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Dynamic Migration Characteristics of Fluorine in Different Saturated and Unsaturated Soils

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Abstract

Elevated fluoride concentrations in ash-sluicing water from coal-fired power plant ash disposal sites have become a major environmental concern for the thermal power industry. In this study, the fluorine-containing ash water from Jianbi coal-fired power plant was selected as the example pollution source, and five representative soil types including Jianbi clay, Beijing silt, Fengrun sand, Tianshengqiao laterite and Fen River loess were selected for the soil column experiments on the adsorption and dispersion characteristics in the five kinds of soils. It was found through experiments that the dynamic adsorption capacity of the 5 kinds of soils for fluorine(F-) was in the order of: Tianshengqiao laterite > Jianbi clay> Beijing silt > Fen River loess> Fengrun sand. The adsorption capacity of Tianshengqiao laterite was much greater than that of other soil types, which was closely related to the total amount of clay minerals in the laterite and the composition of the clay minerals. It was found through the dispersion characteristics test that the pore-water velocity and dispersion coefficient were parameters related to the waterhead; when selecting parameter values in the simulation analysis of the dynamic migration of F-, the water level conditions in the actual projects should be taken into consideration. As a result, the dispersion coefficient and dynamic hysteresis factor of F- in different soils obtained through experiments provided basic parameters for the simulation of the dynamic migration characteristics in soil.

1. Introduction

The disposal and storage of fly ash generated from thermal power plants is one of the important factors limiting the sustainable development of the thermal power industry. At present, about 80% of the fly ash in ash disposal sites is treated by the water-sluicing ash removal method, and the elevated fluoride concentration in ash-sluicing water (namely the ash-sluicing water) has become one of the reasons for the environmental pollution caused by the thermal power industry [1, 2, 3, 4]. During the operation of the ash disposal sites, the fluoride-containing ash-sluicing water leaks into the underlying soil layer. If it is not properly treated, the residue will infiltrate into the soil and groundwater environment through surface runoff and other methods, resulting in groundwater pollution [5, 6, 7, 8], therefore, to a large extent, the influence of fluoride-containing ash-sluicing water depends on the interception and blocking effect of the soil layer. Under normal circumstances, after the fluoride-containing ash-sluicing water has permeated into the soil, the pollutants gradually spread from the leakage point to the surroundings and enter the aquifer through the aeration zone. If the leakage amount of the fluoride-containing ash-sluicing water is relatively small, the diffusion may only occur in the soil or in the aeration zone, otherwise, if the leakage amount is relatively large or it leaks continuously, the pollutants tend to continue to diffuse downward and enter the underground aquifer [9]. The migration and transformation of fluoride-containing ash-sluicing water in the soil layer mainly includes the saturated-unsaturated migration processes in the aeration zone and the aquifer, it is a process of the comprehensive actions of physical, chemical and biological factors, mainly including the adsorption and desorption, and the migration and dispersion with water flow [10, 11, 12].

In terms of the dynamic migration and transformation characteristics of soluble fluorine pollutants in unsaturated soil, with the deepening of domestic and foreign research work, the partition coefficients of the liquid and solid phase concentrations of the soil have gradually been taken into consideration, and Henry, Freundlich and Langmuir isothermal adsorption models have been adopted to solve the problems of the adsorption and desorption of liquid and solid phase concentrations [13, 14, 15]. In terms of the hydrodynamic dispersion coefficient, in some research, constant coefficients have been extended to dynamic parameters that change with the space and the time [16, 17]. In terms of soil water migration, the research has developed from the average pore-water velocity in the unsaturated zone to the movable and immovable water bodies, and the comprehensive interaction between water, gas, pollutant and soil has been taken into consideration [18, 19]. In recent years, most of the existing research results have focused on the

occurrence, adsorption and dispersion characteristics of F^- present in the underground water system, and certain results have been achieved concerning the occurrence rule of F^- in the underground water system. It is believed that the most representative method for classifying the occurrence forms of F^- in soil is to dividing it into water-soluble state, exchangeable state, iron-manganese oxide state, organically bounded state and residue state, etc. [20, 21]; and factors that can influence its occurrence forms mainly include the soil parent material, and the physical and chemical properties, etc [22, 23].

At present, the research on the dynamic migration characteristics of F- mainly uses the indoor dynamic soil-column adsorption-desorption method. According to the existing results, the migration of F- in underground water system can be divided into two types: the migration in a medium (water or soil) in the horizontal or vertical direction; and the migration from one medium into another medium [24]. At the same time, due to the differences in element characteristics and soil environmental capacity, the highly soluble F- might migrate into deeper soil layers, and the direction and degree of migration are affected by multiple factors such as the occurrence form, the geochemical properties of the soil in the unsaturated zone, and other environmental factors, and they are also closely related to the soil moisture content and the hydrodynamic process [25, 26]. Some research used the soil column test to analyse the migration characteristics of F- in the tailing sand, and the research results show that the main factors influencing the F- migration process are the mineral composition and clay content of the tailings sand; since the minerals in the tailing sand are mostly clay minerals such as chlorite and orthoclase, the desorption is dominating the upper-layer tailing sand and the adsorption is dominating the lower-layer tailing sand, the F- content has a trend of increasing with the depth [27, 28]. Zheng et al. [29] adopted the soil column method to study the migration and transformation of F- in unsaturated soil with different pH values under flooding and rainfall conditions, and they believed that under different pH, rainfall and flooding conditions, with the increase of leaching time, the soluble F- content in the leachate gradually increased, and the F- content in the leachate under flooding conditions was lower than that under the raining conditions. Zhang et al. [30] adopted the soil column model to study the migration of F- in the soil of Yuncheng Basin, and concluded that during the downward migration of fluoride ions, due to the adsorption effect, the vertical migration distance was very limited, the fluoride ions is unlikely to leach directly into shallow groundwater directly.

Although some researchers have used the soil column leaching experiment method to study the influence of F- generated by rainfall leaching on the ash residue of the thermal power plant ash disposal sites on the water environment, the only research finding is that the weak-permeable soil in the ash disposal sites has a certain adsorption effect [31, 32]. Therefore, there are still few researches conducted specifically for the migration characteristics of F- in the ash-sluicing water of coal-fired power plants in saturated/unsaturated soil. Targeting at this question, this study selects the fluoride-containing ash-sluicing water from the ash disposal sites of coal-fired power plants as the typical pollution source, and chooses five representative soil types including Jianbi clay, Beijing silt, Fengrun sand, Tianshengqiao laterite and Fen River loess to study the adsorption and dispersion characteristics of fluoride-containing ash-sluicing water in the five kinds of soils; meanwhile, this paper also studies the dynamic migration characteristics of the only research finding is that the weak-permeable soil in the ash disposal sites has a certain adsorption effect on the F- in unsaturated soil such as Beijing silt and Jianbi clay, and obtains the dispersion coefficients, and the static and dynamic retardation factors in different soils, which provides basic parameters for studying the dynamic migration in soil.

