

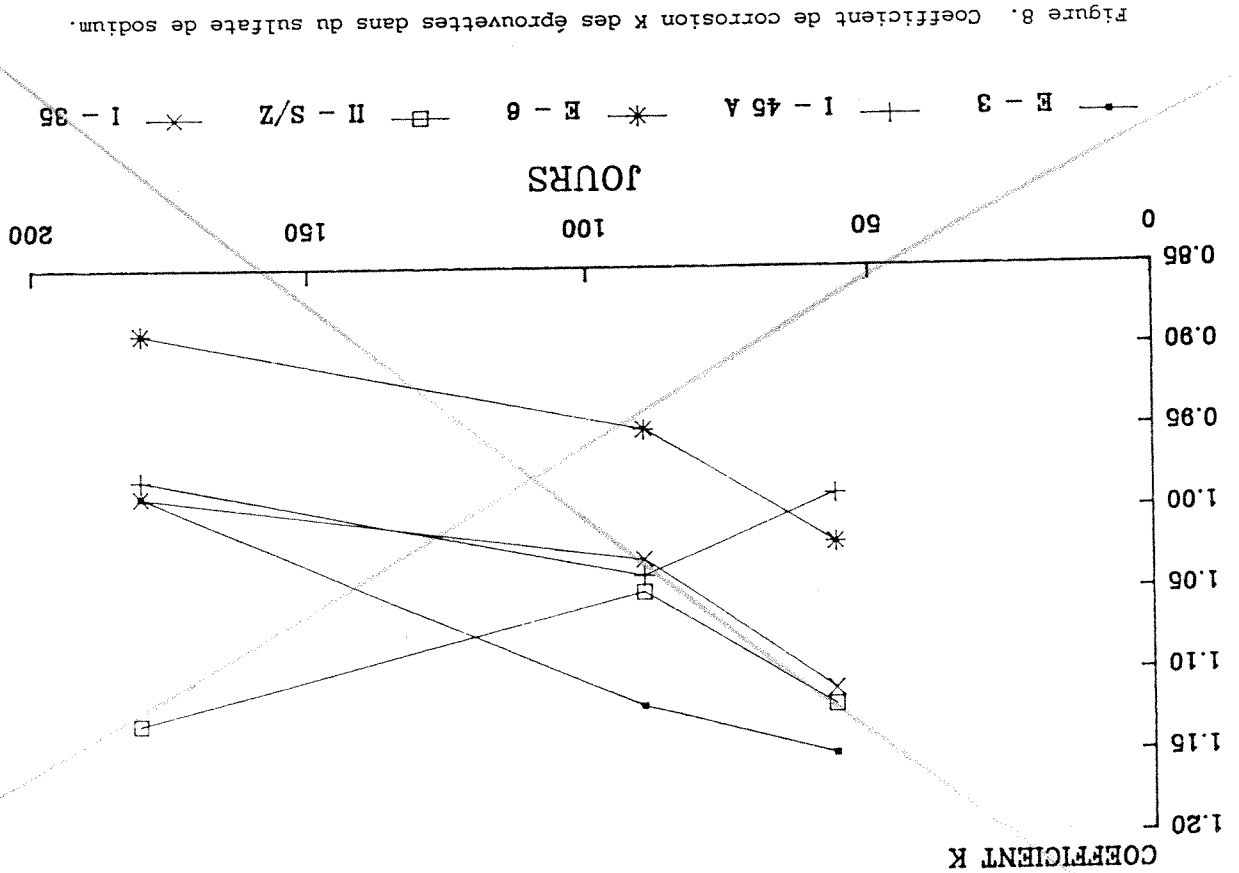
Influence of Microstructure and Water on the Diffusion of CO₂ and O₂ Through Cement Paste

by Y.F. Houst

Synopsis: A knowledge of the diffusion coefficients of CO₂ and O₂ is of considerable importance for a quantitative assessment of the carbonation and corrosion of the reinforcement. Equipment which allows the simultaneous determination of the diffusion coefficients of the two gases as a function of the relative humidity has been developed. Measurements have been carried out on carbonated discs of hydrated cement paste prepared with water/cement ratios between 0.4 and 0.8.

The results show that, if the water/cement ratio is increased from 0.4 to 0.8, diffusion coefficients increase more than ten times. On the other hand, diffusion coefficients are not significantly influenced by the relative humidity in the range 50-90%. The variation of diffusion coefficients as a function of water content and porosity is explained by the microstructure, characterized by water adsorption isotherms and mercury intrusion porosimetry measurements. It is also shown that a simple model based on the hydraulic radius, Knudsen diffusion and total porosity allows us to evaluate diffusion coefficients.

Keywords : Carbonation, carbon dioxide and oxygen diffusion, hydrated cement paste, durability, pore-size distribution, microstructure, gas diffusion modelling.



