

回填材料膨润土对放射性气体滞留能力模拟研究*

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摘要：利用各种分析手段对膨润土的物理特性进行了表征。X射线衍射分析表明钠基膨润土呈典型的六方晶胞，晶胞参数是： a 轴4.913， c 轴5.405；差热分析曲线在低温区和高温区有明显的吸热峰出现；元素分析钠、钾离子的含量大于钙、镁离子的含量，在性能上表现为钠质膨润土具有较强的离子交换能力；显微分析表明其表面呈皱隙状，测定比表面积高达24.52 m²/g；吸水率测定表明膨胀率大，说明它具有密封功能，可有效阻滞地下水的渗入。利用SF₆示踪技术，通过采集不同时间段取样池样品，分析样品中示踪气体浓度，绘制取样池示踪气体浓度随时间的变化关系曲线，根据费克扩散定律计算扩散系数。实验结果表明，随着压实膨润土密度的增大，示踪气体扩散系数迅速减小，当密度大于1.8 g/cm³时，扩散系数降至10⁻⁹ m²/s。研究结果表明，膨润土性能优化是通过在膨润土中添加适量的活性炭，可明显改善其对气体的阻滞能力，增加其对放射性气体滞留能力；添加少量的石英砂增加其机械性能、导热性和减少蠕变性，将引起对气体阻滞能力的下降。综合考虑，在膨润土中各添加5%活性炭和石英砂，既对气体具有较好的滞留能力，又具有较好的工程特性。

关键词：回填材料；膨润土；放射性气体；滞留能力

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A Simulation Study on the Mitigation Capability of Bentonite Backfill to Gaseous Radionuclides*

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Abstract The properties of bentonite were characterized by use of DTA, XRD and SEM analyses. Moreover, the chemical components and the specific surface area of bentonite were analyzed. Sulfur hexafluoride is an ideal non-radioactive gaseous tracer with low ambient concentration (about 10⁻¹³ mL/mL). It is analyzed expediently by gas chromatograph with an electron capture detector. Its analysis sensitivity is very high (about 10⁻¹³ mL/mL). SF₆ tracer is used to simulate gaseous radionuclides to study their adsorption and diffusion in bentonite. The diffusion coefficient of SF₆ in bentonite backfill with different apparent densities was determined experimentally. The results show that bentonite backfill has a good gas mitigation capability. When the apparent density of bentonite backfill is close to 1.8 g/m³, the diffusion coefficient of SF₆ is lower than 10⁻⁹ m²/s. As the engineering characteristic improving agent of backfill, quartz will reduce the mitigation ability of bentonite backfill to gaseous radionuclides. Active carbon is effective to improve the obstruction capability of bentonite backfill. Considering such contrary aspects comprehensively, if 5% quartz is added in bentonite to gain the favorable engineering characteristic of backfill, 5% active carbon should be mixed in it to maintain or to improve the obstruction capability of backfill to gaseous radionuclides.

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Key words Backfill , Bentonite , Gaseous radionuclides , Mitigation capability

1 Introduction

Volatile radionuclides and fission gases , such as ^3H , ^{85}Kr , ^{131}I , etc. , release from the radio-waste repositories. They transfer fast to the earth surface to endanger the public health and the environment. Backfill is one of the important radio-barrier systems to prevent various radionuclides from approaching the surroundings^[1 2]. A large number of experiments have been carried out to assess the diffusivity of a wide variety of dissolved species such as cations and anions in water-saturated clay at differing compactions^[3 4]. Eriksen and Jacobsson summarized these experiments and also discussed the mechanism of diffusion in clay in some detail—especially the influence of the charge , molecular size and hydrolysis of the diffusing species^[5]. The question then arises as to whether the backfilling material will provide any mitigation of gaseous radionuclide penetration through the repository itself. Bauer , using $^{14}\text{CO}_2$ as the radiotracer and scintillation counting instrument , studied its adsorption in and liberation from crushed tuff , bentonite and cement mortar. The results showed that cement mortar had a much better capability of cumbering the liberation and transfer of CO_2 ^[6]. Chen *et al.* investigated the adsorptive and diffusive properties of N_2 , H_2O and Ar and performed diffusion studies using simulation methods for both Ar and He. They found that the adsorptive and diffusive properties depend sensitively on the size of the diffusing species and the concentration c and $(1 - c)$ of the intercalants^[7].

