

# **Gel-induced dew condensation**

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Beysens

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26 condensation on hydrogel grains widely used in agriculture (Aquasorb 3005<sup>TM</sup>). We show that 27 dew condensing on hydrogels is enhanced when compared to a regular bare substrate due to 28 vapor adsorption, which adds to condensation. Hydrogels, which can both capture water by 29 vapor adsorption and condense water vapor with high efficiency, are thus good candidates to 30 harvest water vapor from atmosphere with higher yield than regular bare surfaces.

31

### 32 **1. Introduction**

33

34 Hydrogels are three-dimensional networks of hydrophilic polymers, whose properties are 35 known since more than 50 years (see e.g. Wichterle and Lím, 1960). There are many types of 36 hydrogels (e.g. pH-, temperature-, electro- sensitive, light-responsive, etc.), with several 37 applications related to their extraordinary swelling properties (volume can be multiplied by 38 1000) when immersed in liquid water (for a review, see e.g. Majee, 2016; Ganji et al., 2010). 39 The osmotic pressure attributed to the polymer network is the driving force of swelling. An 40 osmotic gradient indeed forms between the water solvent, low in ionic solute, towards the 41 polymer, rich in ionic solute. The swelling process distends the network and is 42 counterbalanced by the elastic contractility of the stretched polymer network. Due to this 43 osmotic pressure, hydrogels can also exhibit high water adsorption from water vapor (they are 44 hygroscopic), an adsorption which increases with relative humidity *RH* (see e.g. Delavoipière 45 et al., 2018), making them suitable for atmospheric water harvesting (Zhao et al., 2019). 46 Water in hydrogels can be recovered by a moderate  $($   $\sim$  1 bar) osmotic mechanical pressure 47 (Milimouk et al., 2001; Zhang et al., 2017). The osmotic pressure exerted by plant roots in 48 presence of soil water, on the order of 0.1 - 1.2 MPa, can be high enough to extract water 49 from the gel mixed with soil and so provide water to the plant roots (Rudzinski et al., 2002; 50 Puoci et al., 2008). For agriculture in arid and semi-arid environments, there is an obvious

51 interest to swell the gels with water obtained at the place where they need to be used, thus 52 preventing water transportation on long distances. In consequence, collecting water from 53 humid air by adsorption and/or dew condensation is very appealing. 54 The question we thus address in this study is whether, once exposed to humid air at night and 55 cooled near or below the dew point, a typical hydrogel used in agriculture (Aquasorb  $3005^{TM}$ ) 56 could adsorb and/or condense more water than regular surfaces do. It appears that hydrogel 57 can indeed condense water at a larger rate than a bare substrate. In addition, when gel 58 temperature is above the dew point temperature, water adsorption still occurs. 59 The paper is organized as follows. After this introduction, details about the experiments and 60 methods are given. Then the water adsorption process is studied for relative humidity lower 61 than 100%, followed by condensation / adsorption proceeding at supersaturation larger than 1. 62 The paper ends by some concluding remarks concerning the main results of the study. 63 64 **2. Experiments and methods**  65 66 The absorbent materials are samples of Aquasorb  $3005^{TM}$ , manufactured by SNF Floeger, a 67 granular polyacrylamide. The materials are cross-linked copolymers of acrylamide and 68 potassium acrylate, which are water insoluble and have a very high absorption capacity (ratio 69 water weight/hydrogel weight up to 400). Further information can be found in Table 1 and 70 from Aquasorb 3005<sup>TM</sup> (2020). The samples can be found in three sizes presentation 71 (Dabrowska and Lejcuś, 2012): small-size grains (diameter  $0.19 \pm 0.07$  mm), medium-size 72 grains (diameter  $0.70 \pm 0.2$  mm) and large-size grains (diameter  $1.5 \pm 0.4$  mm). Hereby we

73 report results with small and medium grains.

