Diffusion of Cr(VI) in Porous Media
심층 지하에서의 육가 크롬 확산

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요약/Abstract

액체 산업폐기물을 심층지하에 방출시, 폐기물의 이동은 지하매체의 낮은 투수율로 인하여 분자확산에 의해 좌우된다. 한편 확산에 의한 이동은 Fick의 제2법칙으로 예측할 수 있다. 본 연구에서는 실험을 통한 Cr(VI)의 확산 이동계수를 구하였다. 다공질내에서의 Cr(VI)이동을 추적하기 위해 방사성 동위원소인 ^{51}Cr을 사용하였으며, Fick의 제2법칙에 대한 해석해를 구해 Cr(VI)의 확산계수를 결정하였다. 본 연구에서는 온도, ^{51}Cr의 양, 염소 이온의 양, 매체의 건조밀도를 환경적 변화인자로 이용하였다.

Underground Injection Control regulations for Class I injection wells require that the vertical diffusion be considered as a mechanism for transport of contaminants in evaluating containment. Due to the low permeability in the confining aquitard, the movement of contaminants over the long term is controlled by the molecular diffusion. The movement can be predicted, using the Fick's second law of diffusion.

The diffusion coefficient in Fick's law has been determined experimentally in this study. Instantaneous injection of ^{51}Cr was used to trace the distribution of Cr(VI) in soil plugs and an analytical solution was applied to calculate the diffusion coefficients.

This study shows the effect of environmental factors, such as temperature, chloride concentration, applied amount of ^{51}Cr, and bulk density of injection formations on diffusion of Cr(VI)

INTRODUCTION

In the Gulf Coast region, almost 90% of industrial wastewaters are disposed via the deep well injection techniques. The liquid wastes are injected into brackish and saline aquifers which typically are sand formations of 15 to 30 m thickness and are bound by clay or shale aquitards. The interstitial solution within the confining aquitards is not in chemical equilibrium with the fresh injected wastewater. In addition, wastewater velocities in the aquitards are very slow, because of the low permeabilities ($10^{-4}\sim$ 10^{-5} md) (Constant, 1989). Consequently, the vertical movement of hazardous solutes in the zone is controlled by diffusion. The key to the success of the geologic disposal is how fast hazardous solutes are released into the accessible environment. To predict the physical transport rates of solutes in deep well injection zones, bench scale tests were performed with formation soils, obtained from deep well injection zones in Louisiana.

Lai and Mortland (1961) found decreases in the diffusion coefficient of exchangeable cations, such as sodium and calcium ions, with increasing clay concentration. They explained the decreases in coefficient by suggesting that the number of exchange sites present per unit volume affects the diffusion rate. Increasing the amount of clay per unit volume increases the number of exchange sites, thereby increasing the average number of exchanges an ion had to make in a given distance. Phillips and Brown (1964) compared the molecular diffusion and surface diffusion coefficients and found that the magnitude of molecular diffusion was larger than those for surface diffusion in each of the four soil materials. The rate of rubidium (Rb) molecular and surface diffusion was largest in kaolinite clay and was least in montmorillonite clay. Their findings support the conclusions of Lai and Mortland.

On the contrary, some investigators found that the effect of diffusion was increased by the release of cations from exchange sites on the clay minerals (Komiyama and Smith, 1974). Jahnke and Radke (1987) postulated that some cationic adsorption created a surface diffusion path for enhanced ion transport, and showed that this parallel surface transport mechanism could have a significantly adverse effect on the performance of the packing by reducing or completely eliminating sorption retardation.

Jensen and Radke (1988) investigated the counter ionic migration of Cs^+ and Sr^{+2} against Na^+ in Na-Montmorillonite. They found both monovalent cation Cs^+ and divalent cation Sr^{+2} showed enhanced diffusion through the media. When the temperature increased from 22 ℃ to 90 ℃, the Cs surface diffusivities increased approximately four fold (2.2×10^{-6} to 8×10^{-6} cm²/s). The temperature effects on diffusion were also studied by Sadeghi et al. (1988) in water at temperatures ranging from 0 to 50 ℃. In this study, the diffusion coefficients of urea increased almost three fold (9×10^{-9} to 3.2×10^{-8} m²/s) as the temperature increased 50 ℃.

