TECHNICAL SESSION II – SUMMARY
Progress in Partitioning and Waste Forms

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Papers presented: **19**

Overview (*J-P. Glatz*):

Regarding MA partitioning, major progress was presented by U.S., Russia and Japan.

In Japan a simplified PUREX is proposed with co-extraction of U, Pu, Np to be combined with

- TRUEX where salt-free reagents such as hydroxylaminenitrate are used to reduce waste volumes;
- TODGA in the so called ARTIST process aims at discrimination between tetra- and hexavalent Ans;
- Pyroprocessing where large scale deposits of Pu-MA by electrodeposition in liquid Cd and engineering scale casting of Zr based fuels are tested.

In Russia the DOVITA process initially foreseen to fabricate FR fuel by the vibropack technique is now extended to MAs. Irradiation of Np and Am fuels are irradiated and should be extended to higher MAs. Reprocessing of the MA fuels seems to be still somehow problematic.

In the US P&T developments are driven by the wish to avoid in any case the construction of a second spent fuel repository. A dual tier strategy is proposed. In the first tier Np/Pu are recycled in LWRs, in the second tier remaining Np/Pu and other MAs are burned in a fast spectrum combined eventually with ADS. Reprocessing includes DIAMEX/SANEX for MA separation and also Cs/Sr separation. A decision on the process scheme should be made in 2006 and deployment is expected for 2015.

As far as the problematic An/Ln separation is concerned, the following progress was made:

- For aqueous techniques
  - Two of the most promising molecules were compared at FZK-INE. A slightly better performance of BTP over derivates of DTPA was found, the latter has however a better transfer rate. A new small hollow fibre module gave a good separation from Ln with a recovery rate better than 99.95%.
  - At ITU it was shown that a direct selective extraction of MAs from the PUREX raffinate is possible.
  - In CEA derivates of BTP were synthesised with very good hydrolysis stability, glycolic acid improves significantly the back extraction. Only the radiation stability needs to be further improved.

- For the pyro-techniques
  - The use of solid cathodes (Al) allows to achieve an efficient Ln/An separation due to larger differences in the electrodeposition potentials in comparison to liquid Cd or Bi cathodes. Basic thermodynamical and electrochemical data should further enhance the performance of these processes.

The problem of long-lived fission products was addressed several times during the meeting. A flowsheet optimisation, i.e. in the TRUEX process, is proposed. Also new techniques and technologies such as catalytic electrolytic extraction could solve the problem without producing secondary wastes.

If metallic pyroprocessing and oxide fuels are selected in a P&T strategy, conversion processes are required. LiO_2 is one solution proposed, in the future direct electroreduction could be a promising alternative. Fluoride volatilisation of U is completed by electrodeposition in view of a molten-salt reactor development. Alternatives are F_2 and HF; direct solid-gas interaction seems to be more efficient.

As far as the waste issue is concerned, it has to be addressed whether partitioning and transmutation or partitioning and conditioning are adopted. Pyrochlores are proposed as host materials for both MAs and long-lived fission products.

The clean-up of molten-salt after pyroprocessing could happen through a pyrohydrolysis process using the vacuum distillation technique. The process was demonstrated using a Zr surrogate as stand-in material for MAs.

Finally one should mention the safeguards issue, which was briefly discussed during the session. It became evident, that for advanced aqueous and especially pyro-techniques new safeguard regimes have to be developed. In general the tendency is even for the PUREX process to make the schemes less attractive to proliferation, knowing well that an absolute proliferation resistance does not exist.

Technical paper summary (*J. Laidler*):

Dr. Shishalov of SSC/RF-RIAR presented a paper describing progress over the past ten years in the DOVITA programme. This system utilises the Dimitrovgrad Dry Process (DDP) for spent oxide fuel treatment and a vibratory compaction method for recycle fuel fabrication. Dr. Shishalov presented a wealth of information regarding recycle fuel performance and experimental details. The recycle fuel tested has included both (U, Pu)O_2 and (U, Pu, N_p)O_2, and irradiated fuels from both BOR-60 and BN-600 have been processed. A number of fuel rods totalling about 25 kg HM have been recycled to the BOR-60 reactor.

