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Division of  
**BUILDING TECHNOLOGY**

Department of Building Sciences  
Kungliga Tekniska Högskolan

## Alternative approaches to moisture transfer in building materials

the use of natural stable isotopes and tracer gas

by

Kjartan Gudmundsson

Stockholm 2000





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# Alternative approaches to moisture transfer in building materials

the use of natural stable isotopes and tracer gas

Licentiate of Engineering Thesis  
Kjartan Gudmundsson  
June 2000

Kungliga Tekniska Högskolan  
Department of Building Sciences  
Division of Building Technology  
SE-100 44 Stockholm, Sweden

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## Preface

This licentiate of engineering thesis is the result of the author's research during the past three years at the Division of Building Technology at Kungliga Tekniska Högskolan in Stockholm, Sweden. The project has mainly been financed by the Swedish Council for Building Research (BFR) to whom the author wants to extend his gratitude.

The thesis contains three independent papers that share the topic of moisture in buildings and building materials. And while all the papers are about identifying the relevant transport mechanisms of water and water vapour, they approach the subject from different angles.

The first paper is the result of measurements that were done during a two-year period starting in January 1997, the aim of which was to evaluate the moisture properties of the roofs, walls and floors of houses that were built in an "environmental village" in the southern part of Stockholm. The measurement results were then used to estimate the risk of moisture accumulation for various moisture loads using a reference climate from the literature.

The second paper is about the transport of water vapour through porous building materials. The paper contains a review of the transport mechanisms of gases through porous materials and describes how the contribution of each mechanism can be quantified by carrying out tracer gas measurements together with transient measurements of water vapour permeability.

The third paper is about the tracing of leakage in buildings and how this can be done by measuring the concentration of the naturally occurring stable isotopes of Deuterium and Oxygen-18.

The author would like to thank the supervisor, Professor Gudni Jóhannesson at the Division of Building Technology for the support as well as for the numerous creative discussions during the past three years. Thanks are also due to associate Professors Folke Björk and Per Levin, the co-author of the first article, for their advice and helpfulness on matters big and small.

During the year of 1998 the author spent some six months at the ETH in Zürich, Switzerland. The author would like to thank Professor Bruno Keller and his co-workers at the Chair for Building Physics for their help on the subject and how to approach it. The stay in Switzerland was made possible by a scholarship from “Stockholms Byggnadsförening” to whom the author is sincerely grateful.

Stockholm

June 2000

Kjartan Gudmundsson

## List of papers

### **1. Moisture in Constructions with Loose-Fill Insulation and no Vapour Barrier**

*Per Levin and Kjartan Gudmundsson*

*Published in Nordic Journal of Building Physics*

### **2. An Approach to Water Vapour Transport Mechanisms in Building Materials**

*Kjartan Gudmundsson*

*Submitted to Nordic Journal of Building Physics*

### **3. Isotopic tracing of moisture in buildings**

*Kjartan Gudmundsson*

*Submitted to Nordic Journal of Building Physics*



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## 1. Introduction

Corrosion, deterioration of the mechanical strength of materials and fungal growth are some of the signs of excessive moisture content in buildings and building materials that may not only lead to irreparable break down of a construction but can even pose a risk to the health of the inhabitants.

The latest trends in building technology do by no means eliminate those threats, since the effort has mostly been directed to reducing the use of energy and materials, often neglecting the effects of increased insulation and the application of new materials on the moisture properties of the constructions. On the contrary, the risks are greater since there is little or no experience to rely on and are further enhanced when unfounded allegations are made concerning the physical properties of building materials and constructions. It is therefore of principal importance that the moisture properties of constructions are evaluated by the means of both modelling and *in situ* measurements.

This thesis contains the results of such a study whose aim was to investigate the moisture performance of new type of ecological constructions that were built in the southern part of Stockholm. An outline of the study is given in the following text whereas the results are to be found in the first paper of this thesis.

Needless to say the modelling of moisture in buildings and building materials requires that the physical mechanisms of moisture transport be known, as well as how they relate to the properties of the building materials.

This is the subject of the second paper of this thesis. The focus is on the transport of water in vapour phase and how it can be estimated by tracer gas measurements that together with transient measurements of water vapour permeability will enable us to tell apart and quantify the contributions of the different transport mechanisms. The idea originates in previous work done at the Division of Building Technology at KTH [1], where a tracer gas, dinitrogen oxide, was used to simulate the diffusivity of contaminant in a cellulose fibre insulated structure.

The aim was to find a way of assessing the water vapour permeability with tracer gas faster than with the well-known cup-method. In addition this was to be done with the standard equipment that has been used to measure the air exchange in buildings. The first step of the research consisted of a series of measurements

of the tracer gas permeability of light expanded clay aggregate that were compared to the water vapour permeability as measured by the cup method [2]. The results of that work were that the tracer gas measurements could be executed in a matter of hours in, whereas the cup-method measurements had to be carried out for months. The study failed to make clear the relationship between the diffusivity of tracer gas and the diffusivity of water vapour, but the results indicated that the dry-cup diffusivity of water vapour was about 1,5 times the diffusivity of tracer gas. The greatest mistake was perhaps that the specimens where too few, making it difficult to draw definite conclusions.

The next step included a survey of the literature in order to find out how the transport of one gas could be measured and the results used to calculate the potential transport of another. This demanded that the transport processes be identified and formulated as independent functions of material properties and the thermodynamic properties of the gas. The Dusty Gas Model (DGM) of Mason and Malinauskas [3] provides us with this and more since the model even explains how the different transport mechanisms can be combined to give the overall flow of gas through the material.

Further explanations were however required of the concentration dependence of the water vapour permeability, i.e. why the diffusivity increases with increasing relative humidity. The Random Hopping Model of surface diffusion [4] gives such an explanation. The model relates the concentration dependence of the diffusion coefficient to the energies of adsorption of the gas molecules and the energies that are involved in the migration from sorption sites. This is done by connecting the diffusion coefficient to the residence time at the sorption sites, which must depend on the effective energy of the bond that holds the molecule to the site.

Now we do therefore have the means to measure the potential transport of water vapour by measuring the flow of tracer gas. A description of the transport processes is to be found in the second paper of this thesis. The paper does also describe a mathematical model of the diffusion process that enables the deduction of the Fickian diffusion coefficient from transient measurements of tracer gas flow. In addition a mathematical model of surface diffusion, which will reveal the coefficient of surface diffusion, is presented. The latter is linked to the random



hopping model of surface diffusion, thus providing a phenomenological explanation of the physical process.

The third and last paper of this thesis is about the tracing of moisture transport by measurements of the isotopic content of the water. It is explained how water can be characterised by the abundance ratios of deuterium and oxygen-18 to their more common sister isotopes because they do not disintegrate by any mode of decay and do therefore give the water a distinct mark. The idea originates from the field of hydrogeology [5] where it has been proven quite useful. It is known how the meteoric processes modify the isotopic composition of the precipitation and the isotopic signature can therefore be used to trace the origins of groundwater. In a comparable manner measurements of the stable isotopic composition of ice cores from the Greenland glacier have been used to calculate the air temperatures of past climates.

In a similar way the isotopic composition of water in buildings can reveal the history of the water. In some cases the water may not have undergone any reactions that effect its isotopic contents and measurements will give an immediate answer to the question of its origins. In other instances the isotopic content will change as the moisture travels through the building and the building materials because of the different thermodynamic properties of the isotopically unlike water molecules. The paper describes how some of the most common transport mechanisms in buildings effect the isotopic composition of water. It is illustrated by an example how this can be used to determine the source of leakage in a building.

## 2. An outline of the papers

### 2.1 Moisture in Constructions with Loose-Fill Insulation and no Vapour Barrier

Per Levin and Kjartan Gudmundsson

Out of concern for the environment, the traditional polyethylene vapour barrier in lightweight constructions has sometimes been replaced with more diffusion open materials, such as polypropylene fabric. In order to evaluate how this may affect the risk of condensation in the constructions, in-situ measurements of the moisture content and temperature in the walls, roofs and floors of three houses have been conducted. Furthermore, the measurements have been used to establish a model that can be used to predict the moisture performance for design moisture loads. Measurements of moisture content and temperature in the outermost part of the insulation of the constructions have been carried out every three weeks over a two-year period, during which the indoor temperature and relative humidity were continuously registered. Based on indoor climatic data as well as information from a nearby weather station, the moisture conditions have been calculated using a one-dimensional transient diffusion model that takes into account the sorption properties of the materials.

The results of the measurements indicate that for the low moisture loads in the three houses there is no immediate risk of moisture damage. The results of the simulations show good correlation with measurements for the walls and a floor.

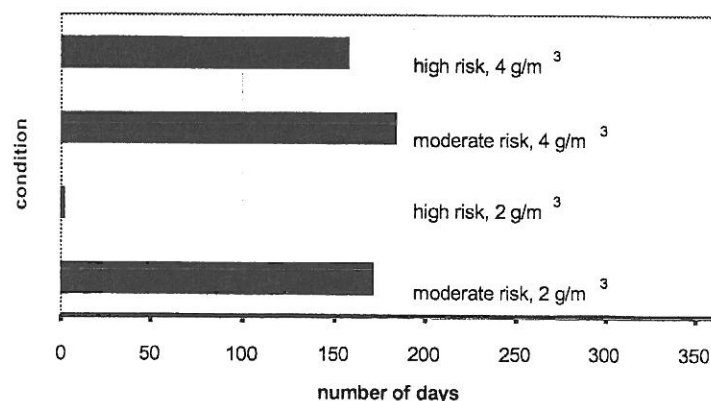


Figure 1 Mould growth risk analysis for the wall construction. Number of days when the criteria of high and moderate risk is met for the moisture loads of 2 g/m<sup>3</sup> and 4 g/m<sup>3</sup> respectively

The calculation model was therefore used to simulate the conditions for a design moisture load of 2 and 4 g/m<sup>3</sup> using a reference climate for Stockholm from the literature.

The results show that even for the lower design load moisture would accumulate and condense in the wall construction. Since high relative humidity would for long periods of time coincide with temperatures feasible for mould growth, the wall construction is not to be recommended.

A similar simulation of the piled floor construction shows that even for moderate moisture loads the risk for condensation is high. A correlation for the roof construction could not be achieved without adjusting parameters and therefore the model was not considered valid for the roof. There are strong indications that this is due to ongoing settling of the loose fill insulation in the roof construction, since no evidence of convection could be derived from the measurement results.

## 2.2 An Approach to Water Vapour Transport Mechanisms in Building Materials

Kjartan Gudmundsson

An analytical model of the different water vapour transport mechanisms in porous materials, based on the literature, is presented. This provides the tools for quantifying the material properties that rule the transport of moisture and thereby the means for modelling the moisture behaviour of constructions, the necessity of which can be stressed by the large number of houses that have suffered from inadequate moisture design.

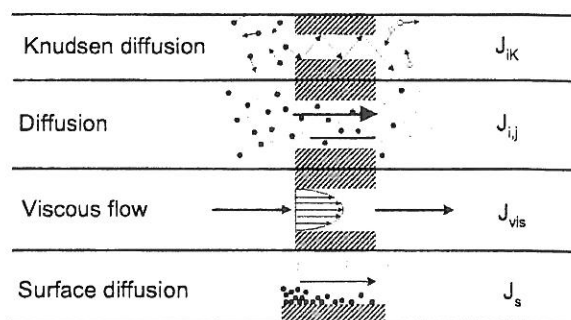


Figure 2 The different transport processes.

The model makes a clear distinction between Knudsen diffusion or effusion, continuum diffusion and surface diffusion. Each transport mechanism is formulated by explicit functions of the textural properties of the material and the thermodynamic properties of the gas.

We also know how the transport processes combine to give the overall flow. The ordinary diffusion is connected in series with Knudsen diffusion and the resulting diffusive flow is connected in parallel with viscous flow and surface diffusion.

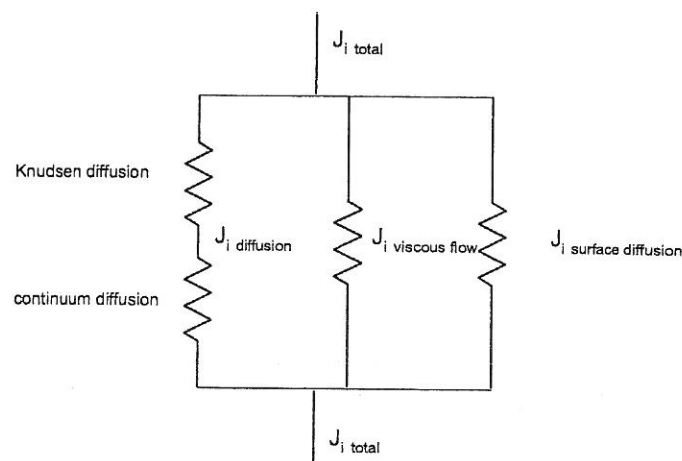


Figure 3 Combined transport

The model can be used to reveal the governing transport mechanisms in porous building materials by tracer gas measurements accompanied with transient measurements of water vapour permeability in a manner that gives a differentiated picture of the physical phenomena involved.

This can be done by first determining the textural properties governing Knudsen diffusion, ordinary diffusion and viscous flow. The permeability that rules the viscous flow can be determined by measuring the flow of a single gas under a pressure gradient. By measurements of the diffusive flows for different total pressures the contributions of effusion and ordinary diffusion can be separated since the latter is pressure dependant while the former is independent of pressure. The potential transport of water vapour due to those mechanisms can then be derived from the relationship between its thermodynamic properties and those of tracer gas.

A comparison with the measured transport of water vapour will then give the contribution of surface diffusion. The surface diffusion coefficient can be

obtained through transient measurements of water vapour permeability without having to solve the equation of diffusion. This can be done by writing the concentration dependent surface diffusion coefficient as an analytical function of the time-lag under the prerequisite that its functional form is known. This is provided by the random hopping model that relates the surface diffusion of adsorbed molecules to the amount adsorbed and the energies involved in adsorption.

### **2.3 Isotopic tracing of moisture in buildings**

Kjartan Gudmundsson

The means of tracing the flows of moisture in a building by using the stable isotopes of oxygen-18 and deuterium are described. It is shown how the knowledge of how the transport mechanisms and reactions involved effect the isotopic composition can be used to identify the sources of moisture. Of central importance is the isotopic content of precipitation as a primary source of moisture. It is explained how the governing reactions involved in transport of moisture in buildings effect the abundance ratios of oxygen-18 and deuterium.

The immediate practical use of isotopic tracing is to determine the source of leakage in buildings.

This is demonstrated by an example from a building in the southern part of Sweden. The isotopic analysis of the samples shows that the leakage water has undergone a reaction that favours the lighter isotopes resulting in an enrichment of both oxygen-18 and deuterium. This is illustrated by the deviation from the meteoric line in Figure 3. Therefore a direct comparison does not reveal the source of the leakage water.

The isotopic differences between the sample of leakage water and the other points that candidate as its sources were calculated. The results are shown in Figure 4. The possible scenarios for reactions and transfer between the point of leakage and the possible sources were then determined. The isotopic separation that was to result from those scenarios was then calculated and compared with the isotopic differences.

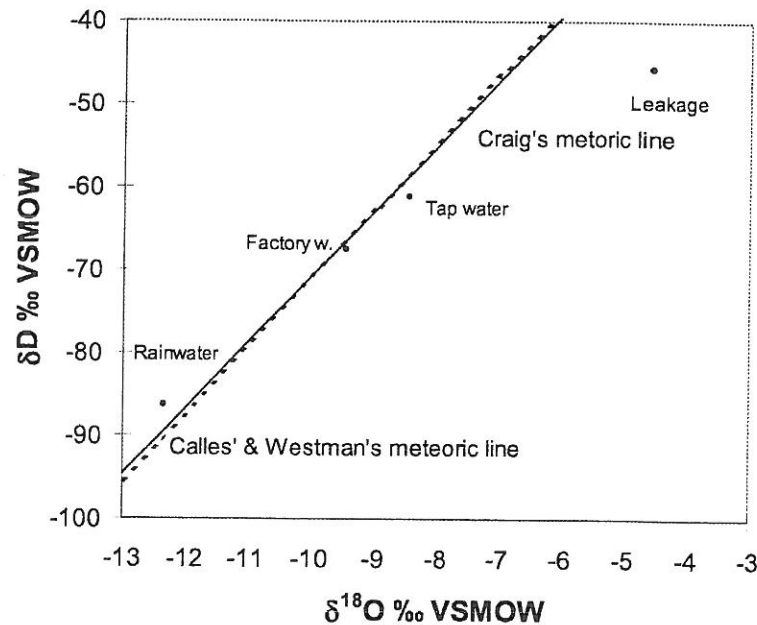


Figure 4 The measured abundance ratios and the global meteoric line of Craig and the local meteoric line of Calles' and Westman

Excessive water from the production at the factory was assumed to be one of the possible sources of leakage, in which case the isotopic content would have to be modified by the cement-water reaction process. Since the calculated isotopic separation from this process exceeds the measured isotopic difference by far it was concluded that the factory water was not a plausible source.

