

A preliminary study on sorption, diffusion and degradation of mustard (HD) in cement

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Abstract

A preliminary study has been done to examine the sorption, diffusion and degradation of mustard (HD) in cement. The sample of dried cement paste is a meso-porous adsorbant with a BET surface area around 40.8 m²/g, which is able to adsorb vapor of HD at room temperature and to result in a multiple-layer isotherm of II type. The molecule of HD seemed to chemically adsorb onto cement surface. Droplet of HD contaminating cement was able to be degraded into less toxic products, but in a very low rate of $k = 4.8 \times 10^{-5} \text{ min}^{-1}$ and $t_{1/2} = 16 \times 10^4 \text{ min}$ at room temperature. Droplet of HD is able to penetrate through the layer of cement, but a cement plate of 8 mm can protect against HD droplets over 48 h. A decrease of thickness for cement layer or addition of sand in cement would lead to lower the protection time against HD droplets. The diffusion coefficient of HD molecule in cement was determined, about $1.3 \times 10^{-4} \text{ cm}^2/\text{min}$ and of a typical diffusion in solid.

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1. Introduction

Although originally used in the first world war as a chemical warfare agent (CWA), the blister agent HD (2,2'-dichloroethyl sulfide, or mustard) has appeared still in our daily life at present. In the northeast of China [1], many HD bombs abandoned by Japanese army in world war two were found. The fate of chemical warfare agents (CWAs) in environmental matrixes is relevant not only to the obvious military concerns of maintaining operations on battlefields, strategic bases, and storage depots but also to civil defense planners as terrorists become evermore sophisticated [1]. One only has to recall the infamous "1995 nerve gas attack in a Tokyo subway" [2] to fully appreciate the latter issues. Common to both interests is the fact that, following a CWA incident; measures must be taken to regain use of the affected area. Most of the modern buildings are built by concrete. On the military side, air bases and their vast expanses of cement are a major concern, as these areas are vital to mission activity. Personnel, aircraft, vehicles, and equipment would necessarily be

in direct contact with these surfaces. Thus, understanding what happens to CWAs in various matrixes would dictate whether natural weathering or other processes innate to a particular material could offer timely and sufficient remediation or more drastic decontamination procedures are warranted.

2. Experimental

The samples of concrete were prepared from cement paste, and simply named as "cement" hereafter. They could be the powders of a size about 10–20 meshes upon crushing dried paste, and also the wafers of different thicknesses between 2 and 10 mm with a diameter of 85 mm. The used cement was a grade of 425 and furnished by Shuangshan Cement Company in Beijing.

An instrument of Autosorb-1 from Quantachrome Company was used to evaluate the structure parameters of the "cement". The experiments for sorption of HD vapor were carried out on the static vacuum adsorption equipment, which was self-constructed in laboratory. Upon degassing the system down to 5×10^{-5} Torr by diffusion pumps, HD vapor was introduced into vacuum space to get certain vapor pressure. The relative quantity of sorption on cement sample would be gotten by a measurement of the variation of quartz spring length.

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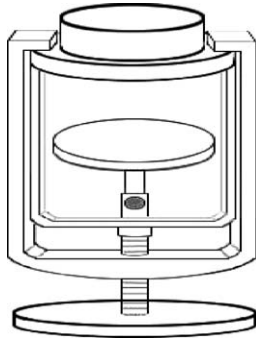


Fig. 1. The clamp equipment to determine the protection time against HD droplet through the wafer of cement at 25 °C.

The experiment to determine protection time against HD droplets for the samples of wafer was effectuated with an equipment of clamp made of stainless steel, as illustrated in Fig. 1. One self-made indicator paper of Chloramines-Congo red could be glued onto the down-side of wafer. A droplet of 80 μL HD was dripped onto the central point of up-side for the wafer. HD vapor would penetrate through the wafer and react with chloramine to produce HCl followed by a successive reaction between HCl and Congo red. A change of color from red to blue would be easily observed through a reflecting mirror once the concentration of HD onto back side surface grew up to 2–4 $\mu\text{g}/\text{cm}^2$. Another equipment of clamp as shown in Fig. 2 was used to determine the diffusion coefficient of HD through the wafer. The key point is to sweep off HD vapor from the down-side surface by air-flow into a solvent once HD vapor breaking through the wafer dripped by a droplet of 80 μL HD, and to determine its amount using a colorimetric method.

