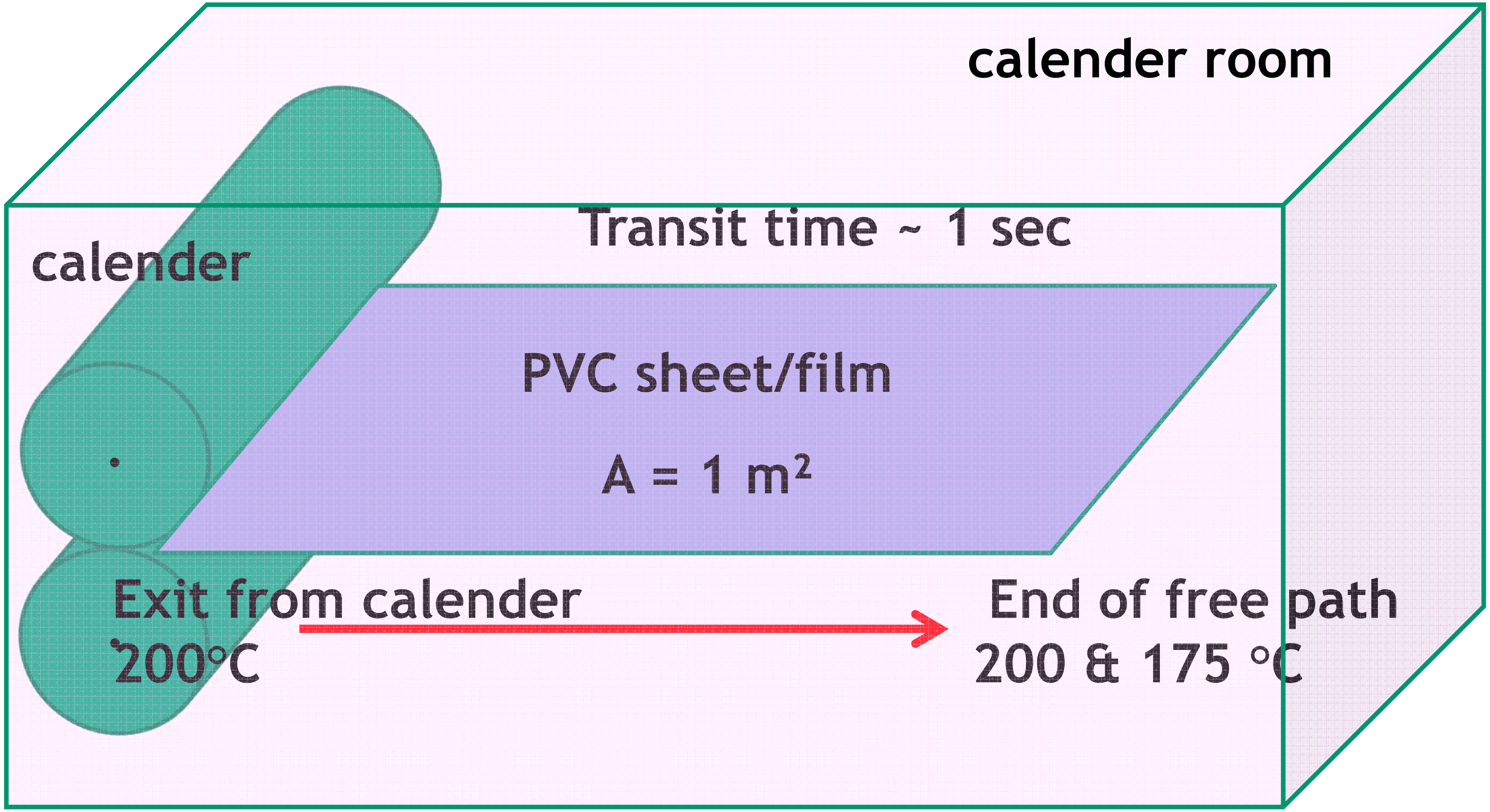
Modelling exposition with Azodicarbonamide (ADCA) during manufacturing of plane Polyvinylchloride (PVC) products

P. Mercea and O. Piringer - *FABES* GmbH
Schragenhofstr. 35, 80992 Munich/Germany
www.fabes-online.de

J. Eckstein - PolyComply Hoechst
Industriepark Höchst, Building F 821, 65926 Frankfurt a.M./Germany
www.polycomply-hoechst.com