Because of its good engineering characteristics and adsorbability , bentonite is the preferred backfill to rad-waste management^[8 9] , but it is necessary to optimize its integrative engineering characteristics. In our research , quartz is added in it to improve its mechanical strength and thermal conductivity , and reduce the creep and active carbon to improve the adsorption and its mitigation ability to gaseous radionuclides.

Sulfur hexafluoride (SF_6) is an ideal non-radioactive gaseous tracer with low ambient concentration (a-

bout 10^{-13}L/L). Its analyzed expediently by gas chromatograph with an electron capture detector. It is analysis sensitivity is very high (about 10^{-13}L/L)^[10]. In this article , SF_6 tracer is used to simulate gaseous radionuclides to study their adsorption and diffusion in bentonite and in its optimized backfilling mixture.

2 Experiment

2.1 Diffusion model

The schematic experimental configuration is shown in Fig. 1. The experimental diffusion cell is a metal column with a certain length (l) of compacted backfilling material , and its diameter was 4 mm. SF_6 tracer with a certain concentration in nitrogen is injected into the source cell , and sampled from the sampling cell.

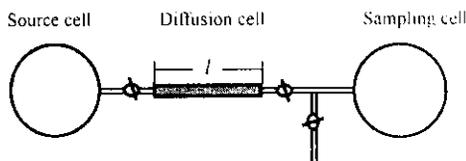


Fig.1 Schematic diagram of the diffusion experiment for tracer gas

The diffusivity of tracer gas within the diffusion cell is described by Fick's second law^[11] :

$$D_i \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \quad (1)$$

where D_i is the diffusion coefficient taking into account the overall tracer diffusion within the diffusion cell , m^2/s , C is the tracer concentration in the diffusion cell , mL/mL , x is the diffusion distance , m , and t is the diffusion time , sec .

The following initial and boundary conditions are assumed to describe the experimental constraints :

$$\alpha(0 < x \leq l, 0) = 0$$

$$\alpha(0, t) = C_0$$

$$\alpha(l, t) \ll C_0$$

The solution (describing the tracer concentration profile within the diffusion cell) is^[5]

$$\alpha(x, t)/C_0 = 1 - x/l - 2/\pi \times \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi x}{l} \exp \frac{D_i n^2 t}{l^2} \quad (2)$$

The total amount of tracer accumulated in the

sampling cell (Q) is obtained by integrating the flux at $x = l$ with t

$$Q(t)/AlC_0 = D_i t/l^2 - 1/6 - 2/\pi \times \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D_i n^2 \pi^2 t}{l^2}\right) \quad (3)$$

where V is the volume of the sampling cell, m^3 , and A is the interfacial area of diffusion cell, m^2 .

As t increases, the exponent in equation (3) decreases fast. Therefore, the concentration of tracer in the sampling cell is given by the asymptotic solution

$$C = \frac{D_i C_0 A}{lV} t - \frac{C_0 Al}{6V} \quad (4)$$

When the tracer gas concentration in the sampling cell at different times is analyzed, the diffusion coefficient D_i can be obtained from the $C \sim t$ curve.

2.2 Reagents and instruments

The main reagents used are 0.038 mm bentonite (Zhejiang Linan Bentonite Chemical Factory), 0.074 mm active carbon (Mianyang Active Carbon Factory), sulfur hexafluoride (purity 99%, China Nuclear Honghua Specialty Gases Ltd.), and 0.370 mm quartz (Yanxi Minerals Processing Factory).