2. Materials and Methods

2.1 Test materials

When selecting sample soil types, both common soil types and special soil types were selected. For common soil types, three types of clay, silt, and sand were chosen, and the corresponding samples were from Eastern China and North China areas; as for the special soil types, the red clay (namely laterite) that is widely distributed in the south and the loess that is widely distributed in the north were selected. Therefore, there were five types of sample soils in all, which can basically represent the soil types at the bottom of ash disposal sites around the country, the samples included acid soil, neutral soil and alkaline soil, and had good representativeness.

(1) The clay samples were taken from the Jingshan ash disposal site of Jianbi Power Plant, so they were called the Jianbi clay. The ash disposal site is an in-use yard located in Jiangsu province, China, the bottom soil layer of the ash disposal site is clay with a natural dry density of 1.23 ~ 1.40 g/cm3 and a natural moisture content of 24.00 ~ 26.00%.

(2) The silt samples were taken from Beijing and called the Beijing silt. The natural dry density was 1.66 ~ 1.72 g/cm3, and the natural moisture content was 12.00 ~ 16.00%.

(3) The sand samples called the Fengrun sand were taken from the ash disposal site of Fengrun Thermal Power Plant. The bottom soil of the ash disposal site was sand with a natural dry density of 1.71 ~ 1.74 g/cm3 and a natural moisture content of 15.00 ~ 21.00%.

(4) The laterite samples were taken from Tianshengqiao, Guangxi province, China, so they were called the Tianshengqiao laterite, the natural dry density was 1.58 ~ 1.74 g/cm3 and the natural moisture content was 16.00 ~ 20.00%.

(5) The loess samples were taken from the Fen River Reservoir area in Shanxi province, China; the area is a typical loess area, so the samples were called the Fen River loess, the natural dry density was 1.51 ~ 1.83 g/cm3 and the natural moisture content was 10.00 ~ 14.00%.

As for the fly ash samples, all were taken from a same batch of dry ash stored in the ash disposal site of Jianbi Power Plant.

2.2 Physical, chemical and mechanical properties of soil and fly ash samples

(1) Physical and chemical properties

The test results of particle size, specific gravity and liquid-plastic limit of 5 kinds of soils and the fly ash samples are shown in Table 1:

Table 1
Particle size, specific gravity and liquid-plastic limit of soils and fly ash

Soil type	Specific gravity	Particle composition %					Liquid limit	Plastic limit
		> 0.5mm	0.05 ~ 0.5mm	0.005 ~ 0.05 mm	< 0.005 mm	< 0.002 mm	%	%
Jianbi clay	2.73	0.9	14.9	27.8	27.8	18.0	49.0	21.0
Beijing silt	2.71	0.2	43.4	42.4	12.2	8.0	27.3	15.9
Fengrun sand	2.64	0.7	93.9	1.1	4.3	3.1	-----	-----
Tianshengqiao laterite	2.80	12.8	46.2	13.2	27.8	22.5	76.1*	43.3*
Fen River loess	2.72	0.5	22.8	68.5	8.2	5.2	33.7	16.5
Jianbi fly ash	2.17	0	14.2	85.8	0	0	-----	-----

The chemical components and pH values of the five soil types are shown in Table 2. These results indicate that the main chemical components of the samples were mainly SiO2, and the Al2O3 occupied a certain proportion. The Tianshengqiao laterite is a special one, its alkali metal, alkaline earth metal and part of SiO2 are leached, and the Fe2O3 and Al2O3 are enriched in the soil.

The x-ray diffractometer was used to analyze the types, contents of the minerals and the relative percentage contents of clay minerals in the five kinds of soil samples, the analysis results are shown in Table 3 and Table 4, respectively. The test results showed that: (1) The laterite had a lowest total mineral content of 22.4%, followed by clay of 56.8%, the mineral contents of other soil types were between 72.3% and 90%. Quartz was the dominant composition in all samples, and laterite contained a certain proportion of hematite. (2) Except for laterite, the main clay mineral in other soils was the mixed-layer minerals of illite and montmorillonite, which accounted for 69–73% in the total clay minerals, the content of montmorillonite in the mixed-layer minerals was about 40 ~ 45%; as for laterite, the main mineral compositions were illite, kaolin and vermiculite.

Table 2
Chemical components and pH values of 5 kinds of soils

Soil type	Chemical composition %								
	SiO_2	Fe_2O3	Al_2O_3	CaO	MgO	Na_2O	K_2O	Loss on ignition	pH
Jianbi clay	65.04	5.89	15.42	0.62	1.46	1.01	2.19	6.82	5.69
Beijing silt	65.30	4.30	11.93	4.95	1.71	1.95	2.41	6.13	7.78
Fengrun sand	83.17	0.83	8.53	0.48	0.35	1.42	2.78	1.35	6.16
Tianshengqiao laterite	50.29	10.02	23.37	0.07	2.03	0.19	3.64	8.38	4.46
Fen River loess	67.41	4.74	12.26	3.23	1.88	1.79	2.39	5.00	8.38

Table 3
Mineral type and content

Soil type	Mineral type and content(%)							Total clay mineral content(%)
	Quartz	Potash feldspar	Sodium Feldspar	Calcite	Dolomite-class	Hematite	Hornblende	
Jianbi clay	46.7	2.0	6.5	/	/	1.6	/	43.2
Beijing silt	40.2	8.0	16.0	8.8	2.4	/	1.3	23.3
Fengrun sand	66.5	12.9	10.6	/	/	/	/	10.0
Tianshengqiao laterite	16.1	0.3	0.5	/	/	5.5	/	77.6
Fen River loess	43.7	6.9	16.1	4.9	/	0.7	/	27.7

Table 4
Relative percentage content of clay minerals

Soil type	Relative content of clay minerals(%)						Mixed-layer ratio(%/S)
	Illite/ Montmorillonite I/S	Illite I	Kaolin K	C	Vermiculite V	Mica/ Vermiculite M/V	I/S
Jianbi clay	69	19	4	3	5	/	45
Beijing silt	71	16	8	5	/	/	40
Fengrun sand	69	21	5	5	/	/	40
Tianshengqiao laterite	/	50	30	/	7	13	/
Fen River loess	73	15	6	6	/	/	45

(2) Compaction and permeability characteristics of soil

Compaction test is generally used to determine the compactness of clayey soil, while relative density test is generally adopted for non-clayey soil. The compaction test results of the 4 kinds of soils are shown in Table 5. Fengrun sand was subjected to the relative density test, and the obtained maximum void ratio and minimum void ratio were emax = 1.08 and emin = 0.53, respectively.