Dr. Yokoo of CRIEPI (Japan) described their work with recovery of uranium and plutonium from a simulated LiCl-KCl salt mixture, using a liquid cadmium cathode. They have progressed to the point at which the actinide solubility in Cd has been exceeded, a very important step in establishing an industrial-scale electrochemical process for metal fuel treatment. He observed the formation of Ucd_{II} and $PuCd_6$ intermetallics and reached 50 wt.% concentration of heavy metal in the cadmium. He also described CRIEPI work with the injection casting process for metal fuel slugs, showing that multi-use of quartz molds has been achieved with acceptable dimensional variances in the fuel slugs.

Dr. Laidler of ANL described the U.S. programme for advanced separation technology development under the scope of the new Advanced Fuel Cycle Programme. He showed that the programme has two major elements, one directed toward the treatment of commercial LWR spent fuel

by 2015 and the other related to the ultimate elimination of minor actinide residues, for the purpose of radiotoxicity reduction. Both programme elements are integral to facilitating spent fuel management in the U.S and together are expected to preclude the need for a second geologic repository. This concern, together with the large number of LWR plants in operation, tend to drive the U.S programme.

Dr. Glatz of the JRC of the EC discussed work at the ITU on the treatment of high active raffinate (HAR). The DIAMEX-SANEX combination of aqueous processing is successful at recovering 99.9% of the Am and Cm in the HAR, and the work has been extended to consider volume reduction of the HAR to produce a High Active Concentrate (HAC) that will enable the use of more compact, and hence less expensive, process equipment. He showed that it is essential to control the concentration factor (CF) to avoid the precipitation of Mo, Zr and lanthanide fission products. He also described what may prove to be a breakthrough in electrochemical separations. Rather than achieve improved separations by adjusting the electrolyte composition, the JRC group obtained a broader voltage discrimination band by varying the composition of the cathode. Using an Al cathode, they were able to achieve good uranium purity in the deposit.

Dr. Hirano of JNC described their research with the SETFICS variation of the TRUEX process, and Dr. Jun-Bo Shim of KAERI discussed excellent and extensive cyclic voltammetry studies aimed at clarifying the behaviour of the lanthanides Nd and Gd in a FLINAK salt.

The KAERI group reported on some valuable insights into the mechanism for electrochemical reduction of UO_2, in a LiCl salt containing a small amount of Li_2O. When lithium oxide contacts UO_2 in the cathode crucible, Li_2O is reduced to metallic lithium and the Li reacts with UO_2 in a replacement reaction to produce metallic U. Reasonable conversion efficiencies have been achieved, but a number of materials issues (both anode and cathode) have been identified. Pyrolytic carbon seems to be a good choice for the cathode.

The Nuclear Research Institute of the Czech Republic is working on an electrochemical process that they propose to use as a supplement to the fluoride volatility process for removal of residual uranium from PWR or FR spent fuel, using FLINA and FLINAK electrolyte salts.

A team from FZK reported on some specialised extractions at very small scale using miniature hollow polypropylene fibers, as a continuation of work reported two years earlier at the Madrid meeting. The miniaturisation allowed them to work with very small fluid volumes, and they obtained excellent Am-Ln separation with BTP in a surrogate Am-La-Gd-Y acid solution.

Dr. Tachimori and colleagues at JAERI described the ARTIST process, which uses advanced amide-based extractants to separate actinides from fission products. The separation produces two streams, U- and TRU-bearing phases that are then solidified and stored for future treatment.

Dr. Fujii and his co-workers from Kyoto University described work with the TRUEX process, evaluating extraction performance as a function of the acidity of the feed solution.