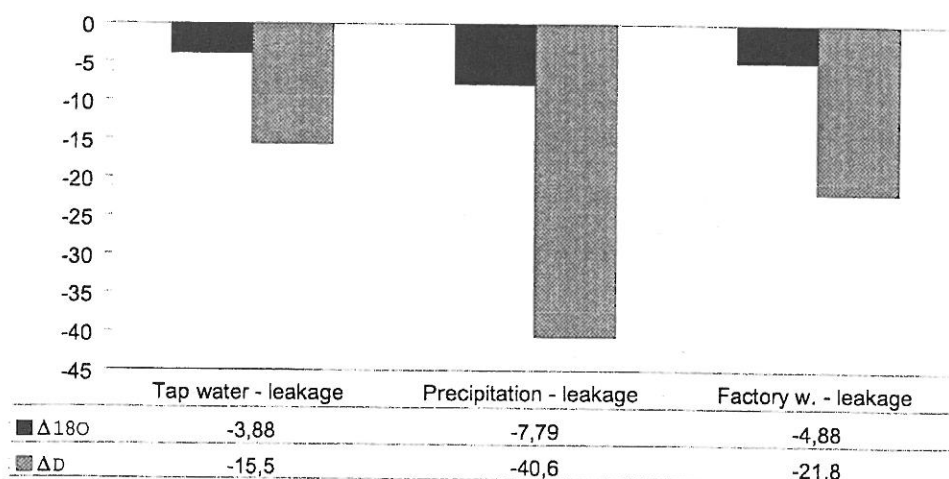


Figure 5 Measured isotopic separation between the leakage water and the other sources

A similar comparison was done for the tap water, which was assumed to have evaporated at 30°C and condensed in the construction at 10°C. And even

though a comparison of the calculated separation and the measured differences indicated that this was a possible series of events it could be discarded since it was contradictory to the temperature conditions in the construction.

The third candidate was precipitation on the building site during erection. It was assumed that the evaporation process had followed a Raleigh-type evolution and that the leakage was rainwater that accumulated during the building period, the half of which had evaporated before seeping through the construction. If this assumption holds the comparison of measurements and calculated isotopic separation gives that the source of leakage is most probably precipitation on the building site during erection.

### 3. Discussion

In this thesis an experimental investigation on site of a new ecological housing project is revised. The study shows that the moisture conditions in walls with an air barrier but open to moisture diffusion could be predicted using standard methods for moisture diffusion. According to the performed measurements and calculations, a wall construction with loose-fill cellulose fibre insulation is not to be recommended because of the risk of condensation and high relative humidity coinciding with temperatures that are feasible for mould growth. Moreover, measurements and calculations indicate that the floor construction involves great risk for condensation. So far measurement results on the roof construction are inconclusive and show poor correlation to the diffusive calculation model. The reasons might be ongoing settling of the insulation material, i.e. changing conditions and perhaps convective moisture transport, even though this was not detected.

The thesis does also include a paper that explains how we can in a fast manner measure the potential transport of water vapour by measuring the flow of a tracer gas. In the simplest case of non-hygroscopic materials, the moisture permeability will be immediately revealed by the tracer gas experiments alone, whereas the potential surface diffusion in hygroscopic materials can be quantified by transient measurements of water vapour permeability. This will make it possible to separate the contributions of each transport mechanism, which will help in the design of moisture-safe constructions and even in improving the moisture performance of building materials. The results of the study are not to be seen as final in the sense that experimental work needs to be carried out in order to verify some of the assumptions that have been made.

The last paper of the thesis is about the use of isotopes to trace the movements of water through buildings and building materials. It has been explained how the isotopic content changes when the water undergoes reactions. For some of the most common reactions and transport processes in buildings those changes have been quantified. It has been shown by an example that this can have a practical application when the origins of leakage water in buildings have to be determined.



It should however be stressed that this method needs further development. An important part of that development would be to carry out more fieldwork but those would preferably be accompanied by laboratory measurements as described in the next section.

#### **4. Future Research**

The next step in the tracer gas study will focus on development of measurement techniques that can be used to verify the model and the assumptions that have been made. This work will start in the year 2000.

The work will include measurements of the pressure dependency of the non-concentration-dependent diffusion and whether that dependency, if found, can in practice be used to distinguish the contribution of Knudsen diffusion and ordinary diffusion. This will be done by placing the specimen between a pair of closed vessels, the pressure in which will be equally increased by pumping in the same amount of air.

It will be investigated whether surface diffusion can be estimated by time lag methods and whether it can be done with sufficient accuracy without separate measurements of the sorption curves for the material. This will be done by transient wet-cup measurements.

Further evaluation and development of the isotopic tracer method will have to include measurements in the field as well as experiments in the controlled environment of the laboratory. That will involve the measurements of how the isotopic composition is effected by the different transport mechanisms as well as an investigation of the effect of condensation and sorption in building materials. The latter will be done by distilling the material in a closed container placed in a climate chamber and collecting the vapour by a series of condensers. Furthermore, methods will have to be developed for collecting water vapour from air in order to make it possible to compare its isotopic content to that of water in building materials.

The purpose is not only the further development of a method for determining the source of leakage water in buildings. It will also be to show how the measured isotopic differences can be used to determine which mechanisms rule the transport of water through the material.

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# **Paper 1**

**Moisture in Constructions with Loose-Fill Insulation and no  
Vapour Barrier**

**Per Levin and Kjartan Gudmundsson**



## Moisture in Constructions with Loose-Fill Insulation and no Vapour Barrier

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*Per Levin, PhD, Associate Professor,  
Department of Building Sciences, Kungl Tekniska Högskolan  
perlev@bim.kth.se*

*Kjartan Gudmundsson, MSc,  
Department of Building Sciences, Kungl Tekniska Högskolan  
kjartan@bim.kth.se*

**KEYWORDS:** vapour barrier, condensation, moisture measurements, transient diffusion model.

### SUMMARY

*Out of concern for the environment, the traditional polyethylene vapour barrier in lightweight constructions has sometimes been replaced with more diffusion open materials, such as polypropylene fabric. In order to evaluate how this may affect the risk of condensation in the constructions, in-situ measurements of the moisture content and temperature in the walls, roofs and floors of three houses have been conducted. Furthermore, the measurements have been used to establish a model that can be used to predict the moisture performance for design moisture loads. Measurements of moisture content and temperature in the outermost part of the insulation of the constructions have been carried out every three weeks over a two-year period, during which the indoor temperature and relative humidity were continuously registered. Based on indoor climatic data as well as information from a nearby weather station, the moisture conditions have been calculated using a one-dimensional transient diffusion model that takes into account the sorption properties of the materials.*

*The results of the measurements indicate that for the low moisture loads in the three houses there is no immediate risk of moisture damage. The results of the*

*simulations show good correlation with measurements for the walls and a floor. The calculation model was therefore used to simulate the conditions for a design moisture load of 2 and 4 g/m<sup>3</sup> using a reference climate for Stockholm from the literature. The results show that even for the lower design load moisture would accumulate and condense in the wall construction. Since high relative humidity would for long periods of time coincide with temperatures feasible for mould growth, the wall construction is not to be recommended. A similar simulation of the piled floor construction shows that even for moderate loads the risk for condensation is high. A correlation for the roof construction could not be achieved without adjusting parameters and therefore the model was not considered valid for the roof. There are strong indications that this is due to ongoing settling of the loose fill insulation in the roof construction, since no evidence of convection could be found from the measurement results.*

## **1. Background**

Since the energy crisis in the 1970-ies, the thermal performance of Swedish lightweight timber-framed constructions has greatly increased. In these multi-layer walls, different materials have been developed to fulfil different functional requirements, e.g. the polyethylene film used as vapour barrier and airtight layer and high-performance thermal insulation. The requirement on U-values in the Swedish building codes governs the thickness of the insulation layer. Most insulation materials used in lightweight constructions are open to water vapour diffusion. In combination of the high thermal performance, which makes the outside of the constructions cold owing to the small heat flux, there is a risk of condensation in winter on the inside of the outer sheathing. This risk was considered in the more prescriptive building codes that were in effect until 1991, where the construction layer outside the insulation should be five times more open to diffusion than the layer inside the insulation. Using the polyethylene vapour barrier normally fulfilled this requirement.

In several project with so called environmentally adapted buildings, the polyethylene vapour barrier have been replaced with a polypropylene fabric or other material open to water vapour diffusion.

This means that moisture can migrate into the constructions in wintertime and a subsequent risk for condensation on the outer sheathing as well as increased thermal conductance.

A number of authors have investigated the effects of omitting the vapour barrier in lightweight constructions.

In a study carried out by (Harderup, 1997) the moisture performance of timber framed walls and attic floors with cellulose fibre insulation were investigated. One of the findings was that, for the relatively low moisture supply of  $1,2 \text{ g/m}^3$ , there was no sign of high moisture content. The author makes a remark on the high moisture resistance on the inside of the insulation in comparison to the outside, roughly five times.

(Sikander, 1996) has written a report on the "moisture safety" of several constructions. The author concludes that choosing cellulose fibre instead of mineral wool has no significance for the moisture safety of the constructions. Furthermore, the author points out the significance of a high moisture resistance on the inside of the insulation in relation to the moisture resistance of the exterior cladding.

## **2. Objective**

In-situ moisture measurements have been performed in floors, walls and roofs of three similar houses without traditional vapour barrier during a two-year period. The objective of this study was to measure the moisture content in the constructions and to simulate the moisture performance for other moisture loads than during the measurements. Of particular interest was the dynamic behaviour of the construction for varying internal moisture loads and outdoor temperature and humidity.

## **3. Construction description**

The three gable-end row houses where the measurements took place are a part of an "environmental" building program that consists of 44 apartments situated in the south of Stockholm. The houses that were built in 1996 are two storey wood-frame constructions, with a living area of about  $160 \text{ m}^2$ . Two foundation methods were used, ventilated crawl spaces and piling, where the terrain was more steeply sloped. The floor constructions were the same. The wall constructions are made out of lightweight studs with cellulose fibre insulation and timber cladding on the outside and gypsum board on the inside.

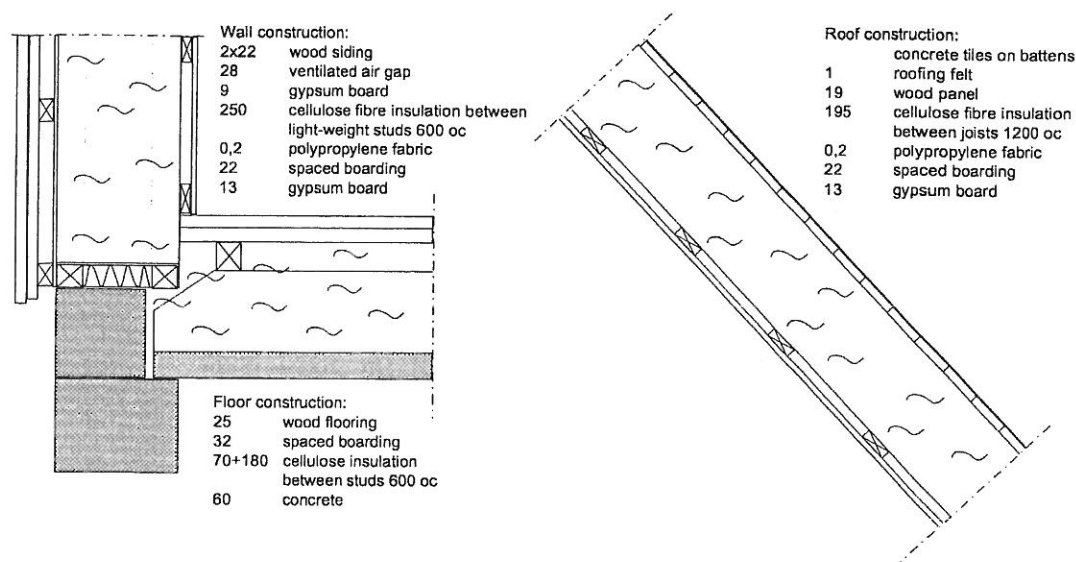


Figure 1. Roof, wall and floor constructions in the houses (measures in mm).

The parallel roofs are timber constructions with cellulose fibre insulation in between light weight Masonite rafters, that are clad with gypsum sheets on the inside, whereas the roofing consists of concrete tiles resting on battens with standard wood panel and roofing felt underneath.

The construction layers for the sloped roof, the wall and the floor constructions are shown in Figure 1. The houses have mechanical exhaust ventilation systems.

#### 4. Performed measurements

Moisture measurements were performed during 1997 and 1998 to find out the moisture conditions in the constructions and the corresponding moisture load from the ambient environment indoors and outdoors.

Moisture measurements in the constructions were made by electric resistance measurements on calibrated plywood sensors that were mounted in the constructions. The sensors have a diameter of about 50 mm and a thickness of 11 mm.

The measured moisture content in the sensors,  $u$  [kg/kg] was then converted to relative humidity, RH [%] of the surrounding air by using the sorption curve for the particular sensor. The sorption curve was provided by the manufacturer of the sensors. A built-in thermocouple gave the corresponding temperature in the measurement points. The sensors were read once every three weeks. In order to find the dimensioning spots, the sensors were placed on the North walls and roofs sides and on places where condensation was most likely to occur.



External wall sensors were mounted on the inside of the external gypsum boards on the middle of the first and second stories. In the floors, the sensors were placed on top of the concrete slab and in the “parallel” roof construction on the inside of the sub roof wood siding. Sensors on the outside of the constructions were placed in the piling foundation of 2 houses, in the crawlspace of one house, in the attic of two houses and at the eaves, as outdoor reference points.

To find the interior moisture load, continuous temperature and relative humidity measurements with hourly resolution were performed in one representative spot in each of the three dwellings, using Mitec satellite data loggers and Vaisala probes. A more detailed revision of the measurements is given in (Levin & Gudmundsson, 2000).

Hourly values of outdoor temperature, relative humidity, wind speed and direction and solar radiation were taken from a nearby climatic station operated by the city of Stockholm.

## **5. Calculation model**

The model used for simulating the moisture condition in the constructions is a numerical solution of Fick’s first law for diffusion under transient conditions, where the sorption properties of the materials is taken into consideration. The moisture transport is assumed to be purely diffusive. Solar radiation is not taken into account. When calculating the temperature distribution the conditions are assumed to be steady-state and daily averages are used. All flows are assumed to be one-dimensional.

In principle, calculations have been carried out with the forward difference method by the MathCad mathematical calculations program. This means that the constructions are divided into segments with nodes in the middle connected by threads having a certain heat and moisture resistance. Thin material layers were combined into layers while the insulation was divided into four segments. For further references see for example (Hagentoft & Harderup, 1995) or (Nevander & Elmarsson, 1994). An iterative process gives an adequate time step of one day, so for each day the net diffusive flow into the nodes is calculated, and added to the water content of the previous day. The vapour permeability of the materials is assumed to be constant.