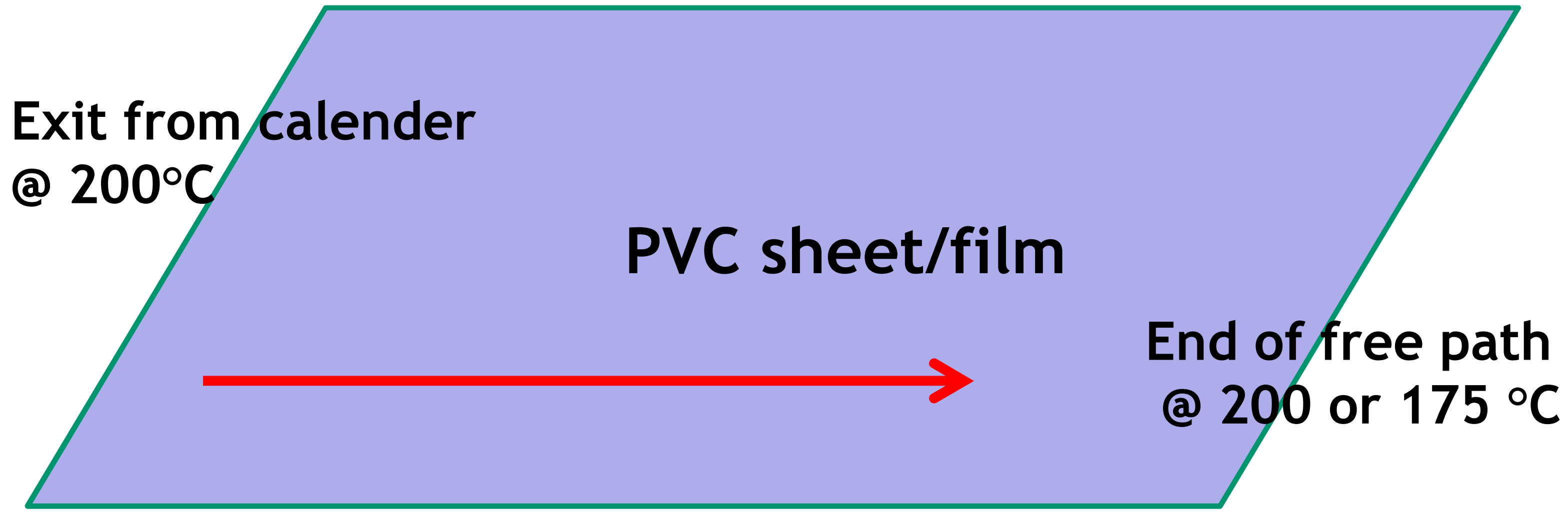
1 . Exposition during calendering of non-plasticized PVC sheet/films



Volume of calender room: V = 10 x 8 x 7m = 560 m³

- fresh air make up

1. Exposition during calendering of non-plasticized PVC sheet/films



PVC sheet/film - thickness 100 to 500 μm, width L= 50 cm
- density @ 25°C   1.35 to 1.40 g/cm³
- initial concentration: ADCA - Cp(0) = 0.1% w/w
- productivity - P ~ 1m²/s = 3600 m²/hour
- time/temperature conditions of free path:
  - i) 200°C for 1 sec - isothermal transit
  - ii) cooling down from 200 °C to 175°C in 1sec

1 . Exposition during calendering of non-plasticized PVC sheet/films

A scenario for the exposition with ADCA

a. Between 200 and 175°C ADCA molecules can diffuse (quite easily) through the PVC matrix to the surface of the sheet/film.

b. From the surface of the PVC sheet/film ADCA can decompose and/or evaporate, at a certain rate, into the surrounding atmosphere.

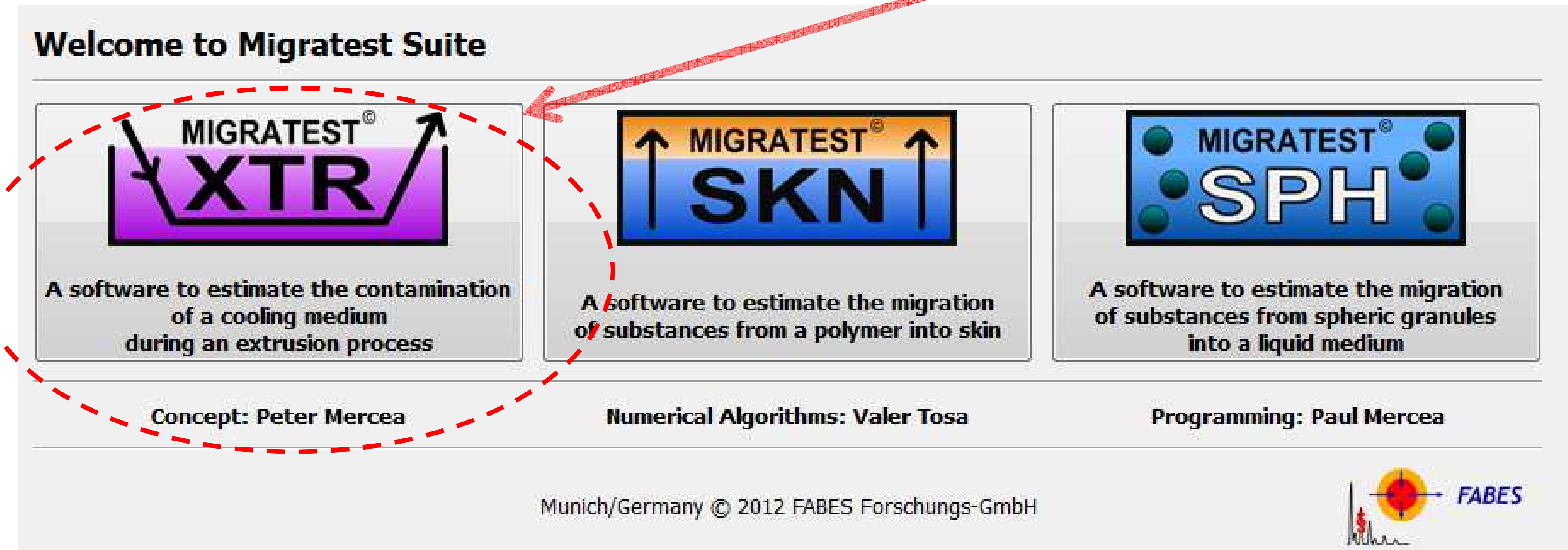
c. ADCA (in form of vapour) can then contaminate the surrounding atmosphere by means of diffusion and convection in air and the circulation of the air in the calender room.

