

From simultaneous heat and moisture transfer models to the modeling of the deterioration of concrete

K. Watanabe, Building Research Institute, Tsukuba, Japan

S. Tada, Nihon University and Texte, Inc., Tokyo, Japan

Existing models for the simultaneous heat and moisture transfer were reviewed and condition to apply them to the deterioration problems of building components especially for concrete were examined. We also discussed the accumulated knowledge and frameworks provided by the simultaneous heat and moisture transfer models in terms of the applicability to the deterioration of concrete.

1 Simultaneous heat and moisture transfer models for concrete

1-1 Review of research

Diffusion-controlled simultaneous heat and moisture transfer model

Since autoclaved aerated concrete may exhibit substantial degradation in thermal insulation performance due to moisture migration, research started early in Sweden. Hanson /1/ reported a simulation of long term moisture variation in walls by applying a cyclic boundary conditions to the conservation equation of liquid and vapor as well as the measurement of transfer coefficients.

The theory of simultaneous heat and moisture transfer developed by de Vries was extensively applied to aerated concrete by van der Kooi /2/. While simultaneous heat and moisture transfer was not taken into account in his simulation, isothermal water diffusivity as well as thermally induced water diffusivity were measured as a function of moisture content. Nicolajsen /3/ measured the coefficients of a set of constitutive equations with gradients of moisture content, temperature and pressure at temperature from 15 to 34 °C and relative humidity from 40 to 70 %. Nielsen /4/ also measured the isothermal water diffusivity as a function of moisture content by the gamma-ray attenuation method. A research group at Lund University executed extensive measurement of moisture properties, of which aerated concrete was still a major object among cementitious materials. These results were used for the simulation of Andersson /5/ in which vapor pressure was used as a driving force, and the simultaneous heat transfer was not taken into account.

Few measurements was made for the transfer properties of the normal concrete except for Daian /6/, while a calculation of the sorption isotherm from the pore structure of HCP by Jonasson /7/ and a power function approximation of the water diffusivity as a function of moisture content by Sakata /8/ was reported. Abe /9/ executed an analysis of the drying of concrete as a simultaneous heat and moisture transfer process based on de Vries model, in which vapor and liquid flow were separated with respective driving forces of concentration gradient and matric potential gradient, and the unsaturated water permeability was given as a function of the matric potential. The transfer properties used for his analysis, however, was quoted entirely from Huang's paper as mentioned later, and the results of the analysis was not verified by experiments.

From the point of view of the applicability to the deterioration problems of concrete, de Vries model may present data of transfer properties of materials which have been measured on the basis of their constitutive equations as well as the experiences of prediction of the long term variation of moisture content in building components. On the other hand, de Vries model appears to provide no framework in which various types of mass flow, other than heat and moisture, indispensable for the deterioration problem should be systematically incorporated.

Convection - controlled simultaneous heat and moisture transfer models

Since the gas release from an accidentally heated PCRV at an occasion of the liner failure may critically control the safety, heat and moisture behavior at very high temperature have been a subject of concrete research. Bazant and Thonguthai /10//11/ constructed a model taking into account the diffusion and convection of heat, water, water vapor and air as well as hydration / dehydration, and a finite element analysis code TEMPOR was developed. The characteristics of Bazant model lies in the simplification where Soret and Dufor effects were considered to be negligibly small and the vapor pressure was used as unique driving force of mass transfer, since a pore pressure may be uniquely determined either by a moisture content and a temperature.

Dhatt, Kadje and Roelandt /12/ executed an analysis of dehydration of concrete up to 500 °C based on Bazant model, and developed their own finite element analysis code. Kamp, Roelfstra, Wittmann and Mihashi /13/ took into account the diffusion flow to analyze hardened cement pastes up to 150 °C, and developed a computer program COUPFLO. Claybrook and Muhlestein /14/ developed a model that took into account the convection of heat, water, water vapor and air, and the release of carbon dioxide gas due to the thermal decomposition of carbonate in concrete, which was incorporated in the conservation equation. The analysis was made for the temperature up to 900 °C with a finite difference code WATRE.