The flow is driven by the gradient of vapour concentration between the nodes. The vapour concentration is calculated in every time step (day) from the relative humidity, which, by using the inverse of the function describing the sorption isotherm, can be based on the water content of the previous day. The net flow into node  $j$  can then be written

$$\Delta g_j = \frac{v_j - v_{j-1}}{Z_j} + \frac{v_j - v_{j+1}}{Z_{j+1}} \quad [\text{kg/m}^2 \cdot \text{s}] \quad (1)$$

where  $v_{j-1}$ ,  $v_j$  and  $v_{j+1}$  are the vapour concentrations  $[\text{kg/m}^3]$  of the previous node, the node in question and the next node, in that order, whereas  $Z_j$  and  $Z_{j+1}$  are the moisture resistances  $[\text{s/m}]$  of the thread preceding the node and the one behind it. This gives an accumulated water content  $\Delta w$   $[\text{kg/m}^3]$ , over the period  $\Delta t$   $[\text{s}]$  that for a node of width  $\Delta x$   $[\text{m}]$  can be written:

$$\Delta w_j = \Delta t \cdot \frac{1}{\Delta x_j} \cdot \left( \frac{v_j - v_{j-1}}{Z_j} + \frac{v_j - v_{j+1}}{Z_{j+1}} \right) \quad [\text{kg/m}^3] \quad (2)$$

## 6. Measurement results

The indoor and outdoor climatic conditions were measured on an hourly basis, and allow the calculation of the indoor moisture supply. Figure 2 shows the moisture supply for all three houses based on the differences in vapour concentration between indoors and outdoors. Measurements started in the beginning of February 1997 and ended in February 1999.

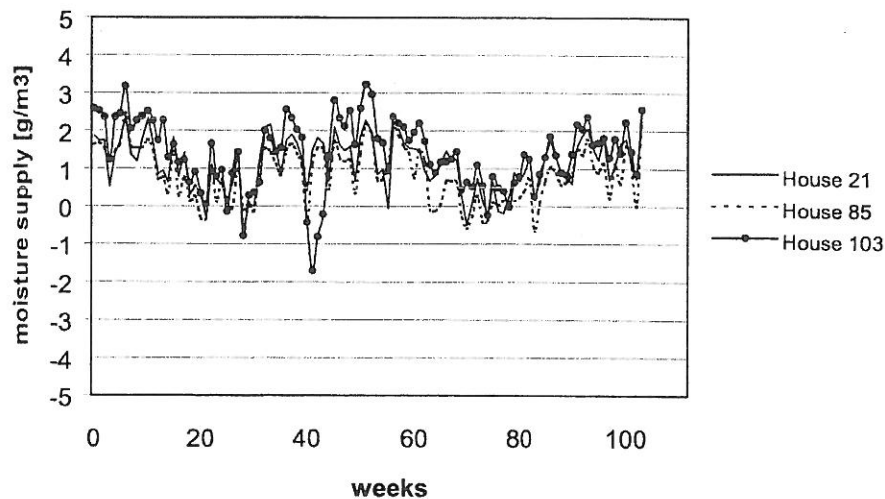


Figure 2. Weekly mean values for the moisture supply for the three houses, starting in February 1997.

The average moisture supply for the two-year period was  $1,1 \text{ g/m}^3$  for house 21,  $0,8 \text{ g/m}^3$  for house 85 and  $1,5 \text{ g/m}^3$  for house 103. The moisture production reflects, among other things, the number of inhabitants ranging from only 2 persons in house 85 to 6 persons in house 103, but is also affected by the living habits and ventilation rate. The sorption and desorption of moisture by interior surfaces can cause some time delay between alterations of indoor and outdoor vapour content. This can result in a negative moisture supply as shown in fig. 2.

Ventilation rates were measured in one winter month of 1998 using a passive tracer gas method with diffusive sampling. The measured air exchange rates were 0,67, 0,48 and 0,69 exchanges per hour for houses 21, 85 and 103 respectively.

The results for the relative humidity, based on measurements, for the walls, the floors and the sloped roof are shown in Figures 3 to 5 versus the number of days since February 2<sup>nd</sup> 1997. As a reference, the relative humidity at the eaves of house 21 is shown in Figure 3.

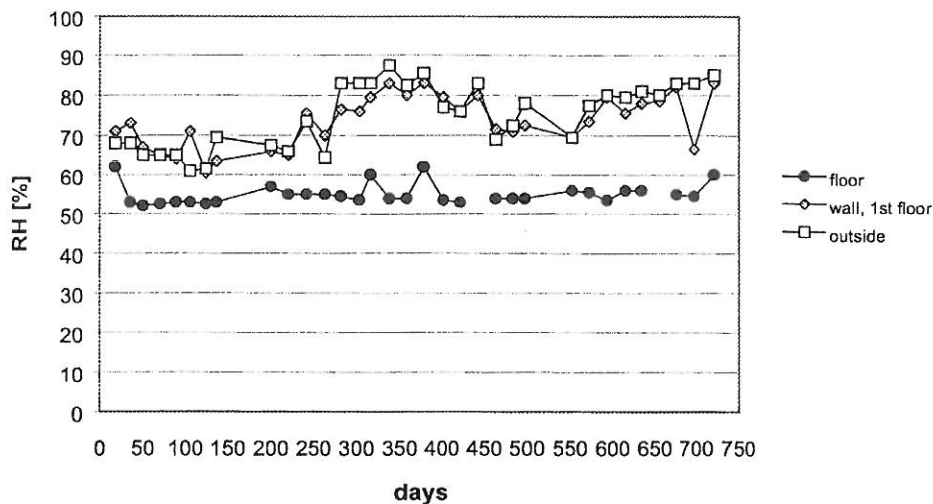


Figure 3. Measurement values of relative humidity in wall, floor and at the eaves of House 21.

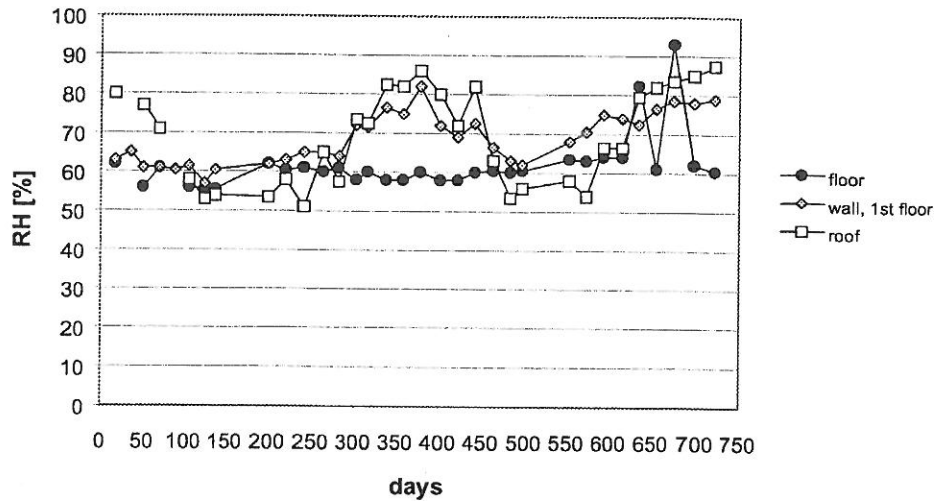


Figure 4. Measurement values of relative humidity in wall, roof and floor of House 85

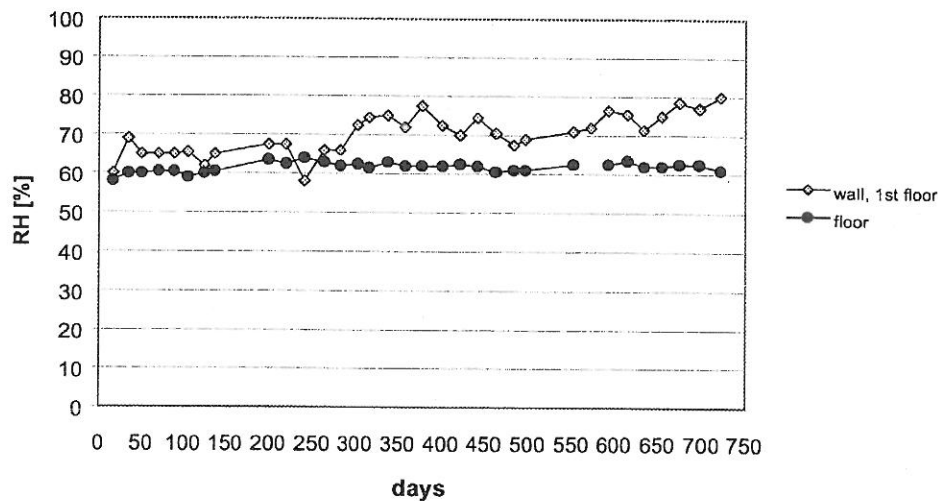


Figure 5. Measur. values of relative humidity in wall and floor of House 103.

## 7. Calculation results

In order to evaluate the performance of the constructions in question over a longer period of time, a simulation was carried out for a 5-year period, which by trial was assumed to be the time it takes the construction to reach equilibrium with the ambient environment.

The climatic data used for verifying the model is the actual daily mean values of vapour concentration and temperature.

The material properties used are assumed to be constant and are listed in Table 1 below. The properties of the cellulose fibre, the polypropylene fabric and the roofing felt are based on information from the manufacturers. The other values presented in the table are to be found in the literature, for example in (Nevander &

Elmarsson,1994). The value for the inside gypsum board includes wallpaper. The value used for the wood siding corresponds to moderate ventilation of the air gap.

In order to calculate the relative humidity from the water content, the inverse function of the sorption isotherm was used. The sorption curves for the gypsum board, cellulose fibre insulation and the wood siding were approximated with polygonal curves.

Table 1. *Material properties used for the calculations.*

Material	thickness	thermal conductivity $\lambda$	thermal resistance $R$	moisture permeability $\delta$	moisture resistance, $Z$
	[mm]	[W/m·K]	[m <sup>2</sup> ·K/W]	$\cdot 10^{-6}$ [m <sup>2</sup> /s]	$\cdot 10^3$ [s/m]
Gypsum, inside	13	0,22	-	-	10
Polypropylene	-	-	-	-	2,7
Cellulose fibre	195	0,039	-	10	-
Gypsum,outside	9	0,22	-	-	3
Wood siding	-	-	0,157	-	11
Roof panel				0,2	-
Roofing felt			-	-	3
Concrete	60	1,4	-	1	-

The water content and the corresponding relative humidity of the sorption curves' breaking points are shown in Table 2. No consideration was taken to whether moisture was being absorbed or desorbed. Instead, a mean value for the two different processes was used.

Table 2. *Breaking points of sorption curves.*

Material	$w_1$	$w_2$	$w_3$	$w_4$	$RH_1$	$RH_2$	$RH_3$	$RH_4$
	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]	[%]	[%]	[%]	[%]
Gypsum board	6,0	12,5	25	100	12,5	50	75	100
Cellulose fibre	7,0	10,2	16	16	75	90	100	-
Wood siding,panel	25	75	150	150	12,5	62,5	100	-
Concrete	24	40	65	130	10	50	70	100

For comparison with measurements for the wall, the vapour concentration of the outside gypsum board has been used. Since the wall sensors are situated just inside the gypsum board they should have a vapour concentration that is marginally lower than that of the board but to some extent higher than in the middle of the outermost segment of the insulation. Figure 6 shows the measured vapour concentration in the

1<sup>st</sup> floor wall of house 21 and values obtained by calculation for a period of two years starting on February the second 1997.

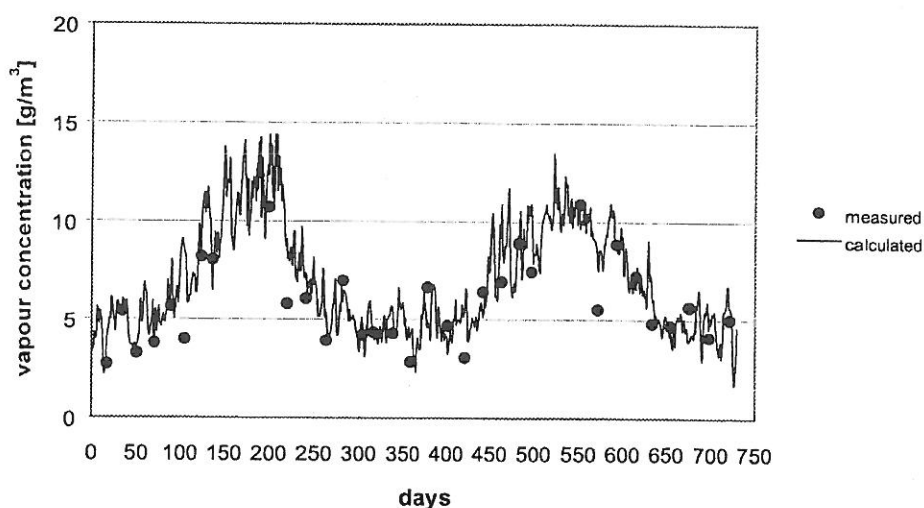


Figure 6. *Measured vapour concentration vs. calculated for the wall of house 21.*

The same sort of calculation has been carried out for the roof of house 85. The results are shown in Figure 7.

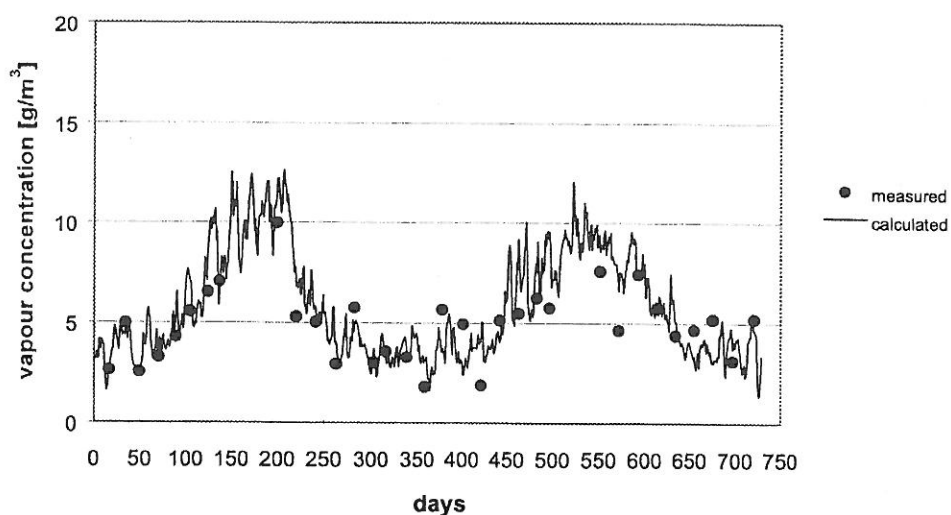


Figure 7. *Measured vapour concentration vs. calculated for the roof of House 85.*

The simulated conditions for the roof did not show as good an agreement with the measurements. Since the measurement results showed both under- and overestimation of vapour content for the whole range of temperature gradients there is no clear indication of natural convection in the roof construction. Furthermore, a thermographic investigation of the roof construction was carried out in order to

investigate the possible role of forced convection as the source of inconsistency between measurements and the model. The pictures taken with the thermal camera did not indicate any air leakage through the roof construction at a pressure gradient of 50 Pa. There are some indications of a relative decrease with time of the thermal resistance of the construction on the inside of the sensor, which may be caused by settling of the insulation. Figure 8 shows the ratio of thermal resistance on the inside of the sensor to the total thermal resistance, based on measurements of the indoor temperature, the temperature in the sensor and the outdoor temperature measured at the eaves. The measurements that were conducted in the mornings succeeding night frost have been omitted in Figure 8.

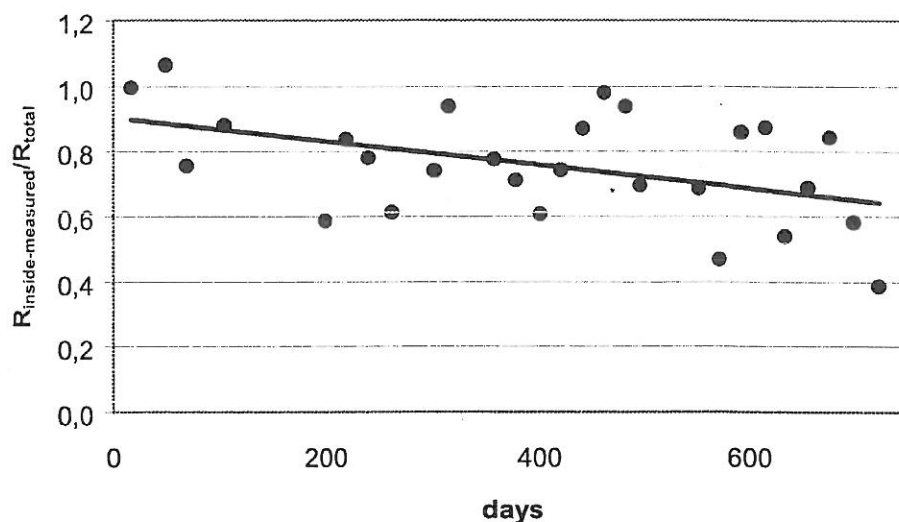


Figure 8. Thermal resistance ratio during the measurement period, based on temperature measurements.

