

A simulation tool for temperature and moisture dependent transport of VOC's in buildings

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SUMMARY:

This work concerns computer simulations of butanol emissions from a heated concrete slab with PVC flooring. Experiments have proved that emissions originate from a chemical reaction when flooring adhesive comes into contact with water entrapped in concrete and if water is of high alkalinity. Due to temperature gradient, moisture from a bottom part of the slab is driven upwards to the flooring surface, where it reaches the adhesive. Our investigation presents moisture content in the concrete after shorter drying, moisture inverse redistribution due to heating and, as a consequence, development and duration of butanol emissions from the slab. For this analysis we have developed a simulation tool, HAM-VOC-Tools, which is capable to analyse distribution of volatile organic compounds (VOCs) in porous building materials under temperature and moisture gradients. Results of HAM-VOC simulations agree well with experiments.

1. Introduction

Building materials can release more than 300 different volatile organic compounds (VOCs). Some of them originate from manufacturing processes, others from a contaminated environment or from chemical reactions that may take place in materials in use. Once present, VOCs can be released under longer time in a building in use. If their quantities exceed certain levels, they may cause human discomfort in some of the following forms: dry throat, eye irritation, sickness, headache, etc. These symptoms of the so-called "sick building" confirm that VOCs are direct air contaminants, and modern indoor air quality (IAQ) considerations enclose (among other things) the assessment of VOCs quantities in indoor environment.

Experimental investigations on material emissions at present are: identification of VOCs in building materials (Won et.al, 2003, Alevantis 2003), determination of their transport properties, (Bodalal et. al., 1999, Meninghaus, 1999, Hansson, 2003), and assessment of acceptable concentration levels for humans in indoor environment (Mølhave et.al. 1997, Alevantis 2003). It is shown that similar physical laws that describe transport of heat and moisture in a building are valid for the storage and release of VOCs (Hansson, 2003, Salonvaara et.al. 2003). This implies that building simulation tools can be used for studying the VOC's distribution in a building, in an analogues way as the transport of heat and moisture.

Transport of VOCs in buildings is driven not only by concentration differences, but also by temperature and moisture gradients. One example is the development of secondary emissions from a wet and heated concrete specimen. Available VOCs simulation tools do not take into account this coupling (Yang et. al. 2001, Zhao et. al. 2002, Haghighat et. al. 2003, Zhang et. al. 2004). Our investigations treat this particular

case, and for that purpose we have developed a simulation tool for combined heat, moisture and VOCs transport analyses in building materials. The tool represents an integrated version of two other simulation programs: one for heat, air and moisture transfer analyses in whole buildings, HAM-Tools (Sasic, 2004), and the other for VOCs analyses in whole buildings, VOC-Tools (Karlsson et al., 2005b). Our simulations on secondary emissions of butanol from a wet and heated concrete specimen agree well with experiments (Törn, 2005), but they also clarify the production, duration and transport of butanol in and out of the specimen.

2. Secondary emissions from a concrete

2.1 Experiments of Sjöberg (2001)

In his doctoral thesis Anders Sjöberg (2001) investigated secondary emissions from a concrete floor with PVC flooring bonded on top. By definition, secondary emissions are gaseous compounds which are produced by a chemical reaction that takes place in a material. In the case investigated, these were alcohols butanol (1- or n-butanol) and 2-ethylhexanol. These alcohols are products of an alkaline hydrolysis (decomposition) of adhesives with binders based on acrylate copolymers. Two conditions must be simultaneously satisfied to cause the production of alcohols. The one is the alkalinity of concrete, or more precisely, of water inside concrete. A common value of 13 pH indicates that this condition is often fulfilled. The other one is that moisture in concrete appears in a liquid phase, which is indirectly described by a critical value of relative humidity. Sjöberg performed experiments on a number of different concrete samples, where he measured emission flow rates. He has also quantified storage and transport properties for the alcohols concerned and our simulations rely in great deal on these data. All measurements were carried out under isothermal conditions.

2.2 Experiments of Törn (2005)

Within a master thesis Törn (2005) performed similar measurements on secondary emissions from concrete, but with specimens heated from one side. Such conditions can be found in a concrete slab with floor heating. Since our simulations attempt to clarify measurements on butanol emissions, the experimental setup is briefly described hereafter.