The main instruments used are the GC-17A gas chromatograph (SHIMADZU), the S-450 scanning electron microscope (HITACHI), the EDAX-9100/60 energy dispersive X-ray spectrometer (PHILIPS), the D/MAX-RA rotating anode X-ray diffractometer (RIGAKU), the WCT-1 type differential thermal analysis (Beijing Optics Instrument Factory), and the ST-03 type apparatus for the determination of specific surface area (Beijing Analytical Instrument Factory).

2.3 Analysis of sulfur hexafluoride

A GC-17A gas chromatograph with an electron capture detector and a 3 mm \times 2 m 5A Molsieve stainless steel packed column was used to determine the concentration of tracer gas sulfur hexafluoride. Samples are directly injected into the instrument using a 6-way valve at a vacuum condition. The detection limit is 7×10^{-13} L/L.

3 Results and discussion

3.1 Bentonite characterization

3.1.1 Component analysis: Bentonite is composed

mainly of aluminosilicate minerals. The main components are Si and Al. Its chemical components are given in table 1. Because the contents of Na and K are higher than Mg and Ca, it is sodium bentonite. It has good a capability of ion exchange and adsorption.

Table 1 The main chemical components of bentonite

Element	Content/%
Na	1.29
Mg	1.74
Al	13.02
Si	72.62
S	1.39
K	4.48
Ca	3.11
Fe	2.36

3.1.2 X-ray diffractometer and differential thermal analysis: The XRD diagram of bentonite is shown in Fig. 2. It can be seen that bentonite has the typical alpha-silicon dioxide hexagonal structure (standard diagram PDF card No. 5-490), $a = 4.913$ nm, $b = 5.405$ nm, and its Space Group belongs to $D_5^4-P_{31}^{21}$. Sodium bentonite is a clay material dominated by montmorillonite and has a very complex chemical structure. The DTA of bentonite (Fig. 3) shows that there is an endothermic reaction at about 100°C for the loss of the sorbed and crystal water, and another one between $730 \sim 930^\circ\text{C}$ for the loss of the most hydroxide radical.

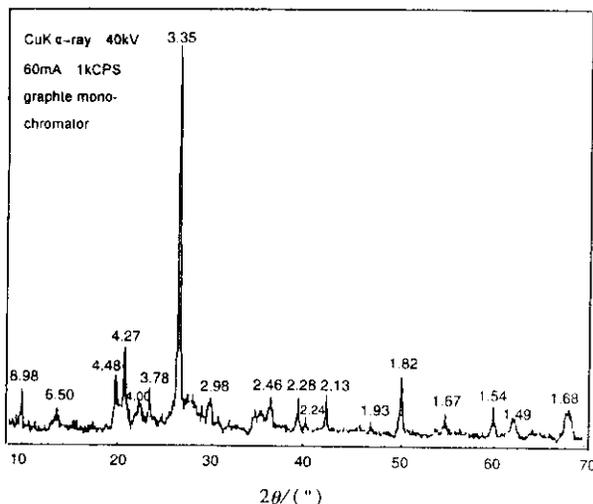


Fig. 2 Plot of the XRD diagram of bentonite

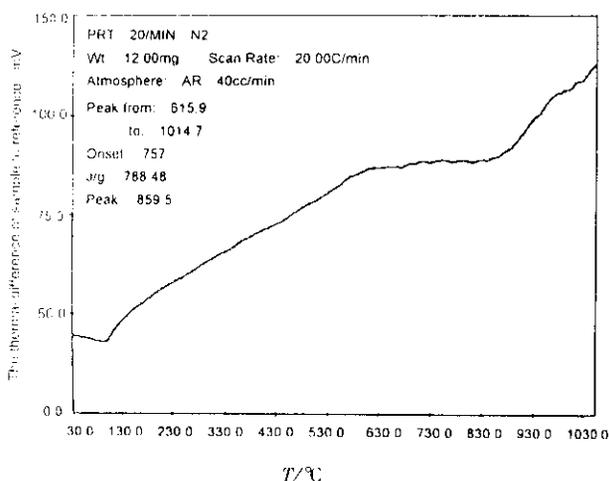


Fig. 3 Plot of the DTA curve of bentonite

3.1.3 The specific surface area and the surface configuration analysis : As shown in Fig. 4 , the surface figure of bentonite particles is irregular with many crinkly

