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Phase Change of Volatile Organic Compounds in Soil Remediation Processes

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Abstract. Liquid-vapor phase change is a central phenomenon in remediation of soils contaminated by volatile organic compounds. An original experimental study leads to validate a law of phase change of heptane in a soil. The dependence of the phenomenological coefficient to liquid content and temperature is established. A simulation of self-removal of heptane in a soil, involving phase change of pollutant and diffusion of the vapor, is compared with experimental results. Finally, treatment by venting of a column of contaminated soil is studied experimentally in order to improve the understanding of the phenomena involved. The results obtained are likely to direct future modelisation of the processes.

1 Introduction

Volatile Organic Compounds (VOCs) are commonly involved in soil pollution cases [1]. Their elimination may occur by self-removal process or by vapor extraction technique. In the first case, the phenomena involved are phase change of contaminant from liquid to gas and diffusion of the vapor in gaseous phase from the subsurface to the atmosphere. In vapor extraction (or venting) method, pumping creates a global movement of the gas phase. Phase change of the liquid is therefore the limiting phenomena. The study of those two processes belongs to the field of heat and mass transfer in heterogeneous media. Their modelisation requires mass balance equations and a set of closure relations such as diffusion and filtration laws as well as the expression of the liquid-vapor relationship. The latter can be assumed to be an equilibrium condition. The vapor pressure is directly deduced from the isotherm of desorption. Such hypothesis should be consistent with experiments if the velocity of the vapor of contaminant is extremely small i.e. if the phase change is not the limiting phenomenon. Nevertheless, experiment shows that this hypothesis is rapidly invalidated. Moreover, for non hygroscopic medium and for isothermal conditions, it follows from equilibrium assumption that the vapor pressure is uniform. Consequently, the transfer of vapor cannot be described by Fick's law that use gradient of concentration. Obviously, it appears that phase change must be taken into account within the framework of non equilibrium thermodynamics. The purpose of this paper is, at first, to present an experimental validation of a law of non equilibrium phase change of a liquid in a soil and the determination of the corresponding phenomenological

coefficient. Next, experiments of self-removal process are presented with the results of numerical simulations. Thereafter, we expose the first experimental results obtained with VOCs removal by venting.

2 Phase Change of a Volatile Organic Compound in Soil

2.1 Law of Phase Change of a Pure Liquid in a Porous Medium

The law of VOCs phase change in a soil is founded on the following description of the problem : the system consists of an inert solid phase, a pure liquid phase and a gaseous phase composed by air and vapor. Mass balance equations for the liquid and the vapor include a term of phase change from liquid to gas. According to linear Thermodynamics of Irreversible Processes, the corresponding phenomenological relation is [1]

$$J = -L \frac{(\mu_v - \mu_l)}{T} \quad (1)$$

J [$kg.m^{-3}s^{-1}$] is the mass of contaminant which transfers from liquid to gaseous phase per unit of medium volume and time. L [$kg.K.s.m^{-5}$] is the phenomenological coefficient of phase change. For a given medium, it depends on the liquid content and the temperature. T [K] is the absolute temperature, μ_v and μ_l are the mass chemical potential of liquid and vapor respectively.

Assuming the perfect gas hypothesis to express the chemical potentials and by means of an original approach based on the introduction of a virtual transformation, Bénet [3] wrote expression (1) for non isothermal case as follows

$$J = \frac{\partial \rho_{veq}}{\partial t} + \nabla \Phi_{veq} - L \frac{R}{M_l} \ln \frac{P_v^*}{P_{veq}} \quad (2)$$

ρ_{veq} [$kg.m^{-3}$] is the virtual mass density of the vapor at equilibrium with the liquid, Φ_{veq} [$kg.m^{-2}s^{-1}$] is the virtual mass flux of vapor induced by the liquid transformation, R [$J.mol^{-1}K^{-1}$] is the perfect gas constant, M_l [$kg.mol^{-1}$] is the molar mass of the contaminant, P_v^* [Pa] is the partial vapor pressure and P_{veq} [Pa] the equilibrium vapor pressure.