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INTRODUCTION

It is well known that carbonation of the concrete cover above the steel reinforcement is one of the decisive factors influencing durability of reinforced concrete structures. According to Tuutti [1], the service life of a structure, from the point of view of reinforcement corrosion, can be subdivided into an initiation stage and a propagation stage. The carbonation of the concrete cover takes place during the initiation stage. The rate of corrosion during the initiation stage is practically zero. It is only during the propagation stage that the rate of corrosion becomes an important factor. The generally accepted idea is that the availability of oxygen at the steel surface influences the corrosion rate, though this point of view is now questioned [2,3]. On the other hand, the water content of the concrete is a very important factor for the rate of carbonation [4] and the rate of steel corrosion [2,3].

The bulk of the experimental data available cannot be understood and interpreted fully because so far there is no comprehensive theoretical concept of the mechanisms involved in carbonation and corrosion of reinforced concrete. Houst, Roelfstra and Wittmann [5] have developed a numerical model to describe the diffusion of carbon dioxide and oxygen into the concrete structure and the drying process, corresponding to the initiation stage. All parameters of the model can be linked with concrete technological data. However, some of these parameters are unknown. This is true in the case of the influence of moisture content on gas diffusion through porous materials. It is the aim of this contribution to show the influence of moisture content on the diffusion coefficients of CO₂ and O₂ through hydrated cement pastes (hcp) prepared with different water-cement ratios.

The one dimensional diffusion of a gas through a porous system can be described phenomenologically by Fick's first law:

$$J = -D \frac{dc}{dx} \tag{eq. 1}$$

where J is the flux of the gas, dc/dx the gradient of concentration and D the diffusion coefficient.

This equation defines the diffusion coefficient of two gases diffusing into one another without hindrance. If the diffusion is hindered by a porous medium, the gases must diffuse through the pores of the material. The distance to cross the material is longer than that in unhindered diffusion. One defines the tortuosity as the distance to cross the material divided by its thickness. Thus only an effective diffusion coefficient can be determined for a specimen having the representative thickness :

$$J = -D_{eff} \frac{\Delta c}{d} \tag{eq. 2}$$

where d stands for the thickness of the representative porous material. The representative thickness is defined as the minimum thickness for which D_{eff} becomes independent of d.

In reality, diffusion processes in capillaries are complex and it is possible to distinguish at least three different transport mechanisms [6,7] :

- As soon as the pores dimensions get smaller than the mean free path of the gas molecules, the Knudsen diffusion begins to take place. The collisions between molecules are negligible in comparison with those between molecules and capillaries walls. This transport mechanism is the same for a partial or absolute pressure gradients, i.e. diffusion and permeability coefficients are the same. The Knudsen diffusion coefficient D_k for cylindrical pores is :

$$D_k = \frac{2}{3} \bar{c} r \tag{eq. 3}$$

where \bar{c} is the average molecular speed and r the radius of the capillary. The average molecular speed is :

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} \tag{eq. 4}$$

where R is the gas constant, T the temperature and M the molar mass.

- In large pores, where the mean free path of the gas molecules is smaller than the pores diameter, normal gas diffusion predominates. Gas molecules move by collisions against one another. This type of diffusion occurs only if the absolute pressure is the same at each end of the pores. At 0°C and 1 atm, the mean free paths of carbon dioxide and oxygen are respectively 40 nm and 65 nm [8]. The normal diffusion coefficient D_n is :

$$D_n = \frac{1}{3} \bar{c} \lambda \tag{eq. 5}$$

where λ is the mean free path which is given by the following equation :

$$\lambda = \frac{R T}{N \pi d^2 P} \quad (\text{eq. 6})$$

where N is the Avogadro number, d the molecular diameter and P the pressure.

- In addition to the two mentioned mechanisms, surface diffusion also can occur at the same time. If pore surfaces are active, gas molecules can diffuse along the pore walls by a succession of adsorption-desorption reactions from one active site to another. In very large pores, surface diffusion becomes negligible.

The diffusion coefficients of moisture through cement paste as a function of the water content can be calculated on the basis of drying experiments [9,10]. Schwiete, Ludwig and Zagar [12,13] have developed an apparatus to measure the diffusion coefficient of oxygen and carbon dioxide through porous ceramic materials. Later Därr and Ludwig [6] used a similar apparatus to measure the permeable porosity of materials. Engelfried [14] has developed a method to measure the diffusion of carbon dioxide through protective films applied on porous substrates. The method can be used only with dry specimens, because of the gravimetric determination of CO₂ which can be altered by water. Tuuti [1] determined the influence of water/cement ratio, concrete cover, curing, type of cement and relative humidity on diffusion coefficient of oxygen. Hurling [15] also determined the influence of water/cement ratio, cement content, as well as duration of curing and storing conditions on the diffusion coefficient of oxygen through concrete.

The permeability of concrete to oxygen is now currently determined and a Cembureau method has been recently published [16]. However, to measure the permeability, the specimen must be dried and the drying process has a very important influence, because of the changes that it causes to pores structure. It has been shown that there is a good correlation between permeability and diffusivity of methane [17] and oxygen [18]. As it is easier to determine the permeability coefficient, so if the correlation between permeability and diffusivity is known, it would be possible to estimate the diffusion coefficient by measuring permeability.

As none of the above mentioned methods allowed us to follow systematically the influence of variable moisture contents on diffusion coefficients, we decided to determine diffusion coefficients of carbon dioxide and oxygen at the same time. We also measured water adsorption isotherms and pore-size distribution by mercury intrusion porosimetry on the same hcp before and after artificial carbonation with the aim of characterizing the porous structure.