From a point of view of the applicability to the deterioration of concrete, simultaneous heat and moisture transfer model developed by Bazant and co-authors may be characterized by the incorporation of chemical reactions into conservation equations upon necessity, since the deterioration of concrete may be associated with chemical reactions of unhydrated cement and water, C₃A and chloride ions, carbonic ions and calcium silicate hydrates. Transfer properties data, however, which is necessary for the long term prediction of mass transfer in concrete may not be provided sufficiently, since the research concentrated in the very short time deterioration associated with a rapid temperature rise.

Non - equilibrium thermodynamics models

Matsumoto /15//16/ presented a diffusion-controlled non equilibrium thermodynamic model in which the chemical potential of water on the basis of free bulk water was used as a driving force of water. Water diffusivity due to either moisture content gradient and temperature gradient as a function of moisture content, and an equilibrium relation between moisture content and chemical potential, were measured for aerated concrete. Moisture and temperature profiles were simulated under variable external conditions not only for the monolithic aerated concrete but for multilayered building components, and

the accuracy was confirmed by laboratory experiments. Sakamoto and Watanabe /17/ executed full-scale experiments of the variation of moisture content in aerated concrete wall as well as multilayered wall over a year, and very good agreement was found between the prediction by Matsumoto model and their experiments. Huang /18/ analyzed the drying of lightweight concrete slab by a non equilibrium thermodynamic model with molar fraction of water vapor as a driving force in the hygroscopic range. From the point of view of the applicability to the deterioration problems of building components especially of concrete, non equilibrium thermodynamic model may provide a basic frame work in which transport phenomena other than heat and moisture relevant to the deterioration of concrete could be rationally incorporated. Experiences in simulation of the long term variation of moisture content in structures based on the diffusion-controlled non equilibrium thermodynamic model may also present useful information.

1-2 Mathematical formulations

The research mentioned above are rearranged in terms of non equilibrium thermodynamics here, and their characteristics are made clear.

Entropy production

It is assumed that the system of concern is a continuum where no chemical reactions take place. The entropy production rate of a given volume may be expressed by the product of fluxes J and the conjugate forces X ,

$$\square T \frac{d_i S}{dt} = \square J_e \cdot X_e + \square J_i \cdot X_i. \quad (1)$$

If fluxes J comprise heat (q), water (l), vapor (v) and dry air (a) only, the dissipation function may be expressed as follows,

$$\square T \frac{d_i S}{dt} = J_q \left[-\frac{\square T}{T} \right] + J_l \left[F \square (\square \square_l)_T \right] + J_v \left[F \square (\square \square_v)_T \right] \square J_a \square P, \quad (2)$$

where F represents an external force, and $J_q = J_e \square H_l J_l \square H_v J_v$, $X_e = X_q = \square \frac{1}{T^2} \square T$, $X_i = X_i^1 + H_i X_e = \frac{1}{T} \left[F_i \square (\square \square_i)_T \right]$, for the last equation, $(\square \square_i)_T = \square \square_i \square S_i \square T$ is used.

Constitutive equations

Provided that the system is not far from equilibrium and a linear correlation between fluxes and forces can be assumed, a set of phenomenological equations may be written from eq.(2),

$$J_q = L_{qq} X_q + L_{ql} X_l + L_{qv} X_v + L_{qa} X_a, \quad (3)$$

$$J_l = L_{lq} X_q + L_{ll} X_l + L_{lv} X_v + L_{la} X_a, \quad (4)$$

$$J_v = L_{vq} X_q + L_{vl} X_l + L_{vv} X_v + L_{va} X_a, \quad (5)$$

$$J_a = L_{aq} X_q + L_{al} X_l + L_{av} X_v + L_{aa} X_a. \quad (6)$$

The phenomenological coefficients L_{ij} may be reduced or even determined to an extent by introducing an assumption of local equilibrium and Onsager's reciprocal theorem, or by the analogy to classical constitutive equations. With the help of the local equilibrium assumption, we may put $\bar{\rho}_l = \bar{\rho}_v$, then we have $X_l = X_v = X_w$. Matsumoto further evaluated the phenomenological coefficients whose contributions to coupling may be negligibly small, and gave practical expressions to the forces. The resulting constitutive equations are as follows.

$$\mathbf{J}_q = -\bar{\rho}_{eff} \nabla T, \quad (7)$$

$$\mathbf{J}_w = -\bar{\rho}_{vlw} \nabla T - \bar{\rho}_{vlw} [(\bar{\rho}_w)_T \nabla F] - \bar{\rho}_{vla} \nabla P, \quad (8)$$

$$\mathbf{J}_a = -k_{va} \nabla P. \quad (9)$$

Among these linear equations, \mathbf{J}_q corresponds to Fourier's law, and \mathbf{J}_w may be the unsaturated Darcy's law under isothermal condition, and may also correspond to Fick's law under isothermal, isobaric and hygroscopic conditions. An advantage of non equilibrium thermodynamic approach may be a unified arrangement of these classical constitutive laws. Matsumoto further gave more practical expressions to the above equations using the moisture content as the apparent driving force whereby unique correspondence between moisture content and chemical potential was assumed.