Some diffusion rates have been shown to be dependent on the concentration of the so-

lute applied and the pH. Phosphorus diffusion in several soils showed a thirty nine fold increase as the rate of added phosphorus increased from 0 to 100 mg/l (Mahtab et al., 1971). Meanwhile, analyzing the diffusion coefficient data in International Critical Tables (Washburn, 1980), it can be said that the diffusion of Cr (VI) in a free aqueous solution is not concentration dependent. In a free aqueous solution, as the Cr(VI) concentration was changed from 0.016 to 0.05 mole at 18°C, it did not show any change in the diffusion coefficient (from 1.17×10^{-5} to 1.17×10^{-5} cm²/sec). Moreover, when the concentration was changed from 0.05 to 0.15 mole, it showed a decrease in the diffusion coefficient (from 1.17×10^{-5} to 1.09×10^{-5} cm²/sec, which is a 6.8% decrease).

The objective of this study is to investigate how environmental factors such as temperature, NaCl concentration, amount of ^{51}Cr in Cr (VI) solution, and soil bulk density can affect the diffusion rate of Cr(VI) in porous media.

MATERIALS AND METHODS

Two formation materials, shale and sand, were obtained from deep well injection zones in St. Charles Parish and St. Bernard Parish, Louisiana, U.S.A. respectively. Both soils were treated and stored as described in Cr(VI) reduction study (pp.191-201).The results of X-ray diffraction analysis of both soils are listed in Table 1.

Temperature Effect : the temperature effect on the diffusion coefficients was determined by

Table 1   X-Ray Diffraction Analysis
(Weight percent)

Bulk Mineralogy		
Component	Shale	Sand
Quartz	57	93
Feldspar	07	06
Plagioclase	04	02
K-Feldspar	03	04
Calcite	–	–
Clay Minerals	36	01
	100%	100%
Relative Abundance of Clay Minerals(Normalized to 100%)		
Kaolinite	06	24
Chlorite	03	04
Illite	18	44
Smectite	73	–
Illite/Smectite **	–	28(50)
	100%	100%

** Values in (   ) indicate precent of expandable smectite interlayers

a method described in Lai and Mortland (1961). Pretreated soil samples were ashed at 550°C for 15 minutes to remove any soil organic matter (APHA et al., 1985). This process prevented Cr(VI) reduction caused by the oxidation of soil organic matter. For same reason, no chloride ion was added into the solution. Shale was mixed with fresh nitric acid of pH −0.62 to yield 37.5% of water by weight. Then this salt free paste was carefully put in a 10 ml disposable syringe from which the tips on both sides were cut off to make a cylindrical figure with a diameter of 1 cm and a height of 6 cm. In case of sand, it was packed every 0.5 cm

to yield bulk density of 1.4 g/cm³, and it was saturated with fresh nitric acid of pH −0.62. Aged nitric acid may produce NO_2 and it may reduce $Cr(VI)$ to $Cr(III)$ (Stollenwerk and Grove, 1985). After covering polyethylene caps on both sides, samples were placed in the water bath for 5 hours to raise the temperature to that of the water bath. Then 100 μL of ^{51}Cr as Na_2CrO_4 solution were placed on the top of the soil as a thin film. Total radioactivity was set to 2 μCi in 100 μL. the syringe was capped to prevent evaporation and placed between two plexiglas plates to ensure the prevention of water evaporation (Fig. 1). The sample syringes were placed in 3 different water baths of 23 ℃, 50℃, and 70 ℃. After 30 days, the syringes were removed from the water baths and the shale and sand samples were frozen prior to segmentation by exposing them to liquified nitrogen gas for 15 seconds. The soil plugs were sectioned in even depth increments of 1.25 mm for shale and 2.5 mm for sand. The same volume of the soil plug in each section

provided same geometry under the radioactivity detector, minimizing detection errors caused by the variable absorption rates of gamma ray. The radioactivity of each section was determined by the Auto-Gamma Multi Channel Analyzer in Nuclear Science Department, Louisiana State University and was summed up to yield the amount at different depths. Solving the following diffusion equation analytically with initial and boundary conditions,

Governing Equation :

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Initial Condion :

$$C(x,t) = \frac{M}{A} \delta(x) \text{ when } t = 0$$

Boundary Condition No. 1 :

$$\lim_{x \to \infty} C(x,t) = 0$$

Boundary Condition No. 2 :

