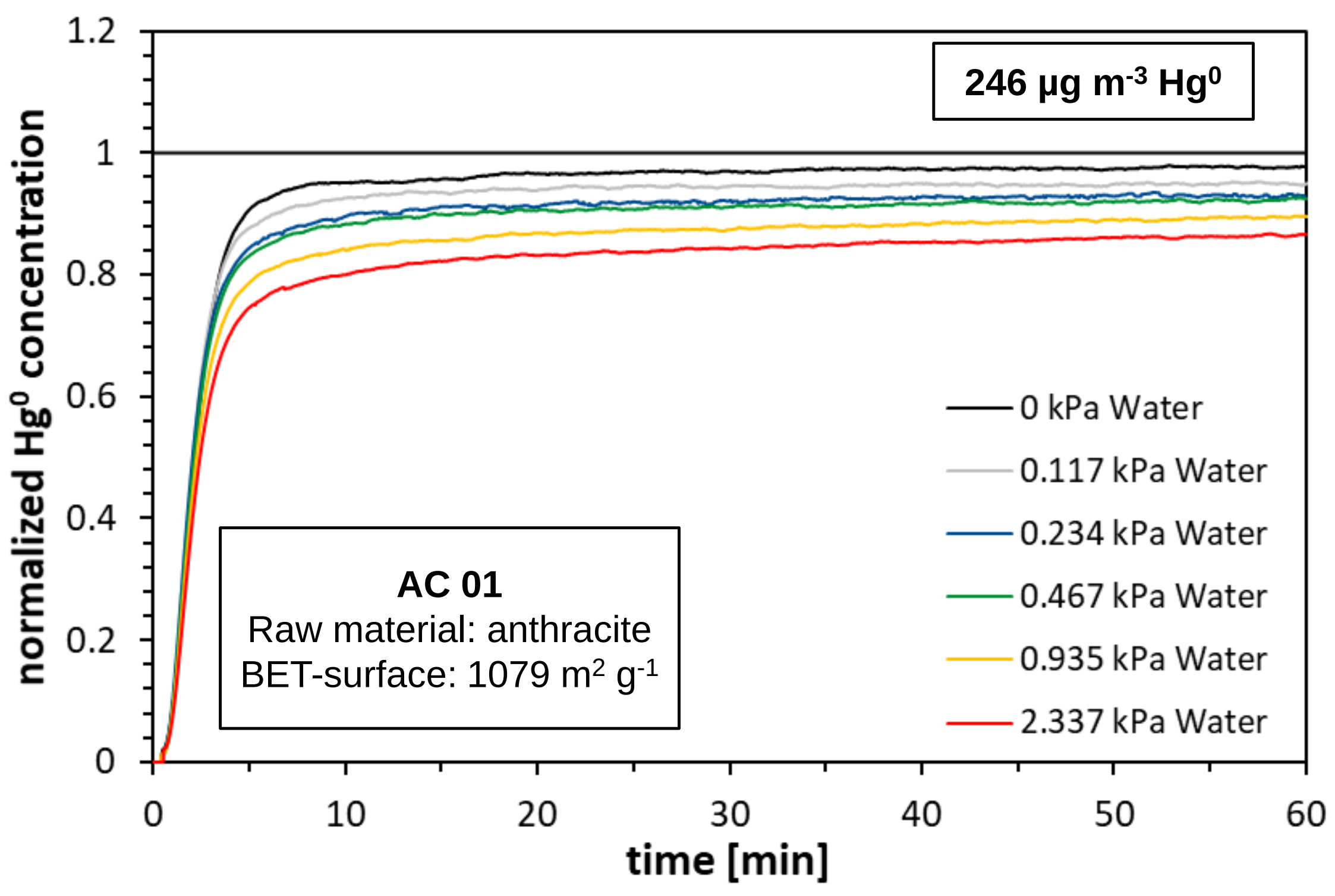

Fig. 3: Breakthrough curves of Hg^0 at 100 °C

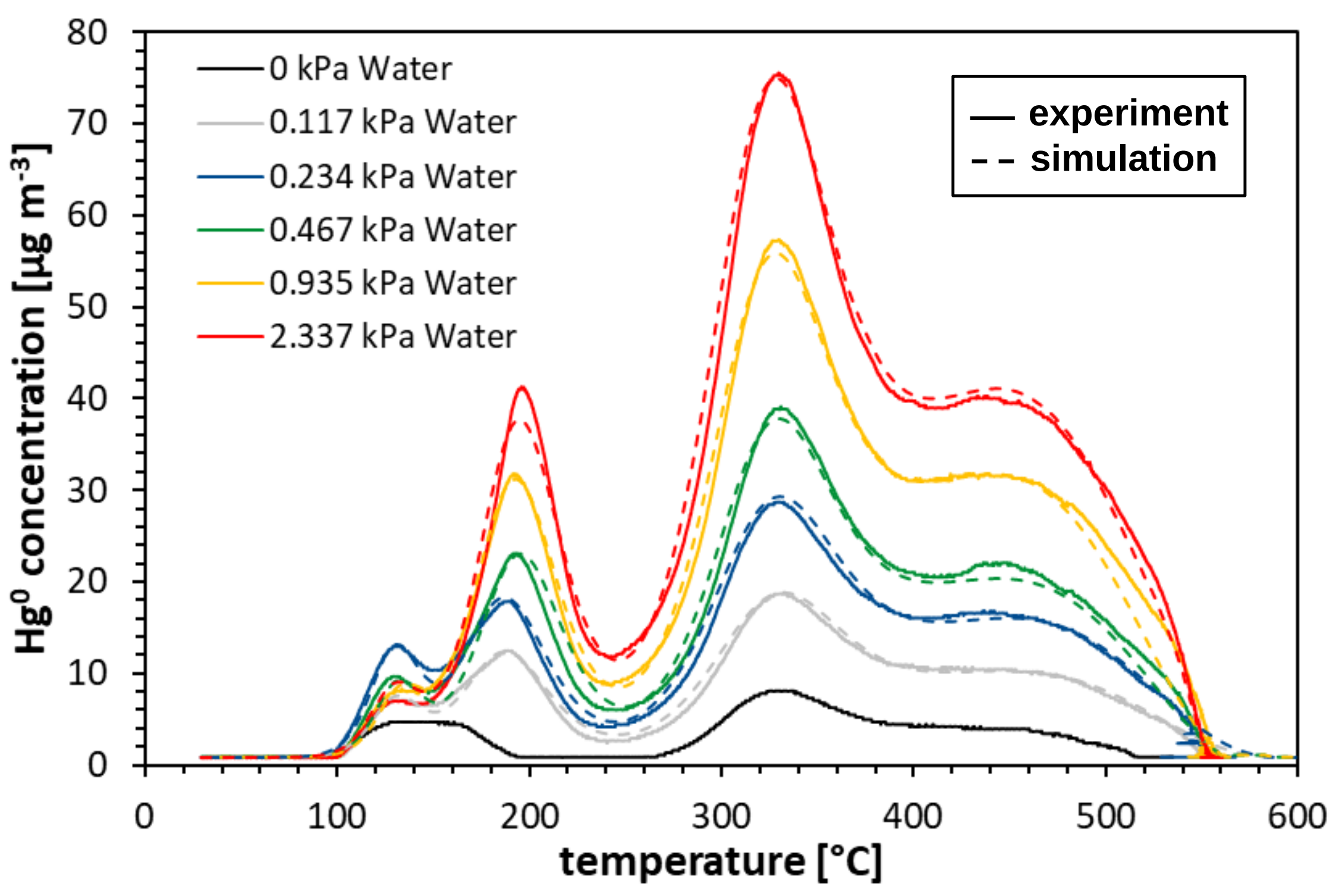

Fig. 4: Hg^0 concentration of TPD experiments

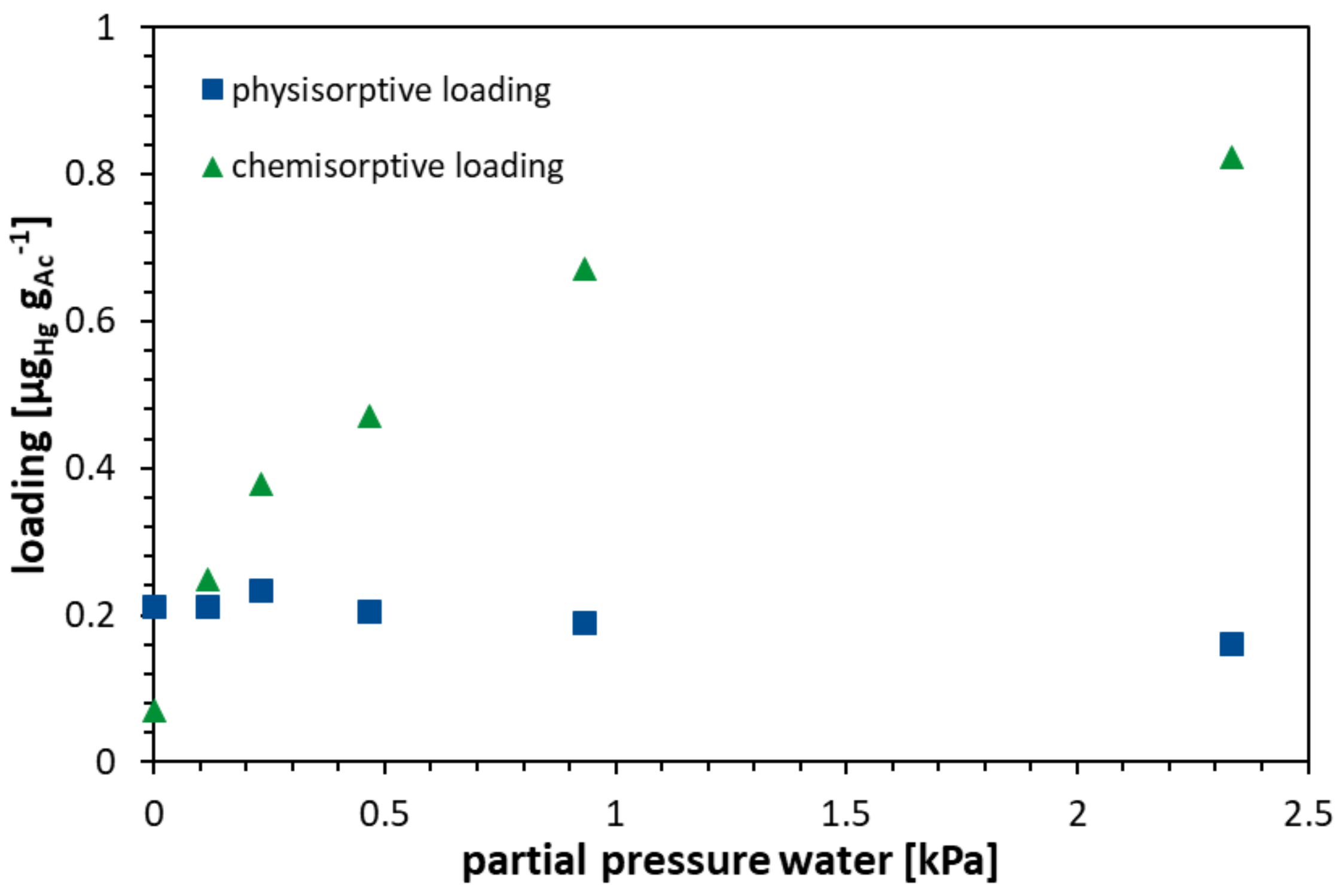

Fig. 5: Desorbed mass during CSA and TPD experiments

Resume and Outlook

The influence of H_2O on the adsorption of Hg^0 was examined by breakthrough curve measurements and TPD experiments. The presence of H_2O in the gas phase promotes chemisorption, in contrast, physisorption of Hg^0 is not influenced. The experimental results could be simulated with an extended transport model. Water probably reacts with Hg^0 and oxygen-containing functional groups to form various surface-water-mercury complexes.

In subsequent work, the complex process of mercury chemisorption on activated carbons should be further investigated. For this purpose, the number of heteroatoms on the surface of the activated carbon could be systematically varied by oxidizing and reducing treatments. These materials should first be characterized in detail by various measurement methods. The basic and modified materials can then be used to study mercury adsorption and desorption.

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