2.2 Experimental Study of Phase Change of Heptane in a Soil

The purpose of the experimental study is to verify the previous law and to determine the coefficient L . To this end, experiments are lead in static conditions so that the macroscopic fluxes can be ignored. The experiment consisted in measuring the temperature, T , and the total pressure of the gaseous phase, P_g^* , of a small volume of soil which contains pure liquid, its vapor and air. From a non-equilibrium initial state for which $P_v^* \neq P_{veq}^*$, the

kinetic of pressure measures show a return to an equilibrium state. In static conditions, and with respect to perfect gas law, the mass balance of vapor in integrated form allows the phenomenological coefficient to be determined [1]

$$\left[\frac{P_v^* - P_{veq}}{T} \right]_t = L \frac{R^2}{\eta_g M_l^2} \int_t^{t_{eq}} \ln \frac{P_v^*}{P_{veq}} dt \quad (3)$$

η_g is the volume of the gaseous phase per unit of volume of soil. t_{eq} is the time when equilibrium is reached, i.e. when $P_v^* = P_{veq}$.

The characteristics of the silty sand soil used are given in table 1. So as for the used VOC, which was heptane as one of the components of gasoline.

Table 1. Soil and VOC characteristics

SOIL	
mineralogy	calcite 50% quartz 40% clay 10%
Atterberg limits	$W_l = 25\%$ $W_p = 14,5\%$
real mass density $\rho_s^*[kg.m^{-3}]$	2650
dry apparent specific gravity $\rho_s[kg.m^{-3}]$	1500
porosity	0,43
HEPTANE as volatilorganic compound	
molar mass $M [kg.mol^{-1}]$	0.1
saturation vapor pressure $P_{vs}(T) [kPa]$	$10^{(6.02167 - \frac{1264.9}{T+216.544})}$
diffusion coefficient in air $D_{va} [m^2.s^{-1}]$	$0.824 \cdot 10^{-5}$
apparent mass density $\rho_l [kg.m^{-3}]$	675.19
latent heat of evaporation (à 20°C) $[kJ.kg^{-1}]$	365.5

The sample of contaminated soil occupied the entire volume of a 12 cm³ cylindrical cell. The cell and its accessories were immersed in a thermostatic bath. The initial thermodynamic non-equilibrium was obtained by replacing the gaseous phase of the soil, first extracted by vacuum, by a vapor-free one. The temperature and total pressure of the gaseous phase of the sample were recorded. After closure, vapor partial pressure of heptane rised to its equilibrium value and could be evaluated at each moment as follows $P_v^*(t) = P_g^*(t) - P_a^*$ where the air partial pressure P_a^* is equal to $P_a^* = P_g^*(t_{eq}) - P_{veq}^*$. The isotherm of desorption for heptane has not been established experimentally. We assume in this paper that it can be deduced from the isotherm of desorption of water in the same soil by means of an ordinate-parallel affinity with a ratio equal to $w_c^{water}/w_c^{heptane}$. w_c^{water} and $w_c^{heptane}$ are the liquid content corresponding to the entrance in the hygroscopic domain respectively for water and heptane.

At the end of an experiment the data are collected by a computer and exploited with a spreadsheet. That allows us to represent the first member of equation (3) versus the integral of the second member. All experimental curves obtained showed two distinct parts. A linear part and a non-linear one. The non linear part corresponds to states the farrest from equilibrium.

Those curves allow us to conclude to the validity of the phenomenological relation (1) in the linear part. The slope of the linear part enables the phase change coefficient L to be calculate according to relation (3).

Figure 1 shows the values of the experimental phase change coefficient of heptane versus the liquid content expressed relatively to the dry mass of solid. The three curves correspond to temperatures of 30, 50 and 80°C. Note that similar liquid content dependence has been found for water in soil [3]. The liquid content corresponding to the maximum value of the coefficient is close to $w_c^{heptane}$ previously defined. The decrease of the coefficient for lower values of liquid content is due to the increase of the energy of bonds between liquid and solid when liquid content decreases in hygroscopic domain. For higher liquid content, the decrease of the coefficient can be explained by the decrease of the connectivity of the gaseous phase when liquid content increases in non-hygroscopic domain. The coefficient reaches zero value when the gaseous phase is entirely occluded.