Table 5
Compaction test results of 4 kinds of soil samples

Sample name	Maximum dry density (g/cm^3)	Optimum moisture content (%)
Jianbi clay	1.63	21.0
Beijing silt	1.75	17.0
Tianshegnqiao laterite	1.27	37.0
Fen River loess	1.78	14.0

Disturbed soil was used in the experiment to carry out permeability test on the 5 kinds of soils with different densities, and deionized water was used as the permeating fluid. The obtained permeability coefficients of Jianbi clay, Beijing silt, Fengrun sand, Tianshengqiao laterite and Fen River loess were respectively 2.0×10 − 5 cm/s, 5.3×10 − 5 cm/s, 3.3×10 − 3 cm/s, 3.2×10 − 5 cm/s and 2.0×10 − 6 cm/s.

(3) Chemical composition of fly ash and ash-sluicing water

The measured chemical composition and content of the fly ash were: except for the loss on ignition (accounting for 2.16%), SiO2 accounted for 59.99%, Al2O3 accounted for 31.51%, Fe2O3 accounted for 2.50%, CaO accounted for 2.37%, MgO accounted for 0.70%, K2O accounted for 0.95%, Na2O accounted for 0.52%, SO3 accounted for 0.33%. These results indicate that SiO2 and Al2O3 contents were relatively higher in the Jianbi fly ash, and their proportions were quite close; and the Fe2O3 content ranked the third.

To study the pH value of the fly ash leachate and the chemical composition of the fly ash, the Jianbi fly ash was subjected to the chemical composition analysis. During the experiment, the fly ash was mixed with deionized water at a ratio of 1:10, the solution was shaken on a constant temperature oscillator for 1 hour, and filtered after standing for 24 hours, and then the K+, Na+, Ca2+, Mg2+, and SO42- contents and pH value of the filtered solution were measured, and the results were: Ca2 + concentration 115.67 ppm, SO42- concentration 53.99 ppm, Na+ concentration 3.80 ppm, K+ concentration 1.51 ppm, F- concentration 1.3 ppm, Mg2 + concentration1.05 ppm, the pH of the leachate was 12.5.

2.3 Test method

The dynamic migration characteristics of F- are usually tested by indoor soil-column test method to obtain the permeation behavior of F- in the soil columns. At the same time, through the processing of the test data of the pollutant permeation, parameters such as dispersivity, dispersion coefficient, pore-water velocity, and retardation factor can be obtained.

The soil column test device adopted in the experiment is shown in Fig. 1. The device consisted of a plexiglass cylinder, a base, and a Markov bottle. During the experiment, water was supplied by the Markov bottle, which provided a stable hydraulic head for the test. The leachate from the soil column flowed into the beaker. When examining the concentration of the pollutant in the leachate, PVC bottle or glass bottle was used to collect the leachate depending on the target pollutant.

The dynamic soil-column adsorption test adopted the vacuum pumping method, the soil column was saturated with the test solution, and then the test solution head was applied by the Markov bottle. The five types of soils were applied by the same water head, the gradient was 5.00, and the direction of the water flow was from top to bottom. The leachate was taken from the bottom of the soil column, the experiment time, the volume of the leachate, the test solution temperature, and the test phenomenon were recorded. In addition, the soil column test method was also adopted for the saturated soil column dispersion test and the pollutant migration test. The water source of the dispersion test was NaCl solution at a specified concentration, the initial concentration of Cl- in the solution was 290 ppm; while the water source of the pollutant migration test was prepared by adding corresponding pollutants in the ash-sluicing water.

3. Results and Discussion

3.1 Dispersion test of saturated soil and the results

In the dispersion test, NaCl was used as the tracer; the test solution was prepared using NaCl and deionized water, and the initial concentration of Cl^- in the solution was 290 ppm. Table 6 lists the dispersion test results of Jianbi clay, Beijing silt, Fengrun sand, Tianshengqiao laterite, and Fen River loess; the dispersion test results and fitting curves are plotted in Figs. 2 (a) ~ (e).

Table 6
Fitting parameters of F^- dispersion test in 5 kinds of soils

Sample name	Dry density ρ_d g/cm^3	Effective porosity n_e	Pore-water velocity v cm/s	Dispersion coefficient D cm^2/s
Jianbi clay	1.47	0.24	4.7×10^{-4}	4.5×10^{-4}
Beijing silt	1.57	0.27	9.0×10^{-4}	1.2×10^{-3}
Fengrun sand	1.46	0.38	3.3×10^{-3}	4.2×10^{-3}
Tianshengqiao laterite	1.14	0.37	2.3×10^{-3}	4.5×10^{-3}
Fen River loess	1.60	0.27	5.3×10^{-4}	7.0×10^{-4}

It can be seen from the test results that: (1) The ratio of effective porosity to porosity was 0.52, 0.64, 0.67, 0.68, 0.85 in the order of Jianbi clay, Tianshengqiao laterite, Beijing silt, Fen River loess and Fengrun sand, respectively. This showed that the coarser the soil particles, the closer the effective porosity was to the porosity, and the high clay content could increase pores at the dead-end of the soil. (2) The dispersion degrees of the five kinds of soils determined by the dispersion test were all near the position of 1 cm.

In order to further compare the influence of soil density on effective porosity, Jianbi clay samples of different densities were subjected to the dispersion test, the test results are listed in Table 5, and the fitting curves are plotted as Figs. 3 (a) ~ (c). In Table 7, the value of effective porosity was only related to the dry density of the prepared soil column sample, its relations with the applied water head and the pore-water velocity were not significant. However, the test solution head had a great impact on the pore-water velocity and the dispersion coefficient; the higher the water head, the greater the potential energy of the water flow, and the faster the water running in the pores, as a result, the hydraulic dispersion effect was larger. These results indicate that the pore-water velocity and dispersion coefficient are parameters related to the water head, and the water level conditions in the actual projects should be considered when selecting parameter values for prediction calculation and analysis.

