

Testing of New Technetium Selective Media TcTreat – 16497

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ABSTRACT

A new zirconium oxide based material TcTreat is under development and testing for the removal of radioactive oxoanionic species (Tc-99 pertechnetate, Ru-106 ruthenate) from solution.

INTRODUCTION

Oxoanionic radioactive species (e.g. ^{99}Tc -pertechnetate, ^{106}Ru -ruthenate and ^{125}Sb -antimonate) are highly mobile in environment and difficult to separate from solution by most conventional methods. Radioactive technetium and ruthenium occur in the waste of nuclear fuel reprocessing plants (NFRP), and ^{99}Tc and ^{106}Ru are often major radionuclides in the marine discharges from the NFRP [1]. The Tc-99 inventories in Hanford and SRS tank wastes are 26,000 Ci and 31,000 Ci, respectively [2, 3] and efficient methods are still sought for their separation of Tc-99 from the tank supernatant solutions. Large amounts of different radioisotopes of antimony, ruthenium and technetium were released in the Fukushima accident and they are obviously present in large quantities in the radioactive water stored in the Fukushima site [4].

While the abatement processes in the NFRPs have greatly improved during the past decades, they do not allow the “zero” level discharges that are highly desirable or even becoming mandatory for the radioactive discharges.

University of Helsinki and Fortum have developed a new zirconium oxide based material (SbTreat) for the removal of radioactive antimony [5], which like Tc and Ru, mostly occurs in oxoanionic form. SbTreat has been successfully tested for the removal of Sb-125 from effluents in Loviisa NPP (PWR, Finland) [6,7]. A related new Zr-oxide material “TcTreat” is under development. It has been tested for ^{99}Tc uptake from common salt solutions sections.

EXPERIMENTAL

Static batch experiments were carried out to measure the distribution coefficients (k_d) of ^{99}Tc for TcTreat in NaNO_3 , NaCl , $\text{Ca}(\text{NO}_3)_2$, Na_2CO_3 and Na_2SO_4 solutions of different concentration (0.01-3 .0 M) that were traced with ^{99}Tc . One set of experiments was carried out in 1.0 M NaNO_3 solutions adjusted to different pH-values (2-12) with NaOH . The experiments were carried out by contacting 20 mg of TcTreat material with 20 mL of solution for 3 days. Thereafter the solution was centrifuged and filtrated with a 0.2 μm disc filter and counted for ^{99}Tc activity using a low-background

1220 Quantulus[®] liquid scintillation counter. The distribution coefficient, k_d for ⁹⁹Tc was calculated from:

$$k_d = \frac{{}^{99}\text{Tc concentration in solid}}{{}^{99}\text{Tc concentration in solution}} = \frac{A_0 - A_{eq}}{A_{eq}} \frac{V}{m} \quad (\text{Eq. 1})$$

where A_0 and A_{eq} are the activity concentrations of ⁹⁹Tc (Bq/L) in solution before and after contact with the solid material, respectively. V is the solution volume (20 mL) and m is the mass of TcTreat (0.020 g) contacted with the solution.

In general, the distribution coefficient for an ion exchange reaction between ions A and B (with charges z_A and z_B) can be expressed for trace ion A as [8]:

$$\log K_D = \log(k_{A/B} [Q]^{z_A}) - \left(\frac{z_A}{z_B} \right) \log[B] \quad (\text{Eq. 2})$$

where $k_{A/B}$ is the selectivity coefficient of A/B exchange, Q is the total ion exchange capacity and $[B]$ is the concentration of ion B ($[B] \gg [A]$ in case A is present at trace level).

RESULTS

Regarding the pH of the solution, the uptake of ⁹⁹Tc in TcTreat from 1 M NaNO₃ had a very broad maximum between pH = 4-10. The level of uptake was very high, the values of k_d being in the range of 500,000 ml/g (Fig. 1). The uptake was however reasonably high also in mildly alkaline solution ($k_d = 30,000$ ml/g at pH = 12) and in mildly acidic solution ($k_d = 80,000$ ml/g at pH = 2).

The increasing salt content had a decreasing effect on ⁹⁹Tc uptake (Fig. 2). In the carbonate solution (Na₂CO₃), the ⁹⁹Tc uptake was much lower than in other salt solutions. This is probably due to the complexation of technetium with carbonate ions in the solution. In the case of nitrate solutions, the slopes $\log k_d$ vs. $\log C$ (Eq. 2, Fig. 2) are close to -1, which is an indication of uni-univalent TcO₄⁻/NO₃⁻ anion exchange. In cases of sulphate and carbonate, the slopes were close to -0.5 pointing to uni-divalent TcO₄⁻/SO₄²⁻ and TcO₄⁻/CO₃²⁻ anion exchanges.

With the exception of Na₂CO₃ solution, even in the 1.0 M salt solutions ⁹⁹Tc uptake was high. The values of k_d being in the range of 100,000 ml/g and above.