The conditions for the floor in House 85, where piling foundation was used, show a relatively good correlation between the model and the measurements as shown in Figure 9.

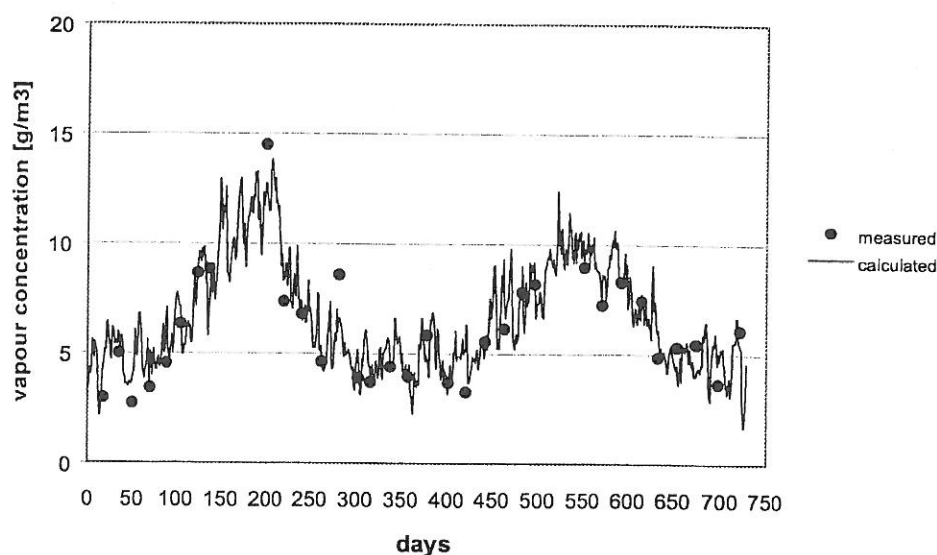


Figure 9. Measured vapour concentration vs. calculated for the floor of house 85.

## 8. 5-year simulation

As the model gave fairly good agreement with the measurements of the floor of House 85 and the walls of all houses, a 5-year simulation was run to see how the constructions would perform during a longer period of time under design moisture load and weather conditions. The climatic conditions used in the simulation are based on monthly mean values for the weather station in Bromma and taken from (Nevander et al 1994). The results of the 5-year simulation for the actual wall construction are shown in Figures 10 and 11 and for the floor constructions in Figures 12 and 13. Two different moisture loads were used, 2 and 4 g/m<sup>3</sup>. The moisture loads were assumed to be constant throughout the year. The node in the gypsum board lies in its middle, whereas the node in the cellulose fibre is 31 mm from the inside of the outer gypsum board.

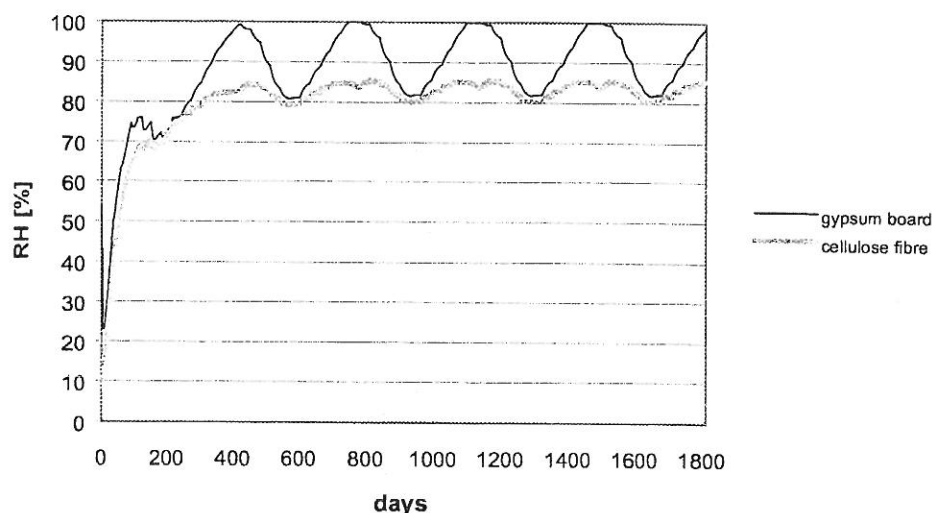


Figure 10. 5-year simulation of wall, for a moisture supply of 2 g/m<sup>3</sup>.



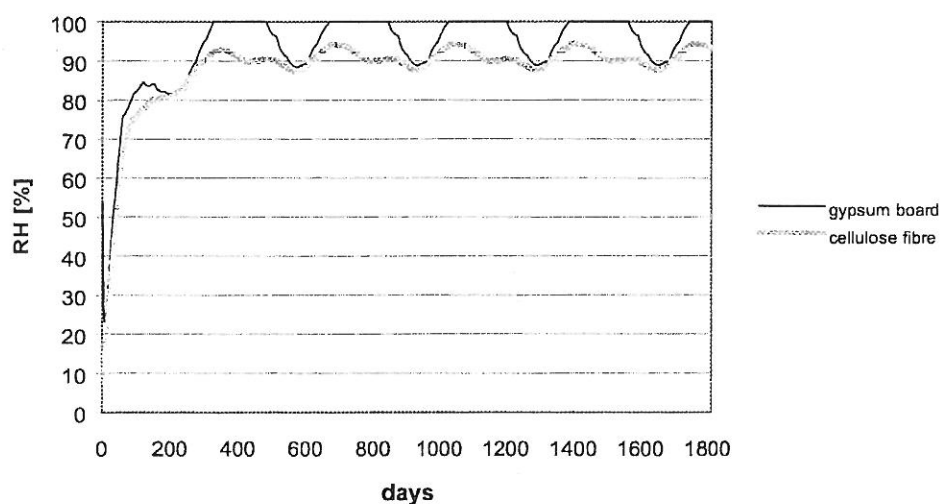


Figure 11. 5-year simulation of wall, for a moisture supply of  $4 \text{ g/m}^3$ .

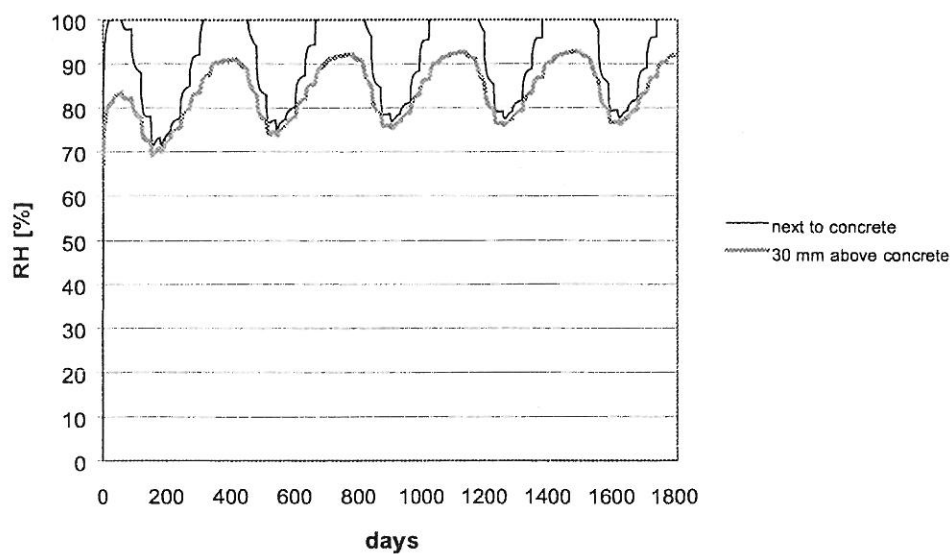


Figure 12. 5-year simulation of floor, for a moisture supply of  $2 \text{ g/m}^3$ .

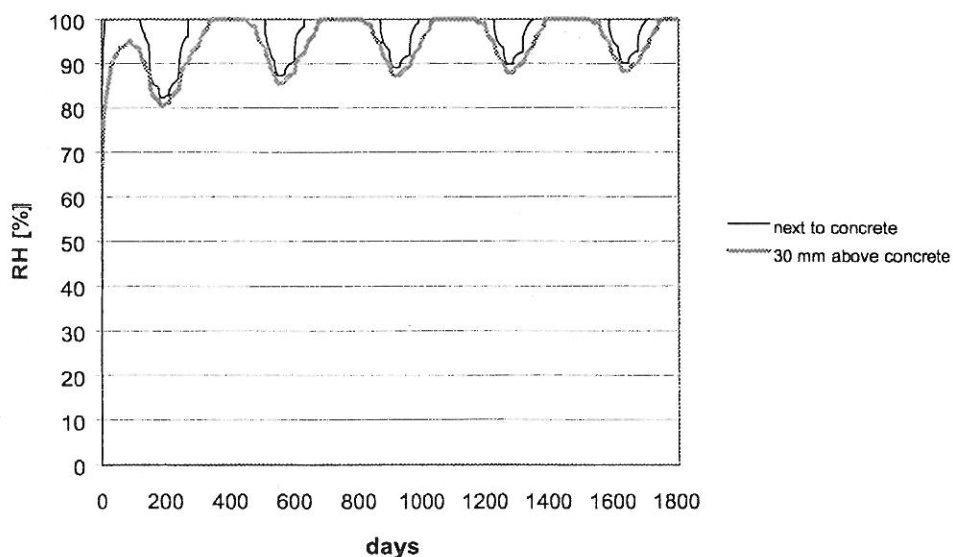


Figure 13. 5-year simulation of floor, for a moisture supply of  $4 \text{ g/m}^3$ .

The significance of the calculated moisture conditions shown in Figures 10 and 11 can be evaluated by counting the number of days when a certain temperature is exceeded at the same time as the humidity rises above a certain level, thus making mould growth feasible. Using the curve of (Nevander & Elmarsson, 1994) these criteria may be set to a temperature of 8°C and a relative humidity of 70% for a moderate risk of mould growth and 85% for a high risk of mould growth. The results for the wall construction are shown in Figure 14.

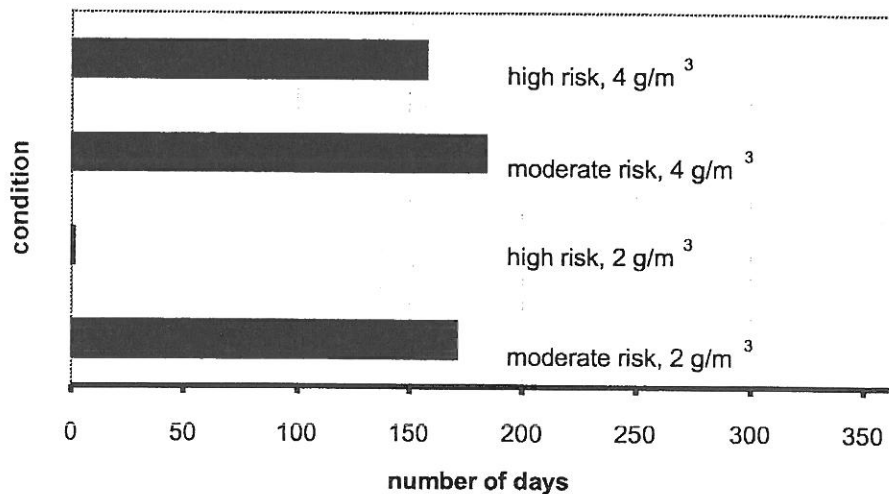


Figure 14. Mould growth risk analysis for the wall construction. Number of days when the criteria of high and moderate risk is met for the moisture loads of 2 g/m<sup>3</sup> and 4 g/m<sup>3</sup>.

## 9. Discussion

The measurements indicate no immediate danger of moisture damage in the walls and floors of the three houses. There are, however, some questions about the moisture safety of the constructions for higher moisture loads.

Calculation of relative humidity for the wall construction, using a calibrated model, standard weather conditions and increased indoor moisture production gave frequent condensation on the gypsum board for a moisture production of 4 g/m<sup>3</sup>, as can be seen in Figure 9.

The long condensation periods in combination with higher spring temperatures indicates a considerable risk for moisture damage at design moisture loads or more extreme climatic conditions. The margin towards potential moisture problems seems to be too small.

Similar 5-year simulations of the floor construction show that even for the floor there is a considerable risk for condensation, even for moderate loads, as can be seen in Figure 12 and Figure 13. It should be mentioned that the model only correlated well for one of the two houses that were built on piled foundations.

For several reasons a simulation of the roof has been omitted. Firstly, there are some indications that the cellulose fibre insulation at the purlin is sinking with time. The deviation from the measured values increased with time and was accompanied with an increased temperature that might even be caused by air leakage. Secondly the obtained overestimation of the vapour content during the summer indicates the effect of solar radiation on the adjacent south slope of the roof.

## 10. Conclusions

This study shows that the moisture conditions in walls with an air barrier but open to moisture diffusion could be predicted using standard methods for moisture diffusion.

According to the performed measurements and calculations, a wall construction with loose-fill cellulose fibre insulation and no vapour barrier might escape condensation and high levels of relative humidity when the moisture loads are low. However, an indoor moisture production exceeding  $2 \text{ g/m}^3$  will cause condensation on the inside of the external sheathing and high relative humidity in the insulation. Using the commonly recommended design value of  $4 \text{ g/m}^3$  moisture will most probably cause damage to the construction.

Moreover, measurements and calculations indicate that the floor construction involve great risk for condensation.

So far measurement results on the roof construction are inconclusive and show poor correlation to the diffusive calculation model. The reasons might be ongoing settling of the insulation material, i.e. changing conditions and perhaps convective moisture transport, even though this was not detected.

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# **Paper 2**

**An Approach to Water Vapour Transport Mechanisms in  
Building Materials**

**Kjartan Gudmundsson**



## An Approach to Water Vapour Transport Mechanisms in Building Materials

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**Kjartan Gudmundsson, MSc,**  
*Department of Building Sciences, Kungl Tekniska Högskolan*  
*kjartan@bim.kth.se*

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### SUMMARY

*An analytical model of the different water vapour transport mechanisms in porous materials, based on the literature, is presented. In this paper it is shown how this model can be used to reveal the governing transport mechanisms in porous building materials by tracer gas measurements accompanied with transient measurements of water vapour permeability in a manner that gives a differentiated picture of the physical phenomena involved. This provides the tools for quantifying the material properties that rule the transport of moisture and thereby the means for modelling the moisture behaviour of constructions, the necessity of which can be stressed by the large number of houses that have suffered from inadequate moisture design.*

*The model makes a clear distinction between Knudsen diffusion, continuum diffusion and surface diffusion. Each transport mechanism is formulated by explicit functions of the textural properties of the material and the thermodynamic properties of the gas. The known properties of the tracer gas can therefore be used to reveal the textural properties of the material, from which the potential water vapour transport, in gas phase, can be derived from the thermodynamic properties of water vapour.*

*The random hopping model is used to explain how the surface diffusion of adsorbed molecules relates to the amount adsorbed and the energies involved in adsorption. Furthermore it is shown how the concentration dependant surface diffusion coefficient can be*

*expressed as an analytical function of the time-lag which makes it possible to obtain the diffusion coefficient through transient measurements of water vapour permeability without having to solve the equation of diffusion.*

## **1. Introduction**

Moisture is the single most common cause of damage to buildings. The adversary effects of excessive moisture content manifest themselves in the deterioration of material properties, such as mechanical strength and thermal conductivity, as well as corrosion of the building materials and fungal growth to name but a few. Subsequently the indoor climate of the building may decline, which can pose a serious threat to the health of the inhabitants.

If these potentially harmful consequences of moisture are to be avoided, it is of paramount importance that the response of the building components, and the building as a whole, to the actual climatic conditions is known. This demands insight into the processes involved in the transport of moisture, which in turn must depend on the properties of the building materials. This becomes even more important when the requirement of optimal utilisation of energy and material resources calls for new construction methods as well as the reinvention of old ones, which in some instances makes it impossible to rely on knowledge gained by experience.

This paper deals with the transport of water vapour through porous building materials. It is shown how a distinction can be made between the key transport processes and how these can be quantified in terms of the textural properties of the materials and the thermodynamic properties of water vapour. It is also shown how these transport processes can be combined to give the overall transport of vapour through the material.

