9-th International Symposium on Supercritical Fluids, 18-20 May 2009, Arcachon, France.

DIFFUSION OF CHLOREX THROUGH THE PAPER IN SUPERCRITICAL AND LIQUID CARBON DIOXIDE

A.A. Murzin[1], D. N. Shafikov[1], and A. Yu. Shadrin[1]
S. I. Bichkov[2], V.V. Bondin[2], I.G. Efremov[2], A.Yu. Zhabin[2]
1 - Khlopin Radium Institute RPA, 28, 2-ndMurinskii av., St. Petersburg, Russia.
2 - Mining and Chemical Combine FSUE, 53, Lenin St., Zheleznogorsk, Russia
shadrin@khlopin.ru

Introduction

Studies preformed in many laboratories throughout the world showed principle feasibility of treatment in supercritical (SC) and liquid CO_2 both for decontamination of the porous materials and for detection of the toxic chemical compounds in the porous materials [1,2]. To evaluate the possibility of the development of the appropriate technology it is necessary to study the diffusion of organic compounds through the porous materials (e.g., through the paper) in SC and liquid CO_2. Chlorex $[(ClCH_2CH_2)_2O]$ was used to study diffusion of halogen-containing organic compounds in this work. The experiments were performed with Chlorex, because it, being close to a series of toxic organic compounds by its physicochemical properties, is significantly less hazardous for human health.

Experimental

In this work, the partition method was chosen to investigate the diffusion kinetics of toxic compounds through the porous materials in the media of liquid gases and supercritical fluids. [3]. Within this procedure, the diffusion of the corresponding compound from one plate with initial concentration $C1$ into the another plate, being with first in contact, with initial concentration $C1$ and duration of the process is selected so that at some distance from the contact area certain sections of the plates retain the initial concentration of the compound in question. Thus, concentration C in the section removed from the contact area at distance x at process time τ can be presented as follows:

$$C=C1+(C2-C1)/(1-\mathrm{erf}\,u), \qquad (1)$$

Where $\mathrm{erf}\,u$ is tabulated for different u values as:

$$u=x/(2(D\tau)½) \qquad (2)$$

Using experimental $C1$, C2, and C for given x and τ, $\mathrm{erf}\,u$ can be calculated using the following expression:

$$\mathrm{erf}\,u=1-2(C-C1)/(C2-C1) \qquad (3)$$

Within given approach, we can also determine the mass-transfer coefficient (the effective coefficient of diffusion). This problem can be strictly solved only for the case of infinite cylinder and laminar flow of the liquid:

$$C1/C2=\omega\Sigma_1^{\infty}(4(Bi)^2/\mu^2+(Bi)^2)e^{(-\mu 2)\tau}, \quad (4)$$

where μ are the characteristic equation roots

$$J0(\mu\ )/J1(\mu)= \mu/(Bi), \qquad (5)$$

and ω is the dimensionless factor

$$\omega=D\eta z/\rho vR^2, \qquad (6)$$

where τ_1 is the time from the moment of the fluid penetration in the layer; D is the diffusion coefficient of extracted compound in the solid state; z is the layer height; w is the flow rate of the liquid; and R is the reduced radius of the cylinder.

Using experimental data on changes in concentration of given compound in the liquid in time τ, $tg\alpha$ in semi-logarithmic coordinates can be determined as follows:

$$tg\alpha=((lgC1/C0)_1-(lgC2/C0)_2)/\tau=0{,}4343D\mu/R^2, \quad (7)$$

It should be noted that $tg\alpha$ is determined after attainment of the steady-state regime, i.e., when the function $lgC_1/C_0=f(\tau)$ becomes linear.

In our work we considered the simplest mode of Chlorex diffusion from the layer with concentration $C1$ into the layers initially containing no compound in question. In our case the initial concentration of chlorex was retained in 1-2 paper sheets in the heap center, whereas the concentration of chlorex in the layers at the heap sides was small (0.01 mg). At the same time, in first paper layers from both sides of the cell the concentration of chlorex increased (to 5-7% of the initial amount). This fact can be explained by precipitation of chlorex from CO_2 at pressure releasing, when the side layers acted as the filters. Taking into account this assumption and known initial and final concentrations of chlorex in all the layers, *erf u* was calculated from Equation (8):

$$erfu = 1 - \frac{2\cdot C}{C_2} \quad (8)$$

Then, using tabular *erf u* values the diffusion coefficients were calculated (9):

$$D = \frac{x^2}{4\cdot\tau\cdot u^2} \quad (9).$$

Experiments were conducted on a laboratory setup presented in Fig 1.