A concrete with water-to-cement ratio of 0.65 is cast in an aluminium test cup with 0.25 m diameter and 0.1 m height. During three days of hardening, the concrete is covered on top with a plastic foil. After the foil is removed, the concrete is left to dry in laboratory environment (stable conditions). The drying takes three weeks, after which an adhesive is spread on the top surface and PVC flooring is bonded, as it is shown in Fig.1. The specimen is left to rest for one day more before it is subjected to heat from the cup bottom side. First measurements of butanol emissions from the cup were taken 74 days after the heating had started.

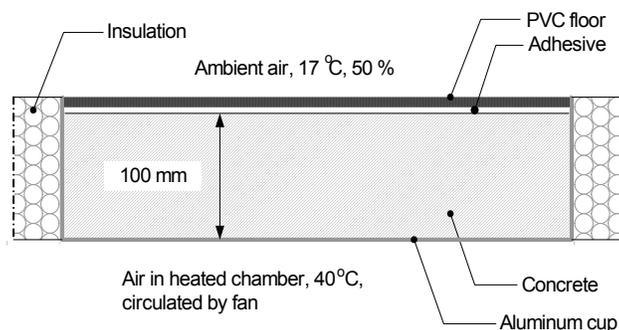


FIG. 1: Concrete in a test cup, heated from the bottom

Our attention is focused on moisture states in the specimen and therefore, three periods are of interest for simulations:

- **DRYING**, i.e. three weeks of drying in laboratory
- **RESTING**, i.e. one day of resting with bonded PVC flooring

- **HEATING**, i.e. from the very moment and on after the heat is applied

3. HAM-VOC simulations

As presented in the introductory section, a simulation tool that we have used here, HAM-VOC-Tools, is an integrated version of HAM-Tools (Sasic, 2004) and VOC-Tools (Karlsson et al., 2005b). The first tool is able to perform one-dimensional heat, air and moisture transfer analyses in building envelope parts and whole buildings, and the second tool regards storage and transfer of VOCs also in the same domains. As parts of International Building Physics Toolbox in Simulink (IBPT, 2002), the tools are developed as open sources, validated and well documented (Hagentoft, 2002, Sasic, 2004, Karlsson et. al., 2005a).

3.1 Moisture profiles during DRYING and RESTING

Since concrete can dry only from the top surface, its bottom part remains moist for a longer time. At the end of the drying period, the moisture distribution inside the specimen is denoted with line “0 h” in Fig.2.

PVC flooring represents a substantial resistance to moisture transfer and the drying is slowed down when it is applied. At the end of the resting period, the moisture profile takes the form, which is denoted as line “24 h” in Fig. 2.

We consider a water-based adhesive. It is estimated that in 300 g of adhesive per 1 m² of flooring, there is about 90 g of water, (Sjöberg, 2001). In practice, adhesive should be left to dry a couple of hours before the flooring is bonded. In the experiment, the flooring is laid on the wet adhesive (immediately), and moisture from the adhesive is redistributed in the concrete. Thus, the moisture transition from the state “0 h” to “24 h” goes over intermediate states which are shown in Fig.2 on right, in a magnified scale. We can see that moisture content at the top briefly goes over 80 % and then drops to 67 %, tending to the value of “24 h”.

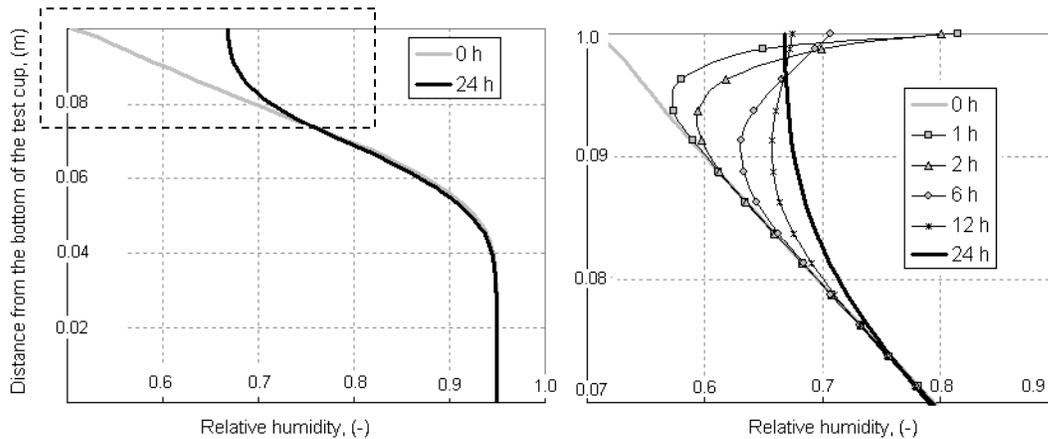


FIG.2: Left: Moisture profiles in the specimen at the beginning and at the end of the resting period. Right: Intermediate moisture profiles during the resting period, enclosed in the squared area from the picture on the left and in magnified scale.