A method of obtaining the textural properties of a porous building material by using a non-absorbing tracer gas together with the sorption isotherms is proposed. In contrast to the commonly used “cup-method” the tracer gas method can be used to identify the relative contribution of each transport mechanism. In addition the tracer gas method provides the means to estimate the moisture permeability many times faster than can be done with the “cup method”.

Moreover, the measurements can be carried out with tracer gas measurement instruments that are commonly used to measure the air exchange of buildings.



The transport processes that the paper deals with are those of Knudsen diffusion, ordinary diffusion and viscous flow as put forward by the Dusty Gas Model of Mason [1] and surface diffusion as described by the random hopping molecule model of Higashi [2].

In the case of viscous flow the flow of the tracer gas as a function of pressure gradient will reveal the permeability of the material and therefore the potential transport of moisture under a pressure gradient can be calculated, given the viscosity of the mixture of water vapour and air.

Knudsen diffusivity can be written as a function of the mass of the effusing particles, the temperature and the Knudsen coefficient which is a structural property of the material and can be assumed to be independent of the sort of gas in question. This means that once we have measured the Knudsen coefficient of the material, with a tracer gas, we can calculate the potential flow of water vapour due to Knudsen diffusion.

Diffusion is dealt with in a similar manner. The diffusion coefficient can be written as the product of the diffusivity of the gas in air times the ratio of porosity to tortuosity. Since the latter is independent of the gas in question, the ratio of the diffusion coefficient of water vapour over the diffusion coefficient of a tracer gas must equal the ratio of the binary diffusion coefficients in air, the values of which can be found in the literature.

In the random hopping model, surface diffusion is pictured as flow due to a gradient of the number density of the hopping molecules. The number density is related to the activation energies required to trigger a jump. This relationship should not come as a surprise since the diffusion coefficient is known to be exponentially dependent on temperature, something that characterises an activated process. This seems to have eluded researchers in the field of building physics though, and whereas surface diffusion is rarely mentioned, it is often vaguely described as a process driven by a gradient of relative humidity.

The amount of gas transported by the surface diffusion mechanism can be evaluated by an experiment carried out with an adsorbing gas. This requires that the structural parameters governing effusion, diffusion and viscous flow be first measured in an experiment with a non-adsorbing gas. Since it has been shown that the continuum diffusion and the free molecule flow are connected in series and that the total diffusive flow is then connected in parallel with viscous flow and surface diffusion, measurements of the total flow of an adsorbing gas will give the contribution of surface diffusion.

In this paper the foundation for the experimental work is laid. A mathematical model of transient vapour transport is introduced. It is shown how the ordinary diffusion coefficient

as well as the concentration dependent surface diffusion coefficient can be derived from measurements by using time-lag techniques.

## 1. Theory

The transport processes that dominate at isothermal conditions are those of Knudsen diffusion, continuum diffusion, viscous flow and surface diffusion (Figure 1.)

With the help of basic kinetic theory they can all be written as separate functions of gas properties and textural properties of the material and combined for the total transport.

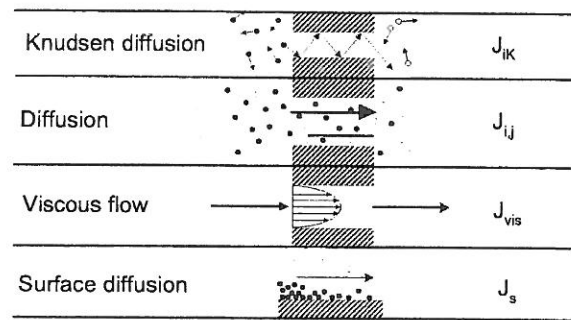


Figure 1 The different transport processes.

### 2.1 Knudsen diffusion

When the diameter of the pores is of the same order of magnitude as the mean free path of the molecules, the different sorts of molecules move independently of each other and diffusion is governed by the collisions of the molecules with the walls.

The free molecule flux,  $J_{iK}$  [molecules/m<sup>2</sup>s], is driven by the gradient of molecular density,  $n$  [molecules/m<sup>3</sup>], and can be written [1]:

$$J_{iK} = -D_{iK} \nabla n_i \quad (1)$$

where  $D_{iK}$  [m<sup>2</sup>/s] is by definition the Knudsen diffusion coefficient. The diffusion coefficient,  $D_{iK}$  is proportional to the mean molecular speed,  $\bar{v}$  [m/s] and therefore directly proportional to the square root of the temperature and the inverse of the square root of the mass,  $m$ . The relationship between the flow of two different gases can therefore be written:

$$\frac{J_{1K}}{J_{2K}} = \frac{D_{1K}}{D_{2K}} = \frac{\bar{v}_1}{\bar{v}_2} = \left(\frac{m_2}{m_1}\right)^{1/2} \quad (2)$$

which is Graham's law of effusion. Notice that  $D_{iK}$  is independent of the pressure.

Given the geometry of a material and the scattering laws of a gas hitting the walls of the pores the value of the Knudsen diffusion coefficient can be calculated [1]. It is however usually much easier to measure it by experiment.

## 2.2 Continuum diffusion

At isothermal conditions where there is no influence of external forces the diffusive flows,  $J_{1D}$  and  $J_{2D}$ , of a binary mixture are [1]

$$J_{1D} = -D_{1,2}^0 \nabla n_1 \quad (3a)$$

$$J_{2D} = -D_{2,1}^0 \nabla n_2 \quad (3b)$$

where  $D_{1,2}^0$  is the diffusion coefficient of component 1 in 2. This equation is also known as Fick's first equation. Addition of the equations reveals that the diffusion coefficients must have the same value  $D_{1,2}^0 = D_{2,1}^0$ .

Under certain conditions (closed containers) a net flow is required to maintain a zero pressure gradient, in which instance the equations become

$$J_{1D} = -D_{1,2}^0 \nabla n_1 + x_1 J_D \quad (4a)$$

$$J_{2D} = -D_{2,1}^0 \nabla n_2 + x_2 J_D \quad (4b)$$

Where  $J_D$  is the net flow  $J_D = J_{1D} + J_{2D}$  and  $x_1 = n_1/n$  is the mole fraction. All flows are diffusive since there is no pressure gradient. The molar density,  $n$ , is directly proportional to pressure and this means that  $D_{1,2}^0$  must be inversely proportional to pressure. Graham showed through experiment that the relationship between the two flows of equation (4) is

$$\frac{J_{1D}}{J_{2D}} = \left(\frac{m_2}{m_1}\right)^{1/2} \quad (5)$$

For a porous material the diffusion coefficient,  $D_{i,j}$ , is substantially smaller than the pure gas diffusion coefficient  $D_{i,j}^0$ . The diffusion coefficient for a porous material is often written in the following manner as a function of the porosity of the material,  $\epsilon$ , its tortuosity  $\tau$  and the pure diffusion coefficient of the gas [1]:

$$D_{i,j} = \left(\frac{\epsilon}{\tau}\right) D_{i,j}^0 \quad (6)$$

The porosity takes into account that only the gas volume is available. The tortuosity has to do with the fact that the length of each pore is greater than a straight line through the material.

### 2.3 Viscous flow

Viscous flow is caused by a pressure gradient. The viscosity of the gas rules its behaviour and is independent of the pressure. The equation for viscous flow is

$$J_{vis} = \frac{Flow}{Area} = -\frac{nB_0}{\eta} \nabla p \quad (7)$$

where  $J_{vis}$  is the viscous flow [molecules/m<sup>2</sup>s],  $n$  is the total number density,  $B_0$  is a flow parameter which is constant for the geometry of the hole [m<sup>2</sup>],  $\eta$  is the dynamic viscosity [Pa·s] and  $p$  is the pressure [Pa]. In viscous flow the gases behave as a single gas since the flow is non-seperative.

### 2.4 Surface diffusion

One of the most common models used to portray the surface flow of physically adsorbed gases is the random hopping model of Hill and Higashi et al [2]. The random hopping model views surface diffusion as a flow due to a gradient of the number density of the hopping molecules. An adsorbed molecule has to gain certain activation energy and it will hop from site to site in the adsorption state before finding rest at an unoccupied site. In Higashi's model it was assumed that when a molecule hit a site occupied by another molecule it would immediately bounce off and continue until finding an unoccupied site, the time of residence being zero, and that the transit time between sites being negligible compared to a residence time when the hopping molecule encountered a site. Yang et al. [3] modified the model by taking into account the residence time at occupied sites.

The residence time  $\tau$  at a site is given by [3]:

$$\frac{1}{\tau} = \nu \cdot e^{-E_s/RT} \quad (8)$$

where  $\nu$  is the vibration frequency of the bond holding the molecule to the site and  $E_s$  is the effective energy of that bond, that is, the difference in energy between the ground vibrational level of the bond and the free mobility of the surface (activation energy of migration).

The surface flow is regarded as a random walk process so the surface flow coefficient  $D_s$  is obtained by Einstein's equation [3],[4]:

$$D_s(\theta_e) = C'\delta^2/\tau \quad (9)$$

where  $C'$  is a constant depending on the tortuosity factor of the porous media and the geometrical configuration of adsorption site,  $\delta$  is the distance between neighbouring adsorption sites and  $\theta_e$  denotes the effective surface coverage of the adsorbed molecules.

If the surface flow is written as a function of the effective amount adsorbed,  $q_e$ , [mol/g] [4]

$$N_s = \rho_{app} D_s(\theta_e) A dq_e/dl \quad (10)$$

where  $\rho_{app}$  is the apparent density of the porous material [ $g/m^3$ ] and  $\theta$  is the amount adsorbed through the monolayer amount adsorbed. Using the total amount absorbed, equation (10) becomes

$$N_s = \rho_{app} D_s A dq/dl \quad (11)$$

and the ratio of the two different gradients is the same as the ratio of their potentials. Equation (9) gives the relationship between the surface diffusion coefficients at different surface concentrations as functions of the residence times:

$$D_s(\theta) = D_{s0} \cdot (\theta_e/\theta) (\tau_{s0}/\tau) \quad (12)$$

where  $D_{s0}$  is the surface coefficient for a single molecule jumping between vacant sites,  $\tau_{s0}$  is the residence time of an adsorbed molecule and  $\tau$  is the expected value of the holding time.

Okazaki et al [4] models the mean residence time as follows: the molecule can be situated on a vacant site or another molecule and hops to a vacant site or onto another molecule which gives four possible combinations of hopping, each having a probability that equals the probability of being on the first site times the probability of landing on the second site.

The expected value of the holding time is then the sum of those probabilities multiplied by the holding time of each combination of hopping as shown in fig. 2.

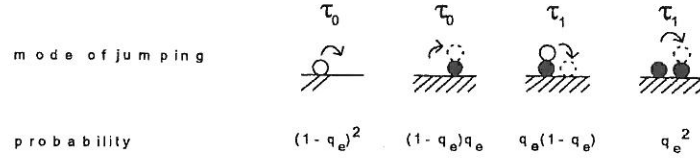


Figure 2. The surface hopping model, from Okazaki [4]

The expected value of the holding time is therefore [4]:

$$\tau = (1-\theta_e)^2 \tau_0 + \theta_e(1-\theta_e) \tau_0 + (1-\theta_e) \theta_e \tau_1 + \theta_e^2 \tau_1 = (1-\theta_e) \tau_0 + \theta_e \tau_1 \quad (13)$$

If we make the approximation that the ratio of the activation energy  $E_{so}$ , [J/mol] and the differential heat of adsorption  $E_{ao}$  is constant,  $E_{so} = a \cdot E_{ao}$ , where  $a$  depends on both the sorbate and the sorbant. The surface diffusion coefficient then becomes [4]

$$D_s = D_{s0} F = D_{s0} (\theta_e / \theta) (e^{-aE_{ao}/RT} - e^{-E_{ao}/RT}) / ((1 - e^{-E_{ao}/RT}) (1 - \theta_e (1 - \tau_1 / \tau_0))) \quad (14)$$

where

$$\tau_1 / \tau_0 = (e^{-aE_{ao}/RT} - e^{-E_{ao}/RT}) (1 - e^{-E_{a1}/RT}) / ((e^{-E_{s1}/RT} - e^{-E_{a1}/RT}) (1 - e^{-E_{ao}/RT})) \quad (15)$$

provided that the differential heat of adsorption  $E_{ao}$  is independent of the amount adsorbed, that is in the case of an energetically homogenous surface.

For an energetically heterogeneous surface the differential heat of adsorption drops monotonously. It has been shown by experiment that the differential heat of adsorption decreases with the amount adsorbed, because adsorption successively proceeds from the site of large heat of adsorption to that of small heat of adsorption. Therefore the molecules have various heats of adsorption,  $E$ . Using the results of Okazaki et al [4] equation (16) becomes:

$$D_s = D_{s0} F = \frac{D_{s0} (\theta_e / \theta) \int_{E_{ao}^0}^{E_{ao}} ((e^{-aE/RT} - e^{-E/RT}) / ((1 - e^{-E/RT}) (1 - \theta_e (1 - \tau_1 / \tau_0)))) g(E) dE}{\int_{E_{ao}^0}^{E_{ao}} g(E) dE} \quad (17)$$

where

$$\tau_1 / \tau_0 = (e^{-aE/RT} - e^{-E/RT}) (1 - e^{-E_{a1}/RT}) / ((1 - e^{-E/RT}) (e^{-E_{s1}/RT} - e^{-E_{a1}/RT})) \quad (18)$$

Here  $g(E)$  is the number of molecules adsorbed which have heats of adsorption between  $E$  and  $(E+dE)$ , and  $E_{ao}$  and  $E_{ao}^0$  are the heats of adsorption at  $\theta_e$  and  $\theta_e=0$  respectively.

In order to calculate the potential surface flow we therefore have to estimate the energies involved in absorption and activation of the water molecules and the different amounts absorbed for varying partial pressures. In other words, estimate the values of  $\theta_e$ ,  $E_{s1}$ ,  $E_{a1}$ ,  $E_{a0}$ , and  $g(E)$  of equations (14) to (18).

In the case of multilayer adsorption only the molecules in the outermost layer contribute to the surface flow, which reduces the effective surface coverage to the coverage of the surface layer. This coverage can be estimated from an adsorption model.

If an adsorption isotherm can be expressed by the Langmuir equation,

$$\theta = \theta_e = c\phi/(1+c\phi) \quad (19)$$

where  $\phi$  is the relative pressure  $[p/p_s]$  and  $c$  is a constant. When an adsorption isotherm obeys the BET equation,

$$\theta_e = \theta(1-\phi) \quad (20)$$

and  $\theta$  is given by:

$$\theta = C \phi / ((1 - \phi)(1 - \phi + C \phi)) \quad (21)$$

The equations above assume that the surface migration has a small influence on the adsorption equilibrium, in which case they can be applied to estimate  $\theta_e$ .

The heat of vaporisation  $E_{a1}$  can be found in the literature.

The activation energy for migration  $E_{s1}$  may be approximately estimated with the Frenkel equation [4] that relates the temperature dependency to viscosity in the liquid state,  $\eta_L$  [Pa·s] and can be found in the literature.

$$\mu_L = KTe^{E_{s1}/RT} \quad (22)$$

The isosteric heat of adsorption  $E_{st}$  is determined from adsorption isotherms at various temperatures using the Clausius Clapeyron equation:

$$E_{st} = -R \cdot \left( \frac{\partial \ln p_1}{\partial T} \right)_q \quad (23)$$

where  $p_1$  is the partial pressure. This heat of adsorption contains both the effects of  $E_{a0}$  in the first layer and  $E_{a1}$  in all the layers above the first layer, when multilayer adsorption occurs.

If the adsorption equilibrium obeys the BET equation,

$$E_{a0} = (E_{st} - RT - \phi E_{a1})/(1-\phi) \quad (24)$$



while when multilayer adsorption does not take place,

$$E_{a0} = E_{st} - RT \quad (25)$$

As  $g(E)$  is the number of molecules adsorbed which have a differential heat of sorption between  $E$  and  $(E+dE)$ ,  $g(E)$  can be easily evaluated from the relation between  $E_{a0}$  and the amount adsorbed.

Okazaki's experiments [4] show a strong correlation of  $D_s/D_{s0}$  and  $F$ . The parameter  $a$  is constant on the same solid. Equation (14) and (17) can therefore be assumed to explain how the surface flow coefficient depends on the amount adsorbed and temperature in the range from less than monolayer to multilayer adsorption.

