

TECHNETIUM MIGRATION EXPERIMENTS UNDER DEEP GEOLOGICAL CONDITIONS

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Technetium-99, one of the important long-lived radionuclides contained in high level radioactive wastes (HLW), is usually considered to be quite mobile in an aqueous environment. In its oxidized form (VII), technetium forms a highly soluble, anionic aqueous species that does not sorb significantly on minerals[1], clayey sand[2] and soils[3]. From actual field observations, technetium can be transported by groundwater through sand aquifer as TcO_4^- [4]. However, it has been suggested that technetium can be removed from solution by reduction of $Tc(VII)$ to $Tc(IV)$, and that ignoring this reaction can lead to an overestimation of the long-term hazardous nature of this isotope[5]. Generally, reducing conditions are expected at depth, due to the oxygen scavenging action of ferrous iron in geological materials.

In crystalline rock, migration is expected to occur predominantly in existing, water-bearing fractures. These fractures are invariably coated with alteration minerals. To study the mobility of technetium under the geochemical conditions that exist at depth, a migration experiment was carried out under similar or in-situ conditions. Highly altered granitic rock samples were obtained from a fracture zone at a depth of about 250 m in a Precambrian batholith and used in a column migration experiment. An experimental system was designed to maintain the original geochemical conditions of the geological material and the groundwater used in the experiments. This system was developed under a JAERI/AECL cooperative program, and was installed in an experimental room excavated especially for this experimental program at the 240 m level of the Underground Research Laboratory (URL) constructed near Pinawa, Manitoba, Canada.

EXPERIMENTAL

Granitic rock was obtained from the fracture zone at a depth of about 250 m. The rock was wet-crushed with a jaw crusher equipped with tungsten carbide jaws and then wet-sieved with groundwater from the fracture zone. The 180-850 μm fraction was selected for the migration experiments and used in columns. The column filling materials consisted of quartz, alkali feldspar, plagioclase feldspar, biotite, chlorite and trace amounts of magnetite. The groundwater used in the experiment was introduced into the column from the fracture zone without exposure to the atmosphere. The pressure of the groundwater supplied to the column was reduced to approximately 0.7 MPa. Flow through the column was controlled by a solenoid valve near the outlet of the column. The monitored values of the groundwater, $Eh=158mV$, $pH=9$ and $conductivity=1340\mu S/cm$ were virtually constant and showed no change in groundwater composition with time over the duration of the experimental period.

The column experiments were performed in an anoxic chamber in the experimental room. High-purity nitrogen gas was used to maintain an anoxic atmosphere within the glove box. The oxygen concentration in the glove box was maintained at less than 10 ppm by volume by constant purification of the gas. The column used in the experiment was made of stainless steel sized 2.54 cm in diameter and 20 cm in length. The internal surfaces of the columns were hard coated with Teflon^{TR}.

A volume of approximately 110 mL of groundwater containing tritiated water and technetium isotopes was injected in the column at a flow rate of 2 mL/h under a pressure of 0.7 MPa. To allow gamma spectrometry, ^{95m}Tc ($t_{1/2}=61d$) was used in addition to ^{99}Tc . The initial ^{95m}Tc and ^{99}Tc concentrations of the solution were 3.9×10^{-12} and 1.9×10^{-6} mol/L, respectively. After the injection of the tracer was completed, the flow was diverted