II. 2. Variation of Pertechnetate Ion Adsorption on Activated Carbons from Different Sources

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Technetium-99 is counted among isotopes presenting promise of useful applications in the near future, and this calls for the establishment of a practical method for extracting Tc from its source, which is high-level liquid waste (HLLW) discharged from nuclear installations 1). For practical application, the beta-decay half-life of $^{99}$Tc amounting to 210,000 y could be found inexpediently long, but this nuclide can be converted by nuclear reaction into other isotopes of much shorter life 2).

A practical method can be ensured by adsorbing onto activated carbon the TcO$_4^-$ contained in the HLLW before solidification. Activated carbon can be derived from various organic sources, and the choice of source material will influence the capacity of the activated carbon to serve its purpose of adsorbing TcO$_4^-$. The present study is aimed at obtaining basic information to serve in selecting the activated carbon to be used, and in optimizing the conditions for the separation of Tc from HLLW.

Adsorption runs were performed applying the method of experiment described in previous paper 3), which also outlined the procedure adopted for producing $^{95m}$Tc. The adsorption equilibrium experiments onto activated carbon were carried out in systems containing solutions of HNO$_3$ and its sodium salt. Fig. 1 compares the four samples of activated carbon derived from different sources 4). In the case of activated carbon from coconut shell (open square symbols in Fig. 1), the acidic region toward left is marked by a rise of Kd with decreasing pH. This behavior is attributable to quickened removal of TcO$_4^-$ in the acidic region 3), with the adsorption onto activated carbon supplement by TcO$_4^-$ reaction with oxonium ions 3) generated by interaction of H$^+$ with the functional groups of activated carbon. Immediately adjoining this acidic region toward right is a stretch around neutral pH 7 that forms a level stage, created by the balance of competition for adsorption onto activated carbon between TcO$_4^-$ and the relevant anion; this is followed further toward right by the basic region of declining K$_d$, where TcO$_4^-$ adsorption comes to be outdone in its competition with OH$^-$. The rise of K$_d$ with increasing acidity noted above for activated carbon from coconut shell has been similarly observed in other runs made with activated carbon from oil pitch
(open triangle), but in the case of activated carbons from coal and bone (closed and open circles), the plots failed to rise in this region.

The foregoing findings would indicate that the activated carbons from coconut shell and oil pitch would be superior to activated carbons from coal and bone for adsorbing Tc from HLLW solutions.

With systems containing 2 M or higher (H, Na)NO₃ (all plots except square, for 1 M (H, Na)NO₃ in Fig. 2), a drop in K₄ distinctly falls beyond a peak that is attained at around pH 0.5, which would thus be indicated as the optimum acidity for adsorbing Tc from a nitric acid system.

In practice, HLLW normally takes the form of an HNO₃ solution of around 3 M concentration (3). This concentration could be lowered down to the above optimum level of pH 0.5 by denitrification to decompose part of the NO₃⁻, or else by partially neutralizing the HNO₃.

The adsorption curves for Cs and Eu ions are shown in Fig. 3 for activate carbon from coconut shell in a 2 M HNO₃ system. Cesium is seen to have presented very low Kd values throughout the entire range covered from 2 M to pH 12; europium has shown a similar behavior in the range below 1 M HNO₃. Above pH 2, Eu cations appear to be adsorbed on the carboxyl group of the surface oxide covering the activated carbon. From the above, it would appear possible to separate TcO₄⁻ from Cs and Eu ions by adopting an HNO₃ system of acid radical concentration of around pH 0.5, which should provide the optimum condition for eliminating Tc from HLLW containing Cs and Eu ions.

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References

4) Ito K., The Third International Conference on Nuclear Fuel Reprocessing and Waste Management, Apr. 16 (1991), Sendai, Japan
Fig. 1. Distribution coefficient $K_d$ of Tc between activated carbon from various sources and 1 M (H, Na)NO$_3$ solution related to pH of solution adjusted by NaOH solution 50 ml TcO$_4^-$ solution, 0.1 g activated carbon: activated carbon from coconut shell: activated carbon from oil pitch: activated carbon from coal: activated carbon from bone.

Fig. 2. Distribution coefficient $K_d$ of Tc between activated carbon from coconut shell and HNO$_3$ of various concentration related to HNO$_3$ concentration and to pH of solution 50 ml TcO$_4^-$ solution, 0.1 g activated carbon from coconut shell: 1 M HNO$_3$: 2 M HNO$_3$: 3 M HNO$_3$: 4 M HNO$_3$.

Fig. 3. Distribution coefficient $K_d$ of Tc between activated carbon from coconut shell and HNO$_3$ solution of various concentration related to HNO$_3$ concentration and to pH of solution 48 ml TcO$_4^-$ solution, 0.1 g activated carbon from coconut shell: Cs: Eu.