74 The experimental apparatus is depicted in Fig. 1. It is placed inside a climatic chamber where 75 air temperature and humidity are controlled. The setup consists of a cooling device, a silicon

(Si) plate of diameter 10 cm and thickness 0.7 mm (condensing surface  $S_c = 7.853 \times 10^{-3}$  m<sup>2</sup>), 77 which holds the considered sample, and a balance to register the overall weight of sample and 78 Si plate. The cooling device is held by a motorized support which moves it from an upper 79 position, where it is in contact with the plate, to a lower position, where the plate is suspended 80 by holders attached to the electronic balance and can be weighted. The Si plate is usually in 81 contact with the cooling device. Each 38 s, the plate is moved to the lower position to be 82 weighed, a step which lasts about 8 s. Temperature of the cooled plate is measured by 83 calibrated thermocouples with an accuracy of 0.1 °C and a sensitivity of 0.01 °C. In the 84 chamber, air temperature  $T_a$  is set at 20  $\pm$  0.5 °C and relative humidity at 50  $\pm$  3 %, which 85 corresponds to a vapor pressure of 1.15 kPa and a dew point temperature  $T_d = 9.3 \pm 0.1$  °C. 86 The gel sample grains are poured on the silicon plate by the help of a circular mold which 87 keeps the sample height less than 1 mm (small and medium grains) to form a thin layer. In 88 order to have identical departure conditions in all cases, all the samples were previously dried 89 at 40 °C during 8 hours and stored in a closed box with silica gel to maintain a low humidity 90 level. For each experiment, the conditions inside the chamber and the cooling device 91 temperature are fixed at their desired value before placing the plate with the gel. 92 Two different conditions were investigated, above or below the dew point, which corresponds 93 to either relative humidity  $RH \le 100\%$  (above the dew point) or supersaturation  $SR > 1$  (below 94 the dew point). Relative humidity and supersaturation are defined from water vapor pressures 95 as

- 96
- 97 SR or  $RH/100 = \frac{p(T_a)}{p_s(T_p)}$  (1)
- 98

Here,  $p(T_a)$  is the water vapor pressure in the air surrounding the plate and  $p_s(T_p)$  is the 100 water vapor saturation pressure at substrate (plate) temperature. In addition to the

101 determination of characteristic adsorption isotherms under various *RH*, typical temperature 102 conditions as encountered at night outdoors were specially investigated: (i) Above the dew 103 point with a plate temperature  $T_p = T_d + 4$  K (adsorption), (ii) below the dew point :  $T_p = T_d - 4$ 104 K.

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106

107

108 Fig. 1. Experimental setup in the climatic chamber. The sample is placed on a silicon plate 109 cooled from below. The cooling device moves vertically (yellow double arrow). In the upper 110 position, the cooling device is in contact with the plate and controls its temperature. In the 111 lower position, the plate remains suspended from the holders fixed to the balance (red arrows) 112 and the weight can be measured. A thermocouple is fixed below the plate to measure its 113 temperature *Tp.*



117

- 118 Table 1. Some data on Aquasorb  $3005^{TM}$  gel (from Dąbrowska and Lejcuś, 2012 and 119 Aquasorb 3005, 2020).
- 120

#### 121 **3. Above the dew point**

122 The dynamics of adsorption is classically governed by two processes (see e.g. Ganji et al.,

123 2010). One process is water molecules diffusing in the gel by Fick's law due to the difference

124 of water concentration between humid air  $(c_0,$  corresponding to water vapor pressure  $p \sim RH$ )

- 125 and water concentration in gel  $(c<sub>c</sub>)$ . The other process is the stretching relaxation of the
- 126 polymer chains.

127 For typical times corresponding to adsorption amplitudes lower than 60% of the limiting

128 saturation value, the adsorption data measured by  $\omega_i = m_w/m_i$  (*m* corresponds to mass with

129 subscript *w* for water and subscript  $i = s$  *or m* for dry small and medium size gel grains) can 130 be fitted to the power law revealing the mode of relaxation:

- 131
	-

$$
\omega_i = m_w/m_i = A_i t^x \tag{2}
$$

133

134 *Ai* is an amplitude and *x* an exponent whose value corresponds to the gel relaxation process. 135 For pure Fickian diffusion,  $x = 1/2$ . For pure gel relaxation,  $x = 1$ . In general, the exponent is 136 between 1/2 and 1, corresponding to both relaxation-controlled transport and diffusion-137 controlled processes. Equation 2 can thus be generalized. With  $A_i, B_i$  corresponding to 138 amplitudes related to the two processes:

$$
\omega_i = A_i t^{1/2} + B_i t \tag{3}
$$

142 For adsorption amplitudes larger than 60% of the limiting saturation value, the approach to 143 saturation can be described in the case of diffusion by the Fick's law. For a spherical particle 144 of radius *R*, initial radius *R*<sub>i</sub> and surface  $S = 4\pi R^2$  one obtains, neglecting the radius change 145 in the concentration gradient as swelling remains small in the adsorption process:

146

147 
$$
\frac{1}{s} \frac{dm_w}{dt} = -D_p \nabla c = D_p \frac{c_0 - c_c}{R} \sim D_p \frac{c_0 - c_c}{R_i}
$$
(4)

148

149 where  $D_p$  is the water diffusion coefficient in the polymer.

150 The adsorbed mass corresponds to water concentration in the gel,  $c_c = 3 m_w / (4 \pi R_i^3)$ . The 151 solution to this equation leads to the following exponential decay evolution, in terms of ratio 152  $\omega_i$ :

153

$$
\omega_i = \omega_{i,\infty} \left( 1 - e^{-t/\tau_i} \right) \tag{5}
$$

155

156 Here  $\omega_{i,\infty}$  is the maximum rate of water in the saturated gel,

157

$$
\omega_{i,\infty} = \frac{4\pi R_i^3 c_0}{3m_i} \propto RH \tag{6}
$$

159

#### 160 and the typical relaxation time,  $\tau_i$ , reads as

161

$$
\tau_i = \frac{R_i^2}{3D_p} \tag{7}
$$

164 Since the diffusion of vapor around the grains limits the process (as in the case of thin film 165 studies by Delavoipière et al. (2018)), the adsorption dynamics depends on the thickness of 166 the diffuse boundary layer, that is the layer where a Peclet number  $Pe = \frac{UL}{D} < 1$ . Here, *U* is 167 the air flow velocity far from the substrate, *L* is the characteristic length of the substrate and *D* 168 is the diffusivity of water molecules in air. In our study, the hydrodynamic conditions are the 169 same for all studied substrates, small or medium grains, and difference in kinetics can be only 170 attributed to *RH* and the grain size.

171 In the case where the gel relaxation dominates the process, a relation similar to Eq. 5 is found, 172 however with a relaxation time which is independent of gel grain radius and relates to the 173 relaxation of the gel network,

174

175 
$$
\omega_i = \omega'_{i,\infty} \left( 1 - e^{-t/\tau'_i} \right) \tag{8}
$$

- 176
- 177 with  $\tau'_i = const.$

178 The evolution due to diffusion plus gel relaxation can thus be written as:

179

180 
$$
\omega_i = \omega_{i,\infty} \left( 1 - e^{-t/\tau_i} \right) + \omega'_{i,\infty} \left( 1 - e^{-t/\tau'_i} \right)
$$
 (9)

181

182 In Fig. 2 are reported typical adsorption isotherms and in Table 2 the results of the fits to Eqs. 183 2, 3 using data in the range  $\omega_i < 0.6\omega_{i,\infty}$ . For small grains, the exponent of single power law, 184 Eq. 2, are found in the range  $[0.58 - 0.79]$ , with mean value 0.69 closer to 0.5 than to 1, 185 showing that vapor diffusion plays the major role in the relaxation process. This is 186 corroborated with double power law fit, Eq. 3, where the amplitude of the  $t^{1/2}$  term is about 10

187 times larger than the *t* term. For medium grains, the relaxation is too long to obtain data close