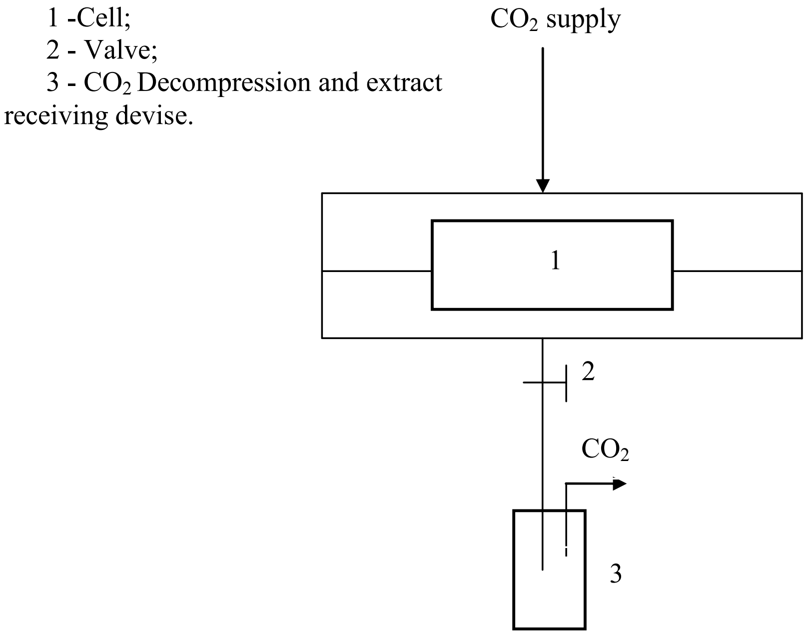

Fig.1 Principal scheme of laboratory setup.

To study the Chlorex diffusion, the paper discs 14 mm in diameter were cut out from the heap of five office paper sheets (TU 5438-016-00253497-2001, white, 80 g/m^2) with a punch. Hereinafter, these five samples are called a layer. The layers of five paper discs were collected in bunches (45 sheets in each).

A fixed volume of chlorex was deposited with a polyethylene pipette on two layers; the amount of deposited Chlorex was controlled by weighing. Then, two layers (5 paper discs in each) were combined (by the planes of deposition) to obtain a pocket of 10 paper discs. This pocket was stored for 10 min for the uniform impregnation. Then, the pocket was weighed to determine the amount of compound (Chlorex) evaporated from the material surface in the course of deposition. The resulting pocket after weighing was placed into cell 1 (Fig 1) between two paper bunches of 45 round discs in each.

The duration of the cell charge with the paper packet was about 1 min. The duration of the temperature attainment was about 1.5 min, and the duration of the carbon dioxide supply no more than 0.5 min. Thus, the total duration of the setup charge with the paper packet (beginning from the deposition of the “polluted” discs to the process start) was no more than 3 min.

The setup was filled with CS or liquefied carbon dioxide using two uniform flows from both sides of the cell. The cell was stored under the steady-state conditions for a required time after setup was filled with CO_2.

After the experiment termination, CO_2 was released by the uniform flows from both sides of cell. The rate of revealing was controlled by valve 2.

The decompression and extract receiving was realized by bubbling of the gas phase through acetone (or methanol). For this purpose, a capillary was immersed up to the bottom of the glass collector (8 mm in diameter), the solvent height was 100 mm. The filling volume of collector 3 was 5 ml

After complete decompression of carbon dioxide from the system the setup was dismantled. The paper from the cell was recovered as a compact briquette. Then, using a pincers, the layers (5 paper discs in each) were separated. Each layer was placed in a sealed container. The duration of the briquette separation was about 3 min. In each container acetone or methanol (1.0 ml) were added. The Chlorex recovery from the paper in the steady-state regime took 4 h. The samples for analysis were taken directly before measurements.

The content of Chlorex was determined from acetone solutions by gas chromatography using nitrogen gas carrier. The measurements were carried out on a Gazokhrom 1106E chromatograph equipped with an electron capture detector; the column was packed with a Chromaton N-HW-DMCS (0.200-0.255 mm).

Results and Discussion

The experimental data on the Chlorex distribution between the paper layers in liquid and supercritical carbon dioxide are presented in Figs. 2 and 3 respectively.