3.2 Temperature and moisture profiles during HEATING

Warm air from the bottom side heats the specimen. Temperature profiles develop in a couple of hours, as it is shown in Fig.3 on the left, and remain constant throughout the entire heating period.

Driven by the temperature gradient, moisture from the bottom of the cup is redistributed upwards. The process is slow compared to the heat transfer, but the moisture inverse is obvious. Eight weeks after the heating has started, the moisture content at the top reaches the critical value of 90 % relative humidity (Sjöberg, 2001). We assume here that conditions for alkaline hydrolysis of the adhesive are fulfilled. Note that the critical moisture content holds for a longer time, certainly for one year.

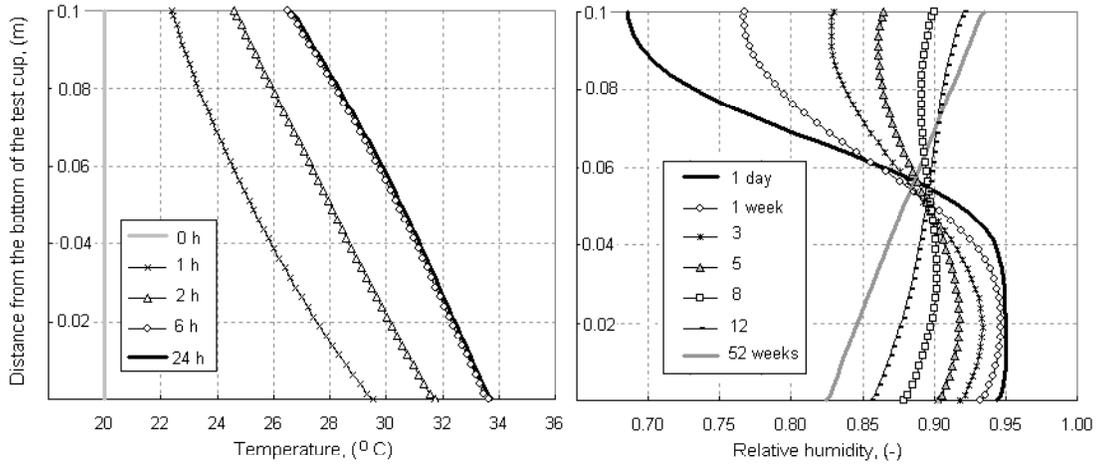


FIG.3: Left: Temperature profiles in the specimen during the first day of heating. Right: Moisture profiles in the specimen during the first year of heating.

Törn (2005) measured also temperature and relative humidity in the specimens. It turned out that these measurements are of limited reliability and therefore, they are used here only to adjust boundary conditions in the model for heat and moisture transfer.

4. HAM-VOC model

4.1 Model for a butanol source

The rate of production of butanol q_{BuOH} starts from zero after the critical moisture level $\phi_{crit} = 0.9$ is achieved, and increases linearly to a maximum value $q_{BuOH,max}$ at $\phi = 1$:

$$q_{BuOH}(\phi) = \begin{cases} \frac{q_{BuOH,max}}{1 - \phi_{crit}} \cdot (\phi - \phi_{crit}), & \phi \geq \phi_{crit} \\ 0, & \phi < \phi_{crit} \end{cases} \quad (1)$$

The quantity of butanol produced is limited by the quantity of acrylate copolymers that can be decomposed in the chemical reaction. It is assumed that 8 % (mass) of adhesive can be turned into butanol. Thus, if 300 g of adhesive is applied per 1 m² of floor area, 24 g/m² of butanol can be produced at maximum (Sjöberg, 2001).

4.2 Diffusion of butanol in concrete

Diffusion of butanol inside concrete is modelled by the following equation:

$$K_{BuOH}(\phi(x), S) \cdot \frac{\partial c_{BuOH}(x, t)}{\partial t} = D_{BuOH}(\phi(x)) \cdot \frac{\partial^2 c_{BuOH}(x, t)}{\partial x^2} + \frac{\partial q_{BuOH}(\phi(x))}{\partial x} \quad (2)$$

where $K_{BuOH}(-)$ is the internal partition coefficient, D_{BuOH} (m²/s) is the diffusion coefficient for butanol in concrete, $c_{BuOH}(x, t)$ (kg_{voc}/m³_{air}) is the vapour phase concentration of butanol inside concrete and x (m) is the space coordinate measured from the top of the cup.