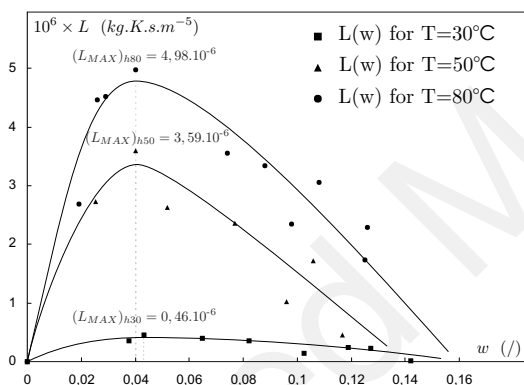


Fig. 1. Experimental phase change coefficient L

Figure 1 also shows the evolution of the maximum value of the coefficient vs temperature. The increase of the coefficient is higher when the temperature rises from 30 to 50°C than from 50 to 80°C. This kind of observations is likely to direct choices when thermo-activated venting treatment of a contaminated site is considered.

3 Self-removal of a contaminant in a soil

Natural diffusion of hydrocarbon vapor from the contaminated zone to the surface can significantly contribute to soil remediation. This so called "self removal process" is the purpose of this section. A numerical simulation is proposed using the phase change coefficient previously determined. Then, we

present some experimental results obtained with heptane. Finally, a comparison between simulations and experiments is performed.

3.1 Simulation

Based on the phenomenological model presented below, whose main equations are recalled in table 2, a one directional simulation of heptane self-removal from a soil is performed.

Table 2. model equations

Liquid mass balance	$\frac{\partial}{\partial t} w = -\frac{J}{\rho_s}$
Vapor mass balance	$\frac{\partial}{\partial t} P_v^* = \frac{RT}{\eta_g M_l} \left(-\frac{\partial}{\partial z} J_v + J\right)$
Phenomenological relation of phase change	$J = -L \frac{R}{M_l} \ln \frac{P_v^*}{P_{veq}^*}$
Phenomenological relation of diffusion	$J_v = -D \frac{\partial}{\partial z} P_v^*$

The diffusion coefficient of the vapor in the gaseous phase of the soil D can be related with the diffusion coefficient in air D_a . Among different relations, we chose the expression proposed by Penman [9] that is $\frac{D}{D_a} = 0.66\eta_g$. In addition the pressure of vapor at equilibrium P_{veq} is expressed by $P_{veq} = a(w) P_{vs}(T)$, where the saturating vapor pressure of heptane is given in table 2 and $a(w)$ is the activity of the liquid given by the isotherm of desorption and from which it is deduced a polynomial approximation

$$a(w) = 10^4 [55.46 w^4 - 6.18 w^3 + 0.19 w^2 + 5.47 \cdot 10^{-4} w] \quad (4)$$

The phenomenological coefficient of phase change at 30°C can be approximated from the curve in Fig.1 by a polynomial expression

$$L = 10^{-4} [6.34w^3 - 2.06w^2 + 0.17w] \quad (5)$$

The above expression of the coefficient L is available close to the equilibrium i.e. when the ratio P_v^*/P_{veq}^* is close to 1. Nevertheless, in practical applications, phase change occurs in conditions that are outside of this linear domain. In these situations, the coefficient L increases significantly as the partial pressure of VOC vapor P_v^* decreases. Thus, a first interpretation of experimental results far from equilibrium is used in the case of water [10]

$$\text{if } P_v^*/P_{veq}^* \leq 0.93 \text{ then } L = -18.4 \cdot 10^{-8} \left(\frac{P_v^*}{P_{veq}^*}\right) + (L_{\text{équilibre}} + 17.1 \cdot 10^{-8}) \quad (6)$$

where L_{eq} is the coefficient given by equation (5). In this study we fitted phase change coefficient far from equilibrium for heptane from relation (6). Finally experiments are set at $T = 30^\circ\text{C}$.

As showed in Fig.2a, simulation is performed in one directional geometry. The space axis is divided in two sections

- soil: from $z = 0$ to $z = h$
- air: from $z = h$ to $z = H$

The initial and boundary conditions are the following

- at $t = 0$
 - $w = w_0$ for $0 \leq z \leq h$
 - $P_v^* = 0$ for $h \leq z \leq H$
- at $z = 0$, $J_v = 0 \forall t$
- at $z = H$, $P_v^* = 0 \forall t$

Integration is performed using Newton method with a time implicit scheme.

