Nitric acid plays an integral role in the reprocessing of irradiated fuel. Thermal and radiolytic degradation of nitric acid results in the formation of redox active NO₃ species. A full understanding of solvent extraction requires us to understand actinide valence states which in turn requires us to understand what NO₃ species are present in HNO₃ solutions and their quantity.

**IR&D Project Aims**
- Gain a better understanding of nitric acid decomposition chemistry in order to optimise plant operations.
- Achieve this through capturing knowledge in a literature review with a focus on thermal and radiolytic degradation of HNO₃, and an emphasis on reactions that generate and remove NO₃ species and on quantifying HNO₃/NO₂ and HNO₂/NO₂⁻ species.
- The information gained from the literature review will provide the basis for a fundamental model of nitric acid for the solvent extraction process.

**Nitric Acid Degradation**
HNO₃ degrades thermally and radiolytically, forming NO₃ species including HNO₂.

Thermal degradation of HNO₃:

\[ 4\text{HNO}_3 \xrightarrow{\Delta} 4\text{NO}_2 + 2\text{H}_2\text{O} + 3\text{O}_2 \]  

(1)

Further thermal reactions:

\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2 \]  

(2)

\[ 2\text{NO}_2 = 2\text{NO} + \text{O}_2 \]  

(3)

\[ 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O} = 3\text{HNO}_2 \]  

(4)

HNO₃ can interact with radiation directly or indirectly through the products of the radiolysis of water (Fig. 2). The fraction of radiation directly absorbed by HNO₃ molecules can be approximated by the fraction of the electron density of HNO₃ in solution (Fig. 3).

Direct radiolysis of HNO₃:

\[ \text{HNO}_3 \xrightarrow{\text{radiation}} \text{HNO}_2 + 0 \]  

(5)

\[ \text{HNO}_3 \xrightarrow{\text{radiation}} \text{H}^* + \text{NO}_2 \]  

(6)

\[ \text{NO}_2 \xrightarrow{\text{radiation}} \text{NO}_2^- \xrightarrow{\text{radiation}} \text{NO}_2^- + 0 \]  

(7)

\[ \text{NO}_2 \xrightarrow{\text{radiation}} \text{NO}_2^- \xrightarrow{\text{add. e}^-} \text{NO}_2^- \]  

(8)

Indirect radiolysis of HNO₃:

\[ \text{e}^- + \text{H}^* \rightarrow \text{H}^- \]  

(9)

\[ \text{NO}_2^- + \text{e}^- + \text{H}_2\text{O} \rightarrow \text{NO}_2\text{O}^- \]  

(10)

\[ \text{NO}_2^- + \text{H}^* \rightarrow \text{HNO}_2^- \]  

(11)

Fig. 3 Fraction of electron density of HNO₃ (as an approximation of dose deposited in HNO₃) vs. HNO₃ concentration.

A number of further reactions occur, creating other NO₃ species. The key products of the radiolysis of nitric acid solutions can be summarised as follows:

\[ \text{HNO}_3 \xrightarrow{\text{radiation}} \text{HNO}_2, \text{NO}_3^-, \text{NO}_2^-, \text{NO}_2O_2, \text{H}_2\text{O}_2 \]  

(12)

**Nitrous Acid Chemistry**

HNO₂ is an important species in solvent extraction as it can have a detrimental effect to the extraction process, even when in very small quantities.

HNO₂ is redox active; a key reaction is the oxidation of minimally extractable Pu(III) to extractable Pu(IV). This can have an adverse effect on extraction yields.

\[ \text{Pu(III)} + \text{HNO}_2 + \text{H}^* \rightarrow \text{Pu(IV)} + \text{NO} + \text{H}_2\text{O} \]  

(13)

This reaction is autocatalytic as subsequent thermal reactions generate more HNO₂ (Eqn. 4), thus even μ-molar quantities can have a large effect. Factors effecting HNO₂ concentration include HNO₂ concentration and radiation type.

Understanding how HNO₂ is generated and removed and thus the species involved and the concentration, the better the extraction process can be controlled and optimised.

**Benefits**
- A model based on a fundamental understanding of nitric acid will improve our understanding of actinide valence states and thus the extraction process providing a better grounding to support plant operations.
- Nitric acid is used throughout the reprocessing of irradiated fuel; a fundamental model of nitric acid will provide a basis from which plant models can be updated.

**References**