

WATER AD- AND DESORPTION ON ACTIVE CHARCOAL: IRREVERSIBLE MODIFICATION OF THE SURFACE BY HUMID AIR AND THE EFFECTS ON WATER-ISOTHERMS AND –SORPTION DYNAMICS, AS WELL AS ON THE PROTECTION PERFORMANCE AGAINST CHEMICAL WARFARE GAS

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ABSTRACT

As it is well known, in many cases high humidity strongly reduces the performance of gas filters with active charcoal. Our studies of the adsorption and desorption of water on active charcoal have shown, that the former humidity and the storage conditions are strongly influencing the final results, and that under normal drying conditions such modifications are non-reversible. The influence of the sample pre-treatment on the isotherm results is shown and described systematically, and proofs for the modification of the carbon surface, as well as quantitative effects on the sorption performance are presented.

INTRODUCTION

In many cases, high humidity strongly reduces the performance of gas filters containing active charcoal. One is expecting from NBC-protection filters an adequate protection against toxic gases even under unfavourable humidity conditions. For the evaluation of high performing adsorption materials, the estimation of the remaining lifetime and the understanding of the water balance is fundamental.

There are rather few reliable water isotherm data available for active charcoals used in NBC-protection, presumably due to experimental constraints. A large series of measurements in our laboratory led to some unexpected results. Follow up studies have shown, that not only the adsorption isotherm, but also the desorption strongly depends on the pre-treatment of the active charcoal. That means, the former humidity and the storage conditions are strongly influencing the final water isotherms. One could even show, that under normal conditions such modifications are non-reversible. By the usual physical drying of the samples at temperatures below 150 °C the initial state cannot be recovered.

EXPERIMENTAL

Two different testing facilities were used to determine the water uptake of the charcoal samples.

The values presented in table 1 were recorded in a commercial HERÄUS-VÖTSCH climatic test cabinet HC 4120, in which a special equipment is mounted to circulate the air at a flow of 2 m³/h through test tubes of 10 cm diameter. Samples of several active charcoal types, in state as delivered, were divided into 13 portions of 50 g. At first the climatic test cabinet was set to 20 °C and 95 %rH and one portion of each charcoal type was prehumidified for 60-65 hours and the water uptake of these samples was recorded gravimetrically. Then, the test cabinet was set to 40 %rH and the prehumidified sample portions, as well as portions in state as

delivered, were mounted in the cabinet and equilibrated for 94-96 hours before the final water uptake was taken. From the recorded weights, the load in g water / g charcoal was calculated. This procedure was repeated with new sample portions at equilibration air humidities of 50, 60, 70, 80 and 90 %rH. The temperature und the water dew point in the cabinet was checked with calibrated instruments: the corrected climate values are 20 ± 0.5 °C and 40, 49, 59, 68, 78, 86 and 91 ± 5 %rH (short time control oscillations).

The further measurements were conducted in a (very stable) laboratory sorption test apparatus. The air flow through the sample is set by mixing dry and humidified air. The humid air flow is achieved by passing the air trough a temperature controlled water saturation column. The sample temperature and the laboratory temperature is controlled as well as the air flow and pressure. Sample weight = 10 g, air flow = 0.36 ± 0.004 m³/h, temperature = 22 ± 0.3 °C, air stream humidity = set value ± 0.2 °C, time for preconditioning = 65 h, equilibration time = 24 h.

Drying of the charcoal:

In the first measuring series one portion of each type of charcoal was dried in an dry air stream ($\tau_{H_2O} < -40$ °C) at +40 °C for 65 hours. The weight loss, regarded as initial humidity, was about 1%M. The calculation of the water uptake in the first series was referred to this state. For the further measurements, the samples were dried previously for 60-65 hours in a vacuum dryer (two stages rotary pump) at 150 °C.

Evaluation of the protection performance against toxic gases:

In this test facility the well defined test air stream is passed through the thermostatic sorption tube of 60 mm diameter and the break through detected by gas chromatography with a flame ionisation detector. The required test air stream is set by a dry air stream (set mass flow control ± 2 %rel), adding water (mass flow control, recording dew point ± 0.5 °C), and mixing with test agent (set mass flow control ± 2 %rel). The temperature control is 20 ± 0.5 °C and the pressure control is 900 ± 5 mbar.

RESULTS AND DISCUSSION

The measuring series from the climate test cabinet in some cases showed a higher desorption equilibrium load at 78 %rH than at 86 %rH, and the same at 59 %rH than at 68 %rH, a doubtful result. (As described, each desorption point was measured with a new sample portion!) A closer check revealed a scattering of the load of the sample portions in the preconditioned state at 91 %rH and, surprisingly, a correlation to the load in the desorbed state (table1)!