The products for the degradation of HD within the wafer of cement over 48 h at 25 °C were identified with HP5890II-5971A GC-MSD. The experiment for degradation of HD droplets in cement was accomplished by properly mixing 1600 mg cement powders with 80 μL HD droplets within a culture glass-dish. The obtained mixture would be collected into the conical flask with brush. A solvent, acetonitrile, was used to extract HD residual in cement upon different time-on-reaction at 25 °C. The degradation rate constant would be gotten from the variation of HD residual along with time-on-reaction.

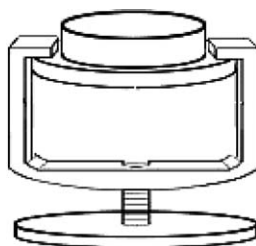


Fig. 2. The clamp equipment to determine the diffusion coefficient of HD through the wafer of cement at 25 °C.

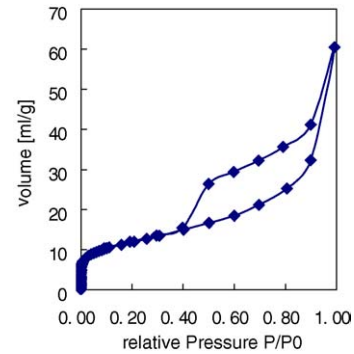


Fig. 3. Isotherm of N₂ adsorption for cement at –196 °C.

3. Results and discussion

3.1. Porous structure for cement

Isotherm for sorption of N₂ at –196 °C was obtained by AUTOSORB-1 instrument after the sample of cement was dried at 100 °C for 2 h, as shown in Fig. 3. One could get a surface area about 40.8 m²/g and a distribution of pore size around 30 Å (Fig. 4), when treating isotherm with BET equation and BJH method.

The surface area of cement measured by nitrogen adsorption varied widely between 5 and 250 m²/g, as reported in literature [3–5]. It was much affected by some factors such as calcium chloride content, temperature of cure, water/cement ratio in paste, drying method and age process. It will become larger if water/cement ratio or aging time increased. The surface area measured with nitrogen is much less than that by sorption of water vapor. Furthermore, different methods to determine surface area, like nitrogen adsorption technique, small angle X-ray (SAXS) and small angle neutron scattering (SANS) and Nuclear Magnetic Resonance (NMR), have been developed over the past 25 years and gave off different values of surface area.

Concrete science classified structural levels as micro ($\leq 1 \mu\text{m}$), meso (1 μm to 1 cm), and macro ($> 1 \text{cm}$) [6]. Internal structures of concrete imply those at micro and meso levels. At micro level, structures are discontinuous and inhomogeneous such as molecular and crystal structures, gels and pores. At meso level, structures are continuous but inhomogeneous such as coarse and fine aggregates, cement hydrates, unhydrated cement

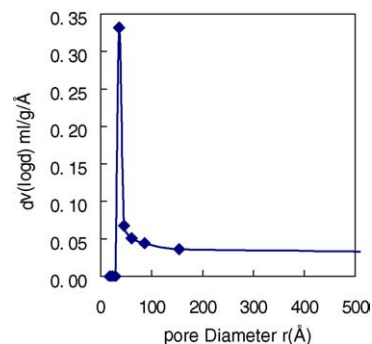


Fig. 4. Distribution of pore size calculated by BJH method.

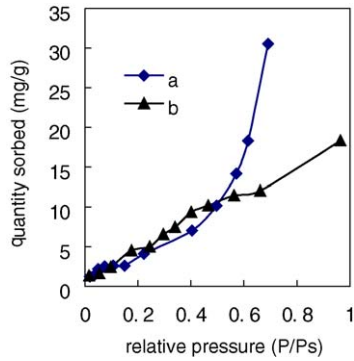


Fig. 5. Influence of water content in cement on sorption of HD at 25 °C (a: pure cement stored in air; b: pure cement dried at 120 °C for 2 h).

particles, pores, and interface. At macro level, concrete is continuous and homogenous [7]. Pore structure is a parameter, which relates to all three structural levels. It includes porosity, pore size distribution and surface area. Pore structure at both micro and meso levels is an important characteristic, which determines macro properties of concrete such as strength [8–14], elasticity, shrinkage [15], durability [16–19] and, etc. Cement paste, mortar, and concrete are all porous materials. Any change in pore structure may lead to sharp changes in performance [20,21]. For the sample of cement, Fig. 4 shows the pore structure at micro level.

3.2. Sorption of HD vapor by cement

For the sample of cement exposed in air, it was experimentally found that the sorption of HD vapor was non-measurable and less than 0.1 mg/g when $P/P_s < 0.1$, and it could grow up to 30 mg/g when vapor of HD approached to saturation. The isotherm for sorption of HD vapor on cement is of multiple-layer, II type, as shown in Fig. 5. If the sample of cement was dried at 120 °C for 2 h and lost some content of water, it would result in a decrease in sorption of HD, as illustrated in Fig. 5. It seemed that more content of water is favorable to sorption of HD onto cement. In addition, it was also experimentally demonstrated that the sorption of HD would obviously decrease when the content of sand in cement increased, as illustrated in Fig. 6.