EXPERIMENTAL

Materials

In order to determine diffusion coefficients, we needed samples thin enough to be completely carbonated and equilibrated at different relative humidities in a relatively short time. For this reason, we prepared Portland cement paste cylinders of 160 mm diameter. After at least six months of curing in lime water, discs of 1-2 mm thick were sawn. As it is not possible to increase the water/cement ratio (W/C) of cement paste above 0.4 without having sedimentation and bleeding, it was necessary to keep cement particles in suspension before setting and hardening. Our ideas were based on previous work by Sereda and Swenson [19] who prepared cement pastes with high water/cement ratio. It was necessary to bring some modifications because of the large diameter of our specimens compared to those of Sereda and Swenson (ϕ 32 mm). Cement and water were mixed under vacuum and the cylindrical mold placed on a roller device for rotating the mix during setting and hardening, usually for a period of 48 to 72 hours. This method allowed us to prepare hcp with a W/C ratio from 0.3 to 0.8. The cement used was an ordinary Swiss Portland cement, corresponding approximately to ASTM type I.

During carbonation in a natural environment, carbon dioxide diffuses through an already carbonated material. Thus, we artificially carbonated our samples at 76% R.H. in an atmosphere of 80% to 90% CO₂. After a complete carbonation, checked by the phenolphthalein test, samples were equilibrated at different relative humidities before diffusion measurements. For water sorption and mercury porosimetry, we used pieces of the same discs of hcp as those used for diffusion studies.

Water Adsorption Isotherms

The samples (pieces of 3 to 5 mm), dried at 105°C, were first placed in desiccators where different relative humidities are obtained by saturated salt solutions. After the equilibrium was reached, the water uptake was measured by weighing. The water content as a function of the relative humidity allowed us to draw the adsorption isotherms. All adsorption experiments were carried out at 18°C on non-carbonated and carbonated hcp.

Mercury Porosimetry

A standard porosimeter (Micromeritics Autopore 9200) which allows the application of pressures up to 415 MPa has been used. This corresponds to a minimum radius of 1.7 nm. After having introduced a

number of simplifying assumptions, the radius r of pores, which can be penetrated by mercury at pressure P , can be related by the following equation:

$$r = - \frac{2 \sigma \cos \theta}{P} \quad (\text{eq. 7})$$

where σ stands for the surface tension of mercury and θ for the contact angle hcp-mercury. A value of 135° for θ was used in this study. The pore-size measurements have been carried out on small pieces of hcp (3 to 5 mm) pre-dried at 70°C .

Diffusion Measurements

We have developed equipment which allows us the simultaneous determination of diffusion coefficients of O_2 and CO_2 as a function of the relative humidity, by a non-steady state method. The heart of the apparatus is a measuring cell which is divided in two rooms by the porous disc of hcp. Once the specimen is built into the measuring cell, nitrogen, with a given moisture content, is introduced into the cell. The flow of pure nitrogen is continued until no more oxygen and carbon dioxide can be measured in the lower room. At this time, the two rooms contain only nitrogen, with the same moisture content. Then, the preconditioned gas (2% CO_2 , 20% O_2 and 78% N_2) enters only the upper room of the cell. After a few minutes the gas composition in this room will be the same as that of the preconditioned gas, which is moistened by bubbling a given part of gas through water. Relative humidities of over 90% are obtained by bubbling all the gas through water at a temperature higher than the room temperature. Oxygen and carbon dioxide diffuse now from the upper room through the hcp into the lower room, where the two gases are monitored as a function of time by gas analyzers using the paramagnetic properties of oxygen and infrared absorption of carbon dioxide (Leybold's Oxynos-1 and Binios analyzers). The humidity of the lower room (the same as that of the upper one) is kept constant by an appropriate saturated salt solution and the gases are homogenized by the pump of the analyzers which work in closed-circuit. In this way, water does not diffuse from one room to the other. But, that is not the case for N_2 which diffuses from the lower room to the upper one, similarly for a non-reactive gas in a real concrete.

All measurements were carried out between 20°C and 25°C . Relative humidity was continuously checked in the two rooms by humidity sensors. The diffusion coefficients are deduced from the curves of gas concentration as a function of time. The duration of the measurements varies between 1 and 3 days, depending on the thickness and porosity of the samples. The equipment and the method, which have been already tested on aerated concrete, are described in more detail in another publication [20].

RESULTS AND DISCUSSION

Microstructure

The water adsorption isotherms of the four different samples of hcp, measured on non-carbonated and carbonated samples, are shown in figure 1. Carbonation causes a decrease of adsorbed water as already observed [21]. The higher the equilibrium moisture content in a non-carbonated hcp, the higher the decrease of moisture content in a similiary carbonated hcp. The adsorption isotherms of carbonated hcp of W/C between 0.3 to 0.8 do not vary in a large extent. For example, the equilibrium moisture content of these hcp at 97% R.H. runs from about 8,5% to 11%. The BET specific surface area was calculated from the data of the adsorption isotherms between 9 and 44% R.H. and the results are reported in table 1. Carbonation strongly reduces the specific surface area to an approximatively constant value of 54 to 59 m^2/g for the three higher W/C.

