ABSTRACT

Radioactive waste is generally classified as low and intermediate level waste (LILW) and high-level waste (HLW), based on their level of radioactivity and the time taken for decay. The low and intermediate level solid/solidified wastes are emplaced in near surface shallow land repository and are termed as Near Surface Disposal Facility (NSDF). A near surface disposal facility (NSDF) is proposed to be built at Kalpakkam, Tamil Nadu. Kalpakkam is situated about 70 km south of Chennai (12°33' N Lat and 80°11' E Long) along the east coast of India. Several of India's nuclear installations like Madras Atomic Power Station, Fast Breeder Test Reactor, Kalpakkam Reprocessing Plant and Indira Gandhi Centre for Atomic Research (IGCAR) are located in Kalpakkam. Typical reinforced concrete trench (RCT) for disposal of low and intermediate level nuclear waste have major portion of RCT being located below the ground surface and above the water table, i.e., in the vadose zone. Available studies on the mineralogical and physico-chemical characterization of clays at Kalpakkam nuclear plant site have not focused on the mineralogical, physico-chemical and hydraulic properties of soils in vadose zone. The physico-chemical properties of soils are important as they strongly affect the fate and mobility of radioactive contaminants in the sub-surface soil. The hydraulic properties of soils in the vadose zone differ from those in the saturated zone owing to dis-continuity in water filled voids that makes the flow path more tortuous; additionally presence of suction in soil voids renders gradient causing flow to vary with the soil moisture content. Strontium is the selected contaminant solute in this thesis as the waste inventory of proposed NSDF

at Kalpakkam shall predominantly contain radioactive strontium and cesium ions. The unsaturated (vadose) zone housing the buried portion of RCT is important as hydraulic characteristics (void ratio, degree of saturation, volumetric water content, suction and unsaturated permeability coefficient) influence the transport of moisture and thereby of the solute dissolved in the moisture to underlying groundwater table, upon breach of the RCT. The physico-chemical properties (pore water chemistry, cation exchange capacity of soils) of the vadose zone soil play significant role in solute transport by way of adsorption/ion-exchange and desorption of the contaminant. Given the significance of hydraulic and physico-chemical properties of the vadose zone soil in influencing solute transport and the lack of studies in this direction in the Indian context, the present thesis examined strontium adsorption and transport for soils obtained from the vadose zone region of proposed NSDF at Kalpakkam, Tamil Nadu, India from 2 pits (termed Pit 1 and Pit 2). Strontium adsorption studies by the NSDF soils were accomplished from batch and miscible displacement column experiments.

XRD analysis showed the presence of illite as the primary clay mineral in the NSDF soil samples. The total salinity in the pore water ranges from 680 to 5747 mg/L for Pit 1 and 342 to 1852 mg/L for Pit 2 samples. The significant variation in salinity of pore water from two adjoining pits (separation distance - 200 m) is attributed to heterogeneity in soil deposition/formation at the test site. Results of the pore-water extracts (pore-water extrusion) indicated that the cationic salinity of Pit 1 and 2 samples are contributed as Na > Ca > Mg > K ions. Chloride, sulfate and bicarbonate ions contributed to the anionic salinity of the pore water. Dissolution of halite mineral apparently contributes to sodium and chloride concentrations in pore water. The

calcium, magnesium, bicarbonate and sulfate ions in the pore water possibly evolve from dissolution of calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$] and gypsum ($CaSO_4$) minerals.

Strontium adsorption by the soil specimens obeyed second order kinetics and the rate is apparently influenced by the number of exchange sites available on soil surface and available strontium ion concentration in solution. Validation of second order kinetics was probed by fitting the experimental data into linear forms of second order equation. The strontium adsorption at equilibrium ranges from 2.42 to 2.64 mg/g for Pit 1 soil specimens and from 2.16 to 2.40 for Pit 2 soil specimens. The experimental maximum strontium adsorption of Pit 1 soil samples range from 2.44 to 2.69 mg/g, while for the Pit 2 soils range from 2.29 to 2.44 mg/g; the experimental values compare reasonably with theoretical values from second order equation. The second order rate constants range from 0.285 to 0.31 (g/mg.min) for Pit 1 soils and from 0.271 to 0.278 (g/mg.min) for Pit 2 soils.

Strontium adsorption by the Pit 1 and 2 soils also obeyed the Langmuir and Freundlich isotherms. The maximum sorption capacities (S_m) from Langmuir isotherms range from 2.21 to 3.41 mg/g for Pit 1 soils and from 2.11 to 2.35 mg/g for the Pit 2 soils as against the maximum adsorption values from experiments are 2.13 to 2.96 mg/g for pit 1 soils and 2.03 to 2.51 mg/g for pit 2 soils. The adsorption intensity values ranged from 0.5 to 0.07 for strontium adsorption by Pit 1 soils and from 0.34 to 0.05 for Pit 2 soils. Adsorption intensity values less than unity imply that strontium adsorption by the NSDF soils is favorable process; further, the larger adsorption

intensity values at lower initial strontium concentration implied that the adsorption is more favored at lower surface coverage.