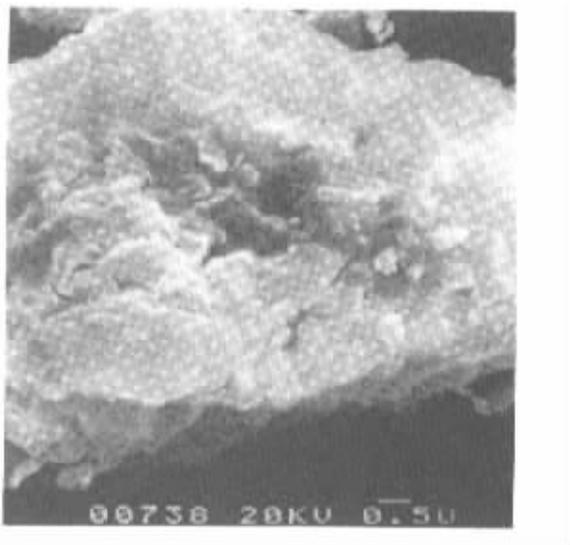


Fig. 4 SEM photograph of bentonite

pores. The surface configuration illustrates that bentonite is of large specific surface area. In our research , the specific surface area of sodium bentonite was detected to be $2.45 \times 10^4 \text{ m}^2/\text{kg}$. The large specific surface area of bentonite dominates its good water sorption capability and large expansion ratio. Such characteristics produce the large capability in gaseous radwaste sorbing and mitigating.

3.1.4 Expansion ratio test : Expansion ratio (e_p) is defined as the enlarged length of bentonite saturated

with water divided by its original length. It could be expressed as :

$$e_p = \frac{h - h_0}{h_0} \times 100\% \quad (5)$$

where h_0 is the original length of the packed bentonite column , m , and h is the length of packed bentonite column saturated with water , m .

For example , a bentonite column with the apparent density (ρ) of $1.6 \times 10^3 \text{ kg/m}^3$ has been tested in our research , $h = 5.8 \times 10^{-2} \text{ m}$, $h_0 = 5.2 \times 10^{-2} \text{ m}$. e_p is calculated to be 11.5%. The result shows that bentonite has a larger expansion ratio after saturated with water. Such expansion gives bentonite the ability to self-seal any cracks that may develop. That was one of the reasons why bentonite was used as backfilling material.

In the bentonite backfill structure , water is important. It participates in various physical and chemical actions , and affects and controls various characteristics of bentonite. There are several forms of water in bentonite. The physical bonding water is firmly bonded to the surface of bentonite particles by electrostatic force and hydrogen bond. The hydrated sheath on the particle surface is formed by the interaction of dipole molecules. Permeation and adsorption water is formed by the destroyed hydrated sheath on the particle surface with the change of temperature and pressure , and is controlled by permeation and adsorption of water molecules. The free water has hydrogen bond connected to bentonite , but not the orient arrangement regulation.

3.2 Sulfur hexafluoride diffusion

With the apparent density of the bentonite packed column increasing , the bed porosity (ε) decreases fast (table 2). After ρ is up to $1.58 \times 10^3 \text{ kg/m}^3$ the decreasing trend of ε slows down.

After diffusing through compacted bentonite diffusion cells with 1.01 kg/m^3 apparent densities , the changes of SF_6 concentrations in sampling cells are shown in Fig. 5.

