Application of Advanced Head End Reprocessing Concepts to a Fluoride Volatility Flowsheet

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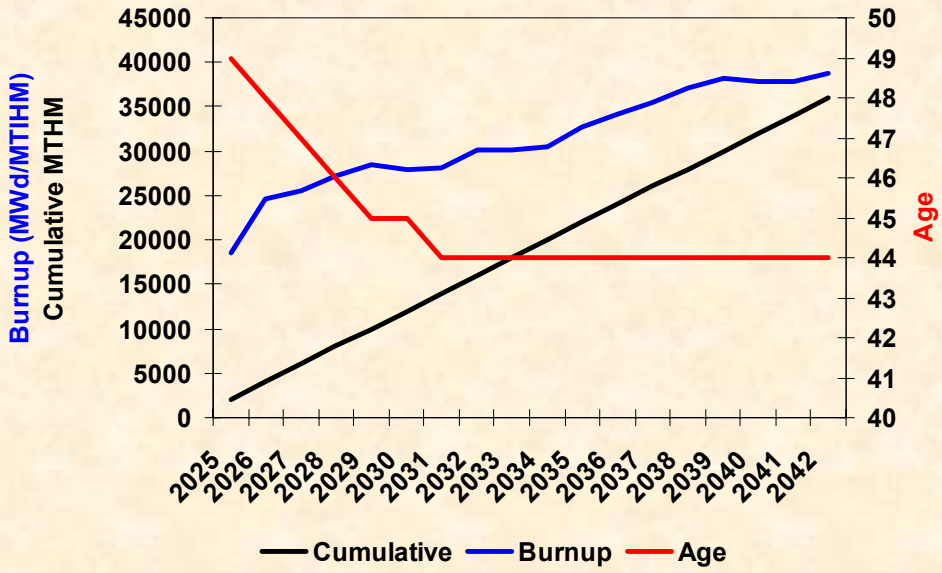
Background

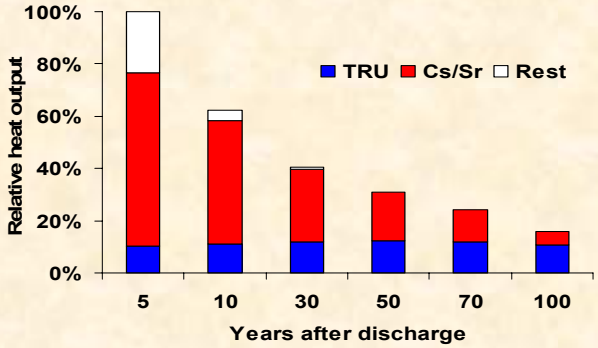
- If direct disposal of spent fuel is done, existing and near-future US spent fuel inventory (to FY 2010) can fill the Yucca Mountain repository
- Major motivation for fuel reprocessing is to reduce volume and heat load sent to the repository, extending its lifetime
- US DOE AFCI program: main reprocessing focus is on aqueous and pyrochemical processes
- *BUT*… AFCI is interested in maintaining awareness of potential alternatives
- We are looking at possible advanced processes based in whole or in part on fluoride volatility

Context

- US existing and near-future spent fuel inventory will be aged for decades before processing, assuming that fuel is processed "oldest-first"
  - Initial reprocessing plant can operate its entire lifetime using fuel aged > 40 years
  - Early processing will be on lower burnup fuel



- Short-half-life FPs are of less concern in this scenario than they are for short-cooled fuel



Fluoride Volatility

- **Fluoride volatility advantages**
  - **Up-front separation of uranium as UF_6 for reenrichment and reuse**
  - **Co-separation of neptunium and plutonium from fission products**
  - **Relative simplicity**
  - **High decontamination factors**
  - **Less secondary waste than aqueous methods**
  - **Amenable to very large industrial-scale operations**