The distribution coefficient for strontium adsorption by NSDF soils were examined for samples collected at 2 m depth from Pits 1 and 2 respectively. The tendency for strontium adsorption reduces with increase in Ca ion concentration. The distribution coefficient reduces from 27.2, 18.8 to 3.3 mL/g with increase in Ca ion concentration from 50, 100 to 600 mg/L for Pit 1 soil. Likewise, the distribution coefficient reduces from 23.2, 15.5 to 3.1 mL/g for similar increase in Ca ion concentration for Pit 2 soil. The distribution coefficient reduces from 25.7, 16.9, 10.6 to 6.8 mL/g with increase in Mg ion concentration from 20, 50, 100 to 150 mg/L for Pit 1 soil and reduces from 22.9, 14.6, 9.4 to 6.1 mL/g for similar increase in Mg ion concentration for Pit 2 soil. The distribution coefficient reduces from 34.5, 27.3, 23.8 to 16.4 mL/g with increase in Na ion concentration from 200, 300, 500 to 700 mg/L for Pit 1 soil and from 32.2, 26.1, 25.6 to 21.4 mL/g with similar increase in Na ion concentration for Pit 2 soil. Reduction in distribution coefficient for strontium adsorption in presence of Ca and Mg ions is attributed to the more favored adsorption of these divalent cations than strontium ions by the soil surface. Reduction in distribution coefficient for strontium adsorption in presence of Na ions is ascribed to the concentration effect, where owing to the large concentration of Na ions, the affinity of strontium adsorption by soil surface reduces.

Miscible displacement experiments brought out that 65 pore volumes were needed to attain breakthrough in absence of co-ions, while only, 29 - 30 pore volumes were needed in presence of co-ions. The cumulative strontium adsorption at

equilibrium (after passage of 29 - 30 pore volumes) in presence of co-ions correspond to 2.5 - 2.7 mg/g, while, 4.4 mg/g of strontium was adsorbed by the soil in absence of co-ions. Reduction in strontium adsorption in presence of co-ions leads to attainment of quicker breakthrough. In absence of co-ions and at equilibrium (represented by the cumulative strontium adsorption at breakthrough pore volumes), 10.1 meq/100 g of strontium is adsorbed by the soil, which corresponds to 67% of cation exchange capacity of the soil. Comparatively about 5.7 to 6.1 meq/100 g of strontium is adsorbed by the soil in presence of co-ions, which corresponds to 38% to 41% of cation exchange capacity of the soil.

The cumulative strontium adsorbed by the soils was further examined for reversible and irreversible adsorption. Calculations showed that 5.7, 4.4 and 5.5 meq/100 g of strontium ions are irreversibly adsorbed on passage of 500 mg/L strontium solution, 500 mg/L strontium solution + 25% strength pore solution and 500 mg/L strontium solution + 75% strength pore solution respectively. Comparatively, 4.2, 1.3 and 0.6 meq/100 g of strontium ions are reversibly adsorbed on passage of the same solutions. In terms of cation exchange capacity it emerged that 29 to 38% of the exchangeable sites are occupied by strongly adsorbed strontium ions, while, 4 to 29% of exchange sites are occupied by weakly adsorbed strontium ions. The results suggest that while the amounts of irreversibly adsorbed strontium are unaffected by the presence of co-ions in the permeant solution, the sites occupied by the weakly held strontium ions are increasingly affected by the presence of cationic co-ions in the permeant solution. Strong adsorption (on leaching by 0.005 M KNO_3 solution) occurs through formation of inner sphere complex, wherein one or more bonds are formed

between the adsorbed ion and that atoms on the colloid surface. Weak adsorption involves formation of outer sphere complex, wherein the water molecules surrounding the cation allow weak electrostatic interaction between the cation and the charged colloid surface.

The soil deposit at the proposed NSDF at Kalpakkam is characterized by 3.2 m thick vadose zone that is inclusive of 0.2 m capillary fringe. The volumetric water content and total suction of the 3 m thick vadose zone ranged between 0.16 (S = 38%) to 0.32 (S = 69%) and 54 to 342 kPa respectively. The sub-surface soil samples predominate in sand (62 to 71%) sized fraction. The unsaturated hydraulic conductivity of Pit 1 soil specimens range from a minimum of $1.08{\times}10^{-12}$ cm/s at S = 10% (θ = 0.044) to $3.1{\times}10^{-5}$ cm/s at S = 100% (θ = 0.45). The unsaturated hydraulic conductivity of Pit 2 soil specimens range from a minimum of $2.77{\times}10^{-16}$ cm/s at S = 10% (θ = 0.044) to $1.42{\times}10^{-4}$ cm/s at S = 100% (θ = 0.44). Diffusion coefficient for strontium migration through NSDF soil corresponded to $1{\times}10^{-6}$ m^2/s, while the molecular diffusion coefficient corresponded to $1.4{\times}10^{-8}$ m^2/s. The diffusion coefficient, velocity of groundwater flow in vadose zone and retardation factor suggested that presence of 3 m vadose zone leads to periods ranging from 500 to > 10000 years for attainment of strontium breakthrough concentration in groundwater (initial strontium concentration = 10 mg/L). In the absence of vadose zone, the strontium breakthrough concentration in groundwater would be attained in 0.09 to 0.8 year. The results of the study thus bring out the importance of maintaining vadose zone below the NSDF to substantially delay contaminant transport to groundwater so that short-lived radioisotopes (half-lives < 30 years) are rendered benign.