Bazant studied the concrete exposed to high temperature, where the pore pressure may increase so substantially that the diffusion terms may be neglected, and derived constitutive equations, by our rearrangement, as follows,

$$\mathbf{J}_q = -\bar{\rho}_{eff} \nabla T, \quad (10)$$

$$\mathbf{J}_w = -(\bar{\rho}_{vla} + k_{va}) \nabla P, \quad (11)$$

where $\bar{\rho}_{eff}$ is the effective thermal conductivity and k_{va} is the air permeability including both vapor and dry air.

Conservation equations

Under normal hygro-thermal working conditions of building components, balances of liquid water, vapor and dry air may be expressed in the following conservation equations.

$$\frac{\partial (\bar{\rho}_l \bar{\rho})}{\partial t} = \bar{\rho} \mathbf{J}_l + I_l, \quad (12)$$

$$\frac{\partial (\bar{\rho}_v \bar{\rho})}{\partial t} = \bar{\rho} (\mathbf{J}_v + \mathbf{J}_a) - I_l, \quad (13)$$

where I_l is the liquid-gas phase change term of water and $\bar{\rho}$ is the porosity. The balance of heat may also be given as follows with heat of fusion C_h ,

$$\rho_s C_s \frac{\partial T}{\partial t} = \rho_s \mathbf{J}_q + C_h I_l. \quad (14)$$

Bazant presented a heat balance equation taking the heat transferred by water flow, the heat of adsorption of water vapor and the heat capacity of free water to be negligibly small,

$$\rho_s C_s \frac{\partial T}{\partial t} = \rho_s \mathbf{J}_q + C_d I_d, \quad (15)$$

where C_d is the heat of decomposition of hydrates, and I_d is the amount of released free water by the decomposition. $\rho_s C_s$ is the heat capacity of concrete except for that of bound water. With regard to the moisture balance, Bazant also took the effect of source term I_d to be substantial particularly at temperature above 100°C, below which the effect may be negative by the progress of hydration, and he derived a following equation,

$$\frac{\partial \rho}{\partial t} = \rho_s \mathbf{J}_w + I_d. \quad (16)$$

1-3 Contribution of simultaneous heat and moisture transfer models

The prediction of the long term variations of moisture content in building components appears to cover the practical range. Provided that the dependency of properties of materials upon their moisture content is given, the degradation or changes in their performance may be estimated by simulating the variation of moisture content, whereas the transfer of mass other than moisture should be taken into account in order to predict the deterioration.

The transfer properties used for the simultaneous heat and moisture transfer models have been extensively measured especially for aerated concrete, while that of concrete, mortar and cement paste are quite few. Non destructive, sensitive methods that could measure the spatial distribution of mass in concrete should be used or developed.

Among simultaneous heat and moisture transfer models, the non equilibrium thermodynamic model appears to provide a unified understanding of various flows, and a principal framework that can incorporate and model the transport phenomena other than heat and moisture in concrete. It is necessary to incorporate the flow of ions and electric current, and chemical reactions to solve the deterioration problems.

2 Coupled flow phenomena in the deterioration of concrete

2-1 Review of research

Electroosmosis

Water flow induced by the electric potential is called electroosmosis and has been used for the pull-out of sheet piles for example, and discussed for an application of the drying of building structures /19//20/. Electroosmosis is a flow of water in conjunction with the electric potential driven flow of ions induced by the externally applied electric field in the electric double layer, which is formed on the microscopic surface of cement paste. It is important to notice that flow of ions, electric current and water are present simultaneously, and an electric potential could be inversely created as a result of water flow by drying for example.