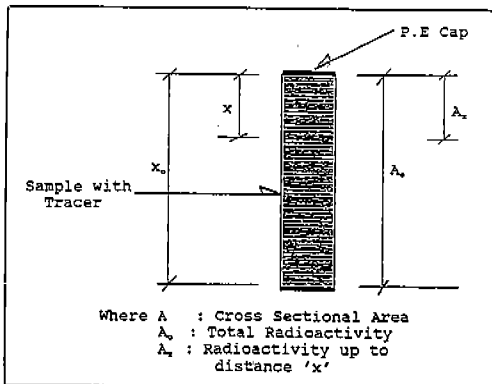$$\frac{\partial C(x,t)}{\partial X} = 0 \text{ when } x = 0$$

and utilizing the solution erf y = A_x/Ao, where y = x/(2(Dt)$^{0.5}$), a plot of y vs x should result in a straight line passing through the origin. Then, the diffusion coefficient "D" can be evaluated from the straight line of slope 1/(2(Dt)$^{0.5}$). The values of A_o and A_x can be obtained from experiments (Fig. 1) and the value of y can be found from erf y in standard probability tables (Abramowitz and Stegun, 1972).

Fig. 1 Schematic Diffusion Experiment Set-Up

^{51}Cr Amount Effect : The ^{51}Cr amount effect study followed the same procedures as those in the temperature effect study. Theree different concentrations were used, 2 μCi, 10 μCi, and 20 μCi per 100 μL. The temperature was set to 70 ℃. This experiment was performed to verify that the radioactive decay term was not necessary in the above diffusion equation.

NaCl Effect : This experiment was necessary to determine the effect of solution density change on the diffusion rate of ^{51}Cr in shale. The shale sample was saturated with 1 N NaCl and washed several times to remove free Na$^+$ and Cl$^-$ ions from the shale. Then, the shale was dried in 102±1℃, crushed to pass No. 100 sieve and strored in a vacuum desiccator. The other procedures were the same as those in the temperature effect study with the exception of two different NaCl concentrations(15,000 and 30,000 mg/L) and of temperature, 70 ℃. The pH was maintained at 8.0 to prevent possible reduction of Cr(Ⅵ) at low pH.

Bulk Density Effect : Dry bulk densities of 1.3, 1.4, and 1.5 g/cm^3 were obtained by packing the sand every 0.5 cm. The soil packing was performed by tamping with a polyethylene syringe plunger, of which the rubber head was cut off and the outer diameter was slightly smaller than the inside diameter of the syringe. The procedures were the same as those in the ^{51}Cr amount effect study except that one concentration was used, 2 μCi/100 μL.

RESULTS AND DISCUSSION

Temp. Effect : Figure 2 shows the effect of temperature on diffusion of ^{51}Cr in sand and shale formations. When the temperature was
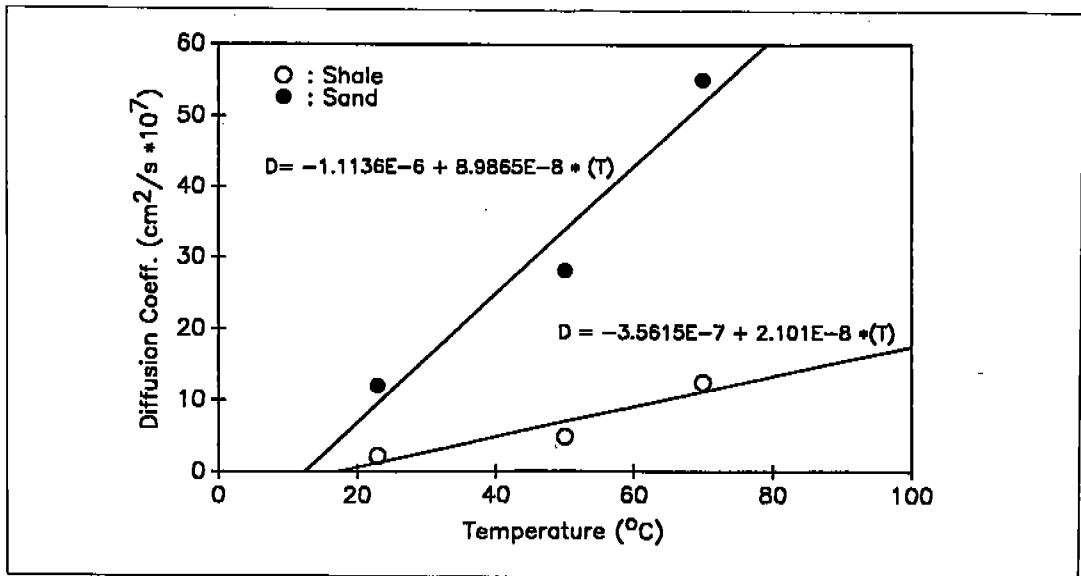