Because bentonite has a good adsorption capability , the tracer gas transferred in the column is almost

Table 2 The characters of bentonite packed diffusion cells

No.	Φ/m	l/m	$\rho/kg/m^3$	$\varepsilon/\%$
1	0.004	0.069	1.01×10^3	40.8
2	0.004	0.058	1.20×10^3	34.0
3	0.004	0.049	1.58×10^3	25.8
4	0.004	0.043	1.83×10^3	22.3
5	0.004	0.040	2.00×10^3	20.4
6	0.004	0.045	2.13×10^3	19.1

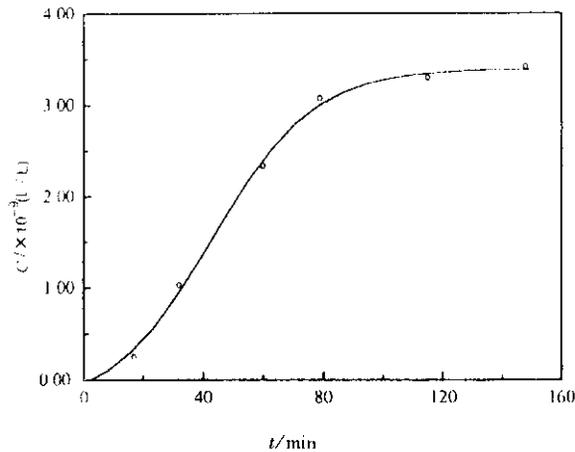


Fig. 5 Relationship between concentration of tracer gas and time in the sampling cell

adsorbed by bentonite. Only a little permeates through the column to the sampling cell. So, at the beginning stage of the experiment, the SF_6 concentration increases very slowly with time prolonging. When the adsorption equilibrium is achieved, SF_6 in the source cell steadily diffuses in the diffusion cell and gets to the sampling cell. Thus, the concentration of SF_6 increases in linear trend. The diffusion coefficient is calculated by the $C \sim t$ linear relationship in this stage (equation (4)). When the concentration difference between the opposite sides becomes small, the diffusion rate of SF_6 decreases sharply. And finally, the concentration of SF_6 in the sampling cell will equal that in the source cell.

The relationship of D_i and ρ is given in Fig. 6. From Fig. 6, it can be found that the diffusion coefficient decreases with the enhancement of the apparent density of the compacted bentonite column. This phenomenon can be explained by the fact that with the ap-

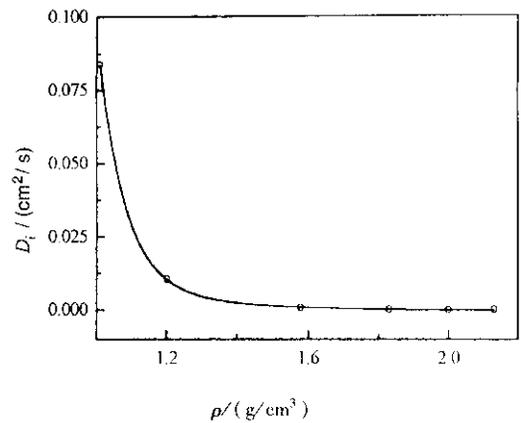


Fig. 6 Relationship between the diffusion coefficient of tracer gas and bentonitic density

parent density increasing, the porosity of the compacted bentonite diffusion cell and the free channel for SF_6 decrease, and then the permeation and diffusion rates decrease.

The data are regressed in such power function as:

$$D_i = 0.0935\rho^{-10.734} \quad (R^2 = 0.99) \quad (6)$$

R is the related coefficient.

When ρ is close to $2.0 \times 10^3 \text{ kg/m}^3$, D_i will be lower than $10^{-9} \text{ m}^2/\text{s}$. Fig. 6 and equation (6) show clearly a common result that D_i decreases fast with ρ increasing. In Fig. 6, it can be found that when ρ is higher than $1.6 \times 10^3 \text{ kg/m}^3$, only a little change of D_i can be observed. This phenomenon is much coincident with the relation of ρ and ε . It can be deduced that the porosity of backfill is one of the most important elements to retard radioactive gases from diffusing, and the high adsorbing capacity of backfill to radioactive gases is one of the essential characteristics for backfilling material to obstruct their permeation. In order to gain an effective mitigation ability to gaseous radiation, the apparent density of bentonite backfill shall be no less than $2.0 \times 10^3 \text{ kg/m}^3$.