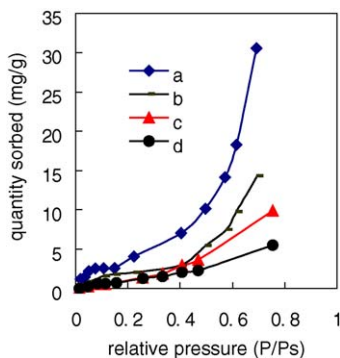


Fig. 6. Influence of sand content in cement on sorption of HD (a: cement; b: cement/sand = 1/2; c: cement/sand = 1/4 and d: pure sand).

Table 1
Parameters from BET equation for sorption of N₂ and HD

Adsorbate	P/P_s	V_m (mg)	S_{BET} (m ² /g)	C	$E_1 - E_L$ (kJ/mol)	E_L
N ₂	0.11–0.31	0.015	40.8	818	16.6	5.6
HD	0.05–0.22	2.3	3.2	8954	22.5	59.8 ± 2.1

Table 1 listed the parameters obtained from BET equation for sorption of N₂ and HD, such as the amount of mono-layer sorption V_m , and the constant C related to sorption heat ($E_1 - E_L$). It can be seen from $E_1 - E_L$ that sorption of HD vapor seemed to be like a physisorption as that of N₂. However, the molecule of sorbed HD was not observed to desorb from cement at room temperature even when the pressure of HD vapor lowered down to 10⁻⁴ Torr. This would indicate a strong interaction between HD molecule and oxide surface of cement. It may be that sorption of HD vapor onto cement surface occurred through a first step physisorption and followed by a second step chemisorption. If one assumed HD molecule to be a sphere model as usual, cross sectional area will equal 38 Å², then S_{BET} for cement would be about 3.2 m²/g. However, HD molecule preferred to a in reality with a cross sectional area about 72 Å². This would result in a S_{BET} about 6.4 m²/g.

3.3. Diffusion of HD molecule through the wafer of cement

With regard to the protection time against HD droplets for the wafer of cement, it was experimentally found that a droplet of 80 μL HD was able to break through the cement wafer of 3 mm thickness in 12 min. This breakthrough time would augment when the thickness of wafer increases, as presented in Fig. 7. Moreover, the breakthrough time would decrease when the proportion of sand in cement increases and this was shown in Fig. 8. It seemed to be resulted from a decrease of HD sorption along with an increase of sand proportion in cement.

The penetration of HD droplet from up-side to down-side through the wafer, $C(x, y, z, t)$, could be written in a mathematic equation based a diffusion process and a degradation reaction of first order as following:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) + kC \tag{1}$$

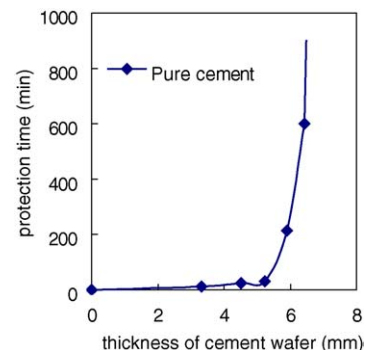


Fig. 7. The time of protection against HD droplet for the wafer of cement at 25 °C.

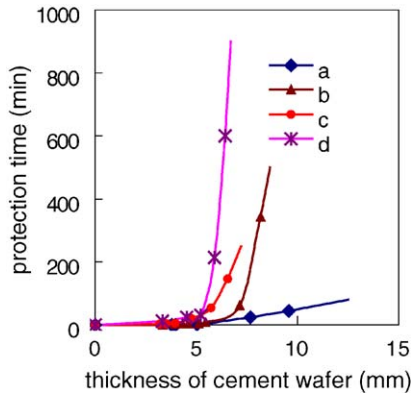


Fig. 8. Influence of sand proportion on the time of protection against HD droplet for the wafer of cement (a: cement/sand = 1/4; b: cement/sand = 1/2; c: cement/sand = 1/1 and d: cement).