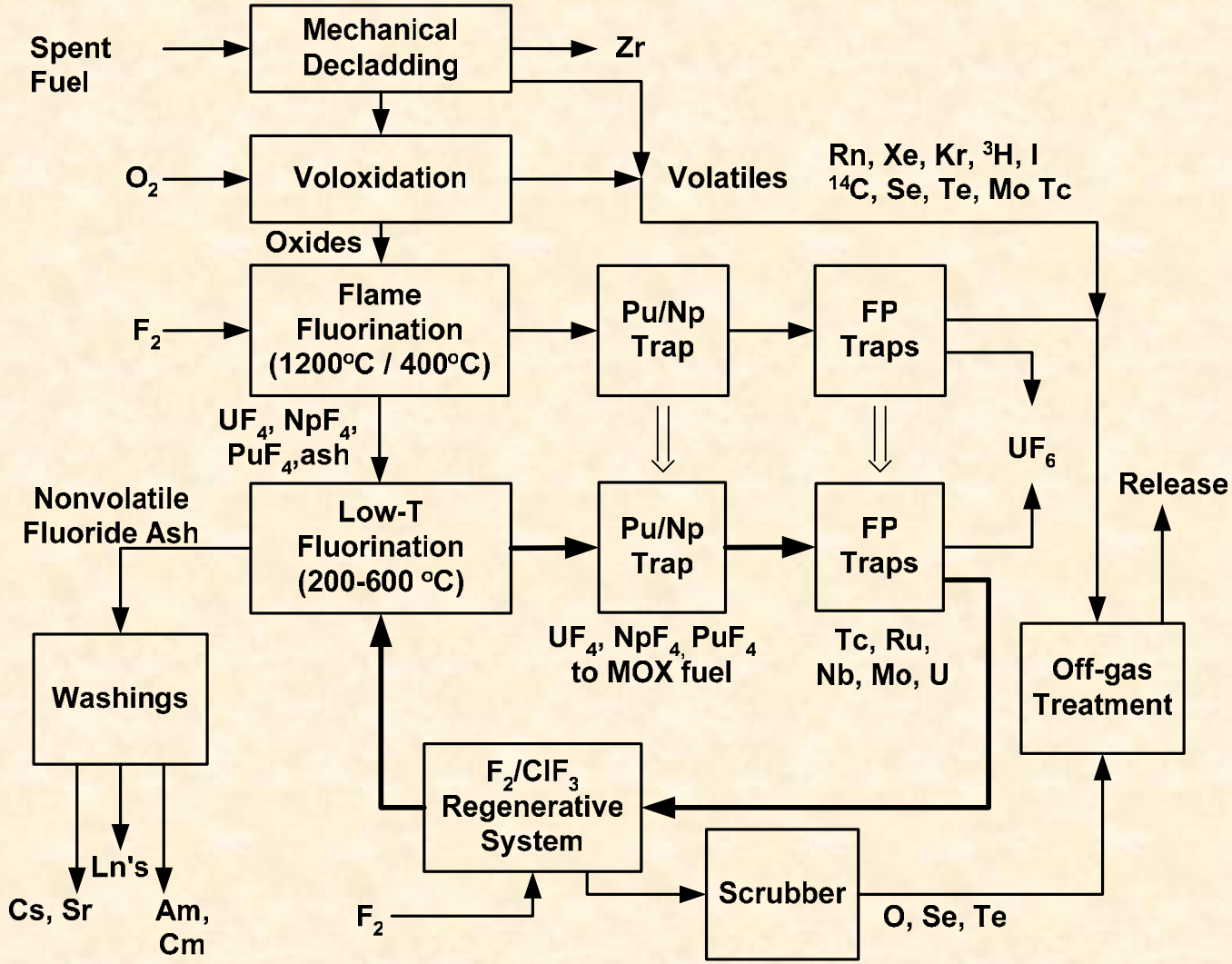
  We recently examined a conceptual fluoride volatility reprocessing method (Trufluor*)
  - **Focus was on technical feasibility**
  - **Head-end was examined only to a minimal degree**

*L. D. Trowbridge, G. D. Del Cul, B. B. Spencer, and E. D. Collins, *Am. Nucl. Soc. Transactions*, **90**, 81 (2004)