d. Exposure resulting from air contanimated with ADCA vapours inhaled by people working in the calender room.

1 . Exposition during calendering of non-plasticized PVC sheet/films

1a. Estimation of ADCA diffusion to the surface of PVC the sheet/film during the transit through the free path.

In a first approximation we use the special software MIGRATEST XTR developed by *FABES GmbH* for the estimation of contamination of a contact medium during an extrusion or calendering process



1 . Exposition during calendering of non-plasticized PVC sheet/films

1a.

The software MIGRATEST© XTR solves with numerical methods Fick‘s mass transport equations:

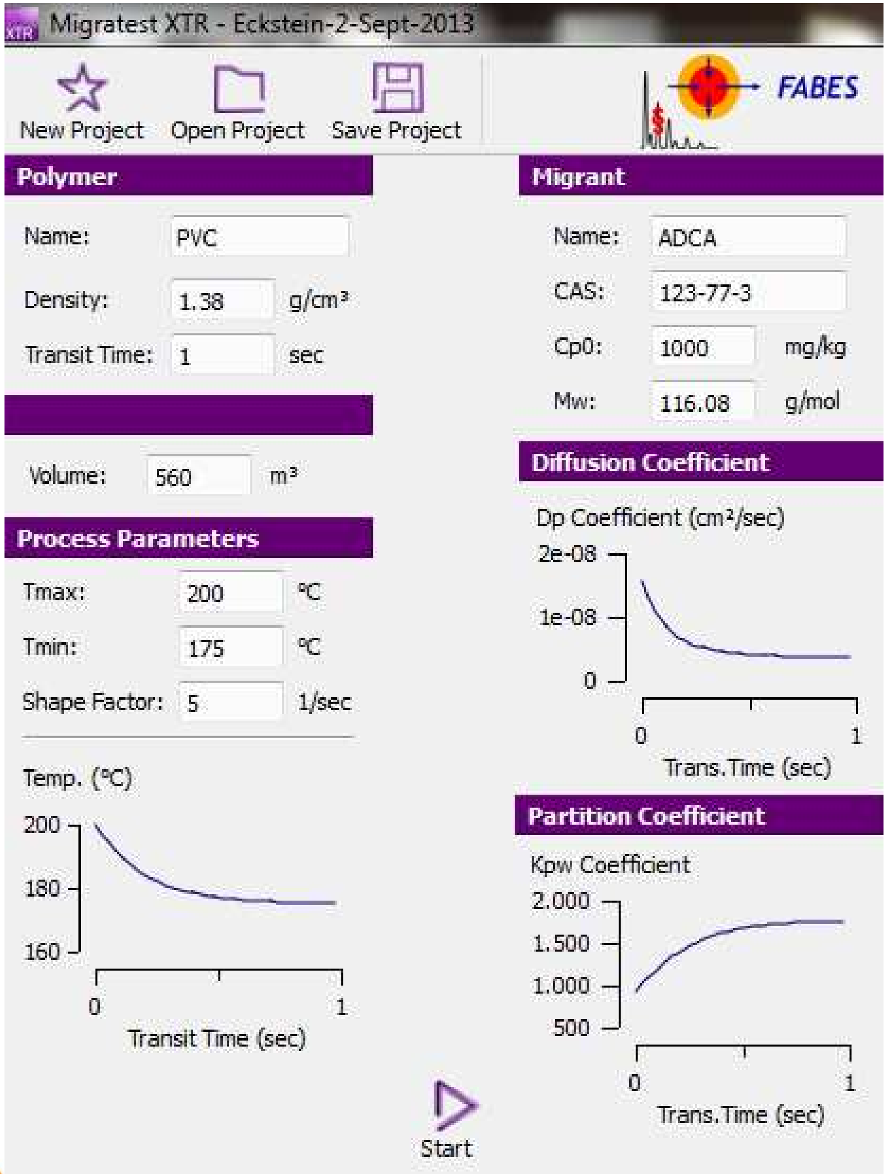
$$\frac{\partial c_k}{\partial t} = D_k \frac{\partial^2 c_k}{\partial x^2}$$

taking into account the fact that during the free path transit the temperature of the polymer sheet/film may decrease (even considerablly) in a very short time.