Fig. 2   Temperature Effect on Diffusion

increased from 23 ℃ to 50 ℃, the diffusion coefficient of sand was increased from 1.2×10^{-6} to 2.8×10^{-6} cm²/sec and when the temperature was increased from 50 ℃ to 70 ℃, it was increased from 2.8×10^{-6} to 5.45×10^{-6} cm²/sec. In shale, the diffusion coefficients were changed from 2.08×10^{-7} to 4.76×10^{-7} cm²/sec, when the temperature was increased from 23 ℃ to 50 ℃. When the temperature was increased from 50 ℃ to 70 ℃, it was changed from 4.76×10^{-7} to 1.24×10^{-6} cm²/sec. The water content applied to shale was 37.5 %. In both formation samples, diffusion coefficients increased linearly as the temperature was increased. This is attributed to the change in density and viscosity of solution as the temperature changes. A less dense and less viscous solution at higher temperatures, enhances the movement of ions or molecules in solution. Thus, it was possible to linearize the relationship between the diffusion coefficient and temperature. It was found that $D = -1.1136 \times 10^{-6} + 8.9865 \times 10^{-8} \times (T)$ with 'r²' $= 0.95$ for sand and $D = -3.5615 \times 10^{-7} + 2.101 \times 10^{-8} \times (T)$ with 'r²' $= 0.87$ for shale. From these equations, the diffusion coefficients at 18℃ for sand and shale could be predicted as 5.04×10^{-7} cm²/sec and 2.203×10^{-8} cm²/sec respectively. These values were compared with the diffusion coefficients of Cr (Ⅵ) in free aqueous solutions without solids. The average diffusion coefficient in free aqueous solution at 18 ℃ was 1.17×10^{-5} cm²s (Washburn, 1980), which was 20 times greater than that in sand pores and 500 times greater than that in shale pores. Table 2 shows the

Table 2 Diffusion Coefficient at Different Temperature

Temperature (℃)	Sand Diffusion (cm²/sec)	Shale Diffusion (cm²/sec)
20	6.837×10^{-7}	6.405×10^{-8}
30	1.58×10^{-6}	2.742×10^{-7}
40	2.481×10^{-6}	4.843×10^{-7}
50	3.38×10^{-6}	6.944×10^{-7}
60	4.278×10^{-6}	9.045×10^{-7}
70	5.177×10^{-6}	1.115×10^{-6}
80	6.076×10^{-6}	1.325×10^{-6}
90	6.974×10^{-6}	1.535×10^{-6}

diffusion coefficients calculated using the above equations.

The variation of the diffusion coefficient with temperature can be expressed by the equation