Table 1: (sample = PCREF-92-2)

Portion	precondition load [g/g]	at %rH	desorption load [g/g]	at %rH	Quotient: load desorbed / load preconditioned
1 ; 2	0.513 ; 0.503	91	0.510 ; 0.501	86	0.994 ; 0.996
3 ; 4	0.524 ; 0.523	91	0.509 ; 0.509	78	0.971 ; 0.973
5 ; 6	0.491 ; 0.494	91	0.465 ; 0.469	68	0.947 ; 0.949
7 ; 8	0.523 ; 0.535	91	0.480 ; 0.491	59	0.918 ; 0.918

From this, we assumed a systematic and non-reversible effect, which transferred the deviations of the preconditioned state to the state after desorption. In this case, not recorded timely oscillations of the climate in the test cabinet could have affected the results. Further measurements on the more stable laboratory test apparatus confirmed our assumptions and showed, that not only the desorption branch, but also the adsorption curve is clearly shifted by the preceding humidifying and storage conditions, as presented in figures 1 and 2.

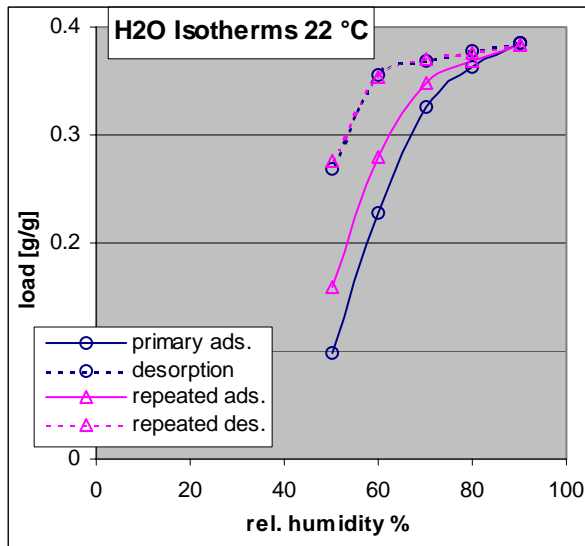


Fig.1: (sample = PCREF-95-1)

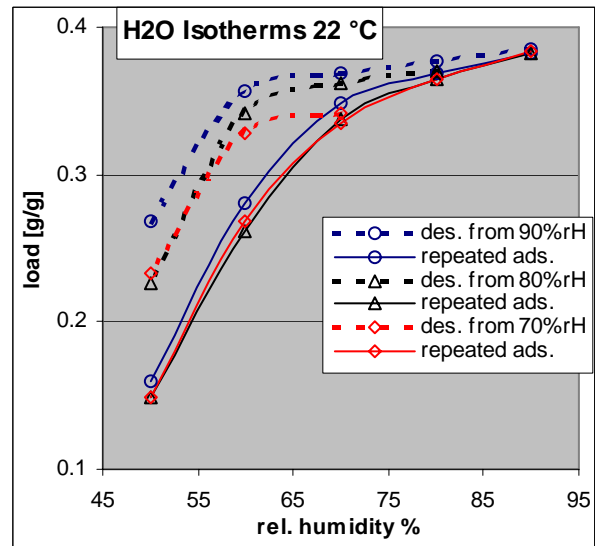


Fig.2: (sample = PCREF-95-1)

Figure 1 shows the primary adsorption curve of the sample in the initial state (as delivered + dried) stepwise equilibrated to 50, 60, 70, 80 and 90 %rH, followed by desorption back to the same points of humidity. Then the sample was dried before repeating ad- and desorption.

In Figure 2, the desorption was measured first after precondition at various maximum humidities, then the samples were dried and afterwards the adsorption measured. The higher the humidity at which the curves were started, the more they are shifted to the left side of the humidity axis! This is a clear proof, that the initial state is not recovered by drying at 150 °C, as well as that the extent of the modification strongly depends on the conditions of prehumidifying.

The results in figures 3 and 4 and table 2 give evidence of the modification of the carbon surface by exposure to humid air. The initial sample (as delivered, humidity < 3 % by mass) was divided, then part A was directly dried, while part B was preconditioned for 24 hours at 22 °C in an air stream of 95 %rH and then dried.

Thermally programmed desorption:

The sample parts A and B were analysed at the university of Granada, under conduction of Prof. C. Moreno – Castilla; for the gas analysis a quadrupole mass detector was used. In comparison to the initial sample (fig.3), the preconditioned sample (fig.4) clearly shows an increased "desorption" of water, carbon monoxide and carbon dioxide, as result of an

increased amount of functional O-groups on the carbon surface. The increased amount of oxygen is also seen by elemental analysis (table 2).