TRUFLUOR—General Methods

- Mechanical decladding
- Voloxidation
  - Increase surface area of oxides
  - Remove some volatiles
- Bulk of uranium is fluorinated using conventional flame fluorination
- Selective fluorination of lower volume remnant
  - Low temperature using ClF_3 and/or
  - Higher temperature using F_2
- Selective, reversible, solid bed trapping of volatile fluorides
- Regeneration of ClF_3 (if used)
- Reliance on conventional steps and well-developed technology where advantageous

Process Overview



Application of Advanced Head End Concepts to TRUFLUOR

- Another paper at this conference* discusses several advanced head-end processing steps
  - Chemical decladding—removal of zirconium by a Cl_2-volatility process
  - Advanced voloxidation—O_2/O_3/steam treatment of UO_2 to produce very high surface area U_3O_8 or UO_3 and release FP's
  - Lanthanide removal from the voloxidation product by treatment with Cl_2 or HCl followed by aqueous rinsing

- Application to TRUFLUOR:
  - Head-end processes (decladding and voloxidation) were included only at a low level of detail
  - This paper discusses the application of the advanced head end steps into the previously described fluoride volatility flowsheet

**Hybrid Processing of Spent Fuel*

Decladding

- Trufluor earlier contemplated mechanical or voloxidation-decladding
- Decladding by reaction with Cl_2
  - Experiments showed that formation and evaporation of $ZrCl_4$ essentially quantitatively removes the zirconium cladding but did not transport any measurable quantity of uranium
  - A small fraction of volatile fission products will be transported to the off-gas in both mechanical and chemical decladding systems
  - The Cl_2 process seems to be viable and mechanically simpler than mechanical decladding

Voloxidation

- Voloxidation was included in the earlier Trufluor flowsheet
  - Assumed to remove a fraction of elements volatilized under these conditions (e.g., noble gases, ^{14}C, Tc, I_2, Se, Te)
- O_3 process/low-temperature examined
  - Intent is to form a higher surface-area UO_3
  - It does not change the character of the voloxidation process, but may increase efficiency of removal of the above elements
  - A higher temperature treatment with O_3 and/or steam can remove other fission products (e.g., Mo, Tc, Cs)
- These treatments could result in reduction or even elimination of the need to separate some elements in later steps
- The product's higher surface area should also improve the efficiency of later fluorination of bulk uranium