MT XTR takes into account that during transit in the PVC sheet/film the parameters determining the diffusion process (diffusion and partition coefficients) may change very quickly during the transit time.

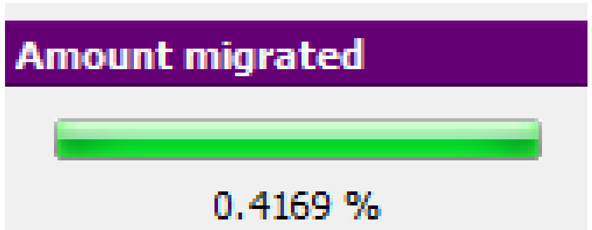
1a.

Inputs for MT XTR:

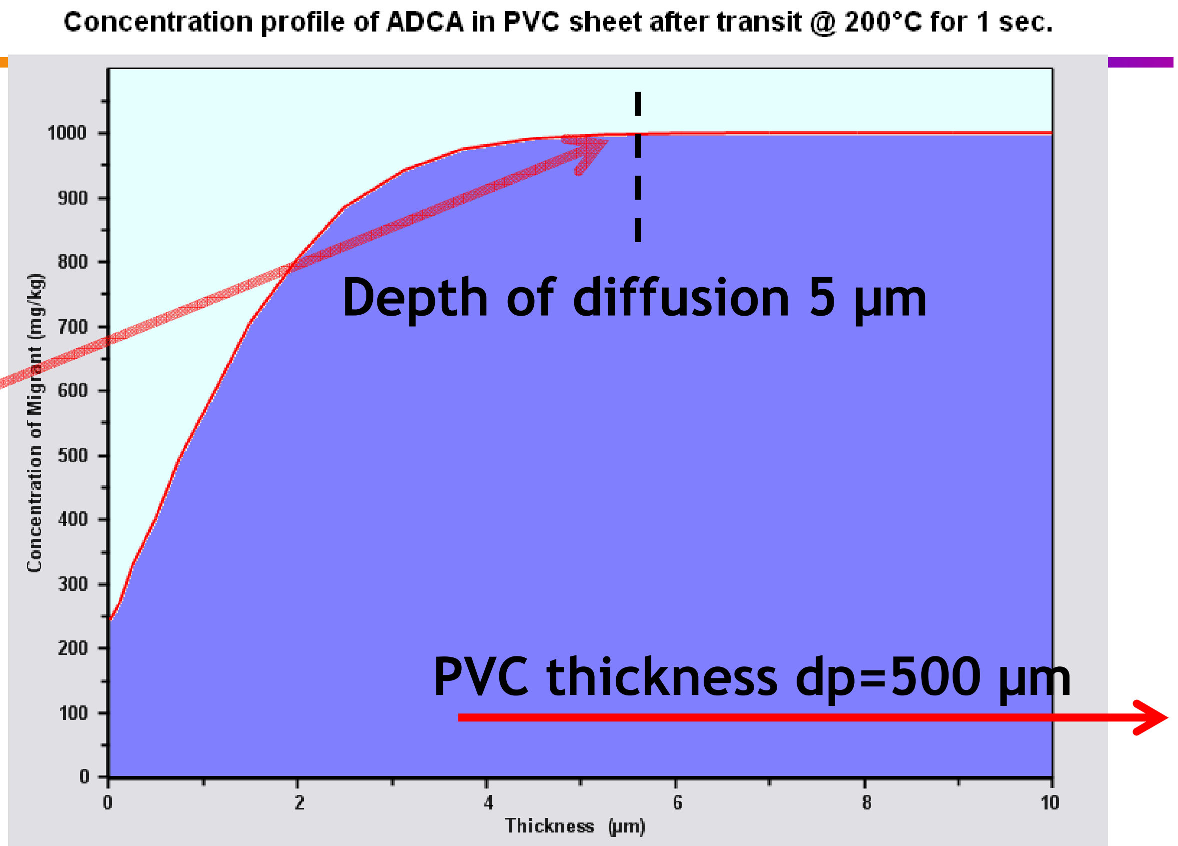


Result:

1a.1) The relative amount of ADCA which may migrate to the surface of a 500 µm thick PVC sheet/film during the transit time after calendering is about:



1a. Results:



ADCA diffuses only from a very thin portion of the PVC sheet/film.

1a.2) The amount of ADCA which may diffuse during the transit time, to the surface of the PVC sheet/film is: ~ 2.2 mg/m²

1a.3) For PVC sheet/films of dp = 100 to 500 µm thickness the amount of ADCA which migrates to the surface during transit does not depend practically on the thickness dp.

1b. Estimation of the rate of ADCA decomposition and evaporation from the surface of the of PVC the sheet/film during the transit time.