The influence of carbonation on the microstructure was quantitatively measured by mercury intrusion porosimetry. The pore-size distribution of carbonated and non-carbonated hcp are shown in figures 2, 3 and 4 for W/C of 0.4, 0.5 and 0.8. Each curve of these figures is an average of 2 to 4 runs. The cumulative pore volume is normalized for non-carbonated hcp and the cumulative pore volume of carbonated hcp is computed with respect to non-carbonated hcp. The results for carbonated hcp of W/C = 0.3 are not given, the samples being not fully carbonated after more than 2 years of exposure to CO_2 .

One can see that the porosity is largely reduced by carbonation (see also table 1). This reduction is greater for low W/C. From figure 2, it is evident that all the pores are affected by carbonation, but specially those with radii below $0.1 \mu\text{m}$. The examination of figure 3 shows that only pores with radii below $0.2 \mu\text{m}$ are affected. The very porous hcp of figure 4 reveals a reduction of the amount of pores with radii below $2 \mu\text{m}$. These results roughly confirm those previously published [21, 22]. However, the history of hcp (hydration duration, type of drying, carbonation, ...) is an important factor for the microstructure and it will be difficult to obtain a definite view of the subject.

Diffusion Coefficients

The diffusion coefficients of O_2 and CO_2 depend, as expected, strongly on water/cement ratio, therefore on the porosity (see figure 6). On the other hand, the influence of water content is weak up to 93% R.H. (figure 5). This result seems to us important, because the diffusion coefficients of O_2 determined by Tuuti [1] and Hurling [15], but on non-carbonated concrete, show a strong influence of the water content. From the curve given for Portland cement concrete by

Tuuti [1], one can see a decrease of twenty times in the value of the diffusion coefficient between 50% and 90% R.H. In this range of humidity, diffusion coefficients determined by us on carbonated material are approximately constant. Such results give also basic values for numerical simulation.

This is not so much surprising if one considers the adsorption isotherms of the carbonated hcp. Indeed, the water content of the studied hcp depends only weakly on the total porosity (or W/C). The influence of water content on diffusion coefficient of water vapor has been determined by Hilsdorf et al. [23] on carbonated Portland cement mortars. They also observed little effect of water content on diffusion coefficient of water vapor, but only in the case of carbonated mortars.

The diffusion coefficients of CO₂ are always lower than those of O₂. This can be explained by the difference in size of the two molecules (3.23 · 10⁻¹⁰ m against 2.92 · 10⁻¹⁰ m; the diameter depending on the method used, but not the ratio). The ratio D_{O₂}/D_{CO₂} of diffusion coefficients given in figure 6 is 0.59, 0.73 and 0.74 for W/C of 0.4, 0.5 and 0.8 respectively. It can be roughly considered as constant.

As already mentioned, after a certain period CO₂ diffuses through carbonated material, as carbonation proceeds by displacement of a front of a few mm thick. That is why all measurements have been performed on a carbonated material. But it is not the case for O₂ which does not react with cement compounds and can be consumed by the cathodic reaction of corrosion in presence of chlorides. Therefore, it would be very useful to determine diffusion coefficients of O₂ through non-carbonated hcp. In this case, a much greater effect of water content on diffusion coefficients can be expected for relative humidities above 90% of R.H., as already observed [1, 15, 18].

Diffusion Modelling

It is possible to model gas diffusion through porous system knowing the pore-size distribution and the transport mechanisms, but it is not a very simple task. That is why we tried to compute diffusion coefficients on the basis of two simple models. The hypotheses of the first model are :

- The complex porosity can be described by cylindrical pores of the same radius and equal to two times the hydraulic radius (The hydraulic radius of a pore system is defined as the volume of the pores divided by their surfaces. The hydraulic radius of a cylinder equals to a half of its geometric radius).
- The only transport mechanism is Knudsen diffusion.
- The diffusion coefficient is proportional to the total porosity.

The hydraulic radius can be calculated from mercury porosimetry data. The results (table 1) show that Knudsen diffusion can be applied

to pores of these radii which are smaller than the mean free path of gas molecules. Knudsen diffusion coefficients, calculated according to eq. 3 and porosities of table 1, are given in table 2. The relation between measured and calculated coefficients is graphically represented in fig. 7. A single bilinear relation was found for diffusion coefficients of O₂ and CO₂. It does not seem realistic to compute two different relations for CO₂ and O₂. Calculated according to eq. 3, the ratio of the two Knudsen diffusion coefficients is 0.85 and an error of 15% can be accepted.

- A second model based on the following hypotheses were tested :
 - The only transport mechanism is normal diffusion.
 - The diffusion coefficient is proportional to the total porosity.

Diffusion coefficients, calculated according to eq. 5 and porosities of table 1, are given in table 2. The relation between these coefficients and those measured is graphically represented in figure 8. Two different relations were found for O₂ and CO₂. It is not surprising, because the ratio of the two diffusion coefficient, calculated according to eq. 5, is 0.52.