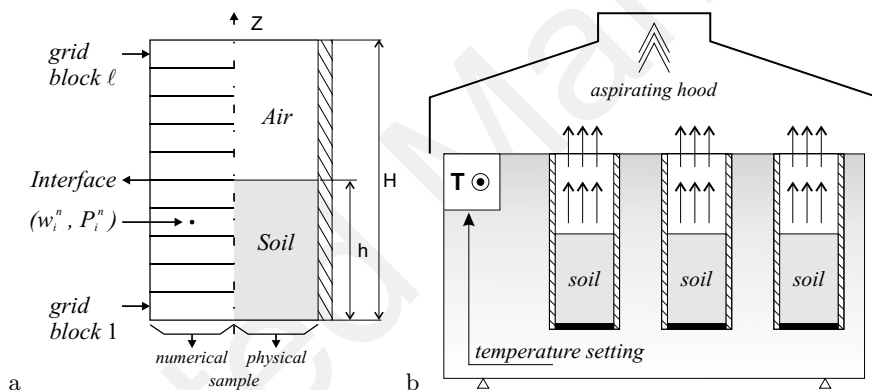


Fig. 2. Heptane self-removal principle a) simulation and b) experiments

3.2 Experimental study

Soil samples contaminated with heptane were placed in cylindrical tubes as shown in Fig.2. Samples were 81,4 mm in diameter and 100 mm height. Tubes were placed under an aspirating hood which allows to assume the heptane vapor pressure being equal to zero at the top of the tubes. Temperature of the samples was regulated at 30°C by means of a thermostatic bath. The initial homogeneous liquid content was about 10%. Vapor of heptane diffused in the air surrounding the sample to the top of the tube. Samples were regularly weighted to determine the global pollutant removal kinetics. Furthermore, some samples are cut in sections for the purpose of establishing

the liquid content profile at a given time. Figure 3a shows experimental kinetics of heptane removal. Final liquid content can be explained at least in part by heptane equilibrium content since no heptane vapor is present in the atmosphere. Liquid content profiles at different times are given on Fig.3b. This figure shows that the removal of heptane does not operate as a front propagation process. The VOC content decreases from the first hours at all level of the sample.

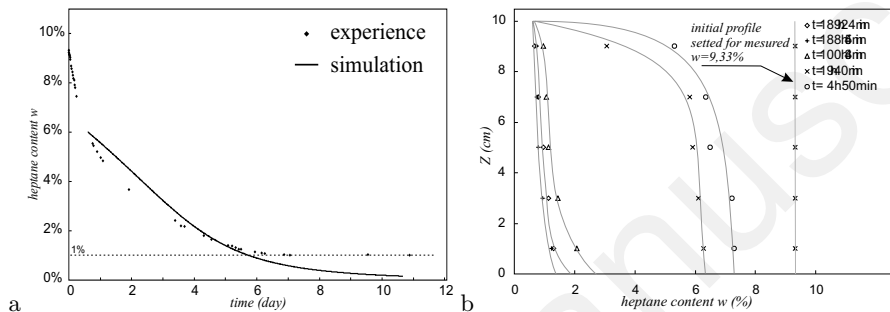


Fig. 3. VOC self-removal test results

a) experimental and simulated kinetics, b) experimental profiles

Figure 3a also illustrates the comparison between experimental and simulated heptane removal kinetics. The general decay of heptane content versus time is well depicted by the model. However, it appears some notable differences. Whereas the simulated kinetic converges to zero liquid content due to the boundary condition at $z = H$. In the same time experimental data tend to a value about 1% of heptane at equilibrium. As said formerly in sec.2.2, the isotherm of desorption for heptane in this soil has not been established experimentally and we don't have yet informations about heptane content at equilibrium in the used soil. The model, indeed, does not take into account the water which cannot be distinguished from heptane in the experimental determination of liquid content. Likewise, the slope of the calculated kinetic at the beginning of the process is not in agreement with the experiment. Possible transport of liquid heptane in the soil, not taken into account by the model, can explain this difference. Moreover, the assumption of strictly diffusive transport of vapor in the atmosphere surrounding the soil can be abusive. Light convective movements of the air can significantly increase the velocity of heptane vapor from soil surface to the top of the tube and consequently increase the heptane removal. Experimental VOC content profiles on Fig.3b shows that liquid content at the surface of the sample ($x = h$) seems to reach the equilibrium rapidly. This can also be attributed to an activated vapor transport by convection in the air of the tube. Finally, the differences between experiments and theoretical simulation can be also attributed to the

coefficient of phase change far from equilibrium that has been inspired by a study of phase change of water in soil.