The squared term in Eq. 2, i.e. the source of butanol, is active only inside a concrete layer next to adhesive. In the present model, the thickness of that layer is determined by a numerical discretization of the domain and it is equal to 1 mm.

Internal partition coefficient represents a lumped storage capacity of butanol in concrete. According to Sjöberg (2001), K_{BuOH} is defined as:

$$K_{BuOH}(\phi, S) = \left(\varepsilon - \frac{w(\phi)}{\rho_w} \right) + \left(S \cdot \frac{w(\phi)}{\rho_w} \cdot \frac{1}{c_{BuOH, sat}} \right) \quad (3)$$

where ε (-) is the porosity of concrete, $w(\phi)$ ($\text{kg}/\text{m}^3_{\text{mtrl}}$) is the moisture content in concrete, ρ_w is the density of water, S ($\text{kg}/\text{m}^3_{\text{water}}$) is the solubility of butanol in water, $c_{BuOH, sat}$ ($\text{kg}/\text{m}^3_{\text{air}}$) is the saturation concentration of butanol in air.

Butanol solubility in water and vapour saturation concentration in air depend on temperature. However, variations are small for a given temperature range (between 25-35°C), and these parameters are presented with values for 30°C (CRC, 2000).

The ratio between diffusion and internal partition coefficients represents a vapour permeability of butanol in concrete, δ_{BuOH} :

$$\delta_{BuOH}(\phi, S) = D_{BuOH}(\phi) / K_{BuOH}(\phi, S) \quad (4)$$

4.3 Binding models

A mechanism of butanol fixation in concrete is not well understood. Chemical references say that butanol solubility in water is limited to $S = 0.077 \text{ kg}/\text{m}^3_{\text{water}}$ at 20°C. It is not certain that the same model can be applied for butanol fixation in air pores, and therefore, Sjöberg (2001) analyzed other binding models. The models are distinguished by the S value and the two of them are presented here:

- “Bound 0”, for $S=0.077 \text{ kg}/\text{m}^3_{\text{water}}$ and
- “Bound 1”, for $S=2.8 \text{ kg}/\text{m}^3_{\text{water}}$.

While the value of S for Bound 0 has a physical reference, the value for Bound 1 is determined from a mass balance. Internal partition coefficients for the selected binding models are calculated by Eq. 3 and illustrated in Fig.4.

The vapour permeability of butanol is also determined according to the binding model, and values for $\phi = 0.65$ are given in Table 1, (Sjöberg, 2001). Using the analogy with water vapour transfer through porous media, where a vapour flow is proportional to the amount of available air pores, δ_{BuOH} is modelled as:

$$\delta_{BuOH}(\phi) \sim \varepsilon - w(\phi) / \rho_w \quad (5)$$

The vapour diffusion coefficients are shown in Fig.4. Note that $\delta_{BuOH}(\phi = 0.65)$ matches the value from Sjöberg (2001).

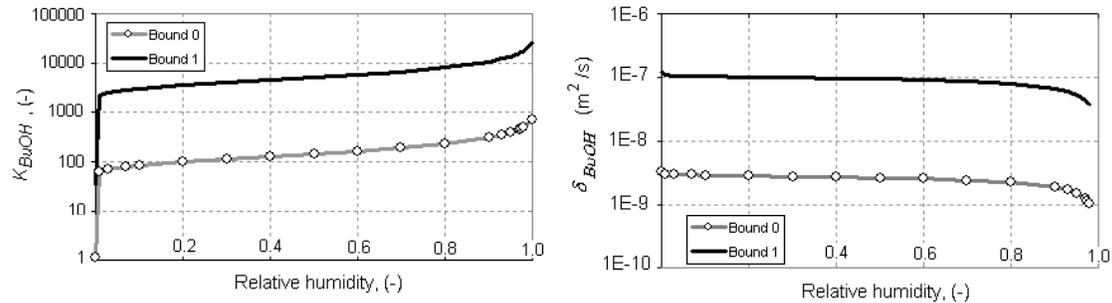


FIG. 4: Internal partition coefficient K_{BuOH} (on the left) and vapour permeability δ_{BuOH} (on the right) for two binding models (see Table 1).

The maximal intensity of a butanol source, $q_{BuOH, max}$, from Eq. 1, depends also on the binding model and the values are given in Table 1.