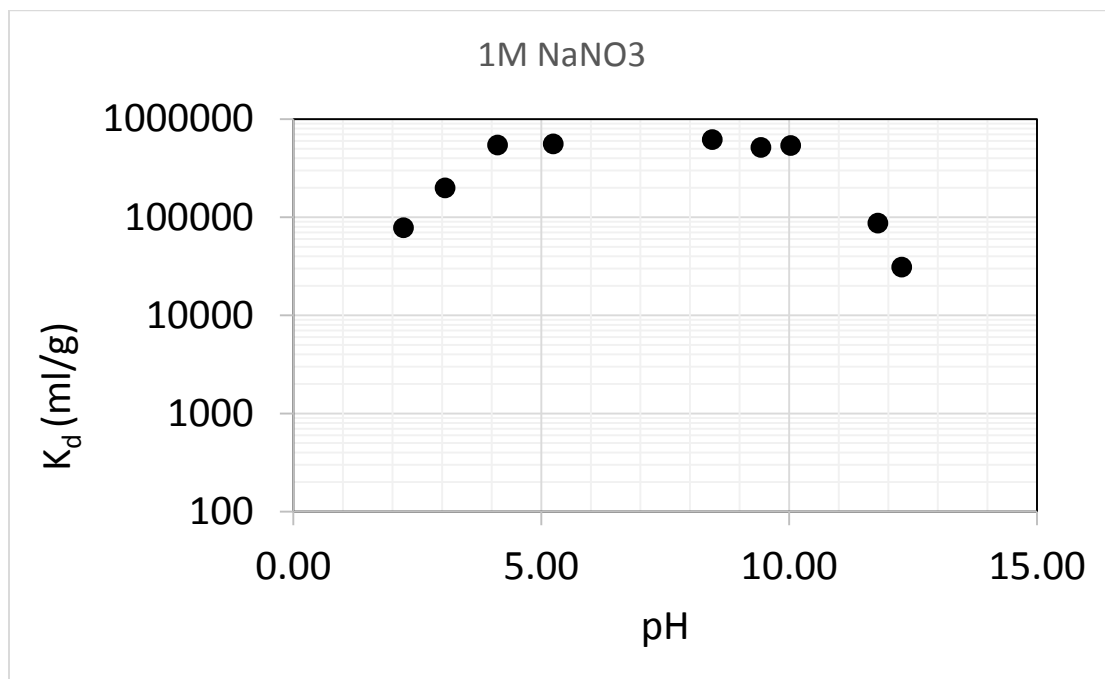


Figure 1. Uptake of ⁹⁹Tc in TcTreat from 1 M NaNO₃ as a function of solution pH

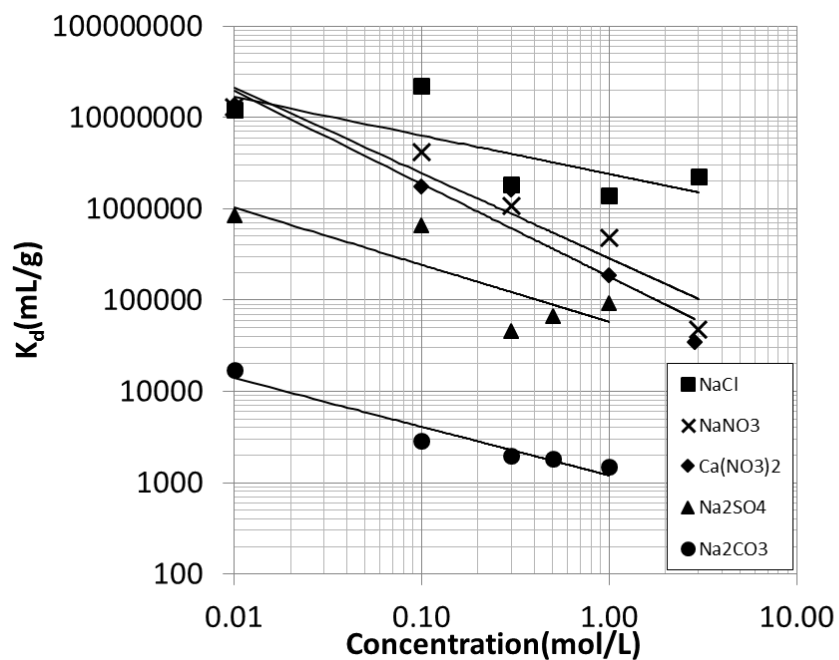


Figure 2. Uptake of ⁹⁹Tc in TcTreat from different salt solutions as a function of salt concentration

CONCLUSIONS

TcTreat exhibited a very high ^{99}Tc uptake over a broad pH-range of 4-10 and the uptake was reasonably high also in mildly alkaline and acidic ranges. Nitrate and sulphate had a decreasing effect on ^{99}Tc uptake but it was still strong ($k_d = 100,000$ ml/g and above) even at 1 molar concentrations.

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