Table 7
Dispersion test fitting parameters

Sample name	Dry density ρ_d g/cm^3	Test water head H cm	Effective porosity n_e	Pore-water velocity *v* cm/s	Dispersion coefficient D cm^2/s
Jianbi clay	1.39	35	0.27	4.7×10^{-4}	4.5×10^{-4}
	1.43	187	0.26	8.5×10^{-4}	8.7×10^{-4}
	1.47	100	0.24	3.7×10^{-4}	3.5×10^{-4}

3.2 Dynamic migration test of saturated soil and the results

To improve the test accuracy, fluoride ions were added to the ash-sluicing water. The specific operation was to mix the fly ash and the deionized water at a ratio of 1:10, the solution was shaken for 1 hour, and filtered after standing for 24 hours; then F- standard solution was added to the filtered solution, since there were Ca2 + in the fly ash solution, after F- was added, CaF2 precipitate was generated, so the solution was stood for 2–3 days and filtered for later use. In the test, the fluoride-containing solution was placed in a Markov bottle, and the concentration of fluoride ions was measured by the fluoride ion selective electrode method, the test device was model-868 ionometer produced by American company Thermo Orion, equipped with the Orion fluorine ion selective electrodes.

Figures 4 (a) ~ (e) are the permeation curves of F- in the five kinds of soils. Parameters such as dispersion coefficient, pore-water velocity, and retardation factor obtained by the fitting curves are listed in Table 6. The adsorption capacity of the soil in the soil column for F- can be measured by comparing the results of the retardation factor, the adsorption capacities of the five kinds of soils from high to low were: Tianshengqiao laterite > Jianbi clay > Beijing silt > Fen River loess > Fengrun sand. The adsorption capacity of Tianshengqiao laterite for F- was substantially higher than that of other soil types, which was largely related to the total amount of clay minerals in the laterite and the composition of clay minerals. Among these five types of soils, Tianshengqiao laterite had a highest total clay mineral content of 77.6%, followed by Jianbi clay of 43.2%. The clay mineral composition of Tianshengqiao laterite was dominated by illite and kaolin, the edge of kaolin particles was positively charged in low pH (acidic) environment and negatively charged in high pH (alkaline) environment. Tianshengqiao laterite is a kind of acid soil with a pH of 4.46, and such soil condition is conductive to the adsorption of F- in the solution. As for the other 4 kinds of soils, the order of their adsorption capacities for anions was the same as clay mineral contents of the soils.

Table 8 also lists the retardation factors calculated using the static test results, and its order was the same as that of the dynamic test, but the values were generally greater than dynamic test values, which was caused by the different test methods. The static isothermal adsorption test reflects the adsorption situation under the conditions that the soil particles and the pollutant liquid are fully mixed and the contact time is sufficient; while the dynamic soil column test simulates the flow of the pollutant liquid through the soil layer; generally, the soil particles in the soil layer are denser, the pores between soil particles are smaller, and the contact area between the pollutant liquid and the soil is smaller than that in the static adsorption isotherm test. Therefore, the F- adsorption capacity of soil in the dynamic soil-column test was weaker than that in the static test, and the difference between the two was reflected through the size of the retardation factor.

Table 8

Fitting parameters of permeation curves of F^- in five kinds of soils

Sample name	Dry density ρ_d g/cm^3	Effective porosity n_e	Pore-water velocity v cm/s	Dispersion coefficient D cm^2/s	Dynamic retardation factor R_d	Static retardation factor R_d
Jianbi clay	1.47	0.24	1.7×10^{-3}	1.6×10^{-3}	16.61	23.61
Beijing silt	1.57	0.28	6.8×10^{-4}	6.8×10^{-4}	3.62	8.09
Fengrun sand	1.46	0.38	1.5×10^{-2}	2.9×10^{-2}	1.55	1.97
Tianshengqiao laterite	1.14	0.37	9.0×10^{-3}	9.6×10^{-3}	20.95	38.44
Fen River loess	1.60	0.28	3.0×10^{-4}	3.1×10^{-4}	2.54	7.85

The fitting curves in Fig. 4 show that, in terms of the F^- adsorption mode of the five kinds of soils, the characteristic difference method could obtain more reasonable parameters for Jianbi clay, Tianshengqiao laterite, and Fengrun sand; while for Beijing silt and Fen River loess, the analytical solutions were better. In fact, for most fitting results, the fitting curves obtained by analytical solution, Crank-Nicolson method, and characteristic difference method were quite close.

This study also took Jianbi clay as an example to compare the migration characteristics under different dry densities and diameters, and the results are listed in Table 7, the permeation curves are plotted as shown in Figs. 5 (a) ~ (c). Table 9 suggests that the retardation factor of F- in the soil is related to the density of the soil; to some extent, increasing the dry density of the soil can help increase the retardation factor and slow down the migration of F-; under allowable conditions, increasing the dry density of the soil can also help reduce the permeability coefficient of the clayey or silty soil, and decelerate the migration of F-. Table 7 also lists the soil-column test parameters with a same dry density of 1.47 g/cm3 and different sample diameters, and the results show that under the same test conditions, the influence of the sample diameter on the test results was not much different.

Table 9

Fitting parameters for F^- permeation curves

Sample name	Dry density ρ_d g/cm^3	Effective porosity n_e	Pore-water velocity v cm/s	Dispersion coefficient D cm^2/s	Dynamic retardation factor R_d	Static retardation factor R_d
Jianbi clay	1.39	0.27	4.3×10^{-3}	6.7×10^{-3}	17.2	20.7
	1.43	0.26	1.7×10^{-3}	6.3×10^{-3}	17.5	22.1
	1.47	0.24	1.5×10^{-3}	1.6×10^{-3}	20.6	23.6
	1.47*	0.24	1.1×10^{-3}	1.2×10^{-3}	18.4	23.6

Note: the diameter of the soil-column was 10cm.

3.3. Test on the dynamic migration characteristics of F^- in unsaturated soil

To study the migration law of F- in unsaturated soil, the test selected Jianbi clay and Beijing silts as the test soils, and the diameter of the soil-column was 5cm. The test device was the same as the test of the saturated soil columns, and the test method was similar as well; the only difference was that after the samples were prepared, the upstream water head had been directly applied to the samples that were not saturated with test solution. To better observe the wetting front, the length of the soil column was set to 30 cm, which was longer than the saturated soil column.