1b.1 Between 200 and 175 °C the ADCA decomposes thermally resulting nitrogen, carbon monoxide and dioxide as well as amonia gases.

1b.2 Technically speaking this ADCA decomposition process is assumed to be „instantaneous“ and „complete“.

1b.3 Physically one can assume that during transit at least 95% of the ADCA, which reached the surface of the PVC sheet/film, decomposes in the above gases.

1b.4 Results that one can assume that, in a „worst case“, the remaining 5% of the ADCA, which reached the surface of the PVC sheet/film, evaporates and diffuses into the surrounding air as ADCA vapours.

1c. Estimation of ADCA vapour contamination of the surrounding air by means of diffusion, convection and circulation.

1c.1 With result 1a.2) and 1b.4) one can calculate in a „worst case“ the amount of ADCA vapour released into the atmosphere by the unit area of PVC sheet/film:

~ 2.2mg/m² * 5% = 0.12 mg/m²

1c.2 For a productivity of 3600 m²/hour this means in a “worst case“ the release of 390 mg/hour of ADCA vapour in the calender room.

1c.3 The ADCA vapours contaminate the surrounding atmosphere by diffusion an convection in and circulation of the air. At room temperature these processes are quite quick.

1c.

1c.4 Assuming that in a „worst case“ no fresh air (make up air) comes into the calender room, after 1 hour of calendering, the mean ADCA concentration in air would be:

$$390\text{mg} : 560\text{m}^3 \sim 0.7\ \text{mg/m}^3$$

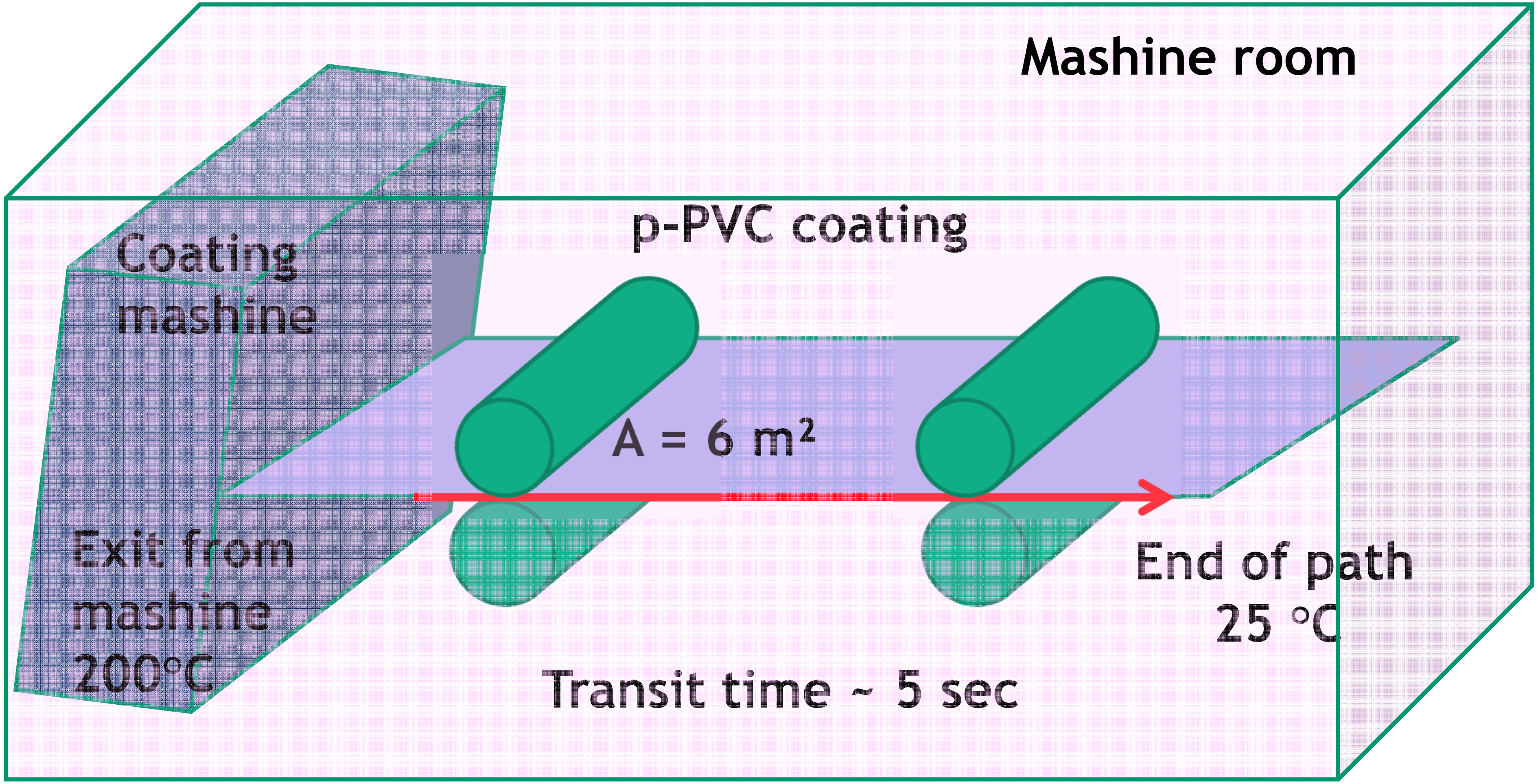
1c.5 In a „worst case“ and without make up air in the room the ADCA vapour concentration limit of 1 mg/m³ air would be reached in about 1.4 hours.