4 VOC Removal by venting

This section is devoted to presenting the first results of an experimental study of venting. In comparison with the self-removal process, venting or vapor extraction introduces supplementary phenomena: filtration of gaseous phase, heat transfer between gaseous phase and other phases and heat conduction within the phases. No theoretical simulation is performed for lack of data about, in particular, the phenomenological coefficients involved in the description of the different phenomena.

4.1 Thin layers experiments

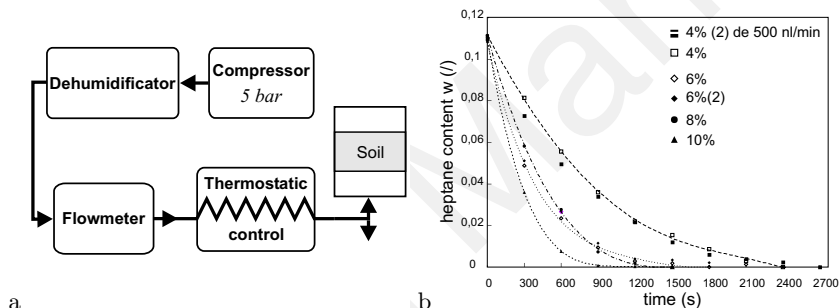


Fig. 4. soil vapor extraction. a) schematic test cell, b) thin layer kinetics

The experimental plant is schematically represented in Fig.4a. Contaminated soil was contained in a cylindrical tube. The diameter was 81,4 mm and the height was 60 mm for experiments with thin layers. The air provided by a compressor was first dried and then heated to the process temperature. Air pressure was controlled by a flowmeter. The samples were weighted regularly to establish the global kinetics of depollution. Holes drilled along the tube permitted to uptake soil at different levels in order to determine profiles of liquid content. The characteristics of the soil were similar to those used in the previous experiments.

Thin layer experiments were intended to determine the influence of the treatment conditions on the removal rate. The influencing parameters are the air flux, its temperature and its saturation relating to VOC vapor that is quantified by the ratio P_v^*/P_{vs} . In this study, we only explore the influence of the air flux. Temperature is 30°C and the partial pressure of heptane vapor at the inlet of the sample is fixed to zero. The small thickness allows the

homogeneity of the sample to be assumed. Figure 4b shows experimental kinetics for 60 mm height samples. The different curves are relating to different air flux: 0.077, 0.116, 0.154 and 0.193 $kg.m^{-2}s^{-1}$. This figure shows that an increase of the air flux logically induces an increase of the removal efficiency.

Exponential approximation of the experimental kinetics permits to calculate derivative functions of the form $dw/dt = k.w$. That makes possible to highlight the dependance of the coefficient k to the air fluxes F_a . The curve obtained suggests a linear type dependance of the form $k = A \cdot F_a$. The influence of temperature and saturation of air relating to vapor of heptane can be taken into account using an expression of the form

$$\frac{dw}{dt} = f_1(T) \cdot f_2\left(\frac{P_v^*}{P_{vs}}\right) \cdot A \cdot F_a \cdot w \quad (7)$$

Experiments have to be completed by the study of the influence of temperature and air saturation in order to propose an expression of $f_1(t)$ and $f_2(P_v^*/P_{vs})$.

4.2 Thick layers experiments

The purpose of experiments on thick layers was to observe the evolution of the profiles of liquid content in the course of time. The samples consisted of five layers of 60 mm thickness. We compacted each layer to obtain the chosen apparent specific gravity ($\rho_s = 1500 kg.m^{-3}$). The inlet air flux was fixed at 0,116 $kg.m^{-2}s^{-1}$. Figure 5a shows some global heptane removal kinetics. The general aspect of the kinetics is similar to the one observed in classical drying processes [7]: a constant rate period, characterized by a linear decrease of the liquid content along the time, followed by a decreasing rate period. In our experiments, the initial rate of heptane removal varies from $1.5 \cdot 10^{-5}$ to $2.5 \cdot 10^{-5}s^{-1}$. Influencing factors can be identified such as the homogeneity of heptane content, the compaction regularity, the control of air flux, and variations of external temperature. The liquid content profiles represented in Fig.5b was measured after 30, 45, 60, 90, and 95 minutes of treatment. These profiles was established from separated experiments that affects the coherence of the curves. One can yet observe following general tendencies: first, the liquid content at the air inlet extremity of the sample, i.e. in $z=0$, reaches the equilibrium value ever since the first minutes of the treatment. Then the removal of heptane progresses by front propagation and by general decrease of the liquid content along the height of the sample. And finally the profiles show higher liquid content near the top of the sample than in the other parts.