3.3 Characteristic optimization of bentonite backfill

Bentonite is an ideal backfill, but its engineering characteristics (mechanical strength, thermal conductivity, and creep) and adsorption capability still need to be improved. So, quartz is used to improve the engineering characteristics of backfill. A certain proportion

of active carbon is mixed in bentonite to optimize its obstructive capability for tracer gas. In order to maintain the essential characteristics of bentonite, the total mixing ratio is set to 10% and kept changeless. A series of experiments have been carried out, changing the ratio of mixed active carbon and quartz, but keeping the apparent densities of diffusion cells the same as $1.41 \times 10^3 \text{ kg/m}^3$. The $D_i \sim t$ curves of SF_6 in the sampling cells are given in Fig. 7 to Fig. 8.

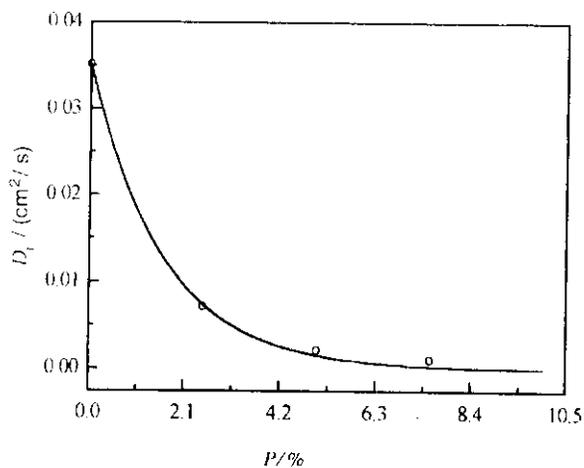


Fig. 7 Relationship between the diffusion coefficient and the active carbon content

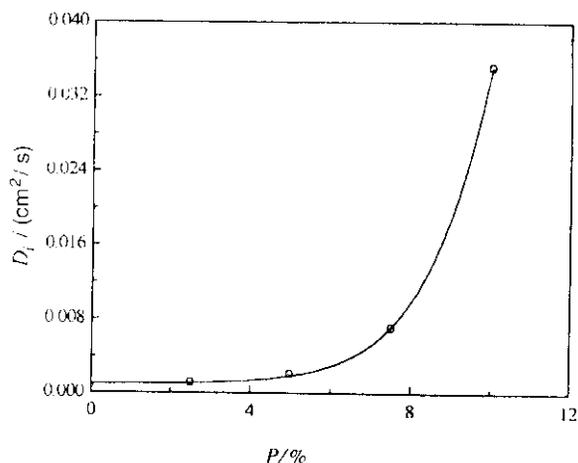


Fig. 8 Relationship between the diffusion coefficient and the quartz content

As shown in Fig. 7 and Fig. 8, when the active carbon mixing proportion P is lower than 5%, the D_i of SF_6 decreases sharply along with P increasing. However, when P is higher than 5%, the decreasing rate of the D_i of SF_6 is very small. On the contrary, the D_i in-

creases because of the quartz added in backfill. In our research, the proper mixing proportion of active carbon is 5%, and that of quartz is 5%, too.

4 Conclusion

Bentonite clay is a kind of feasible backfill. One of the important reasons is that bentonite has good waterproof and sorption capabilities. The diffusion coefficient of gas in bentonite decreases with the increasing of the apparent density of compacted backfill. In order to gain adequate mitigation ability to gaseous radionuclides, the apparent density of bentonite backfill shall be no less than $2.0 \times 10^3 \text{ kg/m}^3$. The diffusion coefficient of SF_6 in such a condition will be lower than $10^{-9} \text{ m}^2/\text{s}$.

As the engineering characteristic improving agent of backfill, quartz will reduce the mitigation ability of bentonite backfill to gaseous radionuclides. Active carbon is effective to improve the obstruction capability of bentonite backfill. Taking into account of such contrary aspects comprehensively, if 5% quartz is added in bentonite to gain the favorable engineering characteristic of backfill, 5% active carbon should be mixed in it to maintain or to improve the obstruction capability of backfill to gaseous radionuclides.

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