A simple realistic model should give a proportional relation between measured and calculated diffusion coefficients. The proportionality ratio can be taken as an evaluation of the tortuosity. For the first model, the tortuosity thus determined varies between 16 and 31 for O₂, and 18 and 39 for CO₂. The tortuosity, calculated according to the second model varies between 83 and 240 for O₂, and 59 and 170 for CO₂. If one admits that the three hcp have not a too different microstructure, the tortuosity should not sensibly vary with W/C. Tortuosity calculated with D_k (first model) corresponds better to this criterion.

CONCLUSIONS

1. Carbonation of hcp causes a decrease of the amount of adsorbed water. The adsorption isotherms and BET specific surface area of carbonated hcp of W/C between 0.3 and 0.8 do not vary in a large extent, contrary to those of non-carbonated hcp.
2. The porosity of hcp is largely reduced by carbonation. All pores are affected, but specially those with radii below 1 to 0.1 mm, depending on W/C.
3. The developed method and previously tested on aerated concrete is also suitable for the determination of diffusion coefficients of CO₂ and O₂ through carbonated hcp as a function of the relative humidity.
4. Diffusion coefficients depend strongly on the porosity. Those of CO₂ are lower than those of O₂.

5. Diffusion coefficients of CO₂ and O₂ through carbonated hcp are little influenced by equilibrium moisture content in the range of 50-90% R.H. In comparison, those hcp's which are not carbonated are greatly influenced by moisture content.
6. A simple model based on the hydraulic radius, Knudsen diffusion equation, and total porosity seems more suitable to evaluate gas diffusion coefficients than a model based on normal gas diffusion.
7. As it is practically not possible to measure diffusion coefficients through carbonated concrete in equilibrium with different relative humidities, it would be necessary to determine the influence of aggregates on diffusion coefficients and to develop a composite material model which allows us to transpose these results to cement concrete.

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Table 1--Total porosity, BET specific surface area and hydraulic radius of the non-carbonated and carbonated hcp

W/C	porosity [%] *		sp. surf. area [m ² /g]		hydr. radius [nm] *	
	non-carb.	carb.	non-carb.	carb.	non-carb.	carb.
0.3	19.05	- **	102	(71.7) **	13.5	- **
0.4	24.05	13.0	123	54.4	15.5	6.0
0.5	32.3	23.5	127	56.9	15.0	13.5
0.8	48.0	42.3	136	59.1	26.0	23.8

* determined by mercury intrusion porosimetry ** not fully carbonated

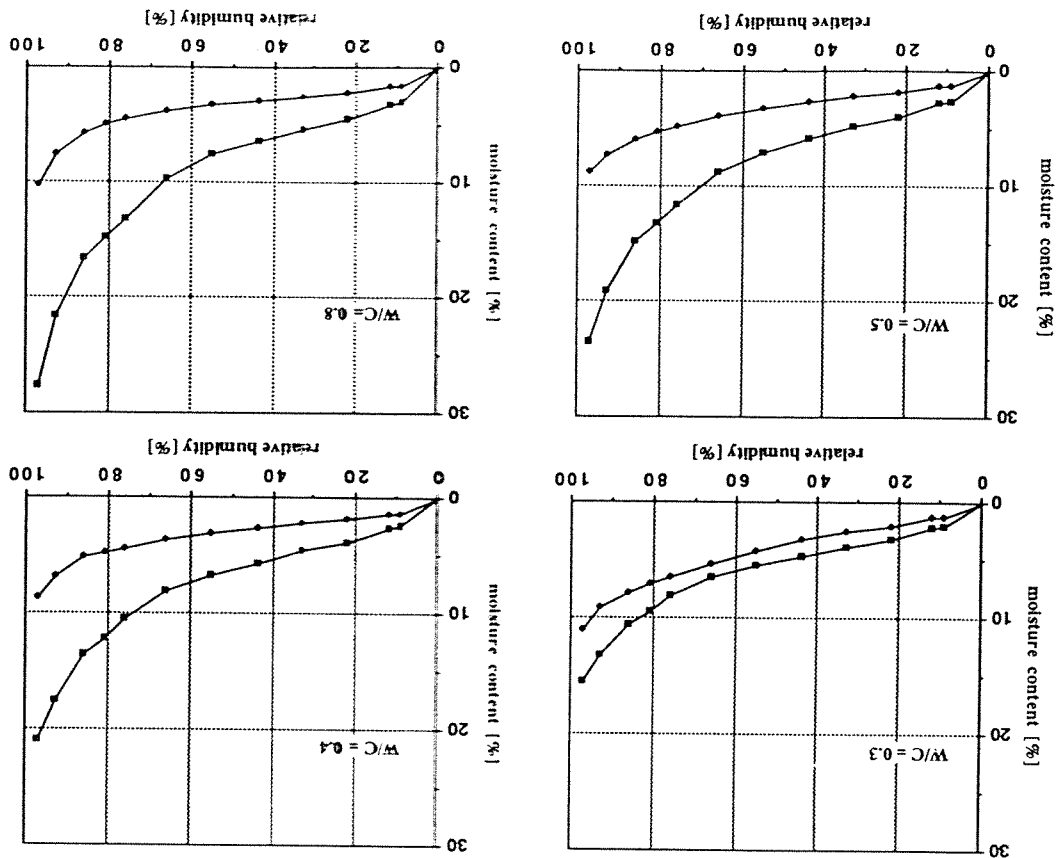
Table 2--Diffusion coefficients [m²/s] calculated for Knudsen diffusion (D_k) and for normal diffusion (D_n) for carbonated hcp (T = 296 K; P = 9.7·10⁴ Pa)