$$D = A * e^{\left(-\frac{E_a}{RT}\right)}$$

where E_a is the activation energy, which works as an energy barrier for the diffusion to occur, A is the activation coefficient, and R is the gas constant (8.314 J/mole °K). The activation energy can be estimated by determining the diffusion coefficient at different temperatures and plotting the ln D versus 1/T. The activation energy E_a is calculated from the slope of the linear plot. Figure 3 shows the Arrhenius plot for the diffusion coefficients of Cr(Ⅵ) in sand and shale. Calculated activation energies for sand and shale are summarized in Table 3. The activation energies of 24.88 KJ/mole for sand and 29.15 KJ/mole for shale were much greater than that for ions in free aqueous solu-
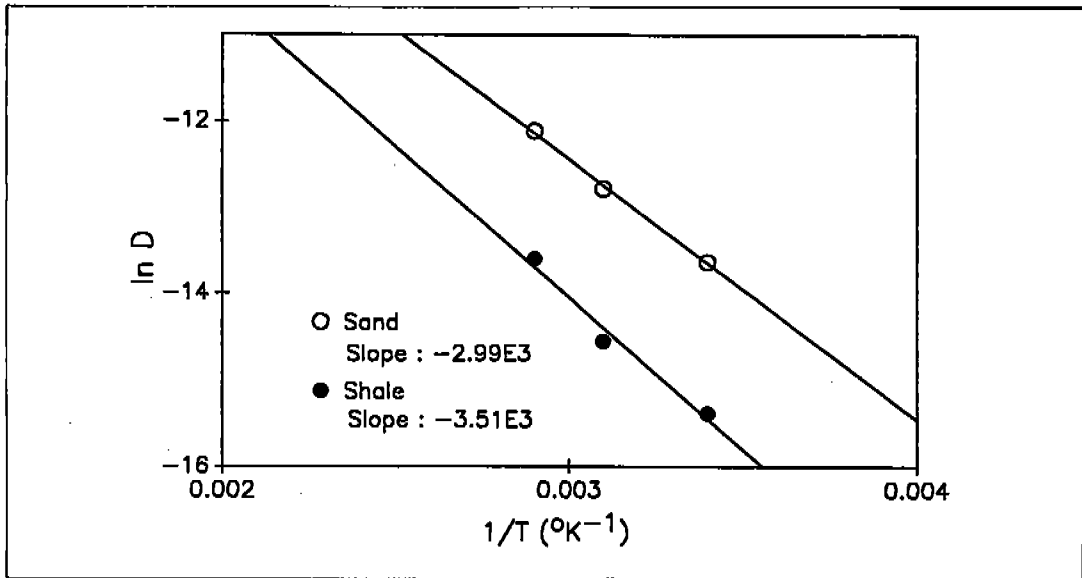
Fig. 3 Arrhenius Plot of Diffusion Coefficients

Table 3 Activation Energy of Diffusion

Soil	Diffusion Coefficient (cm²/sec)	E_a (KJ/mole)	Bulk Density (g/cm³)	Water content (%)
Sand	1.2×10^{-6} at 23 ℃ 2.8×10^{-6} at 50 ℃ 5.45×10^{-6} at 70 ℃	24.88	1.4	—
Shale	2.08×10^{-7} at 23 ℃ 4.76×10^{-7} at 50 ℃ 1.24×10^{-6} at 70 ℃	29.15	—	37.5

tions, which was approximately 17 KJ/mole (Nye, 1979).

The greater activation energy for shale than that for sand shows that the occurrence of diffusion in shale is more difficult than the occurrence in sand, because the greater activation energy implies the greater driving force is required to make the diffusion occur. This explains the cause of smaller diffusion coefficients in shale than the diffusion coefficients in sand.

Bulk Density Effect : Figure 4 shows the bulk density effect on the diffusion coefficients for sandy soil. Regression analysis gave a linear relationship between the bulk density and the diffusion coefficient. At 50 ℃, it was described as $D = 4.03 \times 10^{-5} - 2.682 \times 10^{-5} \times (B.D.)$, and the determination coefficient was found to be 0.98. At 70 ℃, it was described as $D = 9.237 \times 10^{-5} - 6.05 \times 10^{-5} \times (B.D.)$, and the determination coefficient was found to be 0.90. Even though the value of the determination coefficient was lower at 70 ℃, it still gave a strong linear relationship. In the figure, the diffusion coefficients were increased from 1.41×10^{-6} to 2.8×10^{-6}, and 5.58×10^{-6} cm²/sec, when the bulk density was decreased from 1.5 to 1.4 and 1.3 g/cm³ at 50 ℃. At 70 ℃, it was changed from 2.69×10^{-6} to 5.45×10^{-6}, and 1.49×10^{-5}
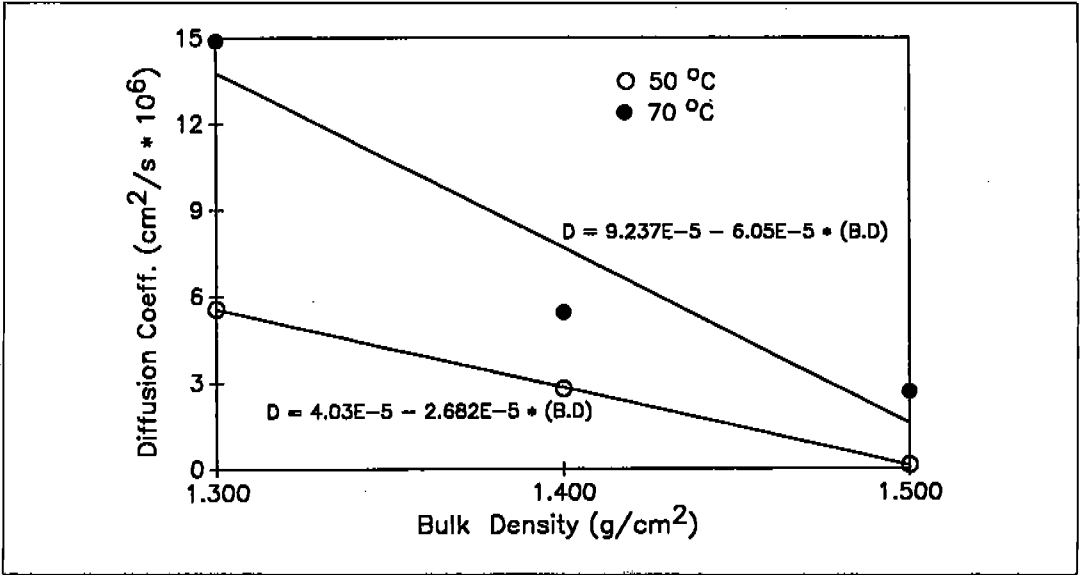
Fig. 4 Bulk Density Effect on Diffusion