1c.6 However, considering for the „worst case“ ADCA vapour evaporation scenario from 1b.4 an air make up of ~10 hours^{-1}, as recommended for factory buildings, the mean contamination in the room would be: ~ 0.065 mg ADCA/m³.

1d.

1d.1 The exposure resulting from an air polution with ~ 0.065 mg/m³ ADCA vapour in the room should be then evaluated.

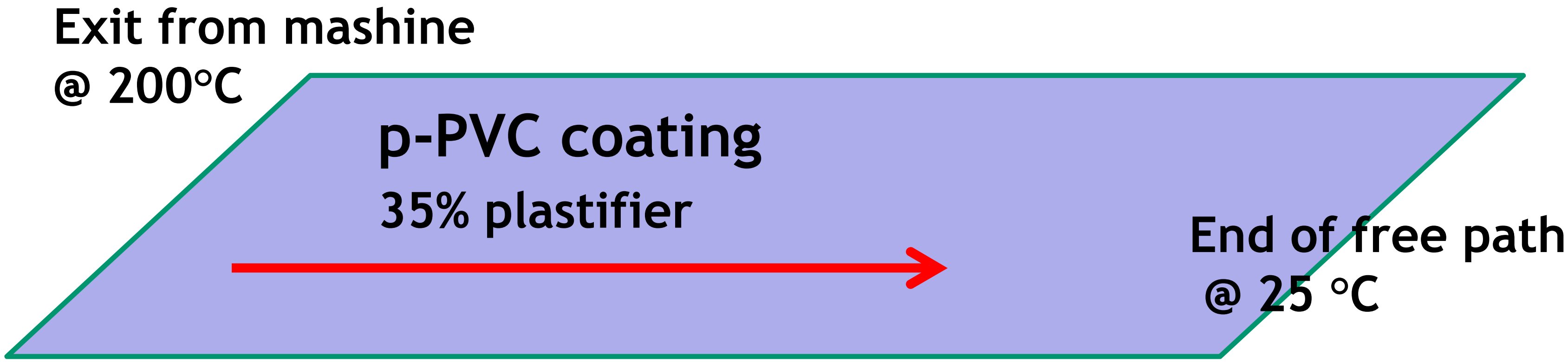
2 . Exposition during manufacturing of plasticized p-PVC coatings



Volume of mashine room: $V = 40 \times 8 \times 18m = 5760\ m^3$

- circulation of fresh air

2 . Exposition during manufacturing of plasticized p-PVC coatings



p-PVC coating

- thickness dp ~ 1000 µm, width L= 200 cm
- speed ~ 0.5 m/sec
- density @ 25°C 1.25 to 1.30 g/cm^3
- initial concentration: ADCA - Cp(0) = 0.1% w/w
- productivity - P ~ 1m^2/s = 3600 m^2/hour
- time/temperature conditions during free path: cooling down from 200 °C to 25°C in ~5 sec

2 . Exposition during manufacturing of plasticized p-PVC coatings

A scenario for the exposition with ADCA

a. ADCA molecules can diffuse at between 200°C and 25°C through the p-PVC matrix to the surface of the coating.