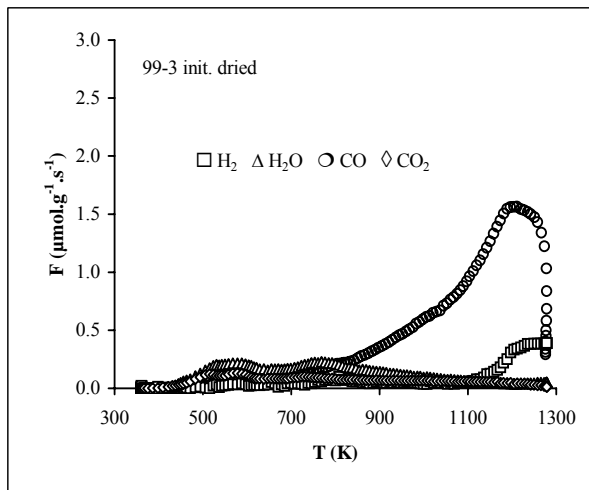


Fig.3: (PCREF-99-3, sample part A)

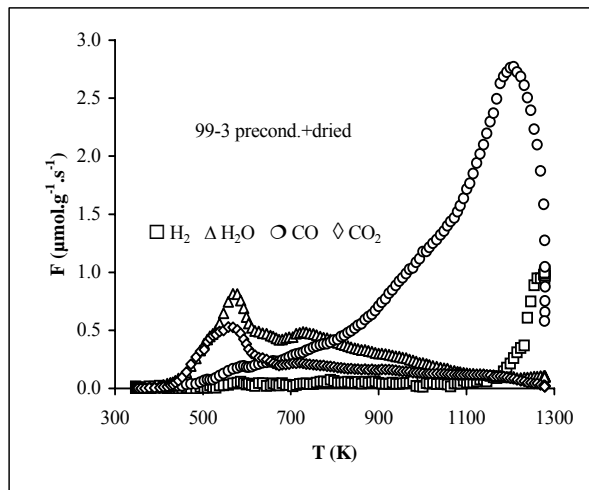


Fig.4: (PCREF-99-3, sample part B)

Table 2: Oxygen content by elemental analysis and enthalpy of immersion in water

Sample	O [%M]	$-\Delta H_i$ [J/g]
PCREF-92-2/A, initial state, dried	10.0	58
PCREF-92-2/B, preconditioned and then dried	10.6	66
PCREF-99-3/A, initial state, dried	3.4	35
PCREF-99-3/B, preconditioned and then dried	4.2	45

According to the publication of Stoeckli et al.^[1], the adsorption of water on active charcoal can be described by the Dubinin-Astakhov equation. Our sample PCREF-92-2 shows a type IV isotherm, which can be fitted by combination of type I and type V isotherms.

Figure 5 shows the measured isotherm points and the empirical fitted D-A curves from the initial adsorption, the repeated adsorption (after precondition of the sample at 95 %rH and drying) and the 'aged' adsorption (after storage of the humid sample for a period of 30 days and then drying). It shows, that after the first contact with water, the modification of the carbon surface is not finished, but it is continuing slowly over weeks and months, a process which is usually known as 'ageing' of the charcoal.

The D-A parameters found are given in table 3, using the relations: $E = E_0 \cdot \beta$ and $W_0 = W_1 + W_2$. For the type I fraction of the curves in the low humidity range the estimation of W_1 , E_1 and n_1 wasn't changed and only E_2 and n_2 were fitted to match the different experimental isotherm points.

From the D-A parameters, the enthalpy of immersion can be calculated (equations and measuring method in ^[2]), the results are given in table 3. These values are not on the same level as the experimental values given in table 2, but the increase by the preconditioning in relation to the initial state is nearly the same.