In the test, it was assumed that the initial soil moisture content was uniform; considering that the adsorption capacity of the soil might vary with the initial moisture content, resulting in different permeation speed, so for each kind of soil, samples with four different initial moisture contents had been prepared. In terms of the selection of initial moisture content, soil saturations with a certain interval were converted into corresponding moisture contents, when the soil moisture contents were respectively 20%, 40%, 60% and 80%, the corresponding moisture contents of Jianbi clay were 6.3%, 12.6%, 18.8%, and 25.1%, and the corresponding moisture contents of Beijing silt were 5.4%, 10.7%, 16.1%, and 21.4%.

(1) Permeation wetting front

In the test, the permeation wet peaks of fluoride-containing ash-sluicing water in soil samples were measured. Since the color of the soil with an 80% saturation was very close to wet soil, the migration of wetting front could not be observed in the test, so no test data had been obtained. For other saturation degrees, the time required for the wetting front to pass through the 30cm soil layer is shown in Table 10.

Table 10
Time required for wetting front to pass through unsaturated soil layer

Sample name	Initial saturation	Dry density	Moisture content	Time for wetting front to pass through soil-column
	%	g/cm^3	%	min
Jianbi clay	20	1.47	6.3	382.1
	40		12.6	28.2
	60		18.8	229.0
Beijing silt	20	1.57	5.4	150.1
	40		10.7	99.5
	60		16.1	941.0

The migration speed of wetting front passing through unsaturated soil varied with the initial moisture content of the soil, generally, the lower the initial moisture content, the greater the adsorption capacity of the soil, and the faster the migration speed of the wetting front. For the two kinds of soils in this test, the migration speeds of 40% saturation wet peaks were faster than those of 60% saturation wet peaks, but the law didn't apply to the 20% saturation wet peaks. In the case of Jianbi clay, the sequence of wetting front migration speeds (according to initial saturation) was 40%> 60%> 20%; as for Beijing silt, the sequence was 40% > 20%> 60%. This phenomenon was largely to do with the low moisture content of the sample under the condition of 20% saturation, at this time, the moisture content of the Jianbi clay sample and Beijing silt sample was only 6.3% and 5.4%, respectively. When preparing the soil columns, in order to

achieve the designed dry density, it required very large impact strength to prepare the dry soil materials. Although the soil-layer of the sample was as thin as 1cm, the middle and bottom soil in the soil-column was relatively loose, the dry density was smaller than the dry density of the sample; while the upper soil was denser, and the dry density was larger than the dry density of the sample. This sample preparation situation made the dry density of the sample uneven, so when the test solution entered the high-density area, the flow rate was decreased naturally, and the decrease was more obvious for higher clay content.

The test results showed that the permeation speed of the wetting front in unsaturated soil was related to the initial moisture content of the soil, and it was also related to the structure of the soil. The denser the soil, the less the large pores and more the small pores, so the permeation speed of the wetting front in unsaturated soil was lower.

(2) Dynamic migration of F^- in unsaturated soil

In the test, after the wetting front passed through the soil column, the water head was maintained constant to observe the permeation process of F- in the soil from unsaturated to saturated conditions. The permeation time of F- in unsaturated soil and the volume of test solution flowing through it are shown in Table 11.

Table 11
Permeation time of F- in unsaturated soil and the volume of test solution

Sample name	Initial saturation	Dry density	Moisture content	Permeation time	Volume of fluoride-containing test solution
	%	g/cm^3	%	Days	ml
Jianbi clay	20	1.47	6.3	35.4	31286
	40		12.6	48.0	33907
	60		18.8	> 166.0	-----
	80		20.6	> 200.0	-----
Beijing silt	20	1.57	5.4	10.3	5922
	40		10.7	8.3	6085
	60		16.1	108.9	5678
	80		21.4	135.8	5336

From the test results, it can be seen that: (1) The moisture content of the sample had a great influence on the permeation time: for Jianbi clay, the permeation time under 20% and 40% initial soil-column saturation conditions was 35.4 days and 48 days, respectively; for soil-column with a 60% initial saturation, its relative concentration only reached 0.28 after 166 days; while for soil-column with an 80% initial saturation, there was almost no water coming out under the test solution head; for Beijing silt, the permeation times under 20% and 40% initial soil-column saturation conditions were close, 10.3 days and 8.3 days, respectively; while the permeation times under 60% and 80% initial soil-column saturation conditions were longer, 108.9 days and 135.8 days, respectively, which were 10 times longer than those under the 20% and 40% initial saturation conditions. (2) The adsorption capacity of the soil can be measured by the total volume of the leachate during the permeation; for Jianbi clay, the total volumes of the leachate under the two initial saturation conditions were quite close, both within the range of 31000 ~ 34000 mL; while in the case of the Beijing silt, the total volumes of the leachate under the four initial saturation conditions were quite close as well, all within the range of 5500 ~ 6000 mL; this indicates that, under different initial saturations, the dynamic adsorption

capacity of Jianbi clay was greater than that of Beijing silt, which was consistent with the results of the static test. (3) The adsorption capacity of unsaturated soil for F- was slightly lower than that of saturated soil. For Beijing silt, the saturated soil columns had an average permeation water amount of about 253 mL for per centimeter soil column length, which was slightly larger than unsaturated soil columns; in the case of Jianbi clay, the relative concentration reached 0.66 after 117 days, and the total volume of leachate reached 19315 ml, the average permeation water amount for per centimeter soil column of saturated soil was expected to be greater than that of unsaturated soil, this is because there were some air trapped in the micro pores in the soil that had not been carried away by the water flow; due to the existence of the small amount of entrapped air, the contact between the soil and the pollutant liquid was reduced, which had affected the adsorption capacity of the soil to a certain extent.

4. Conclusion

(1) The test results of the adsorption of F- in the five kinds of soils showed that, different soils had different dynamic adsorption capacities for F-. The specific adsorption capacities of the soils were Tianshengqiao laterite > Jianbi clay> Beijing silt > Fen River loess> Fengrun sand. The adsorption capacity of Tianshengqiao laterite for F- was substantially higher than that of the other soil types, this was strongly associated with its clay mineral content and the composition of clay minerals. For the F- adsorption modes of the five kinds of soils, the characteristic difference method could obtain more reasonable parameters for Jianbi clay, Tianshengqiao laterite, and Fengrun sand; while for Beijing silt and Fen River loess, the analytical solutions were better.