The last point is partially explained by the increase of the vapor saturation of the air after having crossed through a part of the sample. But, in addition, we observed that the liquid accumulated in the upper part of the column of soil. This accumulation can have two physical origins: either an upward

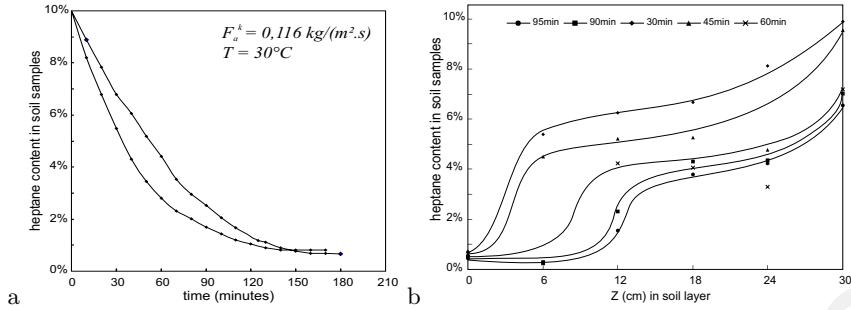


Fig. 5. Thick layers venting test a) kinetics, b) profiles

movement of the liquid mechanically induced by the air flux or a condensation phenomenon due to a decrease of temperature near the surface of the soil or both. Further experiments will have to precise these hypothesis. Theoretical models would have to take into account these phenomena.

5 Conclusion

Phase change appears to be a central phenomenon in remediation of soils contaminated by Volatile Organic Compounds. An original experimental device has been designed to probe the phase change of a liquid in a soil. We demonstrated that the law founded on Linear Thermodynamics of Irreversible Processes was verified near equilibrium and we have determined the phenomenological coefficient of phase change. The results show the dependence of the coefficient to liquid content and temperature. A theoretical model was established to simulate the self-removal of a VOC in a soil by phase change and diffusion of vapor. The model is able to correctly simulate the process. The comparison with experimental results incite to study the phase change phenomenon far from equilibrium and to verify the good agreement of the boundary conditions. Experimental study of venting was instrumental in showing the phenomena involved in the process such as liquid transport induced by gaseous flux and condensation of vapor. The latter phenomenon leads to the study of the reversibility of phase change in porous media and should be experimentally investigated.

References

1. Lecomte P. (1995) Les sites pollués, traitements des sols et des eaux souterraines, Lavoisier, Paris.
2. Bénét J.-C., Jouanna P. (1982) Phenomenological relation of phase change of water in a porous media: experimental verification and measurement of the phenomenological coefficient, Int. J. Heat and Mass Transfer, **25**(11), 1747-1754.

3. Bénet J.-C., Jouanna P. (1983) Non équilibre thermodynamique dans les milieux poreux non saturés avec changement de phase, *Int. J. Heat and Mass Transfer*, **26**(11), 1585-1595.
4. Ruiz T., Bénet J.-C. (2001) Phase change in a heterogeneous medium : comparison between the vaporisation of water and heptane in a unsaturated soil at two temperatures, *Transport in Porous Media*, **44**, 337-353.
5. Chammari A. (2002) Transfert gazeux dans les sols avec changement de phase - Application à quelques aspects de géotechnique environnementale, Thèse de doctorat, Université Montpellier II.
6. Mignard E. (1984) Contribution à l'étude des transferts en milieux poreux par la thermodynamique du non équilibre - cas de la dissolution des gaz dans les sols, Thèse de doctorat, INSA Toulouse.
7. Cousin B., Bénet J.-C., Auria R. (1993) Experimental study of the drying of a thick layer of natural crumb rubber, *Drying Technology*, **11**, n°6, 1401-1413.