## 2.5 Combined transport

Free-molecule and continuum diffusion of gas of sort  $l$  can be combined in the following equation:

$$-\nabla p_1 = \left( \frac{k_B T}{D_{1K}} \right) J_{1D} + \left( \frac{k_B T}{D_{12}} \right) (J_{1D} - x_1 J_D) \quad (26)$$

where  $k_B$  is the Boltzmann constant, and a similar equation is valid for gas of sort 2. This equation describes the diffusion of one component of a binary mixture at uniform total pressure through the entire pressure range between the free-molecule limit and the continuum limit [1].

When there is a gradient of total pressure, it has been shown that, to a high degree of accuracy, these two types of flows can be measured separately and then simply added.

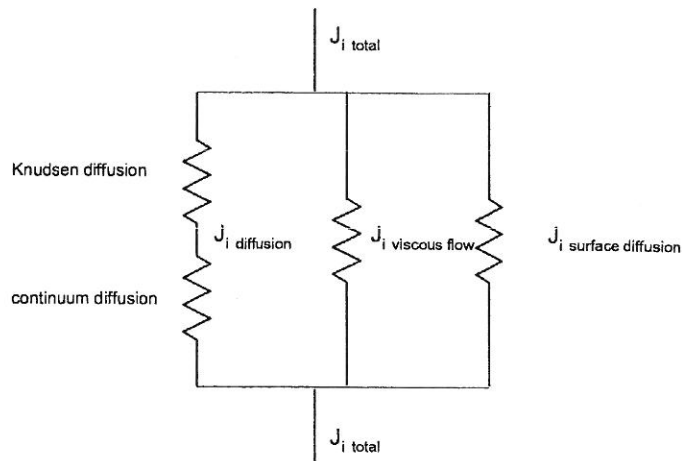


Figure 3 Combined transport

In a similar manner, the surface flux can be added to the diffusive fluxes. The combined transport is shown schematically in fig. 3. This results in the following equation for gas of sort 1 (and a similar equation for gas 2) [1]:



$$J_1 = -D_1 \left( 1 + \frac{D_{1S}}{D_1} + x_1 \frac{(D_{1S} - D_{2S})}{D_{12}} \right) \nabla n_1 + x_1 \delta_1 J + x_1 \gamma_1 \left( \frac{nB_0}{\eta} \right) \nabla p + \frac{x_1}{k_B T} \left( \frac{D_{2S}}{D_{12}} \right) \nabla p \quad (27)$$

where

$$\frac{1}{D_1} = \frac{1}{D_{1K}} + \frac{1}{D_{12}} \quad (28)$$

Since the free molecule flow and continuum diffusion are connected in series, where

$$\delta_1 = \frac{D_1}{D_{12}} = \frac{D_{1K}}{D_{1K} + D_{12}} \quad (29)$$

$$\gamma_1 = \frac{D_1}{D_{1K}} = \frac{D_{12}}{D_{1K} + D_{12}} = 1 - \delta_1 \quad (30)$$

Equation (27) contains a complete phenomenological description of diffusion and flow at isothermal conditions and reveals how the different transport mechanisms relate to each other. The Knudsen diffusion coefficient is for instance independent of pressure while the binary diffusion coefficient is inversely proportional to pressure. At low pressures,  $D_1 = D_{1K}$  and the equation for free molecule flow is recovered. At high pressures  $D_1 = D_{12}$  and the equations for continuum diffusion are recovered if the pressure gradient is zero.

## 2.6 The Dusty Gas Model

Mason and Malinauskas [1] base their Dusty Gas Model, (DGM), on Chapman Enskog theory of gas kinetics. The DGM incorporates the different flow and diffusion phenomena and shows how they relate. The DGM views the porous material and the gas as a mixture where the solid material is pictured as heavy evenly distributed dust particles at rest. How this distribution actually looks is of secondary importance since the geometrical factors are built into the transport coefficients.

### 2.6.1 The complete DGM transport equation

In order to get the complete DGM transport equations Mason and Malinauskas start by combining the diffusive flows that are assumed to be independent and then add the viscous flow contribution.

The resulting transport equations can be written as follows:

$$\sum_{j=1}^v \frac{n_j}{nD_{ij}} \left( \frac{J_i}{n_i} - \frac{J_j}{n_j} \right) + \frac{1-\Delta'_{id}}{(D_{ik})_h} \cdot \frac{J_i}{n_i} + \frac{1-\Delta'_{id}}{(D_{ik})_h} \cdot \frac{B_0}{\eta} (\nabla p - nF) = -\nabla \ln(n_i/n) - \nabla \ln p + F_i/k_B T$$

$$- (n')^{-1} \left( \sum_{j=1}^v n_j (\alpha'_{ij})_{tr} + n_d (\alpha'_{id})_{tr} \right) \nabla \ln T, i, j \neq d \quad (31)$$

where  $F_i$  is the external force on the species. The four terms on the right hand side of equation (31) represent concentration diffusion, pressure diffusion, forced diffusion and thermal diffusion. The last term on the left-hand side of equation (31) is a correction for the net drift due to viscous flow.

It should be observed that equation (31) is one out of  $v$  equations where  $v-1$  are independent. It is noteworthy that the summations do not include the dust particles. For a binary mixture at isothermal conditions in the absence of external forces equation (31) can be reduced to equation (27).

The quantity  $\alpha_{i,j} = -\alpha_{j,i}$  is a generalised thermal diffusion factor which can be said to describe the relative separation of the binary pair for a temperature, even if it is independent of all the species in the mixture. It is the sum of the contributions made by transitional and internal movement, which in most cases can be neglected [1].

The terms involving  $(\alpha'_{ij})_{tr}$  give rise to thermal diffusion, as modified by the presence of the dust and the term involving  $(\alpha'_{id})_{tr}$  gives rise to thermal transpiration, as modified by thermal diffusion among the true gaseous components [1]. The term  $\Delta'_{id}$  is a correction factor that takes into account the effect of gases other than species  $i$  and the dust.

The derivation of the hitherto presented equations is mainly based on molecular kinetic theory arguments. But in order to suit the experimental purposes a presentation based upon molar quantities is called for. Under isothermal condition equation (31) can be written

$$\sum_{j=1, j \neq i}^v \frac{x_i N_j - x_j N_i}{PD_{ij}} - \frac{N_i}{PD_{i,K}} = \frac{1}{RT} \cdot \nabla x_i + \frac{x_i}{PRT} \left( \frac{B_0 P}{\eta D_{i,K}} + 1 \right) \nabla P \quad (32)$$

where we have substituted molecular densities with mole fractions.

The continuum and Knudsen diffusion coefficients as well as the permeability can be measured by using a non-adsorbing tracer gas. By adding the pair of equations we get from (32) we get the following:

$$N - \left(1 - \frac{D_{1K}}{D_{2K}}\right) \cdot N_2 = -\frac{D_{1K}}{RT} \left(1 + \frac{B_0 P}{\eta}\right) \sum_{i=1}^2 \frac{x_i}{D_{i,K}} \nabla P \quad (33)$$

Measurements of the LHS vs. the pressure difference plotted against different total pressure will therefore be straight lines whose gradient reveals the permeability whereas the interception with the axes gives the Knudsen diffusion coefficient. The binary diffusion coefficient can then be calculated from equation (32)

### 2.6.2 The diffusion coefficients

The first Chapman-Enskog approximation of the binary diffusion coefficient  $D_{i,j}^0$ , of gas  $i$  in gas  $j$ , denoted  $[D_{i,j}^0]_1$ , is

$$[D_{i,j}^0]_1 = \frac{3}{8} \cdot \left( \frac{\pi k_B T}{2 \mu_{ij}} \right)^{1/2} \frac{1}{n \pi \sigma_{i,j}^2} \quad (34)$$

where  $\mu_{ij} = (m_i m_j / (m_i + m_j))$  is the reduced mass of pair  $ij$ ,  $n$  is the mole concentration mole/m<sup>3</sup>,  $\sigma_{i,j}$  is an arbitrary distance parameter usually chosen to be equal to the mutual collision diameter for the molecular pair and the collisions are assumed to be elastic [1]. This approximation does not include the dependency of the binary diffusion coefficient on the other species in the mixture.

For different gases with the same mode of scattering an effective Knudsen diffusion coefficient can be written [1]:

$$D_{ik} = \frac{4}{3} K_0 \left( \frac{8RT}{\pi m_i} \right)^{1/2} \quad (35)$$

regardless of the nature of the collisions.

## 3. Applications in moisture mechanics of building materials

The theoretical models described above explain the governing transport mechanisms of vapour transport in porous materials.

Tracer gas simulations can be used to reveal the DGM material parameters that dictate the flow of moisture through effusion, diffusion and viscous flow. Measurements of sorption

isotherms and transient measurements of the flow of water vapour will enable an evaluation of the enhancing effects of the adsorbed water through surface diffusion.

### 3.1 Measuring the Fickian diffusion coefficient with tracer gas

The DGM parameters that rule the viscous flow, diffusion and effusion can be obtained by using equation (22) and (23) as previously described. In the case of many building materials, however, the diffusive flows are principally Fickian. We can therefore obtain the diffusion coefficient of water vapour by conducting a single experiment, using for example  $N_2O$  as a tracer gas. The Fickian diffusion can as usual be expressed by the following equation:

$$\frac{\partial C}{\partial t} = D_{F, \text{tracer}} \frac{\partial^2 C}{\partial x^2} \quad (36)$$

where  $C(x,t)$  is the concentration  $[g/m^3]$ . For steady-state conditions the solution of (36) is trivial. The flow rate  $F(t)$   $[g/m^2s]$  is:

$$F(t) = -D_F \cdot \frac{\partial C}{\partial x} \quad (37)$$

and, for steady-state conditions,  $F(t)$  has a constant value that together with the concentration gradient can be used to retrieve the diffusion coefficient.

For less permeable materials a considerable time may elapse until steady state has been reached. It might therefore be desirable to obtain the diffusion coefficient through transient measurements.

For transient conditions a solution of (36) is readily obtained by using separation of variables or the Laplace transform [5]. For a material of thickness  $l$ , where the concentration is constant on both sides, the boundary conditions are:  $C = C_1, x = 0$ ;  $C = C_2, x = l, t \geq 0$ ;  $C = C_0, 0 < x < l, t = 0$ . The solution of (36) is then:

$$\begin{aligned} C(x,t) = & C_1 + (C_2 - C_1) \cdot \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cdot \cos(n\pi) - C_1}{n} \cdot \sin\left(\frac{n\pi \cdot x}{l}\right) \cdot e^{\left(\frac{-D \pi^2 n^2 \cdot t}{l^2}\right)} + \\ & + \frac{4C_0}{\pi} \cdot \sum_{m=0}^{\infty} \frac{1}{2m+1} \cdot \sin\left(\frac{(2m+1) \cdot \pi \cdot x}{l}\right) \cdot e^{\left(\frac{-D(2m+1)^2 \cdot \pi^2 \cdot t}{l^2}\right)} \end{aligned} \quad (38)$$

The total amount of diffusant  $Q(t)$  [g/m<sup>2</sup>] that has passed through the material at the downstream side in time  $t$  is just the integral of the flow rate  $F(t)$  over  $t$  from 0 to  $t$ , :

$$Q(t) = D(C_1 - C_2) \cdot \frac{t}{l} + \frac{2l}{\pi^2} \sum_{n=1}^{\infty} \frac{C_1 \cdot \cos(n\pi) - C_2}{n^2} \cdot \left( 1 - e^{\left( \frac{-D \cdot n^2 \pi^2 \cdot t}{l^2} \right)} \right) + \frac{4C_0 l}{\pi^2} \cdot \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \cdot \left( 1 - e^{\left( \frac{-D(2m+1)^2 \pi^2 \cdot t}{l^2} \right)} \right) \quad (39)$$

If the initial concentration throughout the material is zero and we keep the concentration at zero on the upstream side by sweeping away the diffusant the total flow  $Q(t)$  becomes as follows:

$$Q(t) = l \cdot C_1 \cdot \left( \frac{D \cdot t}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cdot e^{\left( \frac{-D \cdot n^2 \pi^2 \cdot t}{l^2} \right)} \right) \quad (40)$$

As the time,  $t$ , approaches infinity the flow approaches the line

$$Q(t \rightarrow \infty) = \frac{D \cdot C_1}{l} \cdot \left( t - \frac{l^2}{6D} \right) \quad (41)$$

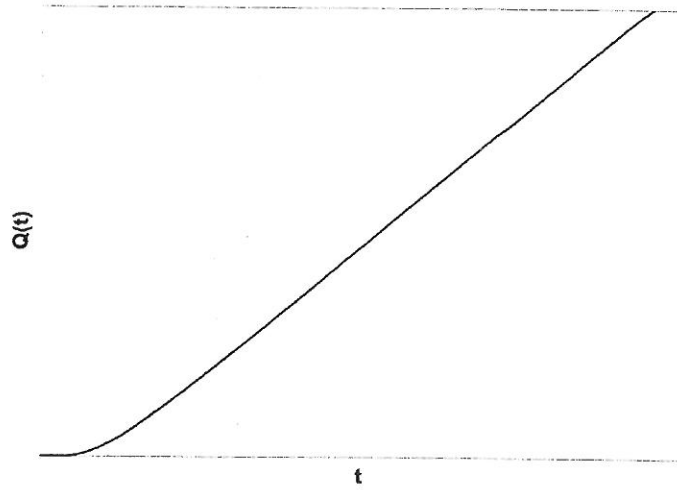
In principle the flow will look as shown in figure 4, where the material properties of concrete have been used for modelling and the time axis stretches over a period of one year. The straight line is the asymptote as written by equation (41).

The intercept of the asymptote of the measured flow with the time axis is the time lag,  $t_{timelag}$  which must equal:

$$t_{timelag} = \frac{l^2}{6 \cdot D} \quad (42)$$

and the diffusion coefficient will be retrieved. As revealed by equation (6), the ratio of the diffusion coefficient for tracer gas, N<sub>2</sub>O through a material over the diffusion coefficient of water vapour through the same material equals the ratio of the diffusion coefficients in air. These might be evaluated by equation (24) or, more conveniently, be found in the literature.

The diffusion coefficient for water in air,  $D_{\text{water,air}}^0$ , is  $2.42 \cdot 10^{-6} \text{ m}^2/\text{s}$  while  $D_{\text{N}_2\text{O,air}}^0$  is approximately  $1.47 \cdot 10^{-6} \text{ m}^2/\text{s}$  [6] and therefore the water vapour permeability of the material



**Figure 4** Total flow  $Q(t)$  through a material after time  $t$ .

will be 1.646 times the diffusion coefficient of the tracer gas.

It is of importance that the tracer gas used does not dissolve or adsorb in the material. In the case of  $\text{N}_2\text{O}$  it has been shown that this requires the material to be dried out in order to prevent the dissolution of the gas in the water in the pores [7].

### 3.2 Measurement of surface diffusion

From the known textural parameters, obtained by tracer gas measurements, the potential Fickian diffusion of water vapour can be calculated. The contribution of surface diffusion is assumed to be independent and connected in series with the bulk diffusion. The contribution of surface diffusion is then simply the measured net flow minus the contribution of Fickian diffusion as described by equation (40). This can be written by the following pair of equations:

$$\frac{\partial C}{\partial t} = D_F \frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t} \quad (41)$$

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial x} \left( D_S \frac{\partial S}{\partial x} \right) \quad (42)$$

where  $S$  is the amount of adsorbate  $[\text{g}/\text{m}^3]$ .

The concentration gradient of adsorbed water may equally well be written

$$\frac{\partial S}{\partial x} = \frac{\partial S}{\partial \varphi} \cdot \frac{\partial \varphi}{\partial x} \quad (43)$$

for steady state conditions the flow due to surface diffusion can therefore be written

$$F_S(t) = -D_S \cdot \frac{\partial S}{\partial \varphi} \cdot \frac{\partial \varphi}{\partial x} \quad (44)$$

which of course is just a rewrite of equation (11). One way of assessing the surface diffusion coefficient would then be to measure the steady state flow in a series of experiments, in different intervals of concentration gradients and use equations (44), (14) and (17) to evaluate the concentration dependency of the surface diffusion coefficient, that is to determine the constant values of  $D_{s0}$  and  $a$ . The other parameters of equations (14) and (17) are readily estimated by the means of sorption measurements.

