
Capability of the Kd model to predict radionuclides behaviour and transport in unsaturated columns under steady flow conditions

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Abstract. In the frame of the IRSN Chernobyl Pilot Site Project, a waste trench containing hot particles was instrumented to study the fate of radioactive pollutants. Results have shown the formation of a ⁹⁰Sr plume in the downstream aquifer, mainly present in the Aeolian layer after 15 years. Laboratories experiments were performed to analyse the transport of ⁹⁰Sr and ¹³⁷Cs in the Aeolian sand in both saturated and unsaturated conditions. Batch experiments were performed to study the chemical equilibrium state of the soil/solution system under static conditions. Stirred flow-through reactor experiments were performed to study the kinetics and reversibility of sorption reactions at the surface of solid particles under dynamic conditions. Column experiments in the structured porous media were also performed in saturated and unsaturated flow conditions. Experimental data pointed out a non-linear, instantaneous and reversible sorption process of ⁹⁰Sr. ¹³⁷Cs exhibits a non-linear behaviour with a partial irreversible sorption process. A suitable cation-exchange model was used to describe the solute/soil reactions. The former model was coupled with transport models to describe behaviour of ⁹⁰Sr and ¹³⁷Cs in both saturated and unsaturated steady flow conditions. Main transport parameters were identified and discussed. An effective simple Kd type approach to describe radionuclides transport properties under unsaturated conditions was evaluated.

1. INTRODUCTION

In mid 1999, the French Institute for Radiological Protection and Nuclear Safety (IRSN) began to manage the Chernobyl Pilot Site (CPS) project [1]. The project was organized through an international cooperation agreement between two Ukrainian (Institute of Geological Science and Institute of Agricultural Radiology) and two French institutes (IRSN and Atomic Energy Commission (CEA)). The project was aimed at characterizing and modelling radionuclide migration from the near-surface radioactive waste burial site containing dispersed nuclear fuel to soils and the geosphere [2].

The study site is located 2.5 km southwest of the Chernobyl Nuclear Power Plant. In 1987, this sector was earmarked for the interim storage of surface soil and contaminated tree trunks. These materials can be found in trenches a few meters deep. In 1999, one of these trenches (N°22) was chosen for carrying out experiments to validate basic models representing radionuclide transfer to soils and aquifers. Trench N°22 and the top layer contain fuel particles that dissolve and release ⁹⁰Sr and ¹³⁷Cs. For 15 years, radionuclides have been penetrating the unsaturated soil zone and the water table at 2-3 m depth with the result that ⁹⁰Sr activity in the water table varies between 10 and 13000 Bq.L⁻¹, while the plume can be seen to spread over a few tens of meters downstream of trench N°22 [2]. ¹³⁷Cs is strongly sorbed by the soil surrounding the trench, and ¹³⁷Cs activity is fixed in a few centimeters from the trench perimeter.

Prediction of contaminant transport in the subsurface is strongly influenced by the hydraulic and chemical properties of the soil. Several factors may cause non-ideal transport [3] in a structured soil or under unsaturated conditions: non-homogeneous soil physical properties (e.g., hydraulic conductivity,

soil-water content, bulk density), physical non-equilibrium, non-homogeneous soil chemical properties (e.g., sorption equilibrium constant), sorption non-equilibrium, sorption isotherm non-linearity and sorption-desorption non-singularity.

This work presents some results on radioactive strontium and caesium transport in the Aeolian sand making up the unsaturated zone on the CPS. Three laboratory techniques were used to identify and quantify the main physico-chemical processes involved in strontium and caesium transport. Batch experiments were performed to study the chemical equilibrium state of the soil/solution system under static conditions. Stirred flow-through reactor (SFTR) experiments were conducted to study the kinetics and reversibility of the sorption reactions at the surface of solid particles under dynamic conditions. Lastly, the transport of radionuclides was studied in the structured porous medium under saturated and unsaturated steady-state flow conditions in laboratory columns. Main transport parameters were identified and discussed. An effective simple K_d type approach to describe radionuclides transport properties was evaluated.