cm²/sec. Here, it should be noted that the diffusion coefficient of Cr(Ⅵ) at 1.3 g/cm³ and 70 ℃ in sand media reached the same order of magnitude as the diffusion coefficient in free aqueous solution at room temperature $(1.45 \times 10^{-5}$ cm²/sec at 25 ℃; Washburn, 1980).

Warncke and Barber (1972) reported that the maximum rate of zinc diffusion did not always occur at a soil bulk density where the diffusion path was least tortuous. This is in contrast to the above results, which showed the inverse relationship between bulk density and the diffusion coefficients. This would be expected, since the bulk density changes affect the physical and chemical properties of a soil. Changes in the physical property are reflected in the tortuosity, while the changes in the chemical property are reflected in the interaction of the diffusing ion with the solid phase.

Initially, at low bulk density, compaction can increase the continuity of the liquid phase by bringing water films in contact. However, the increasing solids per unit volume may increase the tortuosity of the diffusion path. Thus, the net effect of increasing soil bulk density upon the rate of ion diffusion in a soil should be related to the balance between changes in the relative influence of the physical and chemical components. However, the sandy soil in this study was chemically non-reactive and the physical component (tortuosity) was the only one affected. Consequently, while the bulk density was increased, the tortuosity was increased and the diffusion rate was decreased.

[51]Cr Amount Effect : The effect of ^{51}Cr amount applied on diffusion rate was shown in Figure 5 for sand and shale formations. For a given temperature and soil type, the diffusion
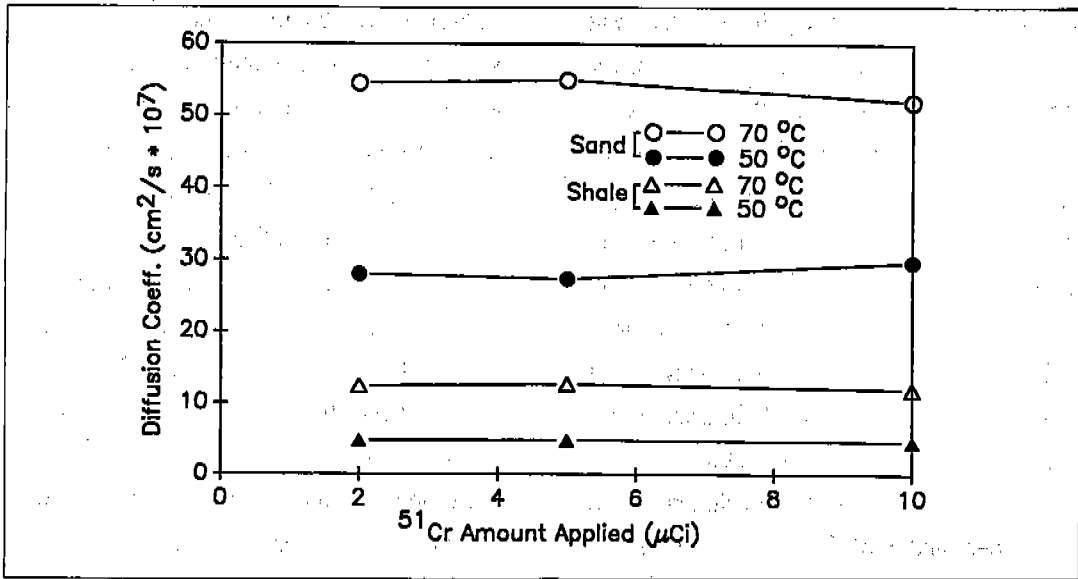
Fig. 5 ^{51}Cr Amount Effect on Diffusion

