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Introduction. An overview of work done on the development of three electrochemical processes that meet the specific needs of low-level waste treatment is presented. These technologies include: mediated electrochemical oxidation [1-4]; bipolar membrane electrodialysis [5]; and electrosorption of carbon aerogel electrodes [6-9]. Design strategies are presented to assess the suitability of these electrochemical processes for specific applications.

Mediated electrochemical oxidation. Mixed wastes include both hazardous and radioactive components. It is desirable to reduce the overall volume of the waste before immobilization and disposal in repositories. While incineration is an attractive technique for the destruction of organic fractions of mixed wastes, such high-temperature thermal processes pose the threat of volatilizing various radionuclides. By destroying organics in the aqueous phase at low temperature and ambient pressure, the risk of volatilization can be reduced. One approach that is attractive is the use of electrochemically generated mediators such as Ag(II), Co(III) and Fe(III). These oxidants react with organics in the aqueous phase, converting the carbon to CO_2. The mediators are reduced, and have to be regenerated by anodic oxidation. We have found that the anodic oxidation is mass-transport limited. Limiting currents have been determined with rotating cylinder electrodes. Organic oxidation occurs via a number of intermediates, which includes aldehydes, ketones, and carboxylic acids. In cases involving nitric acid electrolytes and aromatic compounds, nitro compounds have been found. When possible, intermediates have been identified with GC-MS. Such results have been used as the basis for designing and constructing pilot scale equipment. The design strategy for this process will be reviewed.

Bipolar membrane electrodialysis. In the aqueous processing of nuclear materials, process steps arise that require the neutralization of an acidic stream with a strong base. Ultimately, these neutralized salt solutions become aqueous waste streams, requiring further treatment and disposal. By "splitting" such neutralized salt solutions into their acid and base components, the generation of aqueous mixed waste can be greatly reduced. At LLNL, a bipolar membrane electrodialysis cell has been used to separate neutral solutions of NaCl, $NaNO_3$ and Na_2SO_4 into product streams of NaOH, HCl, HNO_3 and H_2SO_4, which could be recycled. The efficiency of this particular process will be discussed, as well as practical limitations of the technology. Basic principles of engineering design of such systems will be reviewed.

Electrosorption on carbon aerogel electrodes. An electrically-regenerated separation process has been developed for removing unwanted ions from aqueous waste streams as a minimally-polluting, energy-efficient, and potentially cost-effective alternative to ion exchange, reverse osmosis, electrodialysis, and evaporation. Ground water containing various anions and cations are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area and exceptionally low electrical resistivity. After polarization of the stack, impurity ions are removed from the electrolyte by the imposed electric field and adsorbed on the electrode surfaces. Field tests have shown that hexavalent chromium in the form of $HCrO_4^-/CrO_4^{2-}/Cr_2O_7^{2-}$ can be selectively removed from contaminated ground water with substantial total dissolved solids (TDS). The concentration of Cr(VI) can be lowered to levels well below the acceptable level for the regulatory surface water discharge limit of ~ 11 ppb. The mechanism for Cr(VI) separation involves chemisorption on the carbon aerogel anode, a process that can be reversed by cathodic polarization. Cr(VI) removal is not based upon simple double-layer charging. It is believed that the selectivity for chromium observed during this investigation is due to complexation of the oxygen-containing chromium ions with various functional groups on the carbon surface. In additional to carbonyl groups, the carbon surface may also have hydroxyl groups. The exact nature of the comlexaton is not well understood, though it is assumed to involve formation of a weak bond between the Cr, O or H atoms in the ion with C, O or H atoms in the surface. A strategy for the design of such electrosorptive systems is presented.

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