2. RESULTS

2.1 Material and methods

The soil used was an Aeolian sandy deposit representative of the CPS subsurface. It was an average sample from Pripjat Zaton exposure, located 2 km northeast of the CPS. The soil sample was dry sieved and the < 1 mm fraction used for characterization and laboratory experiments (the > 1 mm fraction represented less than 1% of the total sample mass). The main components of the soil were determined by chemical and X-ray diffraction analyses. The mineralogical composition of the sand by percentage mass was: 95-98% quartz, < 5% feldspar. The chemical composition of the sand by percentage abundance was: 95-98% SiO_2 , < 2% $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ (measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) after acid digestion). An average cation exchange capacity (CEC) of 1.2 meq/100g was determined using the sodium acetate saturation method [4]. Sand particle density was assumed to be equal to that of quartz, i.e. 2.65 g/cm^3 [5].

All experiments tests were conducted using a synthetic groundwater, formulated to approximate the composition observed in CPS aquifer samples. The concentrations of major cations chosen for synthetic water were in the range of field concentrations. The composition of the water in equilibrium with the Aeolian sand was determined experimentally. The concentrations of major cations were close to those of the synthetic water. The first conditioning stage of all column and reactor experiments was then reduced.

Synthetic groundwater was prepared by adding cations as sulphate salts to distilled, deionized water, except for K, which was added as chloride, and Ca as carbonate. The pH was adjusted to 6.4 ± 0.2 by adding 0.1 N H_2SO_4 . The theoretical concentrations were then verified by chemical analysis with a capillary ion analyser (Waters).

Known stable strontium and caesium concentration solutions were prepared by adding amounts of respective chloride salt to the previous synthetic groundwater. A wide range of concentrations ranging from $2.5 \cdot 10^{-3} \text{ mol/L}$ up to 10^{-9} mol/L was studied. For radiometric measurements, spiked solutions were also prepared using ^{85}Sr and ^{134}Cs , ^{137}Cs as radioactive tracers.

2.2 Batch and stirred flow through reactors

Sorption properties of caesium and strontium on Aeolian sand have been determined with two different techniques: classical batch experiments for isotherm determination and stirred flow through reactors to study sorption kinetics under dynamic conditions. With the first technique, solid/solution ratio (m/V) was 1 kg/L and characteristic contact time was 24 hours. With the second technique, m/V was 0.21 kg/L and characteristic solution residence time varied from 10 up to 100 minutes depending of flow rates. For a given species, distribution coefficient was defined as the ratio of the sorbed concentration onto the soil to the aqueous concentration.

For strontium a non-linear sorption isotherm was obtained, distribution coefficient being constant for aqueous strontium concentration lower than 10^{-6} mol/L at equilibrium (Figure 1). For higher concentration, a saturation of sorption sites begins and distribution coefficient decreases as strontium concentration increases. SFTR experiments indicate a reversible sorption with a characteristic time lower than 10 min. The same general behaviour was observed for caesium (Figure 2), with a non-linear sorption but sorption mechanisms were different. In the range of concentration studied, the observed isotherm can be successfully modelled with an ion exchange model with two sorption sites. We used PHREEQC (version 2) [6] to determine main sorption parameters: sites concentration, selectivity coefficients and eventually kinetic constants. The first "specific" sites, in low concentration (10^{-7} mol/kg), have a high affinity for caesium with selectivity coefficient relative to Na^+ of $10^{-5.4}$, whereas the "regular" sites in high concentration ($1.25 \cdot 10^{-2}$ mol/kg) have a lower affinity with a selectivity coefficient relative to Na^+ of $10^{-2.3}$. SFTR break through curves (BTCs) analyses allowed us to evaluate characteristic sorption times. For regular sites, sorption is reversible and instantaneous, whereas desorption time for specific sites is higher (20h).