W/C	D _k (O ₂)	D _k (CO ₂)	D _n (O ₂)	D _n (CO ₂)
0.4	2.3·10 ⁻⁷	2.0·10 ⁻⁷	1.4·10 ⁻⁶	7.3·10 ⁻⁷
0.5	9.4·10 ⁻⁷	8.0·10 ⁻⁷	2.5·10 ⁻⁷	1.3·10 ⁻⁶
0.8	3.0·10 ⁻⁶	2.5·10 ⁻⁶	4.6·10 ⁻⁶	2.4·10 ⁻⁶

Table 3--Diffusion coefficients of oxygen and carbon dioxide as a function of the relative humidity and W/C (the given error corresponds to one standard deviation)

relative humidity [%]	W/C = 0.4			W/C = 0.5			W/C = 0.8		
	D _{O2} [m ² /s]	D _{CO2} [m ² /s]	D _{O2} [m ² /s]	D _{CO2} [m ² /s]	D _{O2} [m ² /s]	D _{CO2} [m ² /s]	D _{O2} [m ² /s]	D _{CO2} [m ² /s]	
48	(7.8±1.9)·10 ⁻⁹	(5.9±1.8)·10 ⁻⁹	-	-	(1.8±0.7)·10 ⁻⁷	-	(1.4±0.5)·10 ⁻⁷	(1.6±0.5)·10 ⁻⁷	
55	(1.0±1.8)·10 ⁻⁸	(5.7±1.5)·10 ⁻⁹	(3.0±0.1)·10 ⁻⁸	(2.2±0.1)·10 ⁻⁸	(2.0±0.5)·10 ⁻⁷	(2.2±0.1)·10 ⁻⁸	(1.6±0.5)·10 ⁻⁷	(1.5±0.5)·10 ⁻⁷	
76	(9.2±1.9)·10 ⁻⁹	(4.3±1.7)·10 ⁻⁹	(2.8±0.1)·10 ⁻⁸	(2.1±0.1)·10 ⁻⁸	(2.1±0.5)·10 ⁻⁷	(2.1±0.1)·10 ⁻⁸	(1.5±0.5)·10 ⁻⁷	(1.2±0.3)·10 ⁻⁷	
86	(8.0±1.8)·10 ⁻⁹	(4.3±1.7)·10 ⁻⁹	(2.7±0.2)·10 ⁻⁸	(1.9±0.1)·10 ⁻⁸	(1.8±0.7)·10 ⁻⁷	(1.9±0.1)·10 ⁻⁸	(1.2±0.3)·10 ⁻⁷	(1.2±0.3)·10 ⁻⁷	
93	(6.2±1.5)·10 ⁻⁹	(3.5±1.4)·10 ⁻⁹	-	-	(1.9±0.7)·10 ⁻⁷	-	(1.2±0.3)·10 ⁻⁷	(1.2±0.3)·10 ⁻⁷	

Fig. 1--Water adsorption isotherms (18°C) measured on hcp of different W/C ratio. The upper curve represents the non-carbonated hcp and the lower one the carbonated hcp



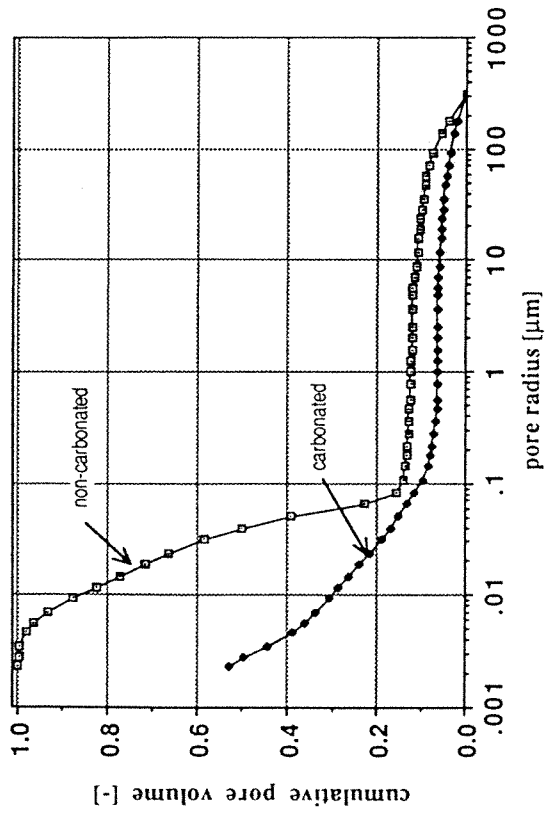


Fig. 2--Cumulative pore-size distribution of non-carbonated and carbonated hcp (W/C = 0.4) measured by mercury intrusion porosimetry