coefficients were not changed significantly. In case of sand at 50 ℃, the diffusion coefficients were 2.8×10^{-6}, 2.73×10^{-6}, and 2.97×10^{-6} cm^2/sec for 2 μCi, 5 μCi, and 10 μCi of ^{51}Cr applied respectively. Afer taking an average of these diffusion coefficients, the deviations of individual values from the mean value were 1.18%, 3.65%, and 4.94% respectively. The standard deviation was 1.234×10^{-7} and the relative strandard deviation was 4.34%. The diffusion coefficients at 70 ℃ were 5.45×10^{-6}, 5.49×10^{-6}, and 5.2×10^{-6} cm^2/sec for 2 μCi, 5 μCi, and 10 μCi of ^{51}Cr applied. After taking an average of the diffusion coefficients, the deviations of individual values from the mean value were 3.35%, 2.04%, and 1.3% respectively. The standard deviation was 1.574×10^{-7}, and the relative standard deviation was 3.1%.

In case of shale at 50 ℃, the diffusion coeffi-

cients were 4.76×10^{-7}, 4.75×10^{-7}, and 4.52×10^{-7} cm^2/sec for 2 μCi, 5 μCi, and 10 μCi of ^{51}Cr applied. The deviation of individual value from the mean value were 1.78%, 1.57%, and 3.35% respectively. The standard deviation was 1.36×10^{-8}, and the relative standard deviation was 2.9%. When the temperature was raised to 70 ℃, the diffusion coefficients were 1.24×10^{-6}, 1.26×10^{-6}, and 1.19×10^{-6} cm^2/sec. The deviation of individual value from the mean value were 0.81%, 2.44%, and 3.25% respectively. The standard deviation was 3.61×10^{-8}, and the relative standard deviation was 2.93%. From the above results, it was found that the deviation of individual values was usually less than the relative standard deviation. Moreover, there is no consistent relationship between the diffusion coefficients and the ^{51}Cr applied. For example, the diffusion coefficient in sand was

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largest at $10\,\mu Ci$, when the temperature was $50\,^\circ C$. But it was smallest at $10\,\mu Ci$, when the temperature was $70\,^\circ C$. The diffusion coefficient in shale was largest at $2\,\mu Ci$ when the temperature was $50\,^\circ C$, but it was largest at $5\,\mu Ci$ at $70\,^\circ C$. Therefore, it can be concluded that the diffusion rate of Cr(VI) in a porous media is independent of the amount of ^{51}Cr applied, and that the consideration of radioactive decay in the governing equation of diffusion is not necessary. Theoretically, the ratio of ^{51}Cr to non-radioactive Cr(VI) in the solution is only 10^{-4} order, and though the ^{51}Cr converts to ^{51}V during decay, its amount is only 10^{-4} order of Cr(VI) ion in the solution. This fact explains why ^{51}Cr diffuses along the non-radioactive Cr (VI) ion (working as carrier), and why the diffusion experiments fit the governing equation without radio-decay term.