Coupled flows associated with carbonation

CSH gels and calcium hydroxide that are the main hydration products of hardened cement pastes may be eventually decomposed by carbon dioxide into silica gels, calcite and water, and may lose their alkalinity. This leads to the abandonment of the role of passivating the reinforcement and is taken for the end of the service life of structures.

Mathematical models for the carbonation problems have been formulated as a simple diffusion process of carbon dioxide gas through concrete whereby the portion that may be fixed as a reaction product has not been taken into account. While in recent models of Masuda and Tadano /21/ and Saetta, Shulefler and Vitaliani /22/, the chemical reaction of carbon dioxide was incorporated as a source term in their conservation equations. Saetta and co-authors in particular solved the diffusion and reaction of carbon dioxide as a simultaneous process of both water and heat transfer.

Kobayashi and Uno /23/ reported coupled transport phenomena of chloride ion and Alkali metal ions in the carbonation process. It was concluded that the carbonation reaction in cement paste is a reaction of carbonic ions and calcium ion in the pore solution, and the reaction rate is controlled by pH value of the pore solution relevant to the solubility of calcium, and a high pH value necessary for the reaction may even be maintained if the alkali metal ions could be provided. Furthermore, Kobayashi, Shiraki and Kawai /24/ have shown that the chloride ions fixed as Friedel salts as well as sulfate ions fixed as ettringite may be released by the carbonation reaction and then migrate towards an uncarbonated zone inside of the cement paste whereas the Alkali metal ions may take the opposite direction.

Migration of chloride ion and alkali metal ions, and the cathodic protection

- Chloride migration has been also modeled as a diffusion process solely of chloride ion, while recently, a simultaneous heat and moisture transfer model presented by Saetta, Scotta and Vitalini /25/ took the chloride ion flow with water, together with the diffusion of chloride itself, into account. Andrade /26/ pointed out the simultaneous transfer of ions and electroosmosis effects which may be present when an accelerated test for chloride diffusivity is made by the externally applied electric current.

It is well known that the only means to prevent concrete including large amount of chloride from corrosion is the cathodic protection, which applies CP current between reinforcement, as a cathode, and external anode placed on the surface of concrete. The CP current may not only protect the reinforcement but also drive chloride ions as well as other anions from the neighbor of the reinforcement to the anode. Ali /27/ reported that among migrations of K^+ , Na^+ , Ca^{++} , Cl^- and Mg^{++} toward the reinforcement under variable CP currents, concentration of K^+ was quite noticeable.

Xu and Hooton /28/ measured the redistribution of alkali metal ions by applying cyclic driving forces of wetting/drying, freezing/thawing as well as constant drying and electric potential for 9 to 12 months. It was shown that the true driving forces were water movement and electric potential, and the most concentrated zone was found to be a drying end under cyclic wetting and drying.

2-2 Mathematical formulations

The research mentioned above are rearranged in terms of non equilibrium thermodynamics here, and their constitutive relations are examined.

Moisture in hardened concrete is in principal retaining in the hardened cement paste and is under strong influences of surface forces. The interaction between water molecule and the solid surface may be imagined when we estimate the thickness of water film less than 2 nm for wet hardened cement paste with moisture content of 20 % due mainly to its large surface area.

Entropy production

The system of concern here is a water film existing on the microscopic surface of the hardened cement paste. With the same assumption as in the section 1-2, and without the effect of gravity, the entropy production of the system may be expressed as follows.

$$\rho T \frac{d_i S}{dt} = \mathbf{J}_q \cdot \frac{\nabla T}{T} + \sum_{i=0}^n \mathbf{J}_i \cdot (\nabla \tilde{\mu}_i)_T. \quad (17)$$

The electrochemical potential of i th species may be given as

$$(\nabla \tilde{\mu}_i)_T = v_i \nabla P + z_i F \nabla \phi + RT \nabla \ln c, \quad (18)$$

where v , z and F are the molar volume, the valence of ion and the Faraday constant respectively. P is the pressure created in the water film and ϕ is the electric potential. The molar concentration c of each mass may be very dilute. By introducing eq.18 to eq.17, and putting driving force for diffusions as the osmotic pressure $\pi = RTc$, and using Gibbs-Duhem equation, we have,

$$\rho T \frac{d_i S}{dt} = \mathbf{J}_q \cdot \frac{\nabla T}{T} + \mathbf{J}_c \cdot (\nabla P) + \mathbf{J}_d \cdot (\nabla \pi) + \mathbf{J}_e \cdot (\nabla \phi), \quad (19)$$

where subscripts q, c, d and e of each flux represent heat, convection, diffusion and electric current respectively. The effect of surface forces is expressed in terms of the pressure P, which may be created within the water film as a function from the solid surface and may be called as the disjoining pressure whereby the difference in thickness could be an apparent driving force to induce a convection.