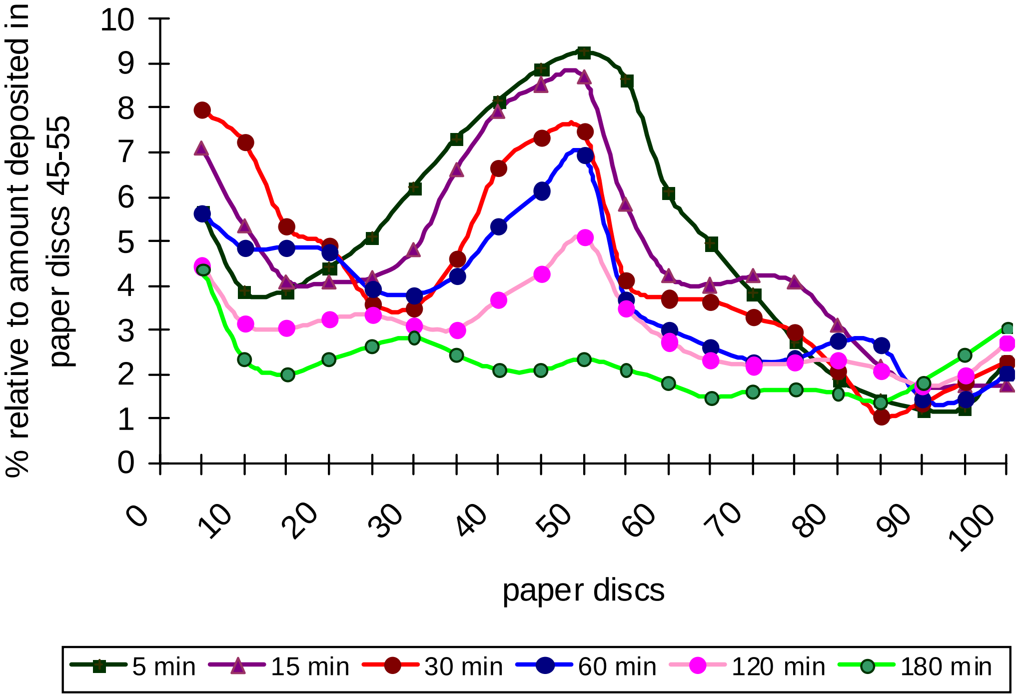

Fig. 2. Concentration of Chlorex in the paper layers at various duration of treatment in compressed CO_2 *(7MPa,25°C).*

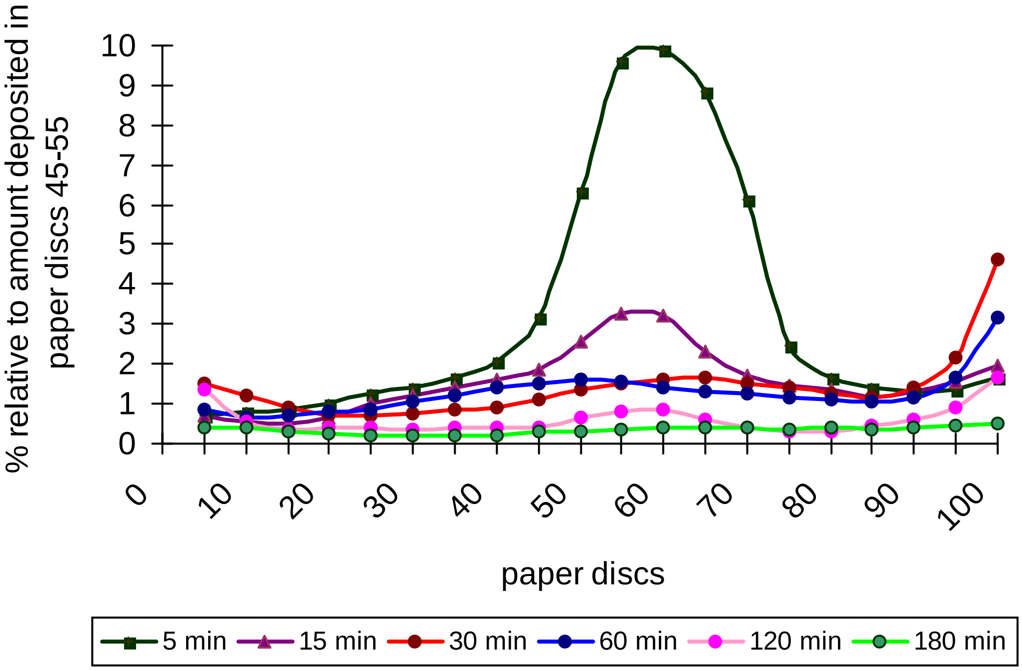

Fig. 3. Concentration of Chlorex in the paper layers at various duration of treatment in compressed CO_2 (25 MPa, 60°C).

It was found that in the case of treatment of relatively volatile liquid Chlorex under the conditions of supercritical fluid the peak of maximal Chlorex concentration shifts toward greater free volume of the cell, which is probably due to the design and features of the cell used. Hence, only concentrations determined in smaller (left) section of the cell were used to calculate the diffusion coefficients. The diffusion coefficients of Chlorex through the paper layers in the medium of liquid and supercritical CO_2 were 0.007 ± 0.003 and 0.018 ± 0.003 mm^2/min respectively, which suggests high penetrability of Chlorex through the paper in liquid and supercritical CO_2.

Conclusion

Applicability of the partition method to determine the kinetics of diffusion of the halogen-containing organic compounds through porous materials in liquid gases was demonstrated. The diffusion coefficients of Chlorex through the paper layers in the media of liquid and supercritical CO_2 were calculated, that were estimated as 0.007 ± 0.003 mm^2/min и 0.018 ± 0.003 mm^2/min respectively.

The work was financially supported by the international Science and technology Center (ISTC project no. 3106).

---

1 Knez, Z., Posel, F., Krmelj, I., High pressure extraction of organics from water, in Supercritical processing of foods and biomaterials. 1991, Blackie and Academic Professional: New York, NY. p. 181.

2 Jya-Jyun Yu, Hung-Chih Wang, Wei-Che Hsiao, Ping-Hsien Shen, Bo-Wen Jeng (Taiwan,China Proceedings of 3rd International Symposium SuperGreen2004, October 23-26, 2004 -Tianjin, China, IL8 (jn CD)
33 G.A. Akselrud, V.M. Lisyanskiy, Ektragirovanie. Sistema tverdoe telo -zhidkost. L, Himiya, 1974, 256 s.