NaCl Effect : Figure 6 shows the effect of NaCl addition on the diffusion rate. At $50\,^\circ C$, as the NaCl concentration was increased, the diffusion coefficients was changed from 4.76×10^{-7} to 4.74×10^{-7}, and 4.62×10^{-7} cm^2/sec. The changes were only 0.4% and 2.5% respectively. At $70\,^\circ C$, the diffusion coefficients were changed from 1.24×10^{-6} to 1.25×10^{-6}, and 1.21×10^{-6} cm^2/sec. The changes were only 0.8% and 3.2 % respectively. In theory, as the NaCl concentration is increased, the solution becomes more dense and the diffusion rate becomes slower. Though this tendency is slightly shown from the above results, it can be concluded that the effect of solution density change due to the addition of NaCl does not contribute significantly to the change in the diffusion rate.
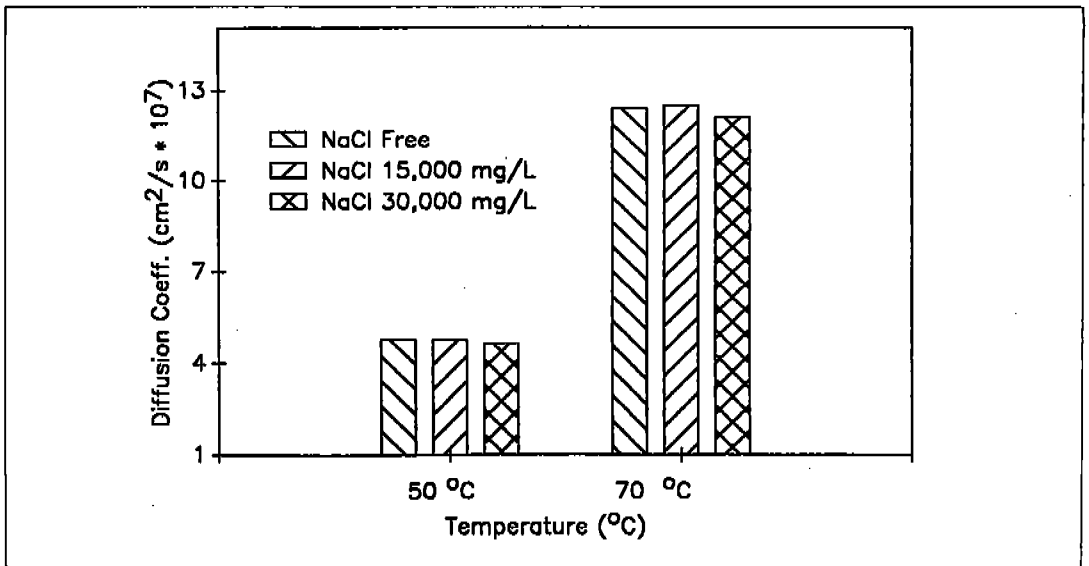

Fig. 6   NaCl Effect on Diffusion

CONCLUSIONS

As the temperature is increased, the diffusion coefficient is also increased. The relationship between the diffusion coefficient and temperature was plotted and calculation of the diffusion coefficients corresponding to different temperature enables the calculation of the activation energy. The activation energies of diffusion in shale and sand (29.15 KJ/mole and 24.88 KJ/mole respectively) were much greater than the activation energy of diffusion in a free aqueous solution(~17 KJ/mole). This fact indicates the difficulties of diffusion occurrence in porous media, compared to the diffusion in a free aqueous solution.

As the bulk density of sand was increased, the diffusion coefficient was decreased due to the increase of tortuosity of the sand. The linear regression provided a relationship between the bulk density and the diffusion coefficient. It was described as $D = 4.03 \times 10^{-5} - 2.682 \times 10^{-5} \times (B.D.)$ at $50\,^\circ C$, and $D = 9.237 \times 10^{-5} - 6.05 \times 10^{-5} \times (B.D.)$ at $70\,^\circ C$.

The amount of ^{51}Cr applied did not affect the diffusion rate significantly in porous media. The deviations of the individual value were less than 5% from the mean value. The result implies that the radio-decay term in the governing equation of diffusion is unnecessary.

The effect of NaCl addition on the diffusion rate was not significant, i.e., the density change due to NaCl in the solution did not contribute significantly to the change of the diffusion rate.

Thus far, several environmental factors have been studied for their effect on the diffusion rate of Cr(Ⅵ) in sand and shale. Some factors such as temperature and bulk density affected the diffusion rate significantly, while others such as ^{51}Cr amount and NaCl concentration in the solution did not significantly affect the diffusion rate. The environments of the deep well disposal zones are too complicated to be characterized by one or two environmental factors. Therefore, more environmental factors such as viscosity, porosity, pH, etc., should be studied to evaluate the behavior of diffusion in deep well disposal zones more accurately.

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