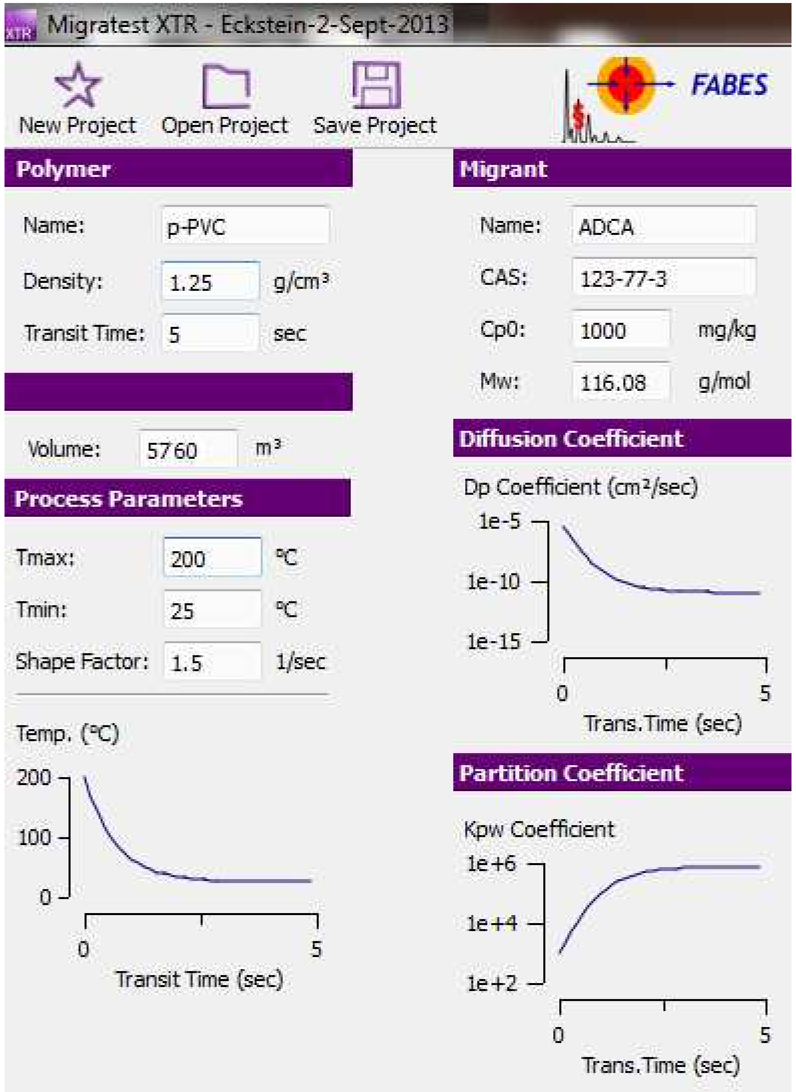
b. From the surface of the p-PVC coating ADCA can decompose and/or evaporate, at a certain rate, into the surrounding atmosphere.

c. ADCA (in form of vapour) can then contaminate the surrounding atmosphere by means of diffusion and convection in and circulation of the air.

d. Exposure resulting from air contanimated with ADCA vapours inhaled by people working in the room.

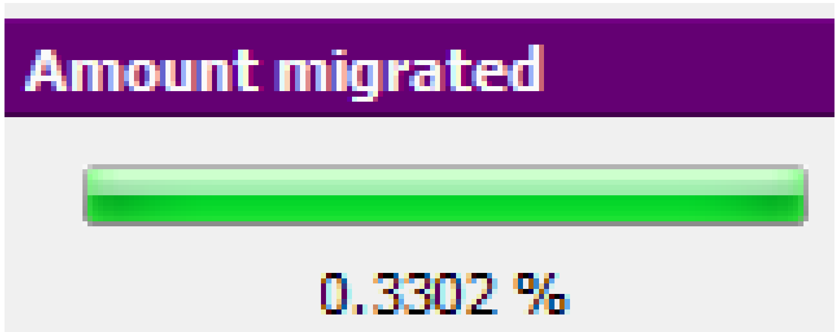
2a.

Inputs for MT XTR:

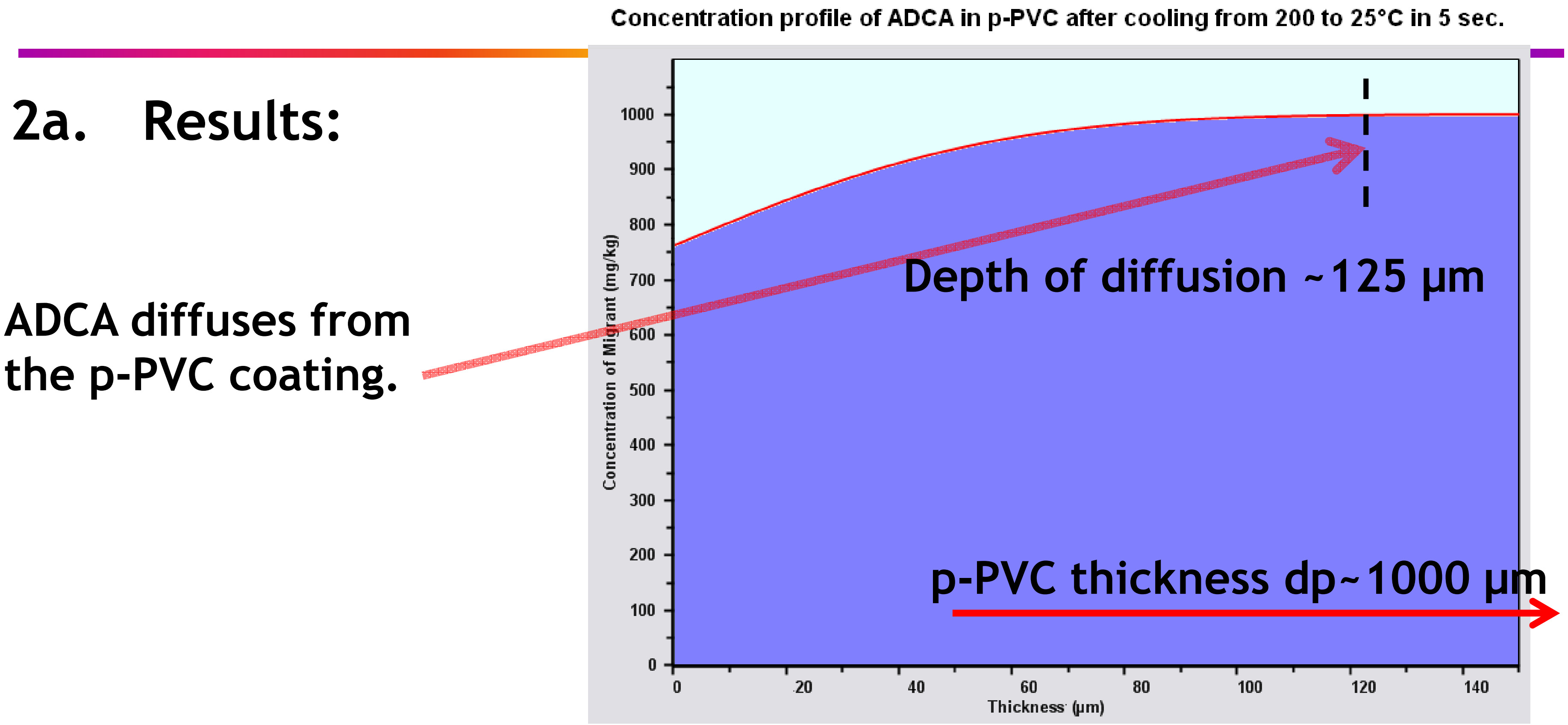


Result:

2b.1) The relative amount of ADCA which may migrate to the surface of an ~1000 µm thick p-PVC coating during the cooling time of t ~ 5 seconds, is about:



2a. Results:



2a.2) The amount of ADCA which may diffuse during cooling from 200 to 25°C, to the surface of the p-PVC coating is about: 4.1 mg/m²

2a.3) For p-PVC coatings of dp = 500 to 1000 µm thickness the amount of ADCA which may migrate to the surface does not depend on the thickness dp.

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2b. Estimation of the rate of ADCA decomposition and evaporation from the surface of the of p-PVC coating during the cooling time.

2b.1 The temperature of the p-PVC coating is between 200 and 175°C only for about 1 second during the cooling process. During this time about 90% of all ADCA diffusing from the polymer during cooling reaches the surface of the coating.

2b.2 Technically speaking the ADCA decomposition during the above 1 second can be assumed to be „instantaneous“ and „complete“.

2b.3 During the last 4 seconds of the cooling there is almost no decomposition of ADCA and little additional diffusion from the matrix of the p-PVC coating.

2b.

2b.4 In absence of experimenal data on evaporation rates of ADCA between 170 and 25°C let's assume again that 5% of the ADCA, which reached the surface of the p-PVC coating during cooling, evaporates and diffuses into the surrounding atmospherer as ADCA vapours.

2c.

2c.1 With result 2b.2) and 1b.4) one can calculate in a „worst case" the amount of ADCA vapour released into the atmosphere by the unit area of p-PVC coating:

$$4.1 \text{mg/m}^2 * 5\% \sim 0.2 \text{ mg/m}^2$$

2c.2 For a productivity of 3600 m^2/hour this means in a"worst case" the release of ~ 725 mg/hour of ADCA vapour in the room.

2c.

2c.3 Assuming that in a „worst case“ no fresh air (make up air) is ventilated into the room, after 1 hour, the mean ADCA concentration in air would be:

725 mg :1560m^3 ~ 0.46 mg/m^3

2c.4 In a „worst case“ and without make up air of the room the ADCA vapour concentration limit of 1 mg/m^3 air would be reached in about 2.1 hours.

2c.5 However, considering in the „worst case“ ADCA vapour evaporation scenario from 2b.4 an air make up of ~10 hours^{-1}, as recommended for factory buildings, the mean contamination in the room would be about:

0.046 mg ADCA/m^3.

2d.

2d.1 The exposure resulting from an air polution with ~ 0.046 mg/m³ ADCA vapour in the room should be then evaluated.

Notes & Conclusions

1. The estimation of the ADCA diffusion processes in the PVC sheet/films and p-PVC coatings have been performed with mathematical algorithms and diffusion data similar to those developed *by FABES GmbH* in the framework of the FACET project.

2. For all other estimations of the ADCA decomposition and evaporation processes little if any experimetal data can be found in the literature. Therefore the estimations were made using similitudes to available data for other substances.

3. Due to the handicaps mentioned in 2) the estimations of the contamination of the atmospheres in the rooms with ADCA vapours shoud be regarded as first (and relatively crude) approximations.

Notes & Conclusions

4. The accuracy of the theoretical estimations done in this work can be considrably augmented by:

- addapting and improving the calculation models and algorithms to the specifics of the processes investigated (specific software development)

and

- aquisition of data which describe the processes involved in the contamination of air with substances used in manufacturing processes (experimental work to quantify the processes involved in the air contamination)


Thank you very much
for your attention !