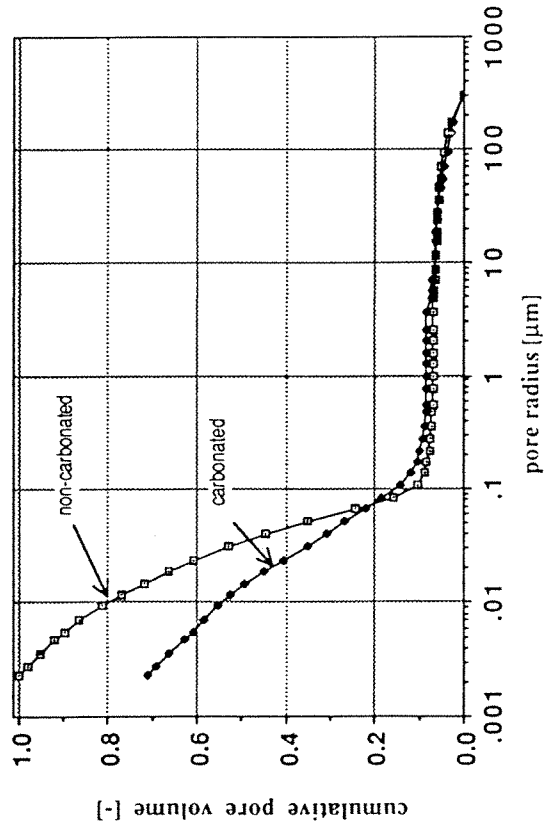


Fig. 3--Cumulative pore-size distribution of non-carbonated and carbonated hcp (W/C = 0.5) measured by mercury intrusion porosimetry

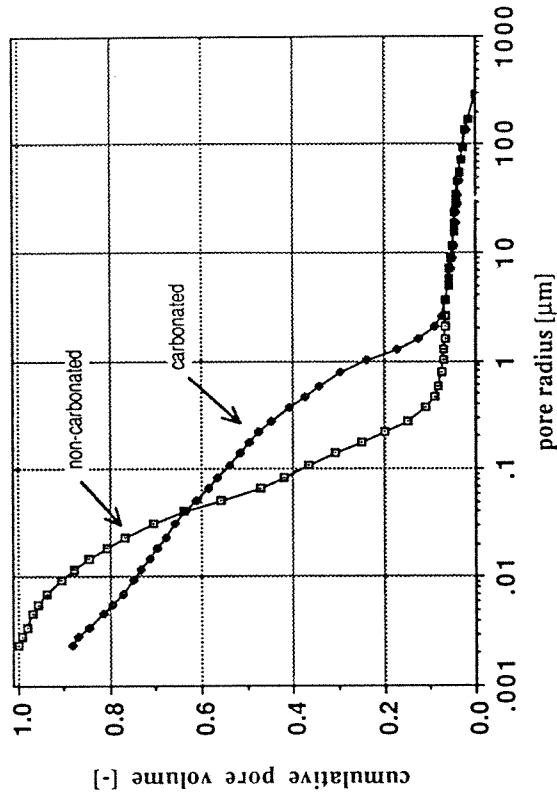


Fig. 4--Cumulative pore-size distribution of non-carbonated and carbonated hcp (W/C = 0.8) measured by mercury intrusion porosimetry

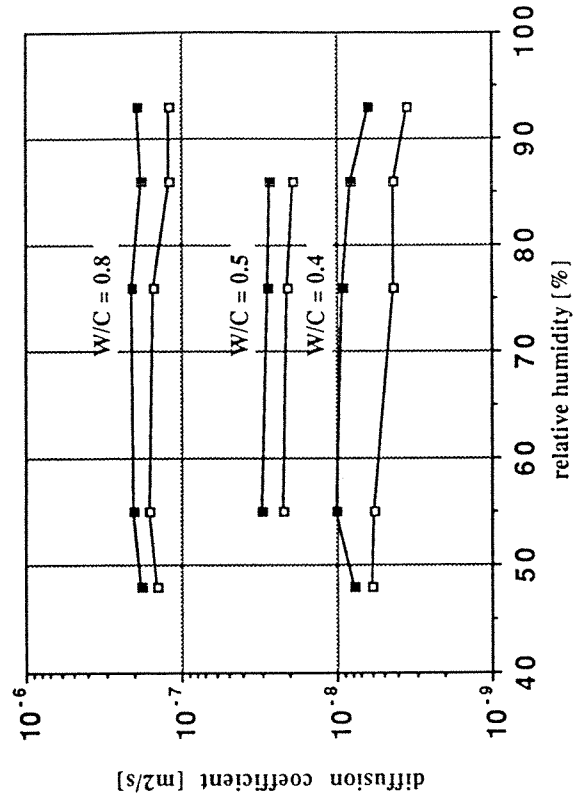


Fig. 5--Diffusion coefficients of O₂ and CO₂ measured as a function of equilibrium relative humidity for W/C = 0.4, 0.5 and 0.8