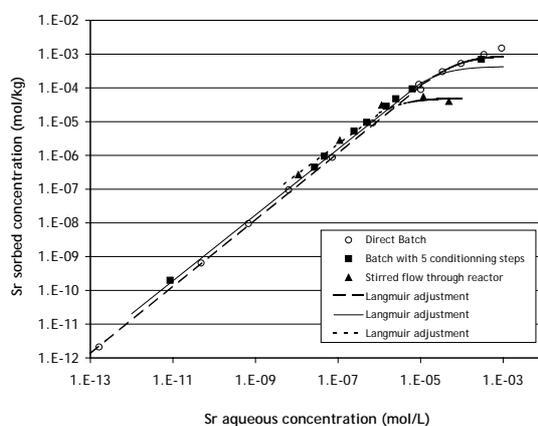


Figure 1. Strontium sorption isotherm in batch and SFTR experiments. Experimental and calculated data with a Langmuir model.

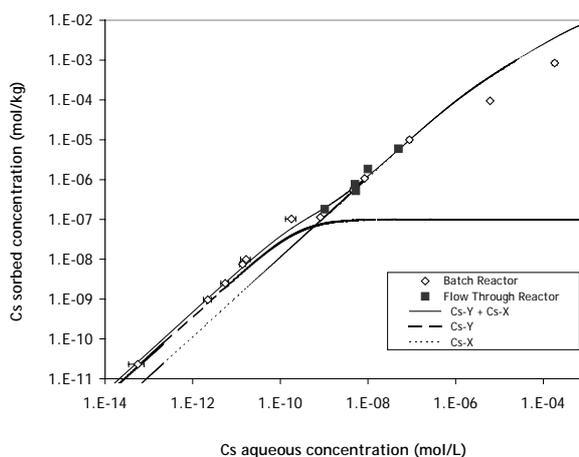


Figure 2. Caesium sorption isotherm with batch and SFTR experiments. Experimental and calculated data with a 2-sites ion exchange model.

2.3 Column experiments

Column experiments were realized to simulate real transport phenomenon both in saturated and unsaturated conditions. In our experimental conditions, solid/solution ratio varied from 5.4 kg/L, for saturated columns, up to 11 kg/L for unsaturated columns depending of soil volumetric water content, θ ($L.L^{-1}$). θ varied between 0.34 down to 0.16.

Transport properties of sand packed columns have been determined with an inert tracer (3H). Classical advection-dispersion model (ADM) described successfully tritium BTCs under saturated flow conditions, whereas a mobile-immobile model (MIM) was required to describe asymmetrical BTCs in unsaturated conditions. The MIM assumes that the porous medium contains a mobile water phase in which convective-dispersive transport of solutes occurs, and a immobile water phase with which solutes can exchange [7], [8]. In the range of saturation level tested, we observed that the fraction of immobile water ($\beta = \frac{\theta_{im}}{\theta}$) was constant and represented 10-20 % of the total water

content. The characteristic time of the advection in the mobile fraction is defined by $t_a = \frac{L}{V_m}$,

with L the length of column and V_m the pore water velocity in mobile phase. In our case, t_a varied from 1 up to 23 hours depending of flow rate conditions. To compare, the characteristic dispersion time $t_D = \frac{D_m}{V_m^2}$, with D_m (cm^2/h) hydrodynamic dispersion coefficient, is less than 0.5 min. For

unsaturated conditions, the characteristic time of mass transfer between mobile and immobile fractions is defined by $t_M = \frac{\theta_{im}}{k_M}$ [9], with θ_{im} the fraction of immobile water and k_M the mass transfer

coefficient. In our experiments t_M is of the order of 0.17 hour. As $t_a \gg t_M$, transport by advection in the mobile phase is the predominant process whatever the flow conditions. As $t_M \gg t_D$, mass transfer rate between the mobile and immobile region is the predominant process for broadening the BTCs (Table 1). Since dispersion is blurred by mass transfer resistance, the local equilibrium assumption does not hold.