In fact, both diffusion and reaction processes happen at the same time, but we could suppose that the process can be divided into the reaction following the diffusion in a short time interval, dt . The change of HD concentration in the cement could be expressed in operator splitting method as Eq. (2):

$$\frac{\partial C}{\partial t} = \frac{\partial(C_1 + C_2)}{\partial t} \quad (2)$$

The diffusion could be expressed in Gauss diffusion, as shown in Eq. (3):

$$\frac{\partial C_1}{\partial t} = D \left(\frac{\partial^2 C_1}{\partial x^2} + \frac{\partial^2 C_1}{\partial y^2} + \frac{\partial^2 C_1}{\partial z^2} \right) \quad (3)$$

The solution in spherical coordinate was obtained and shown in Eq. (4):

$$\frac{\partial C_1}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r^2} \left(r^2 \frac{\partial C_1}{\partial r} \right)$$

$$C_1(x, y, z, t) = \frac{Q}{8(\pi Dt)^{3/2}} \exp \left[-\frac{1}{4Dt} (x^2 + y^2 + z^2) \right] \quad (4)$$

where Q is the mass of HD liquid dripped onto the wafer of cement. $Q = \int_{-\infty}^{\infty} \int \int C \, dx \, dy \, dz$

The reaction could be expressed in Eq. (5):

$$\frac{\partial C_2}{\partial t} = \frac{dC_2}{dt} = kC_1$$

$$C_2(t) = \frac{Q_0}{8(\pi Dt)^{3/2}} \exp \left[-\frac{1}{4Dt} (x^2 + y^2 + z^2) \right] e^{kt} = C_1 e^{kt} \quad (5)$$

Therefore the solution of Eq. (1) becomes Eq. (6):

$$C(t) = C_1(t) + C_2(t) = C_1 + C_1 e^{kt} \\ = \frac{Q_0}{8(\pi Dt)^{3/2}} \exp \left[-\frac{1}{4Dt} (x^2 + y^2 + z^2) \right] (1 + e^{kt}) \quad (6)$$

For one droplet of 80 μL HD onto the wafer of cement over 48 h at 25 $^\circ\text{C}$, an extraction of the contaminated wafer was effected with a solvent of CH_2Cl_2 . It was experimentally demon-

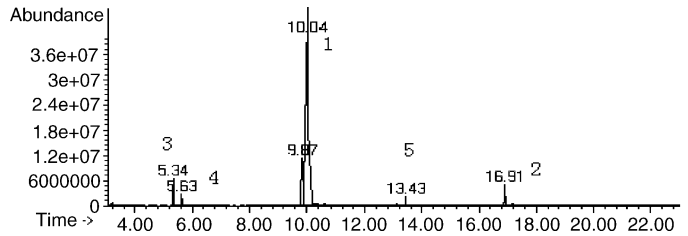


Fig. 9. Chromatogram for the extraction solution (CH_2Cl_2) of 80 μL HD droplet dripping onto a wafer of cement at 25 $^\circ\text{C}$ over 48 h.

Table 2
GC-MS/MS used to identify the product

t_R (min)	Structural formula	Fragment Peak (M+)
10.04	<chem>ClCCSCCCl</chem>	45, 63, 73, 109, 123, 158
16.91	<chem>ClCCSCCSCCCl</chem>	45, 61, 73, 91, 109, 123, 156, 182, 218
5.34	<chem>C=CCSCCCl</chem>	45, 57, 58, 59, 60, 73, 122, 123
5.63	<chem>C1CCOCC1S</chem>	28, 29, 46, 61, 74, 76, 104
13.43	<chem>ClCCSSCCl</chem>	45, 59, 63, 64, 65, 79, 92, 128, 155, 190, 192

strated by GC-MS (Fig. 9) that HD molecule has been partially degraded into several different products as listed in Table 2. This was probably due to a reaction between HD molecule and base sites in cement (Fig. 10). The rate of this degradation was investigated with a model of reaction between cement powders and HD droplets. A rate constant of degradation could be obtained from Fig. 11, $k = 4.8 \times 10^{-5} \text{ min}^{-1}$ and $t_{1/2} = 16 \times 10^4 \text{ min}$. This would indicate that the rate of HD degradation is kinetically too weak to be taken into account for the determination of diffusion rate in the case of HD penetrating through the wafer of cement.

Since the penetration of HD through the wafer processed in one dimension in reality and the degradation of HD could be negligible, one can then get a simplified equation as follow:

$$\frac{dC}{dt} = \frac{d}{dx} \left(D \frac{dC}{dx} \right) \quad (7)$$

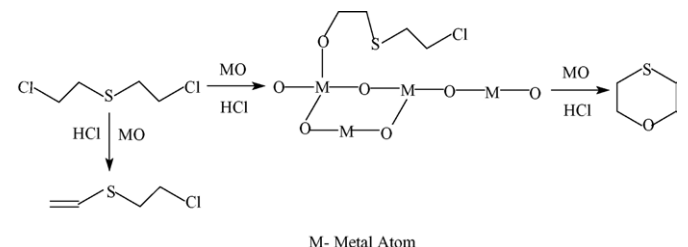


Fig. 10. Scheme for the reaction of HD molecule with the cement.