188 to saturation, then the fit to exponential decay Eq. 5 is made over all the data range, which 189 gives an estimation of  $\omega_{m,\infty}$ . Data are then fitted to power laws in the range  $\omega_m < 0.6\omega_{m,\infty}$ . 190 The results of the fit to the exponential relaxation, Eq. 5, are reported in Table 2. According to 191 Eq. 5, the relaxation times  $\tau_m/\tau_s \approx (R_m/R_s)^{2} \approx 13.6$ . The measured ratio is smaller,  $\tau_m/\tau_s \approx$ 192 4.88, confirming that gel relaxation also matters. Considering only water diffusion in the 193 polymer, one infers  $D_p \sim 10^{-11} \text{ m}^2 \text{ s}^{-1}$ , a typical value in gels. 194 Data (Fig. 2a) show, as expected (see e.g. Delavoipière et al., 2018), that *RH* is the only 195 parameter for the adsorption amplitude  $\omega_{i,\infty}$  (see the isotherms at  $T_a = T_p = T_d + 11$ K and  $T_d$ 196 + 4K with air at same temperature than the substrate and *RH* = 78%)*.* Adsorption where the 197 plate temperature is at a temperature lower than air  $(T_p = T_d + 4K)$ , air at  $T_a = 20$  °C and *RH*= 198 50% ) would correspond to a mean isotherm at *RH* ≈ 64%. Medium grains isotherms (Fig. 2b) 199 correspond to the last case  $(T_p = T_d + 4K)$ , air at  $T_a = 20^{\circ}\text{C}$  and  $RH = 50\%$ ).

200



203 Fig. 2. Evolution of sorption isotherms ( $\omega_{i=s,m}$ , log-log plot,  $RH < 100\%$ ). The full straight 204 lines are power law fits to data 60% below the saturation value (Eq. 2, darker points)) and the 205 interrupted curves are exponential fits to data above 60 % of the saturation value (Eq. 5) (see

206 Table 2). (a) Small grains. (b) Medium grains, where exponential fit is made with all data (see

207 text).

208



209

210

211 Table 2. Results of the fits of the adsorption data. Uncertainties: One standard deviation.

212

213 **4. Below the dew point** 

214

215 When the substrate temperature is set below the dew point temperature, condensation takes

216 place. Condensation on gels exhibits specific features when compared with condensation on a

217 bare surface.

218

219 *4.1. Region of inhibited condensation.* 



234 and the condensation pattern was determined within a small region.

235



- 236
- 237

238 Fig. 3. Examples of region of inhibited condensation (RIC) around a thin (<1 mm) layer of

- 239 (a, b) small size grain at  $t = 25$  s. (b) is the (a) picture with outlined gel and RIC contours. (c)
- 240 Medium size grains,  $t = 25$  s. ( $T_a = 22$  °C at 47 % RH,  $T_p = T_d 6.7$  K).

Figure 4 reports the evolution of the RIC width  $\delta^*$ , which decreases with time. This RIC 244 decrease can be attributed to the increasing impregnation of the gel with adsorbed water. 245 When the gel is saturated, condensation on gel proceeds with the same way as on the bare 246 substrate, as seen in Section 4.2. The RIC width should be at that time the same as the RIC 247 observed around each water drops or hydrophilic dots (corresponding to the lyophilic patches 248 of Schafle et al., 2003), as a result of the surrounding water vapor gradient (see e.g. Beysens, 249 2018). The mechanism behind the RIC evolution is thus different to what happens with a 250 solute sample (e.g. a salty drop as in Guadarrama-Cetina et al., 2014), which comes from a 251 reduction of saturation pressure (Raoult law) or around an ice crystal where the constant drop 252 in saturation pressure makes the RIC width constant (Nath et al., 2018). (Further analysis is 253 out of the scope of the present study).

254 The evolution of the gel radius increase,  $\Delta R_g = R_g(t) - R_g(0)$ , is also shown in Fig. 3. The 255  $\Delta R_g$  growth rate decreases after about a time  $\sim 100$  s for medium grains, a value near the time 256 where the condensation rate exhibits an inflection corresponding to the lowest influence of the 257 adsorption process (see Fig. 5). The  $\Delta R_q$  increase is due to both adsorption and condensation 258 processes and is proportional to the collected increasing water volume per unit surface, *h ,*  259 (see Eq. 11). The prefactor is, however, difficult to precisely evaluate because it depends on 260 the grains packing. It is clear in Fig. 4b that the rate of growth is larger at early times, as in 261 Fig. 5. Note that the  $\Delta R_g$  behavior can be affected by the grains rearrangement during their 262 swelling, which presumably explains the different behavior between small and medium grains 263 and the oscillations in the  $R_g$  evolution as observed in Fig. 4b.