Lanthanide Removal

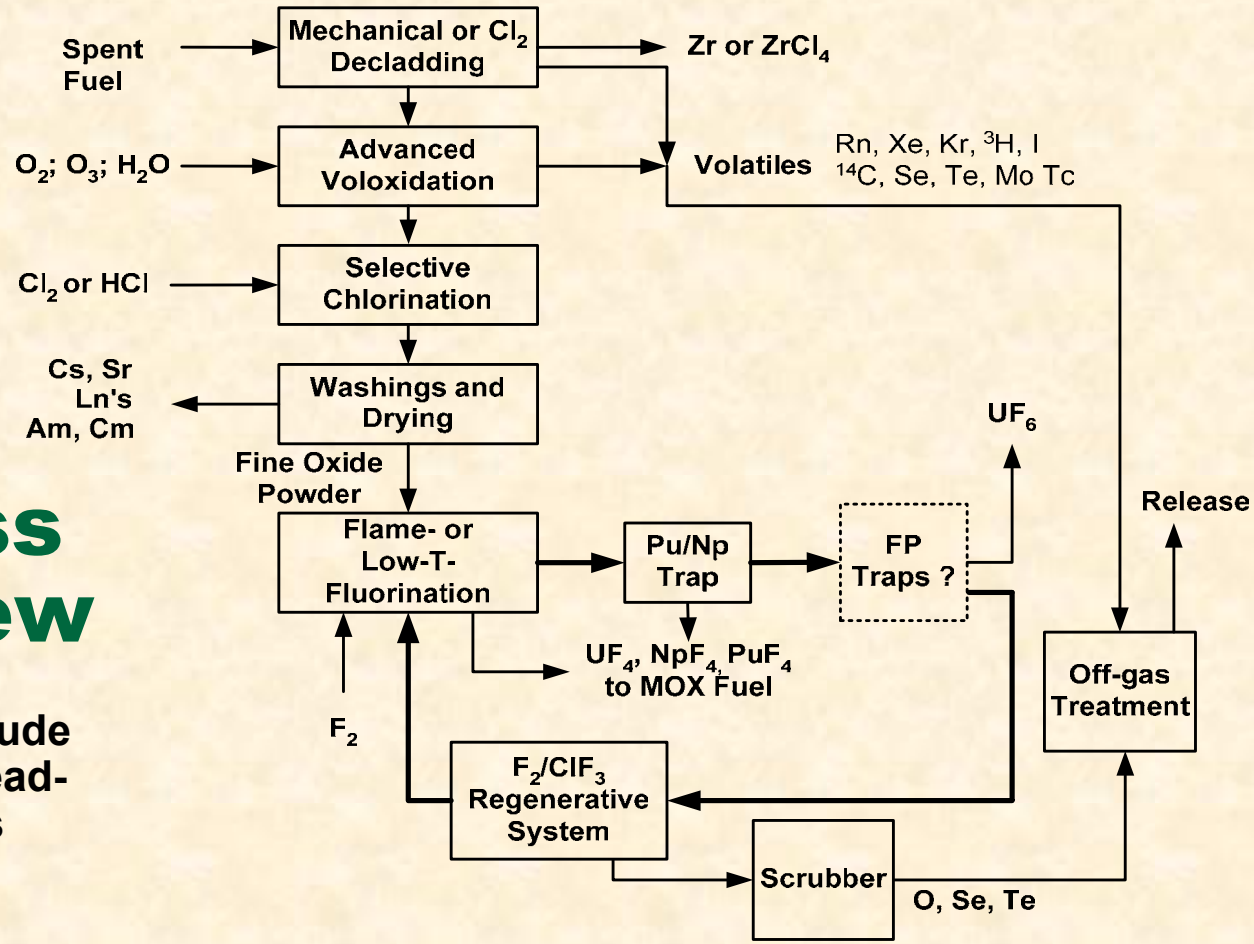
- Cl_2 or HCl treatment of the voloxidation product can result in enhanced solubility of lanthanides by formation of chlorides or oxychlorides
  - An aqueous wash removed a substantial fraction of the lanthanide in addition to other fission product elements (cesium and stronium)
  - Significant U was not lost in the rinse
- This process step, if optimized to remove nearly all the lanthanide content prior to bulk fluorination, could have a significant impact on subsequent processing
  - Due to chemical similarity, americium and cesium likely will behave similarly to lanthanide elements
  - Second, removal of lanthanide species, americium, cesium and other soluble FPs could leave an oxide residue consisting primarily of U, Np, and Pu
  - If adequately efficient, this eliminates postfluorination and washing steps included in the 2004 TRUFLUOR flowsheet

Summary of Effects on Process

- The product of the head-end process will feed into the following bulk fluorination step
- Removal of approximately 90% of the uranium (e.g., by high-temperature fluorination with F_2 or lower temperature fluorination using the ClF_3 catalytic regeneration cycle), creates two streams
  - Relatively pure UF_6 for reenrichment and
  - U/Np/Pu solid residue of the approximate composition desired for MOX fuel
- Depending on the efficiency of prefluorination removal
  - Gas purification traps could be reduced in scale or in some cases eliminated
  - Postfluorination wash of the U/Np/Pu ash might be minimized or eliminated

Process Overview

Modified to Include Advanced Head-End Steps



In Conclusion

- Advanced head-end steps appear to create no complications specific to fluoride volatility reprocessing
- If their initial promise is borne out, they could provide valuable alternatives to existing separation steps
- If efficiency is high enough, separation of elements in the head end may reduce in scale or eliminate separations later in the flowsheet