Computer simulation of technetium scrubbing in PUREX systems

Shekhar Kumar* & S B Koganti
R&D Section, Reprocessing Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, 603 102, India.

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Technetium interferes in reductive partitioning of uranium and plutonium by catalysing destruction of hydrazine, a stabiliser added to prevent oxidation of U(IV) by nitrous acid. In this communication, computer simulation results of technetium removal step by using a high acid scrub have been compared with the results from a published flowsheet.

Consumption of uranous nitrate reductant is observed to be more than stoichiometric requirement during reductive partitioning of uranium and plutonium. Many researchers have investigated this problem. It was further established that cyclic reactions causing oxidation of process reactant U(IV) and product Pu(III) were influenced by several operational factors like place of reductant introduction in the cascade, aqueous HNO₃ concentration and temperature. Presence of fission product technetium, even in trace amounts, was found to accelerate the rate of destruction of "holding" reactant hydrazine leading to increased oxidation of reductant U(IV). Technetium was reported to be extracted significantly in HA cycle inspite of its low distribution coefficient. A value of unity for OF₇₆ was reported by Garrawal as well as Oenniss and Phillips. It was reported that extraction of technetium was enhanced by increased organic uranium loading as well as amount of Zr extracted into organic phase. Several mechanisms suggesting co-extraction of technetium (in several forms) along with uranium and zirconium were reported.

In LWR/PWR/FBR fuels, at high burn-up the amount of technetium is quite significant. Fission product technetium is estimated to be present in gram/kg-HM quantities in irradiated FBTR fuel. Thus, study of technetium behaviour during partitioning operation is of interest.

* For correspondence

Modelling of technetium behaviour in HA cycle

Technetium behaviour in the PUREX process conditions is quite complex. It can be extracted separately as well as in the form of pertechnetate TeO₄⁻. Presence of uranium, Pu or Zr significantly enhances technetium extraction. Garraway and co-workers reported the effect of other elements (Sr, Zn, U, Ce(IV), Mg, Pd, Co, Zn, Ca and Sc) on the extractability of pertechnetate. Kolarik and Dressler suggested extensive numerical models for extraction of technetium in presence of Zr, uranium and plutonium. For technetium extraction a basic DT₆ was proposed which was based on "free TBP" (TBP₅₅ : TBP₇₇₇₇₉₇) and aqueous acid concentration. In presence of uranium, plutonium and Zr, related factors causing enhancement in distribution over this basic DT₆ were proposed. In this scheme, interaction of U, Pu and Zr with technetium is well-accounted. This approach has been integrated in the in-house developed simulation code SIMPSEX (SIMulation Program for Solvent EXtraction).

Options for minimising destructive action of technetium

Action of technetium in partitioning can be minimised by two ways:

- Process parameters can be suitably altered to limit the rate of hydrazine destruction. This route is possible primarily due to the work done by researchers at Sellafield. Denniss and Phillips gave a detailed description of the improvements in the process. This scheme is implemented in IBX partition cycle at THORP. By changing the mode of operation of the partition column to solvent continuous and optimisation, effect of technetium was minimised in active trials in a scaled process unit.

- By using a high acid scrub to backwash technetium into aqueous phase prior to partitioning. This option is primarily due to the French efforts, mainly by Boullis and co-workers. In this option a high acid scrub (typically 5 kmol.m⁻³) is used to backwash technetium from the loaded organic phase (solvent product from HA contactor assuming partition in IBX). Loaded uranium and plutonium are not affected because of high acidity of the scrub. Technetium scrubbing is affected mainly by decreased metal loading (due to additional solvent.
input from organic scrub). This operation is required to be performed only after scrubbing the loaded organic phase with a moderate acidic scrub otherwise DF₂ will be degraded. Miles¹⁴ reported technetium scrubbing from a moderately loaded organic stream (30% TBP, uranium 85 gL⁻₁ and technetium 92.4 mgL⁻¹, 65% solvent utilisation). A battery consisting of 12 stages was used. For technetium, only end concentrations were reported in a qualitative fashion i.e., 98% removal in the aqueous waste. Stage profiles were not reported. Operating conditions are shown in Fig. 1.

**Computer simulation of technetium scrubbing**

In computer simulation of technetium scrubbing step using SIMPSEX, operating conditions reported by Miles were adopted and operating temperature was assumed to be 298 K. Stream flow rates were reported constant even after extraction. Given, concentrations in the exit streams were calculated by mass balance using reported stream flow-rates and qualitative rejection. To make a comparison, simulated concentrations were corrected for the reported stream flow rates.

On comparing the given, and simulated values it was observed that simulated technetium concentrations in the exit aqueous and organic streams were 72.44 mgL⁻¹ and 1.75 mgL⁻¹ against reported 72.04 mgL⁻¹ and 1.47 mgL⁻¹. Thus, a good agreement between simulated and given values was observed. Technetium mass balances for given and simulated end concentrations were 99.986% and 99.837% respectively which were also in good agreement. Fig. 1 shows simulated technetium stage profiles for aqueous and organic phases.

**Application to FBTR fuel reprocessing**

Composition of the first core of FBTR is 30% U + 70% Pu³⁹. It is proposed to dilute this feed with uranium to achieve a feed composition 70% U + 30% Pu. For a burn-up of 50 GWdTe⁻¹ and 120 day's cooling, estimated technetium concentration in HAF (72 gL⁻¹ up) will be around 75 mgL⁻¹. Thus if partitioning is desired, results of simulation work reported in this paper can be readily extended for FBTR fuel reprocessing.

**Conclusion**

A published flowsheet for technetium removal was successfully simulated by computer code SIMPSEX. If required, these results can be extended for technetium removal in U70% + Pu30% flowsheet prior to partitioning step.

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**Nomenclature**

- **BWR** = Boiling Water Reactors
- **DF** = Decontamination factor
- **FBR** = Fast Breeder Reactors
- **FBTR** = Fast Breeder Test Reactor
- **HA** = Highly Active Cycle of PUREX Process
- **LWR** = Light Water Reactors
- **PUREX** = Plutonium Uranium EXtraction process
- **THORP** = Thermal Oxide Reprocessing Plant (BNFL, Sella Field)

**References**