Fig. 4. Evolution of the RIC width  $\delta^*$  (squares) and gel radius increase  $\Delta R_g$  (circles) as

268 observed in Fig. 3 of (a) small grains and (b) medium grains. The curves are data smoothing.

269 (*T<sub>a</sub>* = 20 °C, *RH*= 50%, *T<sub>p</sub>* = *T<sub>d</sub>* − 4 K).

270

- 271 *4.2. Condensation rates*
- 272

273 In order to compare the adsorption volume with respect to condensation on a bare substrate, 274 one considers the surfacic adsorbed volume or equivalent water film thickness,  $h$ . With  $\rho$  the 275 water density, this layer is expected to grow proportionally to time as 276

277  $h = \frac{m_w}{\rho s_c} \sim t$  (11)







280 Fig. 5. Evolution of condensation (*SR* = 1.32) on gel medium grains (blue dots) and bare 281 substrate (red dots) under same conditions  $(T_a = 20 \text{ °C}, RH = 50 \text{ °6}, T_p = T_d - 4 \text{ K})$ . Left 282 ordinate: water volume per unit projected area, *h*. The continuous curve is a fit of gel data to 283 Eq. 12 and the interrupted line is a fit of bare substrate to Eq. 11. The dotted line is the initial 284 slope for condensation on gel. For the sake of comparison, the sorption isotherm at  $T_a = 20$ 285 °C,  $RH = 50\%$ ,  $T_p = T_d + 4$  K is also reported (orange dots; right ordinate; see Fig. 2b).

287 In Fig. 5 is reported condensation on gels and bare substrate. The bare substrate condensation 288 is proportional to time with slope  $(dh/dt)_b = 1.4207 \times 10^{-3} \pm 2 \times 10^{-6}$  mm·min<sup>-1</sup> (uncertainty: 289 1 SD). Gel exhibits a larger initial rate up to time  $\approx 100$  min. where the rate progressively 290 decreases to reach the bare substrate value, corresponding to condensation and imbibition of 291 the gel as if it were a bare substrate. The swelling ratio at which this inflection occurs  $(0.2)$ 292 is far less than the maximum swelling ratio of  $\sim$  370 and cannot be attributed to the vicinity of 293 this limit. One notes that further to this inflection the slope becomes comparable to what is 294 found on the bare surface. This rate decrease towards the bare substrate value can be related to 295 the corresponding decrease of the RIC width and decrease of the rate of gel radius growth, 296  $\Delta R_a$ , which occurs during the same time period, and which corresponds to the approach of the 297 saturation of adsorption. In order to assess this point, the gel data have been fitted to the sum 298 of condensation as if the gel were a bare substrate, Eq. 11 and the adsorption evolution, in 299 volume per unit surface as in Eq. 11:

300

$$
h = \left(\frac{dh}{dt}\right)_b t + h_{m,\infty} \left(1 - e^{-t/\tau_m}\right) \tag{12}
$$

302

303 From Table 2, the amplitude value of the adsorption data at  $T_d + 4K$  can be expressed in 304 volume per projected gel surface area,  $h_{m,\infty} = \omega_{i,\infty} m_i/S_c = (0.201 \pm 0.002)$  mm. Figure 5 305 reports the condensation data on gel and bare substrate at  $T_d - 4K$  and the adsorption data at 306  $T_d$ +4K. Gel condensation data are fitted to Eq. 12 with  $(dh/dt)$ <sub>b</sub> free and imposed. The results 307 are listed in Table 3. When all parameters are left free,  $(dh/dt)$ <sup>b</sup> is found somewhat smaller 308 than on the bare substrate, presumably because of the lack of data at very long times. The 309 adsorption time is found somewhat lower (195 s) that at  $T_d + 4K$  (300 s). The amplitude (0.24 310 mm) compares relatively well with what is expected (0.207 mm). With (*dh/dt*)*b* imposed, the 311 typical adsorption time is 3 time smaller than expected and the adsorption amplitude is too 312 small (0.106 mm). When the adsorption time is fixed at the value at  $T_d$  + 4K ( $\approx$  300 s), the 313 amplitude (0.165 mm) increases but still remains smaller than the value at  $T_d$ +4K. With the 314 latter amplitude imposed at 0.207 mm the adsorption time (391 s) becomes closer to the time 315 at  $T_d$  + 4K (300 s), with however a  $\chi^2$  somewhat larger than the two previous fits. (A more 316 detailed analysis would need more data and is out of the scope of the present study). 317