(2) The retardation factors obtained in static tests were generally greater than those obtained in dynamic tests; since static isothermal adsorption test reflects the adsorption situation under the conditions that the soil particles and the pollutant liquid are fully mixed and the contact time is sufficient, while the dynamic soil column test simulates the flow of the pollutant liquid through the soil layer, therefore, for the prediction analysis, referring to dynamic test results is closer to the actual situation than the static test results.

(3) With Jianbi clay as an example, the value of effective porosity was only related to the dry density of the soil column sample, its relations with the applied water head and the pore-water velocity were not significant, the pore-water velocity and dispersion coefficient were head-dependent parameters; when selecting parameter values in the simulation analysis of the dynamic migration of F-, the water level conditions in the actual projects should be taken into consideration; in addition, the retardation factor of F- in the soil was related to the density of the soil, to some extent, increasing the dry density of the soil can help increase the retardation factor and slow down the migration of F-; under allowable conditions, increasing the dry density of the soil can also help reduce the permeability coefficient of the clayey or silty soil, and decelerate the migration of F-.

(4) The migration speed of F- in unsaturated soil was related to the initial soil moisture content, soil type, soil adsorption capacity, and soil structure. Under normal conditions, the lower the initial moisture content of the soil, the greater the adsorption capacity, the faster the permeation speed of F-. The dynamic adsorption capacity of Jianbi clay at different saturations was greater than that of Beijing silt, and the adsorption capacity of the two kinds of unsaturated soils for F- was slightly lower than that of saturated soil. Through the dynamic migration test of fluoride-containing ash-sluicing water in different soils, the selection of ash-sluicing water seepage-control measures in the ash storage yards should be selected according to the type of bottom soil. Soils such as laterite or clay with a certain thickness and strong adsorption capacity could effectively prevent the migration of pollutant factors during the operation of ash disposal sites.

Declarations

Author Contribution

Jun Yan: Resources, Supervision, Conceptualization, Methodology, Investigation, Writing - Original Draft.Pengfei Dou: Formal analysis, Writing - Original Draft.Zhiao Li and Wei Wang: Data Curation, Validation, Writing-Review& EditingYiding Ma: Writing; Writing - Review & Editing. Junxue Ma: Supervision, Writing -Review & Editing.Fan yu: Preparing figures, Writing -Review & Editing.

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Figures

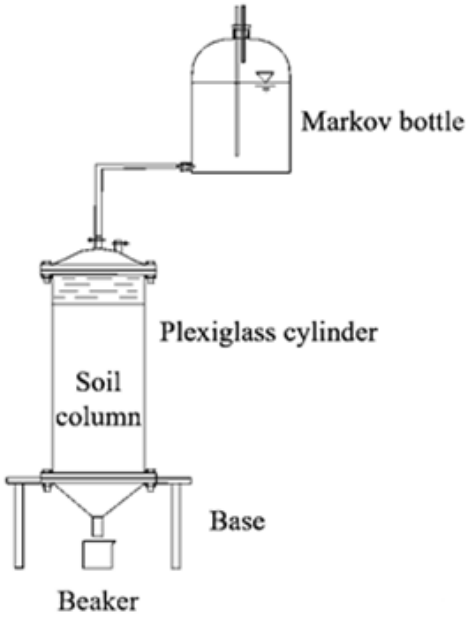


Figure 1

Soil column test device

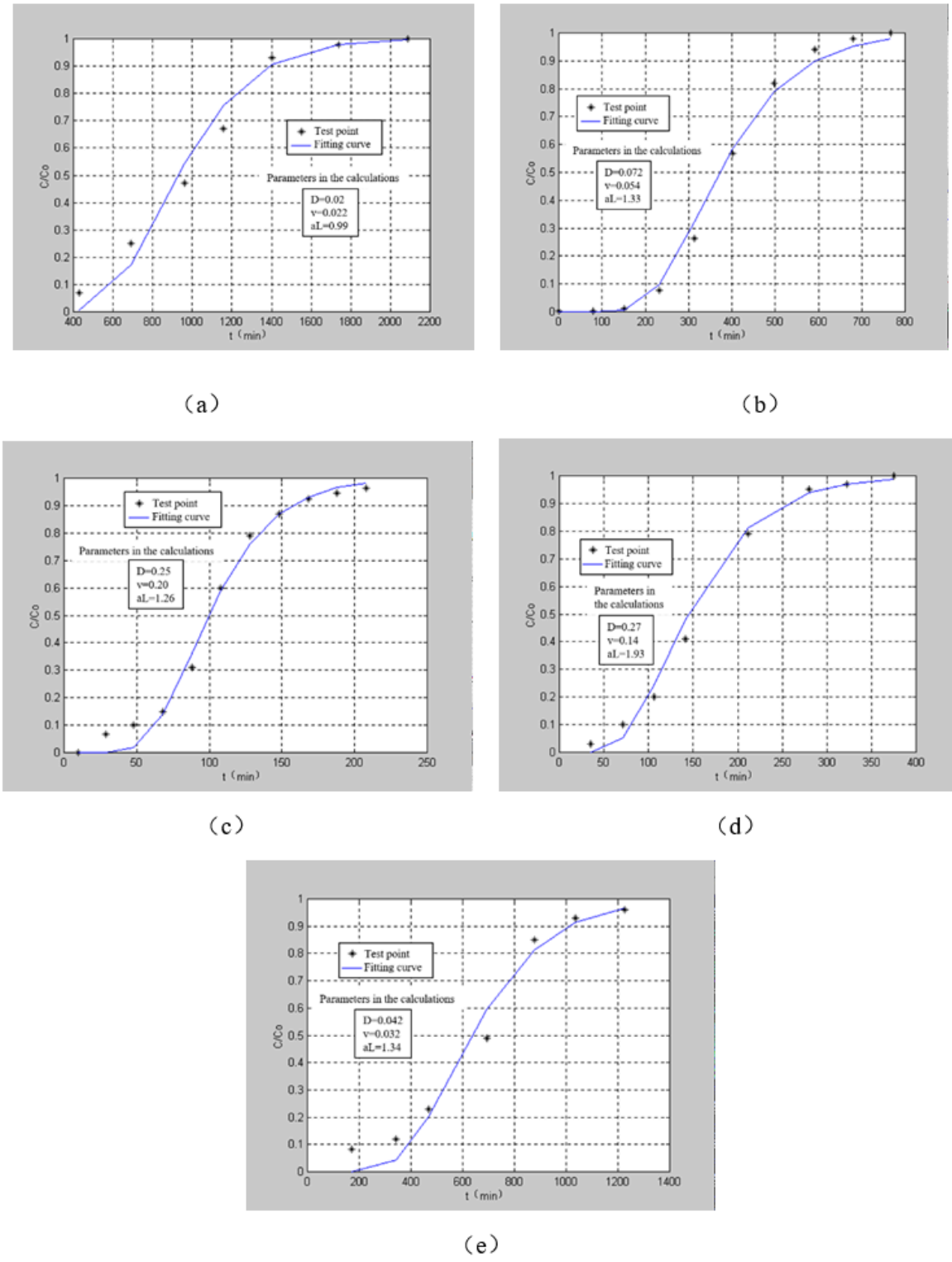


Figure 2

Results of dispersion test of five kinds of soils

(A) Jianbi clay (b) Beijing silt (c) Fengrun sand (d) Tianshengqiao laterite (e) Fen River loess.