5. Results

Butanol vapour flow from the specimen or the emission factor EF can be measured by a special measuring chamber, in which the butanol is captured by pure air, extracted and concentrated on an adsorber (Sjöberg, 2001). Having a zero butanol concentration in the capturing air, the emission factor is calculated as:

$$EF = c_{BuOH,surf} / R_{c,BuOH} \quad (6)$$

where $c_{BuOH,surf}$ is the concentration of butanol in air pores at the top of the concrete, and $R_{c,BuOH}$ is the resistance of PVC flooring to butanol vapour flow. The flow is commonly expressed in $\mu\text{g}/\text{m}^2\text{h}$. The values for butanol vapour flow resistance and water vapour flow resistance for the PVC flooring, R_{p,H_2O} , are given in Table 1.

Emissions from the specimen are calculated for the two binding models, Bound 0 and Bound 1, and results are shown in Fig. 5. The total amount of butanol, which is stored in the specimen is shown in Fig. 6.

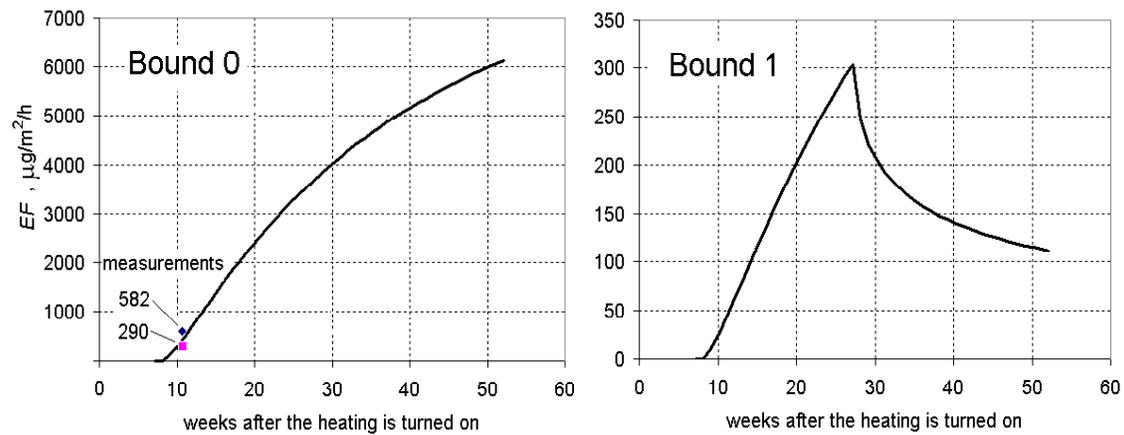


FIG. 5: Calculated emissions from the specimen for the two binding models.

The two different binding models give very different results for EF . According to Bound 0, where the storage capacity of butanol in concrete is lower, emissions are approximately 10 times higher than in Bound 1. Faster penetration of butanol into concrete is also supported by a higher vapour diffusion coefficient for Bound 1, Fig.6. Finally, the greater rate of production of butanol in Bound 1 results in a faster exploration of the source - 27 weeks after the heating has started (see the peak emission in Fig. 5 and the limit in Fig.6).

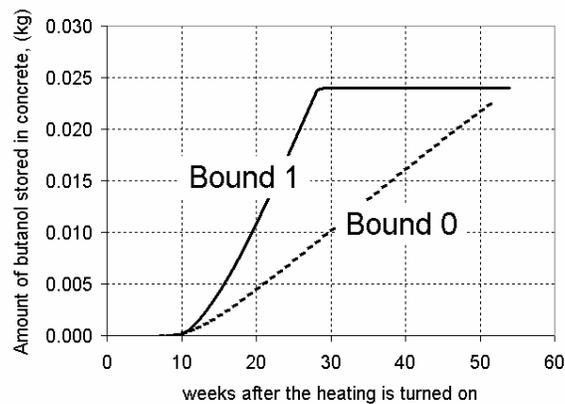


FIG. 6: The calculated quantity of butanol that is stored in the specimen for the two binding models. The total amount produced is 24 g.

6. Discussion

It is straightforward to decide which binding model represents better the true case. Measurements of Törn (2005) from two samples are indicated with markers in Fig. 5. They agree very well with simulated emissions for Bound 0, and they are much higher than for Bound 1.