Table 1. Characteristic timescales (in hours) of predominant processes involved in Sr and Cs reactive transport.

| | Reactor experiments | | Column experiments | | |
|-----------------------------|---------------------|------------|-------------------------------|------------------------------------|------------------------------|
| | Saturated | | Saturated | Unsaturated | |
| Solid/solution ratio (g/ml) | 1-0.21 | | 5.4 | 5.4 up to 11 | |
| Process | Sorption | Desorption | Advection (t_a) | Advection (t_a) | Mass transfer rate (t_M) |
| Strontium | < 0.17 | < 0.17 | 1.6-23 ($\theta = 0.34$) | 2-17 ($0.29 < \theta < 0.19$) | ~ 0.17 |
| Cesium | < 0.17 | > 20 h | 1 ($\theta = 0.32$) | 10 ($\theta = 0.16$) | ~ 0.17 |

Different miscible displacements experiments were performed to study reactive unsaturated transport. BTCs and profiles of caesium and strontium were successfully modelled with PHREEQC code using sorption parameters determined in SFTR study. The implicit assumption made here is that all the solid is in contact with water and that the reactivity of surface in contact with mobile and immobile water is the same. In other words, the proportion of sorption sites in contact with the mobile fluid to the total number of sorption sites is numerically equal to β . This assumption based on the nature of the Aeolian sand has been often made [10], [11]. The sand packed in the column is structure less and disaggregated. In this case there is no reason to suppose that the concentration of sorption site (X) in the immobile region of the soil is higher than the concentration of sorption site in the mobile region. The opposite statement was made by [12] for a synthetic porous medium containing reactive

micro-aggregates of clay minerals sorbents glued together. The cumulative grain size distribution of the Aeolian sand is monomodal, and scanning electron microscope was used to image sand particles that did not revealed the presence of clay micro-aggregates.

For strontium experiments, slight adjustments of most sensible sorption parameters (sorption site concentration, X^-) allowed us to match experimental data (Figure 3).

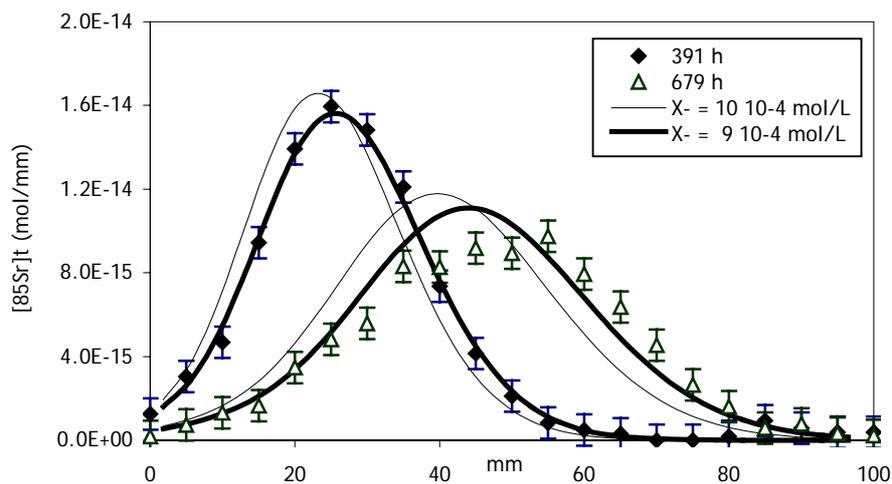


Figure 3. Sr concentration profiles along a sandy column under unsaturated conditions ($\theta = 0.16$) respectively 51 and 88 pore volumes after tracer injection. Experimental and calculated profile using MIM coupled with ion exchange model.

For caesium, a first order desorption kinetic has been implemented to better describe profiles along the saturated sand column (Figure 4) because advection timescale was smaller than reaction characteristic time (Table 1). In this case chemical non equilibrium is the predominant process that affects Cs transport.