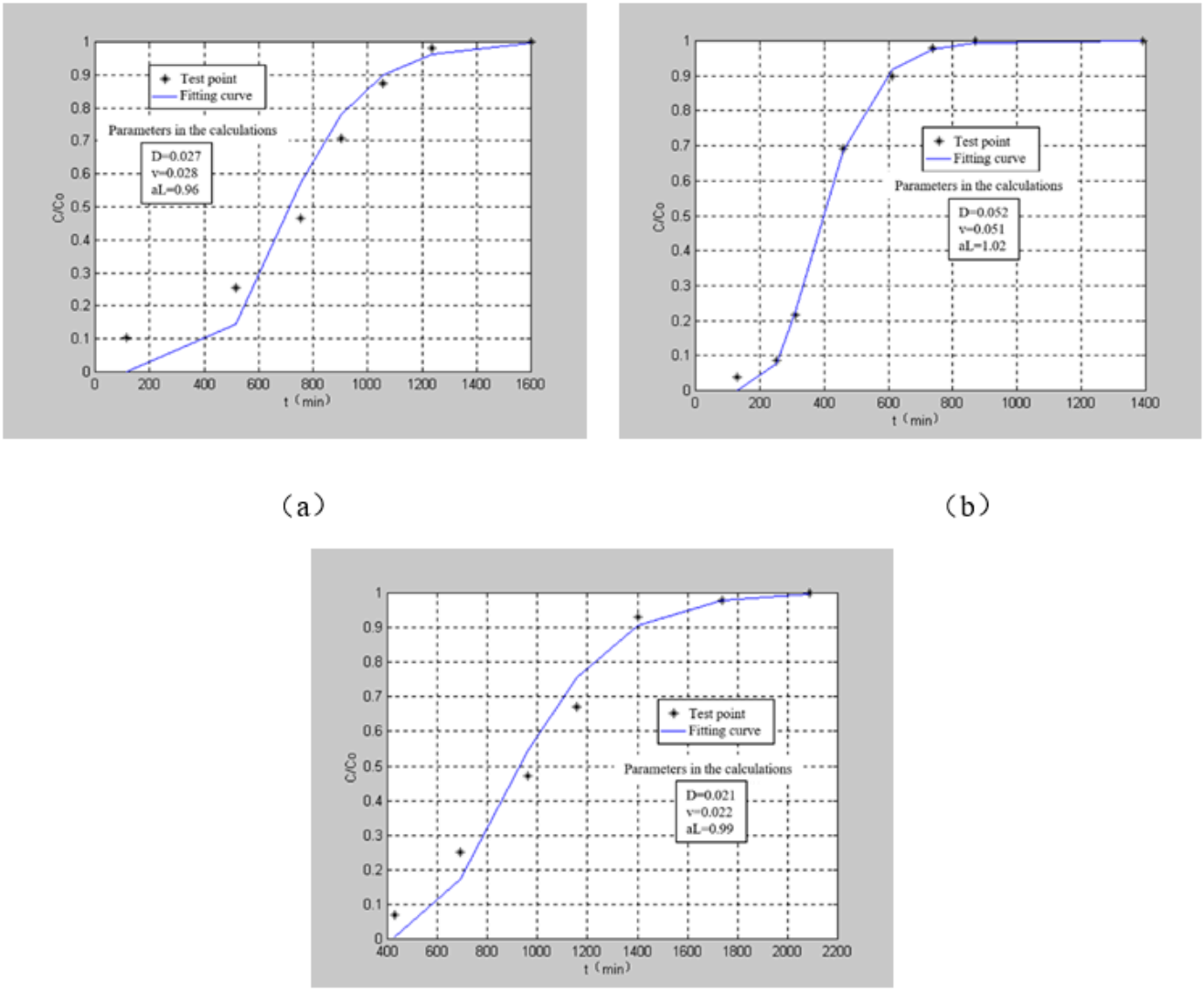


Figure 3

Dispersion test results of Jianbi clay soil columns with different dry densities

(A) ρd=1.39 g/cm3 (b) ρd=1.43 g/cm3 (c) ρd=1.47 g/cm3

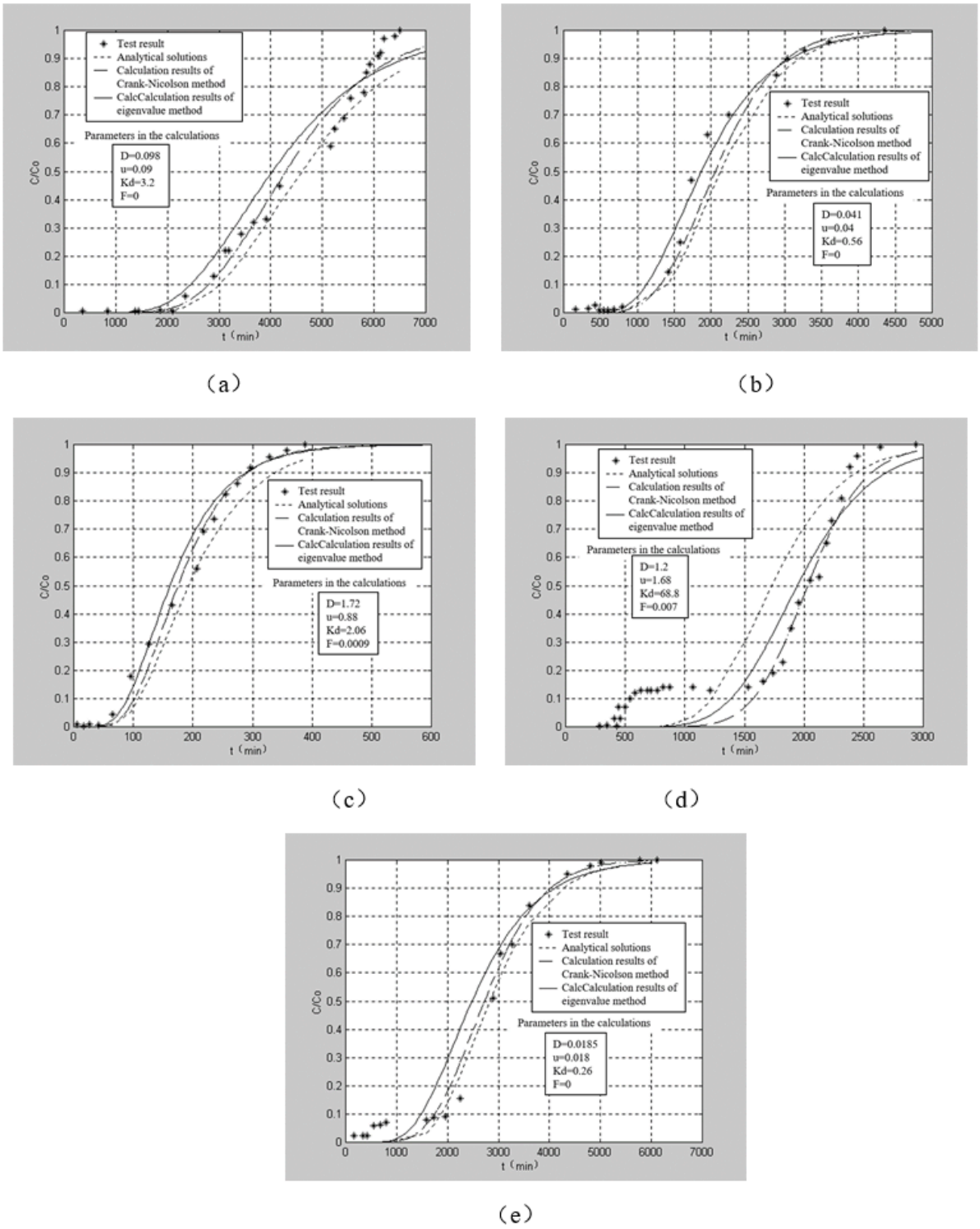


Figure 4

Permeation curves of ash-sluicing water F- in soil columns of 5 kinds of soils