Constitutive equations

From eq.19, we may write constitutive relations of heat and mass transfer within the water film in the hardened cement pastes as follows.

$$\mathbf{J}_q = L_{qq} \left[\frac{\partial T}{\partial x} \right] + L_{qc} \left[\frac{\partial P}{\partial x} \right] + L_{qd} \left[\frac{\partial \phi}{\partial x} \right] + L_{qe} \left[\frac{\partial \psi}{\partial x} \right], \quad (20)$$

$$\mathbf{J}_c = L_{cq} \left[\frac{\partial T}{\partial x} \right] + L_{cc} \left[\frac{\partial P}{\partial x} \right] + L_{cd} \left[\frac{\partial \phi}{\partial x} \right] + L_{ce} \left[\frac{\partial \psi}{\partial x} \right], \quad (21)$$

$$\mathbf{J}_d = L_{dq} \left[\frac{\partial T}{\partial x} \right] + L_{dc} \left[\frac{\partial P}{\partial x} \right] + L_{dd} \left[\frac{\partial \phi}{\partial x} \right] + L_{de} \left[\frac{\partial \psi}{\partial x} \right], \quad (22)$$

$$\mathbf{J}_e = L_{eq} \left[\frac{\partial T}{\partial x} \right] + L_{ec} \left[\frac{\partial P}{\partial x} \right] + L_{ed} \left[\frac{\partial \phi}{\partial x} \right] + L_{ee} \left[\frac{\partial \psi}{\partial x} \right]. \quad (23)$$

There are sixteen phenomenological coefficients, while they may be reduced or even determined by using Onsager's reciprocal relations or analogy with the classical constitutive relations. The most effective means to reduce the above phenomenological coefficients is to estimate the practically negligible flows by experiments and reduce the terms from the above equations whereas the experimental data available to support the estimation appears to be still insufficient.

The necessary experiments to promote the study of the deterioration of concrete more objectively should be executed with special attentions to the coupled flow of energy and masses that could be inevitably accompanied by the flow of a mass [29]. For the carbonation problem, flow of ions, water and gas may be at least taken into account. For chloride attack problem as well as CP/desalination/realikalization issue, interaction of ions, water and electric current may also be considered.

3. Conclusions

The principal results of simultaneous heat and moisture transfer models were reviewed concerning the applicability to the study of the deterioration of concrete. Among simultaneous heat and moisture transfer models, non equilibrium thermodynamic approach is considered to be providing a basic framework in which rational incorporation of various flows other than heat and moisture associated with the deterioration of concrete could be possible.

The deterioration of concrete is often associated with chemical reactions, which are represented only in the source terms of conservation equations in the existing models, while the constitutive relations are not always very clear. The estimation of the practically negligible flows may be based on the experiments, which should be executed with spatial attentions to coupled flows which may be associated with the flow of a mass.

The deformation especially the plastic deformation that is relevant to the deterioration of concrete is not studied in this paper whereas it may not be neglected even for the construction of a mass transfer model.