There are other measurements (cited in Sjöberg, 2001), which show butanol emissions of several hundreds of $\mu\text{g}/\text{m}^2\text{h}$ from older specimens (5 years). Therefore, we have analyzed longer application time of the concrete floor with seasonal interruptions in heating (5 months). Variations in moisture distribution for this case are shown in Fig. 7 on the left, and the corresponding emissions for Bound 0 are illustrated on the right. We can see that Bound 0 gives high rates for years. In the same situation, emissions according to Bound 1 drops to $50 \mu\text{g}/\text{m}^2\text{h}$ already during the second year.

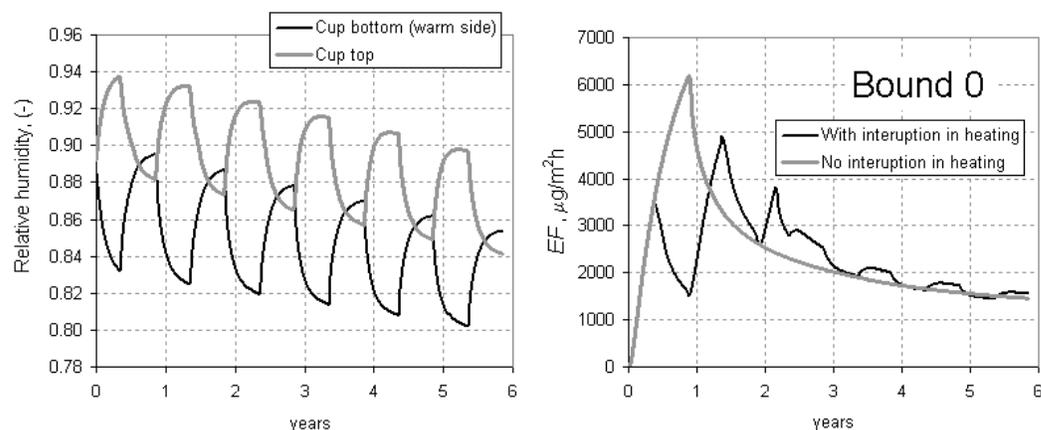


FIG. 7: Left: Relative humidity variations in the specimen with seasonal interruptions in heating. Right: Emissions from the specimen for Bound 0, with and without interruption in heating.

Table 1: Input data for simulations, (Sjöberg, 2001)

Quantity	Unit	Bound 0	Bound 1
$q_{\text{BuOH},\text{max}}$	$\text{kg}/\text{m}^2\text{s}$	$2.6 \text{ E-}9$	$7.3 \text{ E-}9$
S	kg/m^3	0.077	2.8
$\tilde{\delta}_{\text{BuOH}} (\phi = 0.65)$	m^2/s	$2.5 \text{ E-}9$	$93 \text{ E-}9$
$R_{\text{c,BuOH}}$	s/m	$3.7 \text{ E-}6$	
$R_{\text{p,H}_2\text{O}}$	$\text{m}^2\cdot\text{s}\cdot\text{Pa}/\text{kg}$	$3.7 \text{ E-}12$	

separated by the test material. Contaminated air is introduced in one chamber, while pure air constantly ventilates the other chamber. The amount of stored and diffused toluene is determined from mass balances. The same could be possible for butanol and concrete, and even for different relative humidities. Finally, with known storage capacity and vapour diffusivity, the intensity of butanol source could be estimated from measurements of Sjöberg (2001) or of Törn (2005).

There is another reason to give legitimacy to Bound 0 – a definition of the storage capacity of butanol in a wet concrete has its physical background (see section 4.3). If so, there are two parameters to be estimated – vapour diffusivity and intensity of butanol source. We believe that the vapour diffusivity can be obtained from measurements, similar to those performed by Hansson (2003). In brief, Hansson studied diffusion and sorption of toluene in a gypsum board by an experimental setup, consisting of two steel chambers

7. Conclusions

Our experience from the work presented is summarized in the following conclusions:

- Secondary emissions of butanol from a wet and heated concrete specimen represent a complex case of coupled heat, moisture and VOCs transport.
- An integrated simulation tool, such as the one used here, can be a reliable way to clarify and explore the combined processes. Such a tool can be used to organize similar experiments by identifying critical moments and determining the duration of those.

- Material properties are crucial for the reliability of simulations results. While moisture transport properties are well defined, further investigations are needed on transfer and storage of butanol in concrete.
- It is straight forward to integrate simulation tools with the common developing platform, such as the one described in IBPT (2002), and by using the graphical user interface.
- For the future work it would be interesting to extend the investigation on IAQ of an adjacent air space, where such floor is a part of a building construction. The same calculation tool can be used for the investigation.

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