318

320 Table 3. Results of the fit to Eq. 11 of condensation data on gel (Fig. 5). The values under 321 brackets are imposed in the fit. The gel mass is  $m_m = 6.94$  g. Notations: see text.

322

323 It thus results a net increase of water absorbed on gel when compared to the bare substrate 324 under same conditions, with value on the order of 0.1 mm. This behavior can be explained by 325 the fact that two phenomena are present: (i) an initial adsorption of water vapor, giving a 326 vapor concentration gradient above the surface of the gel larger than on the bare substrate, at 327 the origin of a RIC, followed by (ii) a steady condensation with the same concentration 328 gradient as found above the water drops on the bare substrate. Water will continue to 329 condense on the gel until it reaches its maximum swelling. As a result of the initial large 330 water absorption rate, water absorbed by the gel is thus found in greater amount than water 331 condensed on the bare plate.

332 Note that if instead of gel particles, one considers a gel film, one should obtain similar 333 enhancement as the adsorption phenomenon is not due to the macroscopic shape of the gel but 334 to the intrinsic properties of the polymer network. A gel film will then equally serve to 335 condense water vapor and the swelling mechanism due to adsorption plus condensation will 336 be the same. The only difference would be the value of the exposed area to condensation, 337 which is smaller, then the condensation rate will be lower. The maximum swelling volume 338 capacity, proportional to the gel volume, will also be smaller. As a matter of fact, such gel 339 film condensation has already been reported by Delavoipière et al., 2018. On the other hand,

340 if there were any non-water vapor absorbing hydrophilic powder on the surface instead of the 341 gel particles, one would simply expect no adsorption. Only filmwise condensation will occur 342 (coefficient  $h_{m,\infty} = 0$  in Eq. 12).

343

#### 344 **5. Concluding Remarks**

345

346 Common hydrogels grains used for soil in agriculture (Aquasorb  $3005<sup>TM</sup>$ ) can collect water 347 even for relative humidity less than 100%. They also exhibit interesting properties when used 348 in supersaturation conditions (conditions of dew formation) since they collect more water than 349 a bare hydrophobic substrate with same projected surface area. The measured gain is on order 350 0.1 mm of water / day, which is an important gain when compared to the current values found 351 for dew yield (0.1 - 0.6 mm/day). This enhanced condensation of water is due to the initial 352 water vapor adsorption, which adds to condensation. As noted in the introduction, such 353 condensed water stored in gels can be either used in agriculture where the osmotic pressure 354 exerted by the roots is sufficiently high to extract water or removed by moderate  $($   $\sim$  1 bar) 355 mechanical pressure for human use (Milimouk et al., 2001). Another way is to evaporate 356 water and condense it in e.g. a solar still (see e.g. Zhao et al., 2019 where details on needed 357 energy and time duration are given). Although the use is one and only in agriculture where the 358 grains are definitely mixed with the soil, water extraction by pressure or evaporation has to be 359 cyclically repeated. There is, however, a possible limitation to the number of cycles due to the 360 absorption of  $CO_2$  gas from the atmosphere.  $HCO_3^-$  ions are indeed added in the solutions, 361 screening the polymer charges and thus progressively reducing the swelling amplitude (see 362 e.g. Rička and Tanaka,1984 for ions influence). Precise evaluations remain to be carried out. 363 In addition, although the above study has been performed in laboratory by contact cooling, 364 preliminary experiments under outdoor radiative cooling (Beysens, 1998) give, at least



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