More conveniently we would like to be able to determine the concentration dependence of the diffusion coefficient by carrying out transient measurements of the surface diffusion. Unfortunately, though, we do not have an analytical solution of equation (42). We can however, express the time lag as a function of the diffusion coefficient without having to solve the diffusion equation explicitly. Let the boundary conditions be:  $S = S_0$ ,  $x = 0$ ;  $S = 0$ ,  $x = 1$ ,  $t \geq 0$ ;  $S = 0$ ,  $0 < x < 1$ ,  $t = 0$ . The flow rate  $F(t)$  through the downstream side,  $x = 1$  is:

$$F_S(t) = -\left(D_S \cdot \frac{\partial S}{\partial x}\right)_{x=1} \quad (45)$$

And the total flow through the surface  $Q_S(t)$  in time  $t$  is give by:

$$Q_S(t) = \int_0^t F_S(t) dt \quad (46)$$

As shown by Crank [5] integration of both sides of (42) over  $x$  from  $x$  to 1 followed by an integration over  $x$  from 0 to 1 and consequently an integration over  $t$  from 0 to  $t$ , gives after some rearrangement:

$$Q_S(t) = \frac{1}{l} \left( t \int_0^{S_0} D_S(u) du - \int_0^l \int_x^l S(z,t) dz dx \right) \quad (47)$$



The asymptote  $Q_{as,s}(t)$  to  $Q_s(t)$  is

$$Q_{as,s}(t) = F_s(t - t_{\text{timelag}}) \quad (48)$$

and therefore the time-lag must equal

$$t_{\text{timelag}} = \frac{\int_0^l \int_x^l S_{\text{steadystate}}(z) dz dx}{\int_0^{S_0} D_S(u) du} \quad (49)$$

Integration by parts gives us

$$t_{\text{timelag}} = \frac{\int_0^l x \cdot S_{\text{steadystate}} dx}{\int_0^{S_0} D_S(u) du} \quad (50)$$

It has been shown that [5]:

$$\int_{S_{\text{steadystate}}}^{S_0} D_S(u) du = \frac{x}{l} \int_0^{S_0} D_S(u) du \quad (51)$$

This can be used to rewrite equation (50). We then get the following (in [5] the lower limit of the inner integral is set to zero):

$$t_{\text{timelag}} = \frac{l^2 \int_0^{S_0} w \cdot D_S(w) \left( \int_w^{S_0} D_S(u) du \right) dw}{\left( \int_0^{S_0} D_S(u) du \right)^3} \quad (52)$$

Since we know the functional form of the diffusion coefficient as described by equations (14) and (17) the measurement of the time lag for different concentrations  $S_0$  allows the constant parameters of  $D_S$  to be determined and thus  $D$  as a function of the surface concentration.



## 4. Discussion

We have seen how the transport of vapour through porous materials, by diffusion, surface diffusion, Knudsen diffusion and viscous flow can be written as separate functions of the thermodynamic properties of the vapour and the textural properties of the material. The previously given physical model explains how the viscous flow is governed by the pressure gradient, while the ordinary diffusion coefficient depends on the total pressure, whereas the Knudsen diffusion coefficient is independent of pressure. It also explains how the surface diffusion coefficient depends on the amount adsorbed and the energies involved. Together with the knowledge of how these different transport mechanisms combine, this provides us with the means to identify the relative contribution of each transport process to the overall flow.

The significance of the model for measurements of vapour transport through porous building materials is twofold. First of all, we will be able to measure the potential transport of water vapour by measuring the flow of a tracer gas, by using standard equipment. In the most simple case of non-hygroscopic materials, the moisture permeability will be immediately revealed by the tracer gas experiments alone, whereas the potential surface diffusion in hygroscopic materials can be quantified by accompanying sorption measurements. Secondly it will be possible to separate out the contributions of each transport mechanism, which will help in the design of moisture-safe constructions and even in improving the moisture performance of building materials.

We have shown a mathematical model of the diffusion process that enables the deduction of the Fickian diffusion coefficient from transient measurements of tracer gas flow. In addition a mathematical model of surface diffusion, which in combination with measurements of the sorption isotherms, will reveal the coefficient of surface diffusion, has been presented. The latter is linked to the random hopping model of surface diffusion, thus providing a phenomenological explanation of the physical process.

The next step of the research will focus on development of the measurement techniques that can be used to verify the model and the assumptions that have been made.

Further research will preferably involve the extension of the model to the transport of water in liquid phase.

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# **Paper 3**

**Isotopic tracing of moisture in buildings**

**Kjartan Gudmundsson**



## Isotopic tracing of moisture in buildings

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*Kjartan Gudmundsson, MSc,  
Department of Building Sciences, Kungl Tekniska Högskolan  
kjartan@bim.kth.se*

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### SUMMARY

*The means of tracing the flows of moisture in a building by using the stable isotopes of oxygen-18 and deuterium are described. It is shown how the knowledge of how the transport mechanisms and reactions involved effect the isotopic composition can be used to identify the sources of moisture. This is illustrated by an example from a building in the southern part of Sweden.*

### 1. Introduction

Water can be characterised by the composition of its isotopes, in particular by the abundance ratios of deuterium and oxygen-18 to their more common sister isotopes. Those isotopes are stable, in the sense that they do not disintegrate by any mode of decay and do therefore give the water a distinct mark.

Besides the isotopically unlike water molecules have different thermodynamic properties, which means that reactions change the concentration of the product compared to that of the reactant.

This has been proven quite useful in the field of hydrogeology [1]. It is known how the meteoric processes modify the stable isotopic composition of precipitation and the isotopic signature of the water is now commonly used to trace the origins of groundwater. In a similar manner measurements of the stable isotopic composition of ice cores from the Greenland

glacier have been implemented in paleogeographic studies. Since freezing conserves the isotopic composition, the glacier can and has been used as an archive of past climates.

And even the isotopic composition of water in buildings can tell us the history of the water. Knowledge of the isotopic content of the water at two different points in combination with the understanding of which transport mechanisms may be involved in the travel of moisture between them as well as how these transport processes affect the isotopic composition will help us in two ways.

Firstly this can provide us with the means to identify the source of the water, which in the case of leakage is of principal importance.

Secondly the isotopic abundance ratios might tell us what transport processes the water has undergone and thus give aid in quantifying the contribution of the various transport processes.

In this paper the means of gathering information on the isotopic composition of water in the built environment are described. Of central importance is the isotopic content of precipitation as a primary source of moisture. It is explained how the governing reactions involved in transport of moisture in building effect the abundance ratios of oxygen-18 and deuterium.

Furthermore it is illustrated by an example how this can be used for an identification of leakage in buildings. It is shown how the isotopic separation between the leakage and its possible origins together with the calculated isotopic differences that are associated with transfer of water from the sources to the leakage point can be used to point out the most probable cause of the leakage.

## 2. Terminology

Stable environmental isotopes are measured as the ratio of the two most common isotopes of the element. For oxygen it is the ratio of  $^{18}\text{O}$ , with a terrestrial abundance of 0.204 %, to its more frequently found sister isotope  $^{16}\text{O}$  which represents 99.796 % of terrestrial oxygen [2]. The relative isotopic concentration is expressed as the difference between the measured ratios of the sample and reference over the measured ratio of the reference. Mathematically the error ( $\epsilon$ ) between the apparent and true ratios is cancelled.

Using the  $\delta$  notation this can be written:

$$\delta^{18}O_{sample} = \frac{m(^{18}O/^{16}O)_{sample} - m(^{18}O/^{16}O)_{reference}}{(^{18}O/^{16}O)_{reference}} \quad (1)$$

$$\delta^{18}O = \left( \frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{reference}} - 1 \right) \cdot 1000\text{‰} \quad (2)$$

the reference normally used is the VSMOW or Vienna Standard Mean Ocean Water. A positive  $\delta^{18}O$  ‰ value, say +10‰, signifies that the sample has 10 permil or 1% more  $^{18}O$  than the reference, that is enriched by 10‰.

In similar manner the relative isotopic concentration of Deuterium can be written

$$\delta D = \left( \frac{(D/H)_{sample}}{(D/H)_{reference}} - 1 \right) \cdot 1000\text{‰} \quad (3)$$

Another commonly used notion is the deuterium excess that is defined by the following equation:

$$d = \delta D - 8\delta^{18}O \quad (4)$$

The higher the deuterium excess, the lighter the water.

Isotope fractionation takes place in any thermodynamic reaction because of the different reaction rates of the different isotopes. The reaction thereby leads to an altered ratio of one isotope over the other. This change is expressed by the fractionation factor  $\alpha$ , which is the ratio of the isotope ratios for the reactant and product:

$$\alpha = \frac{R_{reactant}}{R_{product}} \quad (5)$$

As an example, for the evaporation of water the fractionation factor for oxygen is written:

$$\alpha^{18}O_{water-vapour} = \frac{\left( \frac{^{18}O}{^{16}O} \right)_{water}}{\left( \frac{^{18}O}{^{16}O} \right)_{vapour}} \quad (6)$$

The isotopic difference in parts per thousand is defined by the equation (7)

$$\varepsilon_{X-Y} = \left( \frac{R_X}{R_Y} - 1 \right) \cdot 10^3 = (\alpha - 1) \cdot 10^3 \quad (7)$$

and the isotopic separation,  $\Delta$ , between two compounds, is defined as

$$\Delta_{X-Y} = \delta_X - \delta_Y \quad (8)$$

The  $\Delta$ -values can be used for comparing the measured separation with the isotopic difference calculated from the theoretical fractionation.

A number of isotopic reactions follow a Rayleigh-type evolution, for example the change in the abundance ratios of oxygen-18 and deuterium during evaporation. According to the Rayleigh distillation equation the isotope ratio,  $R$ , of a diminishing reservoir is a function of the isotope ratio of the reservoir at the start of the reaction,  $R_0$ , the fraction left of the reservoir,  $f$ , as well as the fractionation factor for the reaction,  $\alpha$

$$R = R_0 \cdot f^{(\alpha-1)} \quad (9)$$

### 3. Theory

The isotopic composition of moisture at different locations can be used to trace the transport of moisture through a building and its envelope. This requires that we know how to measure or calculate the isotopic concentrations of the various sources as well as how the transport processes and reactions involved effect the abundance ratios of Deuterium and oxygen-18.

In the following section the means of obtaining the isotopic content of the most common sources of water is described. The isotopic composition of precipitation is of central



importance since it must be the primary source of all water in buildings and their environment. Furthermore the fractionation factors for the principal transport mechanisms are described.

### 3.2. Sources of moisture in buildings

The sources of moisture in buildings are numerous. Rainwater constitutes the dominating external load, seeking its way directly through the roofs and walls and from the ground underneath and surrounding the building. In addition the indoor air contains water vapour that can be the source of condensation and accumulation in roofs and walls as the vapour is transferred through the constructions by diffusion or carried by the flow of air.

Collecting samples of water for isotopic analysis is simple when we have access to free water, as will often be the case when we want to measure the isotopic content of precipitation or groundwater or even tap water in those instances when a broken piping is suspected to be the source of leakage.

Samples of the indoor air can be taken with the help of a cold trap, i.e. by using a pump that collects air into a condensing device. In order to obtain representative values this should be done for a period of 24 hours. The water vapour in the indoor air should preferably be collected in the room adjacent to building envelope at the place where we suspect that air is driven out by diffusion or convection. If the governing sources of the indoor water vapour are known as well as their quantitative contributions we might even calculate the isotopic content of the indoor air.

### 3.1 The isotopic composition of precipitation

There is a strong correlation between the relative concentration of  $^{18}\text{O}$  and that of  $\text{D}_2$  in rainwater, as shown by Craig. In [3] Craig presented the following equation for the relationship between the concentration of  $\text{D}_2$  and  $^{18}\text{O}$ :

$$\delta D = 8\delta^{18}\text{O} + 10 \quad (10)$$

We can even obtain an estimate of the isotopic content at a specific site by calculating it from the mean monthly temperature. As shown by Dansgård the temperature,  $T_m$  correlates with  $\delta^{18}\text{O}$  of the precipitation [2].

Calles and Westman [4] carried out measurements of the isotopic content at several weather stations in Sweden. The authors presented the following equation for the temperature -  $^{18}\text{O}$  relationship for their measurements at the weather station at Arup

$$\delta^{18}\text{O} = 0,239 \cdot T_{\text{monthlymean}} - 11,460 \quad (11)$$

which can be seen as a moderation of Dansgård's equation but the correlation has a root-mean-square correlation factor of only  $r^2 = 0,53$ .

Calles and Westman [4] even investigated the relationship between the concentration of  $\text{D}_2$  and  $^{18}\text{O}$  in precipitation at a number of weather stations in Sweden. For the weather station at Arup the authors got the following linear relationship:

$$\delta\text{D} = 7,893\delta^{18}\text{O} + 8,112 \quad (12)$$

with a correlation factor  $r^2 = 0,94$ . Other weather stations showed the same strong correlation.

### 3.3 Isotopic fractionation by transport processes and reactions

When it comes to continuum or ordinary diffusion the mass differences lead to fractionation. The diffusion, which is driven by the concentration gradient, is directly proportional to the diffusion coefficient. For water vapour diffusing through air the molecular flow by continuum diffusion can be written:

$$g_{wD} = -D_{w,air}^0 \nabla v_w \quad (13)$$

If we assume elastic collisions, the diffusion coefficient can be written as

$$D_{w,air}^0 = \frac{3}{8} \cdot \left( \frac{\pi k_B T}{2\mu_{w,air}} \right)^{1/2} \cdot \frac{1}{n\pi} \quad (14)$$

Where  $k_B$  is Boltzman constant and  $\mu_{w,air}$  is the reduced mass  $\mu_{w,air} = (m_w m_{air} / (m_w + m_{air}))$ .

The ratio of flows of the different molecules is therefore directly proportional to ratio of the diffusion coefficients in air, which gives the following fractionation factor for diffusion:

$$\alpha_{1,2} = \frac{m_{iso2}(m_{iso2} + m_{air})}{m_{iso1}(m_{iso1} + m_{air})} \quad (15)$$

This is valid for binary diffusion of gases in porous materials as well as in air, given that the material resistance is the same for all gases.

For small pores the diffusion process is ruled by the collisions of the water molecules with the pore walls. This is called Knudsen diffusion or effusion and can be written as a function of the concentration gradient and the Knudsen diffusion coefficient:

$$g_{wK} = -D_{w,K} \nabla v_w \quad (16)$$

Where the Knudsen diffusion coefficient is:

$$D_{wk} = \frac{4}{3} K_0 \left( \frac{8RT}{\pi m_i} \right)^{1/2} \quad (17)$$

This gives the following fractionation factor for effusion:

$$\alpha_{1,2} = \sqrt{\frac{m_{iso2}}{m_{iso1}}} \quad (18)$$

Fractionation by phase change depends on the temperature at which the phase change takes place. Majoube describes the temperature dependency on the fractionation of oxygen-18 and Deuterium by the following equations [2]:

$$10^3 \ln \alpha^{18}O_{w-v} = 1,137(10^6 / T^2) - 0,4156(10^3 / T) - 2,0667 \quad (19)$$

$$10^3 \ln \alpha^D_{w-v} = 24,844(10^6 / T^2) - 76,248(10^3 / T) + 52,612 \quad (20)$$

Figure 1. below illustrates this dependency.