(A) Jianbi clay (b) Beijing silt (c) Fengrun sand (d) Tianshengqiao laterite (e) Fen River loess.

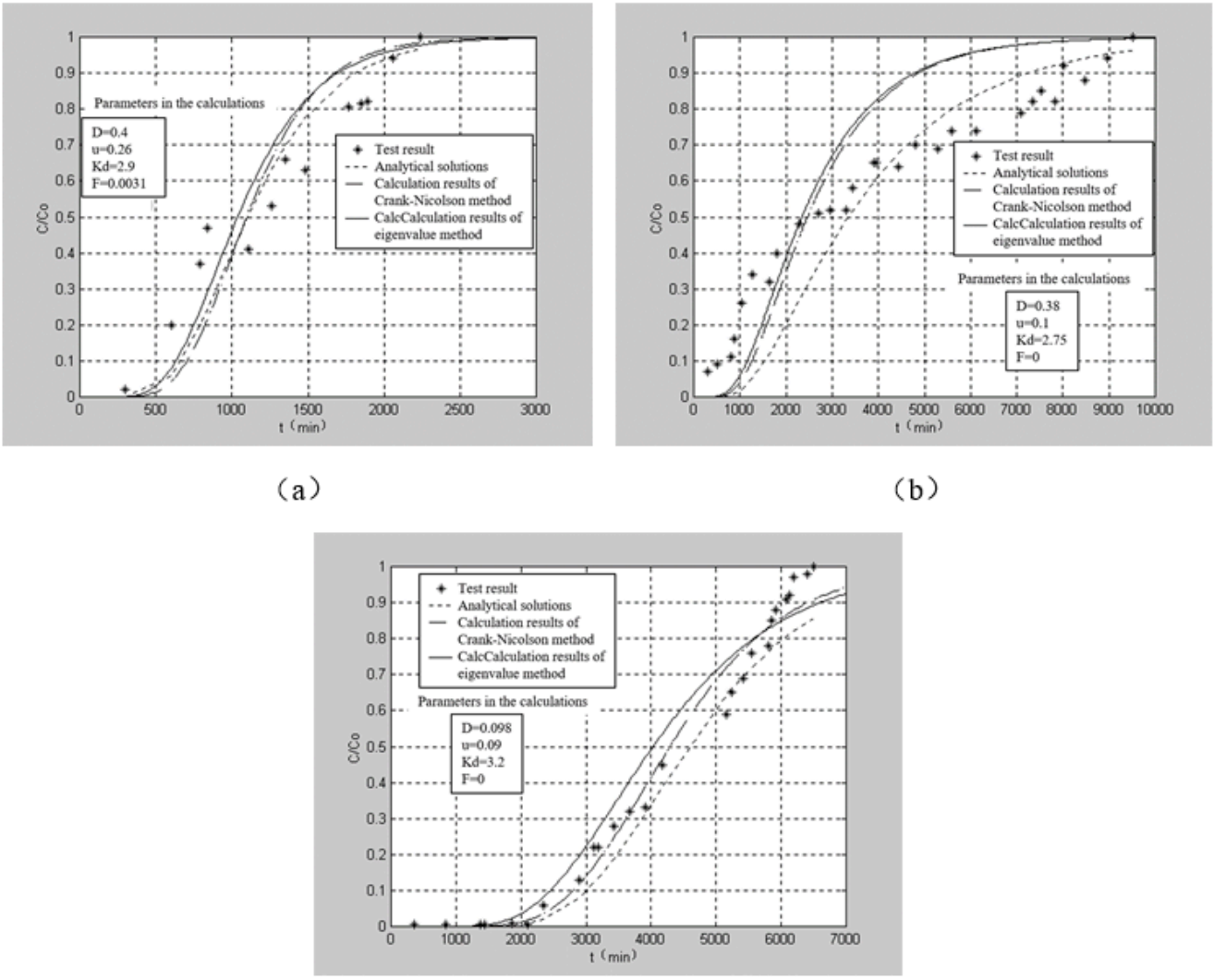


Figure 5

Permeation curves of ash-sluicing water F- in Jianbi clay soil-columns with different dry densities (a□ρd=1.39 g/cm3 □b□ρd=1.43 g/cm3□c□ρd=1.47 g/cm3