

Technetium removal from alkaline active liquid wastes

Background

Under normal aerobic conditions, Tc exists as the soluble TcO_4^- anion, which is able to migrate through porous rock/clay as it does not adsorb on such media. Disposal of simple immobilised wastes is therefore unacceptable. Also due to the volatility of TcO_2 , Tc containing wastes are unsuitable for high temperature immobilisation processes. If Tc could be removed selectively from Tank Supernates, it would enable disposal of the latter as low-level waste.

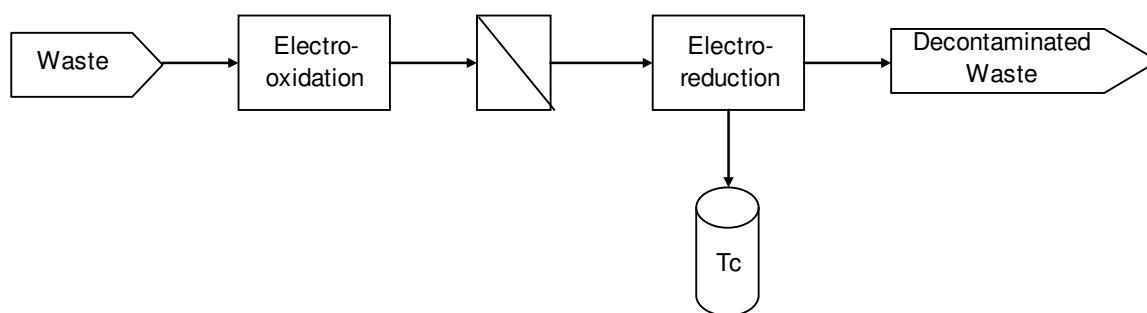
While Tc can be recovered by adsorbent/ion-exchangers, these are limited in their effectiveness ($\text{DF} < 4$) – thus preventing the decontamination factor target being achieved. Accentus Tc recovery technology is able to overcome these difficulties to achieve DF's of $15 > 200$.

Process objective

The goal of the Accentus process is to recover and separate Technetium from liquid wastes – including alkaline wastes high in dissolved nitrate salts. This can either be in the form of a solid (Tc/TcO_2) that could then form part of an encapsulated waste package, or else could be recovered as a concentrated liquid for separate treatment for disposal. The process is protected by US patent.¹

Process overview

Wastes low in organics can be treated directly by electroreduction at a high surface area cathode in a flow-through electrochemical cell. The TcO_4^- anion is reduced to TcO_2 and then to Tc – both of which are insoluble. Re-dissolution is prevented by retaining a protective negative potential. After completion of deposition, the cell can be drained of the feed solution and immobilised. Sacrificial metal components in the cell design are then able to retain this anaerobic condition within the waste package into geological disposal.



If organics are present in the waste, a pre-oxidation step (e.g. at the separated anode of the cell) mineralises these – thus deactivating their complexing power – and releasing the Tc for

¹ US 5,894,077 (April 13, 1999) Radioactive effluent treatment Jones, Fennell, Fletcher.

electroreductive removal. Normally the waste would then be filtered prior to the Tc electroreductive stage to prevent cell fouling.

If the waste also contains chromate, the selection of alternative cathode materials is able to allow reduction to Chromic ions, while at the same time enabling deposition of insoluble TcO₂ on the electrode. If desired, Tc recovery can then be achieved simply by re-dissolving in a dilute acid under mild oxidizing potential control. Further purification from any cationic content is then possible by a conventional electro-dialytic separation process.

Co-decontamination

Ru is also removed by the Accentus process – giving similar significant Decontamination Factors. If additional elemental decontamination is required (e.g. for iodine), this can normally be achieved by simple modification of the overall process flow sheet – e.g. by seeding the stream with selective absorbers prior to the filtration step, or as a conventional IX/adsorber column.

Experience

Bench-scale work has been conducted at Harwell and Sellafield by Accentus on both synthetic and genuine Medium Active Liquid Waste Concentrates (pH 10.5) – the latter in collaboration with BNFL. Additional pilot scale work has also been carried out by BNFL on full-scale flow cells. Volume reduction factors of >1000 and DFs of >35 were achieved.

In addition, as part of the TWRS programme, synthetic and genuine Hanford tank wastes were treated by the process at Harwell at bench-scale. The target DF of 5 was easily exceeded in tests on all tank waste types – with typical DFs of 10->40.

Status of demonstration/development

The process principles have been demonstrated with genuine wastes, and inactive pilot-scale work has demonstrated the scalability of the process, using conventional industrial units.

While BNFL were involved initially in a joint study (1995-6), and LMAES in the TWRS programme (1997), the process has not as yet been commercialised.

There has been no contact with Cogema to date.