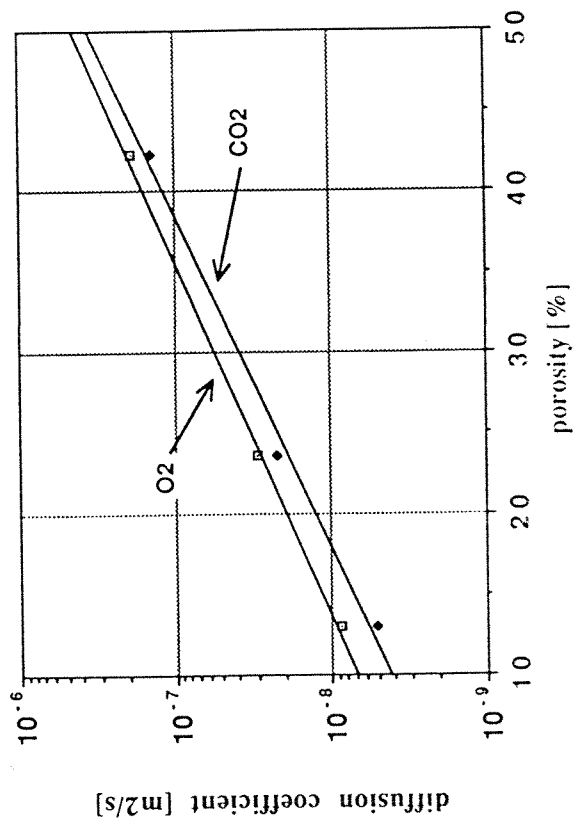


Fig. 6--Diffusion coefficients of O₂ and CO₂ as a function of total porosity

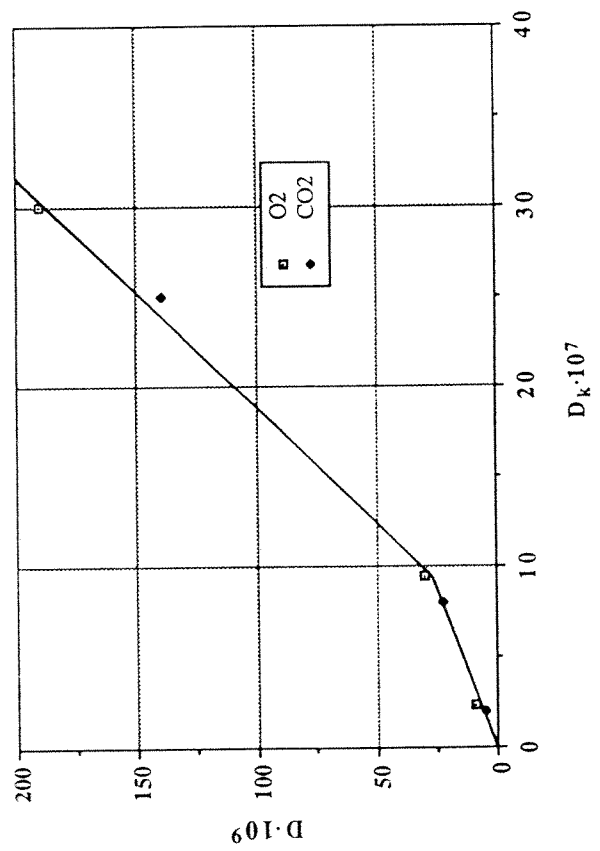


Fig. 7--Relation between calculated diffusion coefficient according to Knudsen (D_k) and measured diffusion coefficient (D)

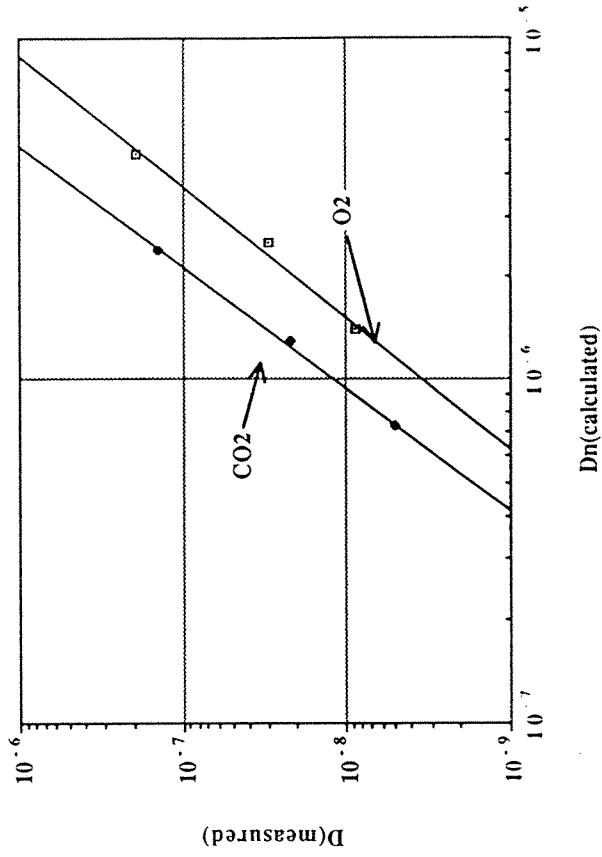


Fig. 8--Relation between calculated diffusion coefficient according to normal diffusion (D_n) and measured diffusion coefficient (D)

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