References

1. Hanson, R., Moisture in light-weight concrete roofs, Proc. RILEM Symp. Light Weight Concrete, Goteborg, 405-431, 1960
2. Kooi, J. van der, Moisture transport in cellular concrete roofs, Proc. 2nd Int. Symp. Moisture Problems in Building, Rotterdam, 2.5.5, 1974
3. Nicolajsen, A., Moisture transfer coefficients of cellular concrete (Danish), Report 25, Tech. Univ. Denmark, Lyngby, 124p, 1973
4. Nielsen, A. F., Moisture distribution in cellular concrete during heat and moisture transfer (Danish), Report 29, Tech. Univ. Denmark, Lyngby, 219p, 1974
5. Andersson, A-C., Verification of calculation methods for moisture transport in porous building materials, Document, Swedish Council for Building Research, D6:1985, 223P, 1985
6. Daian, J-F., Condensation and isothermal water transfer in cement mortar, Transport in Porous Media, 3, 563-589, 1988
7. Jonasson, J-E, Moisture fixation and moisture transfer in concrete, Trans. Int. Conf. Struct. Mech. React. Technol., 8th, 235-242, 1985
8. Sakata, K., A study of moisture diffusion in drying and shrinkage of concrete, Cement and Concrete Research, 3, 216-224, 1983
9. Abe, T., A mathematical model of heat and moisture transfer in concrete, Bulletin of Fukui Technical College, Vol. Science and engineering, 21, 149-160, 1987
10. Bazant, Z. P., Thonguthai, W., Pore pressure in heated concrete walls: theoretical prediction, Magazine of Concrete Research, 31(107), 67-76, 1979
11. Bazant, Z. P., Chern, J-C., Thonguthai, W., Finite element program for moisture and heat transfer in heated concrete, Nuclear Engineering and Design, 68, 61-70, 1981
12. Dhatt, G., Kadge, C., Roelandt, J-M., Coupled heat and mass transfer in ceramics at high temperature, Numerical Methods in Thermal Problems, 2, 830-842, 1985
13. Kamp, C. L., Roelfstra, P. E., Wittmann, F. H., Mihashi, H., Diffusion mechanisms and drying of concrete at elevated temperatures, Trans. Int. Conf. Struct. Mech. React. Technol., 9, 137-179, 1987
14. Claybrook, S. W., Muhlestein, L. D., WATRE: A program for computing water and gas released from heated concrete, US DOE Report, Conf-85410, 2, 775-782, 1985
15. Matsumoto, M., Simultaneous heat and mass transfer in porous wall and analysis of internal condensation, Int. Seminar Heat and Mass Transfer, Dubrovnik, 1, 45-58, 1978
16. Matsumoto, M., A periodic solution of moisture condensation and re-evaporation process in the building wall, Numerical Methods in Thermal Problems, 1, 819-829, 1985

17. Sakamoto, Y., Watanabe, K., Verification of the simultaneous heat and moisture transfer model using full-scale test wall, *J. Archit. Plan. Environ. Engng*, AII, 457, 39-47, 1994
18. Huang, C. L. D., Multi-phase moisture transfer in porous media subjected to temperature gradient, *Int. J. Heat and Mass Transfer*, 22, 1295-1307, 1977
19. Wittmann, F. H., Hollenz, C, On the significance of electroosmosis in hardened cement paste, *Cement and Concrete Research*, 4, 389-397, 1974
20. Wittmann, F. H., Kann das Prinzip der Elektroosmose zur Trockenlegung von Mauerwerk angewendet werden?, *B+B*, 4(4), 126-132, 1981
21. Masuda, Y., Tadano, H., Prediction model for progress of concrete carbonation, *France-Japan Workshop on Mass and Energy Simultaneous Transfer*, Tsukuba, No.11, 13p, 1992
22. Sætta, A. V., Schrefler, B. A., Vitaliani, R. V., The carbonation of concrete and the mechanism of moisture, heat and carbon dioxide flow through porous materials, *Cement and Concrete Research*, 23, 761-772, 1993
23. Kobayashi, K., Uno, Y, Carbonation mechanism of concrete (Japanese), *Concrete Research and Technology*, 1(1), 37-49, 1990
24. Kobayashi, K., Shiraki, R., Kawai, K., Migration and concentration of chloride, sulfides and alkali compounds in concrete caused by carbonation (Japanese), *Concrete Research and Technology*, 1(2), 69-82, 1990
25. Sætta, A. V., Scotta, R. V., Vitaliani, R. V., Analysis of chloride diffusion into partially saturated concrete, *ACI Material J.*, 90(5), 441-451, 1993
26. Andrade, C., Calculation of chloride diffusion coefficients in concrete from ionic migration measurements, *Cement and Concrete Research*, 23, 724-742, 1993
27. Ali, M. G., Migration of ions in concrete due to cathodic protection current, *Cement and Concrete Research*, 22, 79-94, 1992
28. Xu, Z., Hooton, R., Migration of Alkali ions in mortar due to several mechanisms, *Cement and Concrete Research*, 23, 951-961, 1993
29. Tada, S., Degradation of cement-based materials associated with the simultaneous mass and energy transport, *France-Japan workshop on simultaneous energy and mass transport*, Tsukuba, 10p, 1992