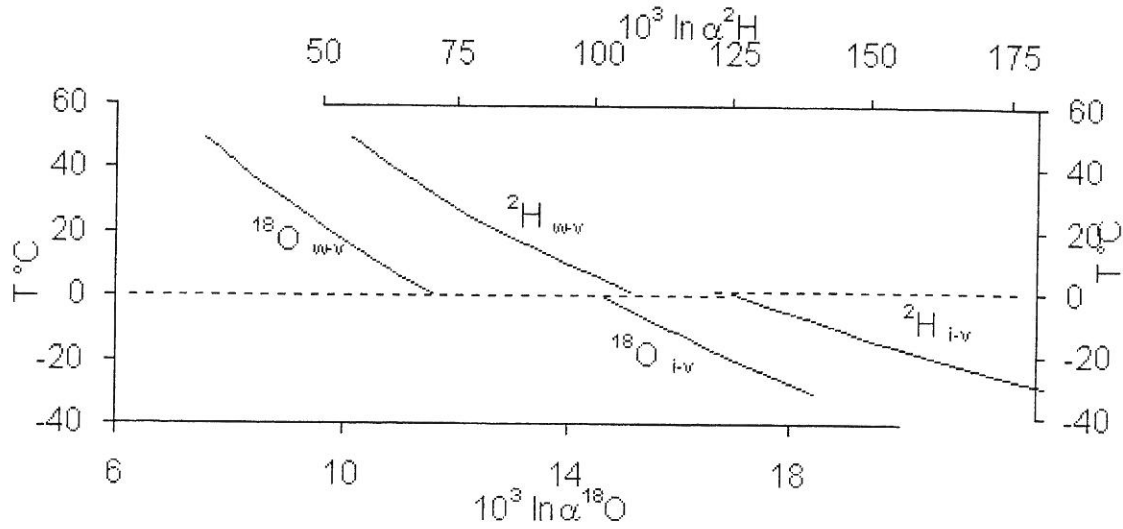


Figure 1. The fractionation of  $^{18}\text{O}$  between water and vapour, from [2]

However the fractionation factor does not only vary with temperature but also the relative humidity of the ambient air. This is because evaporation is a stepwise transfer from the water to the boundary layer from where it diffuses through a transition zone. For relative humidity lower than 100% this diffusion causes fractionation that depletes the vapour from the heavier isotopes. Gonfiantini [2] describes this kinetic effect, which in terms of humidity can be written with the following equations:

$$\Delta\epsilon^{18}\text{O}_{bl-v} = 14,2(1 - RH)\text{‰} \quad (21)$$

$$\Delta\epsilon D_{bl-v} = 12,5(1 - RH)\text{‰} \quad (22)$$

The total fractionation between the water and the open air is then written:

$$\delta^{18}\text{O}_l - \delta^{18}\text{O}_v = \epsilon^{18}\text{O}_{l-v} + \Delta\epsilon^{18}\text{O}_{bl-v} \quad (23)$$

Cement reactions, that is the hydration of Calcium and Silica oxides leads to fractionation. The isotopic difference can be calculated from the water-hydroxide fractionation factor [2]:

$$10^3 \ln \alpha^{18}\text{O}_{\text{H}_2\text{O}-\text{OH}} = 40\text{‰} @ 25^\circ\text{C} \quad (24)$$

When there is a surplus of water from the cement hardening process the isotopic content of the remaining water can be calculated by using equation (9).

### **3.4 Non-separative processes**

It is worth noting that transport by viscous flow is non-separative. This includes both the transfer of water vapour by the means of viscous air flow and capillary transport. Depending on the reactions involved, however, the absorption and condensation of vapour in the building materials may lead to fractionation.

## **4. Experimental work**

In a building project in the southern part of Sweden it was found out that water had accumulated in a prefabricated concrete cassette deck that constitutes the ceiling of one of the apartments. Since the cause of leakage could not be determined it was decided to see if the isotopic content of the leakage water could be used to reveal its origins. It was assumed that the possible sources were precipitation, tap water and water from the production of the cassette decks. Therefore samples of the leakage as well as the possible sources were sampled for analysis.

### **4.1 Method**

Samples were taken of the leakage water as well as the three points that were assumed to be the possible sources of the leakage. The water was stored in PET-bottles and frozen to ensure conservation of the isotopic compositions. The samples were then sent to the laboratory of the department of Geophysics at the Science Institute of the University of Iceland.

In brief, the  $^{18}\text{O}$  content of the water is measured by equilibrating the water with  $\text{CO}_2$  and then analysing the  $\text{CO}_2$ . The sample should have a pH value lower than 4,5 to ensure a fast exchange of oxygen between the water and the carbon dioxide. The fractionation factor of this reaction has been examined by a number of authors. The precision of determining the  $^{18}\text{O}$  content in this manner is usually better than  $\pm 0,2\%$ .

The deuterium content of the samples is determined by a method resembling that of Coleman et al. [5]. 2  $\mu\text{l}$  of degassed water are reduced with 15 mg of zinc metal in a sealed quartz tube at about  $450^\circ\text{C}$  for 10 minutes. The zinc pellets are then heated up to  $700^\circ\text{C}$  in order to transfer the remains of the zinc to the walls of the sample tubes by evaporation and

condensation. Then the samples are again kept at 450°C for 20 minutes. The accuracy of the measurements is 0.7‰.

The isotopic separation of the leakage water and the three possible sources can then be calculated and compared with the isotopic differences that can be calculated from the fractionation factors of the reactions that can be assumed to be involved in the transfer from the sources to the point of leakage.

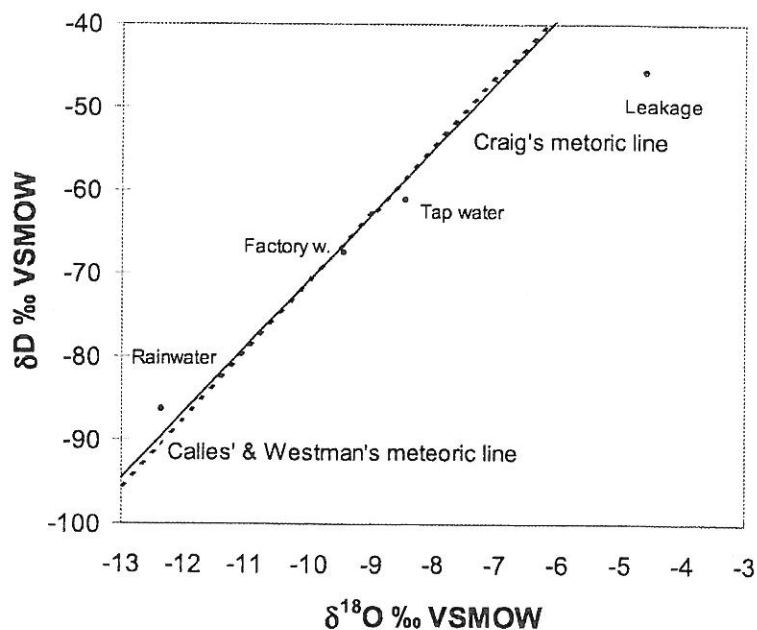
## 4.2 Results

The isotopic analysis gave the results shown in table 1.

**Table 1** *The abundance ratios of deuterium and oxygen-18 of the samples*

Point of measurement	$\delta D$	$\delta^{18}O$
Leakage	-45,7	-4,57
Tap water	-61,2	-8,45
Rainwater	-86,3	-12,36
Water from factory	-67,5	-9,45

Figure 2. shows the abundance ratios of oxygen-18 and deuterium of the samples and the meteoric line of Craig as well as the meteoric line of Calles and Westman for the weather station at Arup that lies in the vicinity of the building where the samples were taken.



**Figure 2.** *The measured abundance ratios and the global meteoric line of Craig and the local meteoric line of Calles' and Westman*

The precipitation sample lies close to the meteoric line. The slight deviation that may be due to local variation is to be expected. The water sample from the factory lies very close to the meteoric line as does the sample of tap water, which indicates that both samples are of meteoric origin. The distinct offset of the leakage water indicates that the water has undergone isotopic fractionation due to reaction.

The isotopic separation between the leakage water and the other samples is shown in Figure 3.

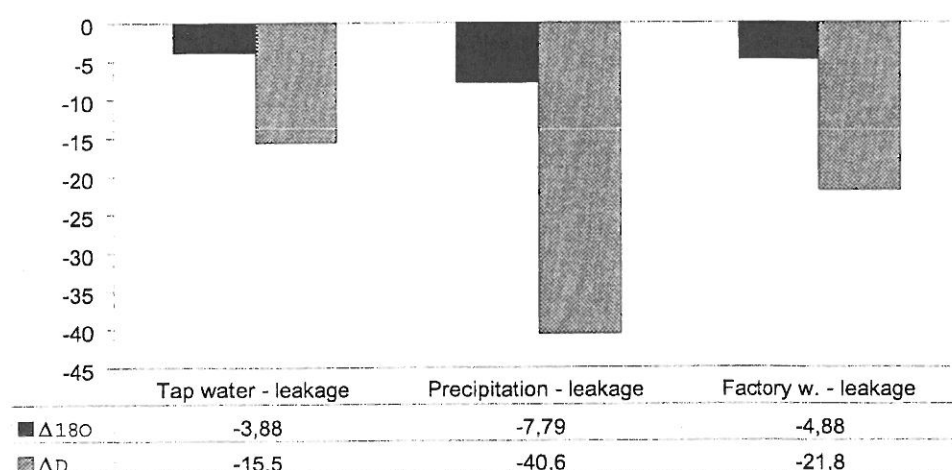


Figure 3. Measured isotopic separation between the leakage water and the other sources

If we compare the abundance ratios of the rainwater and the leakage water we can see that if rainwater is the source it must have undergone fractionation that most likely is due to evaporation. Not only must this be valid for the sample of rainwater that was analysed but all precipitation that follows the meteoric line. The isotopic differences due to evaporation can be calculated with eq. (19) and (20) and are shown in Figure 4, where the temperature ranges from  $-10$  to  $25^\circ\text{C}$ .

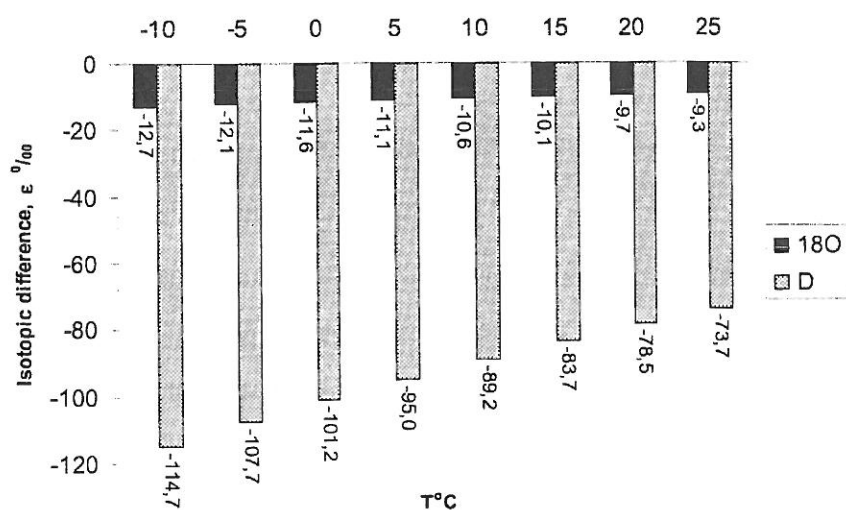


Figure 4. Calculated isotopic differences,  $\epsilon$  of deuterium and oxygen-18 due to evaporation in the temperature range of  $-10$  to  $25^\circ\text{C}$ .

As can be seen in Figure 4 the calculated isotopic differences exceed the measured isotopic separation between leakage and precipitation. It may however be assumed that the evaporation process follows a Rayleigh-type evolution in which case the isotopic ratio of the diminishing reservoir can be calculated according to eq. (9). Figure (5) shows the evolution of the abundance ratios, starting with the values of the rainwater sample.

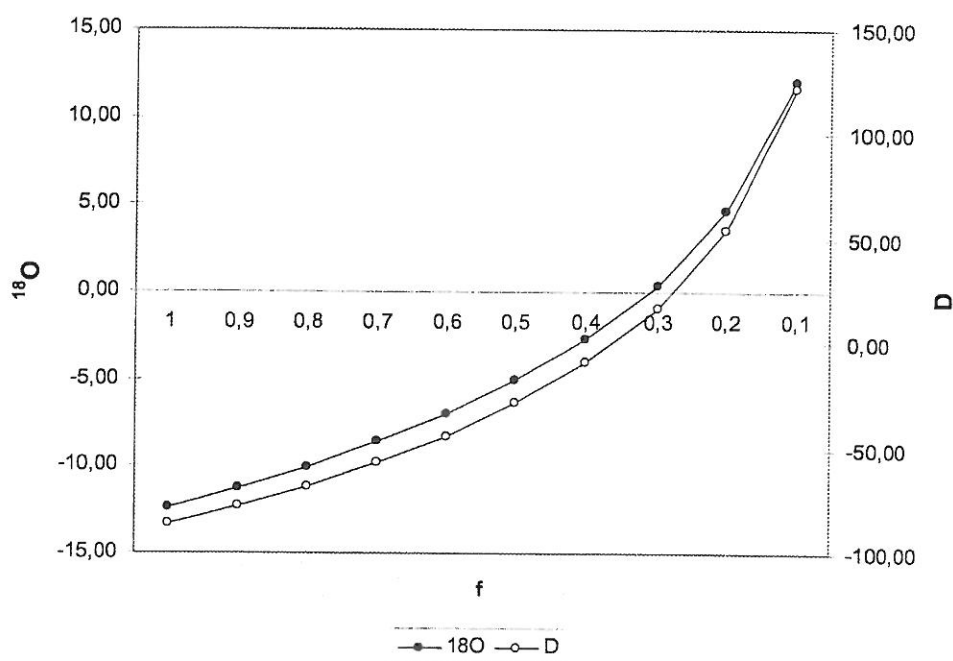


Figure 5. Calculated abundance ratios for evaporating rainwater following a Rayleigh evolution at 10°C.

If we compare the measured abundance ratios for the leakage water shown in Table 1 with the calculated values of Figure 5 it may be concluded that the leakage is possibly rainwater that accumulated during the building period, the half of which has evaporated before seeping through the construction.

A comparison of the water from the concrete factory with the leakage water gives us the  $\Delta^{18}\text{O}$  value of  $-4,88$   $\Delta\text{D}$  value of  $-21,8$  for the separation between the two samples. It is of interest to compare these  $\Delta$ -values with the isotopic differences that we are to expect because of the water-cement reactions in the concrete. If we follow the example of [2] and assume that 2 out of 3 water molecules are redundant we can calculate the isotopic differences of oxygen-18 from eq. (24) together with eq. (9) using  $f = 0,67$ . This gives us an isotopic difference  $\epsilon^{18}\text{O}$  of 16 ‰, which is roughly three times the  $\Delta^{18}\text{O}$  value. Given that the sample from the factory is representative for the water used when the elements were constructed it is therefore not plausible that the cause of leakage is the excessive use of water in the production.



The third candidate for the source of leakage is the tap water from the apartment. Under the assumptions that the tap water evaporates at 30°C and then condenses at 10°C in the construction, eq. (19) and (20) give us the isotopic differences of  $\epsilon^{18}\text{O} = -1,71$  and  $\epsilon\text{D} = -21,57$ . If we compare these values with the isotopic separation between the leakage and the tap water, with  $\Delta\text{D} = -15,5$  and  $\Delta^{18}\text{O} = -3,88$  it seems possible that the leakage is in fact condensed and accumulated moisture from the indoor air. The deviation between measurements and calculation might in that case for example be caused by the kinetic effect as formulated by equations (21) and (22). This is, however, contradicted by the position of the leakage and the temperature conditions that can be expected in the construction.

Based on the isotopic analysis of the samples as well as the calculations we can draw the conclusion that the leakage water has undergone a reaction that favours the lighter isotopes resulting in an enrichment of both oxygen-18 and deuterium. Moreover we can conclude that the most probable source of leakage is rain on the building site during erection.

## **5. Discussion and future research**

The effect of many physical and chemical reactions on the isotopic composition of water is well known. Many of these that are relevant to the transport of moisture in buildings have been described and thereby the means are provided for tracing the movements of water and water vapour through and within the building envelope.

An example has been given of how this can be used to identify the source of leakage in buildings. The comparison of the isotopic composition of leakage water and the possible origins of leakage reveals precipitation on the building site as the most probable source.

Nevertheless it is obvious that the use of isotopic analysis as a way of determining the source of leakage will in some cases be speculative because of the numerous possible scenarios. In some cases the method will, however, undoubtedly provide swift and certain identification, namely on those occasions where there has been no separation of isotopes.

Further evaluation and development of the method will ultimately involve a number of case studies together with experiments in the more controlled environment of the laboratory. The laboratory work should among other things include further investigations of how moisture transport in building materials in combination with absorption and condensation effects the isotopic content of the water.

We have in [6] shown how the thermodynamic properties of water vapour relate to the different transport mechanisms in porous building materials. And since we know how the thermodynamic properties of the isotopically water differ we will not only be capable of using the isotopes as tracers but even able to use the measured isotopic separation to quantify the contribution of the various transport processes.

## 6. References

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