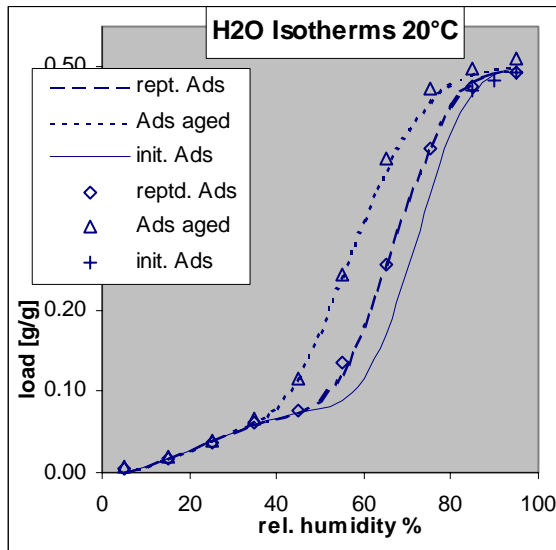


Fig.5: (sample = PCREF-92-2)

Empirically fitted D-A parameters	init. state, dried	pre-condit., then dried	aged, then dried
W_1 [cm ³ /g]	0.100		
E_1 [J/mol]	3500		
n_1	2		
W_2 [cm ³ /g]	0.4		
E_2 [J/mol]	900	1100	1500
n_2	3	3	3
calc. $-\Delta H_i$ [J/g]	37.6	41.9	50.4

Table 3:

Quantitative effects on the protection performance against toxic gases

The variety of effects of different humidity pre-treatment on the breakthrough time of active charcoal filters against toxic gases is shown by a few examples. Table 4a, with standard test conditions for product quality audits, shows the problem of ageing for the physically sorbed chloropicrin as well as for the chemically sorbed cyanogen chloride and hydrogen cyanide. Table 4b shows the effects of different precondition climate, of ageing and of bed depth (the latter to get some kinetic information).

Table 4a: Dynamic sorption test results

Sample: PCREF-95-1, water content (humidified) 27.4 %M, bed depth 152 mm
 Test air: velocity = 96 mm/s, temperature = 20 °C, rel.humidity = 70 %
 Test concentrations; Chloropicrin: challenge = 16 g/m³, breakthrough = 5 mg/m³
 Cyanogen chloride: challenge = 5 g/m³, breakthrough = 5 mg/m³
 Σ{HCN + (CN)₂} Hydrogen cyanide: challenge = 2 g/m³, breakthrough = 2 mg/m³

Test agent	Sample precondition	Breakthrough time t_b [min]	Quotient % t_b aged / humid.
Chloropicrin	Humidified at 90 %rH	180	83
	+ 100d aged	150	
Cyanogen chloride	humidified at 90 %rH	190	74
	+ 100d aged	140	
Hydrogen cyanide	humidified at 90 %rH	325	69
	+ 100d aged	225 ((CN) ₂ !)	

Table 4b: Dynamic sorption test results (next page)

Sample: PCREF-92-1 (with TEDA)
 Test air: velocity = 85 mm/s, temperature = 20 °C, rel.humidity = 70 %
 Test concentrations: challenge = 10 g/m³, breakthrough = 5 mg/m³

Test agent	Sample precondition	H ₂ O content of sample [%M]	Bed depth [mm]	Breakthrough time t _b [min]	Quotient % t _b 24/36 mm	Quotient % t _b aged / humid.
Chloro-picrin	humidified at 90 %rH	28.4	36	50	40	
			24	20		90
	+ 100d aged		36	45	40	90
			24	18		
	humidified at 80 %rH	27.0	36	54	48	
			24	26		70
	+ 100d aged		36	38	50	73
			24	19		
Cyanogen chloride	humidified at 90 %rH	28.3	36	24	42	
			24	10		92
	+ 100d aged		36	22	41	90
			24	9		
	humidified at 80 %rH	26.9	36	29	48	
			24	14		79
	+ 100d aged		36	23	48	79
			24	11		

CONCLUSIONS

The former humidity and storage conditions of active charcoals are strongly influencing the adsorption equilibrium at a given climate as well as the desorption. Under normal drying conditions these effects are non-reversible, that means: *By physical drying of the samples at temperatures below 150 °C the initial state cannot be recovered.*

Modification of the carbon surface is provable by several methods and corresponds within the framework of the D-A theory to the shift of the adsorption curves. The effect is found with different types of active charcoal, coconut 'base' or anthracite 'base', with or without chemical impregnation for NBC protection.

The resulting protection performance of filters containing active charcoal is affected for physical sorption processes as well as for chemical sorption. The sorption capacity of the charcoal may be affected as well as the kinetics of the sorption process.

That means, with regard to the humidity precondition, test procedures for NBC filters, as well as test facilities, have to be evaluated and defined very carefully to obtain correct and reproducible results. For modelling of sorption processes and prediction of the filter performance, the understanding of the described effects is essential, so our study will be carried on.

LITERATURE

- [1] Stoeckli F., Jakubov T. and Lavanchy A., J. Chem. Soc. Faraday Trans., 1994, 90(5), 783-786
- [2] Bansal R., Donnet J.B., Stoeckli F., Active Carbon, New York: M. Dekker, 1988, 147-159