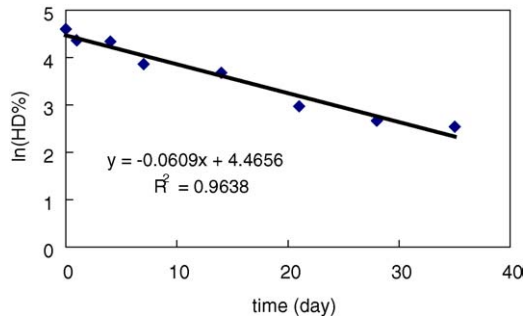


Fig. 11. Variation of the proportion for degradation of HD droplets in cement along with time at 25 °C.

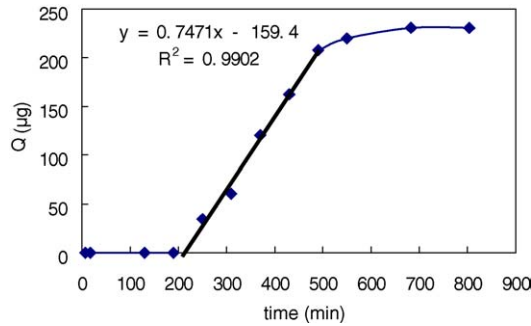


Fig. 12. Diffusion of 80 µl HD droplet through the wafer of cement in 4 mm thickness at 25 °C.

if diffusion coefficient is independent of HD concentration,

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad (8)$$

For initial condition: $C(x,0) = 0$

For boundary condition: $C(0,t) = C_m$; $C(d,t) = 0$

$$C = C_m - C_m \frac{x}{d} - \frac{2C_m}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi x}{d} e^{-n^2\pi^2 Dt/d^2} \quad (9)$$

Then to integrate from $t = 0$ to t ,

$$Q_t = \frac{C_m DA}{d} t - C_m \frac{C_m dA}{6} - \frac{2C_m dA}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} e^{-n^2\pi^2 Dt/d^2} \quad (10)$$

When t is so large as to the exponential term it may be ignored, then

$$Q_t = \frac{C_m D}{d} t - \frac{C_m d}{6} \quad (11)$$

When the diffusion achieves a stable state, Q_t will increase with t in a linear trend. When $Q_t = 0$, $t = \tau$. Then, we could obtain the following equation to calculate diffusion coefficient in cement:

$$D = \frac{d^2}{6\tau} \quad (12)$$

When one droplet of 80 µL HD contaminated the wafer of 4 mm thickness, the amount of HD breaking through the wafer was determined along with time, as presented in Fig. 12. An

intercept in t , about 212 min, could be obtained. Then, the diffusion coefficient for HD in the wafer of cement would be calculated as follow:

$$D = \frac{0.42}{6 \times 60 \times 212} = 2.2 \times 10^{-6} \text{ (cm}^2/\text{s)}$$

The determined coefficient would indicate that the diffusion of HD molecule in cement seems to be a typical diffusion in solid since D , $2.2 \times 10^{-6} \text{ cm}^2/\text{s}$, was less than $10^{-5} \text{ cm}^2/\text{s}$.

4. Conclusions

The sample of dried cement paste is a meso-porous adsorbant with a BET surface area around $40.8 \text{ m}^2/\text{g}$, which is able to adsorb vapor of HD at room temperature and to result in a multiple-layer isotherm of II type. The cement started to obviously adsorb vapor of HD when P/P_s passed over 0.1 and a saturated sorption could be over 30 mg/g . Loss of water through drying or addition of sand in cement would lead to decrease the amount for sorption of HD. The molecule of HD seemed to chemically adsorb onto cement surface. Droplet of HD contaminating cement was able to be degraded into less toxic products, probably due to the base properties of cement, but in a very low rate of $k = 4.8 \times 10^{-5} \text{ min}^{-1}$ and $t_{1/2} = 16 \times 10^4 \text{ min}$ at room temperature. Droplet of HD is able to penetrate through the layer of cement. A decrease of thickness for cement layer or addition of sand in cement would lead to lower the protection time against Mustard droplets. The diffusion coefficient of HD molecule in cement was determined, about $1.3 \times 10^{-4} \text{ cm}^2/\text{min}$ and of a typical diffusion in solid.

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