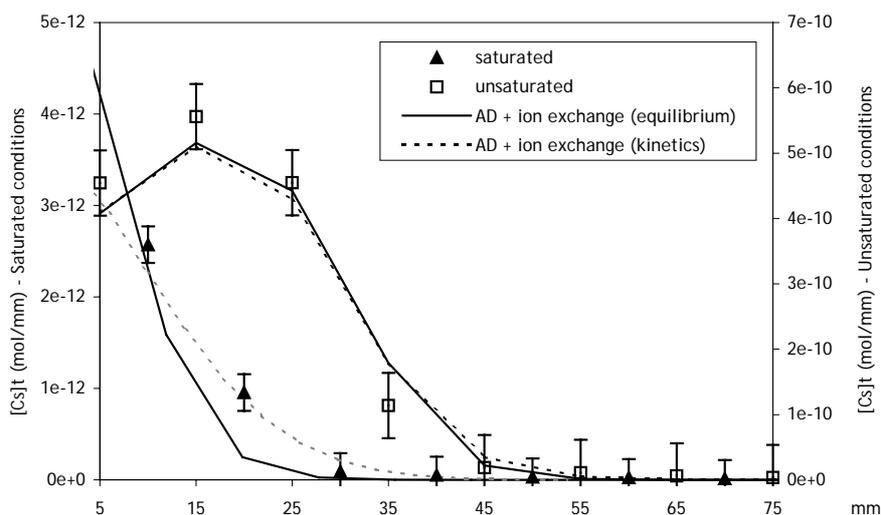


Figure 4. Cs concentration profiles in both saturated and unsaturated conditions ($\theta=0.17$). Measurement time: 87 pore volumes after tracer injection. Experimental and calculated profile using AD model coupled with ion exchange model and with first order sorption kinetics.

The analyse of characteristic times of sorption and transport phenomenon and the use of different experimental techniques show that non-linear sorption and non-equilibrium mass transfer between mobile and immobile region dominate the BTCs of strontium under unsaturated conditions. Non-linear sorption and sorption/desorption non-singularity dominate the BTCs of Cs whatever the water content especially for experiments with high pore water velocity (near saturation of the sand). In both cases, all parameter values had been determined previously in independent experiments under completely saturated conditions except k_M and β introduced in the MIM.

3. OPERATIONAL PARAMETERS AND SIMPLIFIED APPROACH

Previous results can help us to estimate operational parameters to describe transport in steady-state conditions. Because of non-ideal sorption properties of caesium, a simple model cannot be used. Thus distribution coefficient of Cs varies with time and space as a function of the pore water velocity that is also dependent of the water content under unsaturated conditions. However, the problem is different for Sr where sorption is instantaneous, reversible and perfectly described by the same ion exchange model under saturated and unsaturated flow conditions. Thus the same range of K_d values can be used to describe soil/solution interaction whatever the water content.

In simplified field model, a retardation factor R is often used to describe transport in saturated conditions. For strontium in our experimental conditions, a modified relation can be used to describe the transport in unsaturated conditions. The modified retardation factor R_{unsat} is defined as:

$$R_{\text{unsat}} = 1 + \frac{\rho_d}{\theta} K_{d,\text{sat}}(^{90}\text{Sr}) = \frac{T_s(^{90}\text{Sr})}{T_s(\text{water})} \quad (1)$$

with ρ_d , the mean soil bulk density, θ the mean water content, $K_{d,\text{sat}}(^{90}\text{Sr})$ the strontium distribution coefficient determined under the same conditions but at saturation of the porous medium, $T_s(^{90}\text{Sr})$ and $T_s(\text{water})$ the residence time, respectively for ^{90}Sr and water in the unsaturated zone.

In the case of CPS, stable strontium aqueous concentration is about $5 \cdot 10^{-6}$ mol/L containing traces of ^{90}Sr . From laboratories reactors studies, the K_d of strontium varied from 1 to 10 ml/g. Assuming a mean water content in the unsaturated zone of 0.2, the retardation factor may vary between 9.5 and 86.

In field tracer test and field activities measurements allowed to estimate the ^{90}Sr retardation factor $R_{\text{sat}}(^{90}\text{Sr})$ in the aquifer. The obtained value was $R_{\text{sat}}(^{90}\text{Sr}) = 12$ and the subsequent back calculated $K_{d,\text{sat}}(^{90}\text{Sr}) = 2$ ml/g, which is in the range of predicted laboratory experiments.

5. CONCLUSION

Different laboratory techniques were used to characterize the transport of caesium and strontium in both saturated and unsaturated conditions. Main parameters controlling transport in sandy soil columns were identified. Successful transport modelling using ion exchange model to describe sorption properties were performed in steady-state conditions. For strontium, a simplified approach using a modified retardation factor could be used to describe transport behaviour in unsaturated conditions.

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