Use of Uranyl Peroxide Precipitation as a Means to Clean up Irradiated Uranyl Sulfate Target Solutions

Chemical Science and Engineering Division

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prepared for

U.S. Department of Energy, National Nuclear Security Administration,

Office of Defense Nuclear Nonproliferation

February 28, 2012

USE OF URANYL PEROXIDE PRECIPITATION AS A MEANS TO CLEAN UP IRRADIATED URANYL SULFATE TARGET SOLUTIONS

Several methods were considered by Argonne National Laboratory (Argonne) for periodic cleanup of the irradiated uranyl sulfate SHINE target solutions. These methods included (1) conversion to nitrate media followed by UREX processing, (2) direct solvent-extraction process for uranyl sulfate, (3) anion exchange of uranyl sulfate complexes, and (4) precipitation of uranyl ion as uranyl peroxide. A final version of a report discussing these four options was sent to Morgridge Institute for Research (MIR) on August 10, 2011. The report was based on both literature and Argonne experimental data. It concluded that only two of the four options, options 1 and 4, had any chance of success.

The most developed and straightforward method was option 1; however, Argonne was asked to perform further experiments on the uranyl-peroxide precipitation method to see whether its flaws could be overcome.

In principal, the precipitation should be straightforward; the solubility product ($K_{sp} = [\text{UO}_2^{2+}] \times [\text{O}_2^{2-}]$) for uranyl peroxide is 1.3×10^{-36} (Djogic et al. 2005). However, there are many factors that influence the concentrations of free UO_2^{2+} ions and free O_2^{2-} ions, and therefore the completeness of the precipitation. For uranyl ions, there are pH-dependent hydrolysis reactions that form the species $\text{UO}_2\text{OH}^{1+}$, $\text{UO}_2(\text{OH})_2$, and $\text{UO}_2(\text{OH})_3^{1-}$, as well as sulfate complexes UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, and $\text{UO}_2(\text{SO}_4)_3^{4-}$. The free peroxide-ion concentration is also affected by the pH, due to formation of the weak acids H_2O_2 and HO_2^- . The relative concentrations of uranyl-sulfate complexes are also related to pH through the equilibria of sulfate ions with HSO_4^- and H_2SO_4 . Further complications to the precipitation are that peroxide ions can also form complexes with uranyl ions $\text{UO}_2(\text{O}_2)_2^{2-}$ and $\text{UO}_2(\text{O}_2)_3^{4-}$.

Low pH will increase uranyl-ion solubility by keeping the concentration of peroxide ions very low. As the pH is increased, the free uranyl ion concentration will drop due to an increase in the importance of hydrolysis reactions, complexation with sulfate, and eventually complexation with peroxide ions.

Once the precipitate is filtered/centrifuged and washed, the standard procedure is to thermally treat it to form UO_3 . This thermal process must be carefully performed to minimize reduction to U_3O_8 , which would be more difficult to dissolve in sulfuric acid (Sheft et al. 1950). The last step is the dissolution of UO_3 in sulfuric acid to prepare a solution for recycle. It should also be possible to dissolve the uranyl peroxide in sulfuric acid directly.

The processing steps are as follows:

1. Conditioning the irradiated solution for optimal uranium recovery and purity.
2. Peroxide precipitation.
3. Filtering and washing the precipitate.

4. Thermal conversion of UO_4 to UO_3 .
5. Dissolution of UO_3 in sulfuric acid.
6. Reconstituting the uranyl-sulfate/0.1-M sulfuric acid target solution.
7. Treatment of waste streams generated for storage and final disposal.

Steps 4–6 could be replaced by direct dissolution of the precipitate in sulfuric acid.

Development activities for this option were (1) to find optimized conditions for performing this precipitation and (2) to measure decontamination factors from other irradiated-solution components. As well as the pH dependence, conditions for stirring and peroxide addition must be developed that allow formation of a highly crystalline, filterable precipitate. Under typical conditions, the precipitate will resemble a “buttery” precipitate and will be difficult to separate by filtering or centrifugation. Thoroughly washing the precipitate is vital to achieving high decontamination factors for the uranium.

Following this report additional experiments were performed on the uranyl-peroxide precipitation, but we were unable to find conditions that would produce a precipitate that could be successfully filtered or centrifuged on a commercial scale. Therefore, no further experimental work was performed, this option was abandoned, and Argonne only recommends the conversion to nitrate media followed by UREX processing option.

The flowsheet for conversion to nitrate media followed by UREX processing will have 10 processing steps, all of which are commercially viable at the scale required for SHINE target solution cleanup. These steps are as follows:

1. Addition of $\text{Ca}(\text{NO}_3)_2$ dissolved in 1-M HNO_3 to the irradiated uranyl sulfate solution in a stirred vessel; addition rate and stirring speed are important.
2. Passing the slurry into a filtration system to collect and wash the precipitate (minimize uranium losses).
3. UREX processing of the filtrate.
4. Anion exchange step to remove pertechnetate and iodine from uranium product stream.
5. Precipitation of uranium as ammonium diuranate and its filtration.
6. Conversion of the precipitate to UO_3 .
7. Dissolution of UO_3 in sulfuric acid.
8. Reconstituting the uranyl-sulfate/0.1-M sulfuric acid target solution.

9. Potential recycle of uranium from ammonium diuranate filtrate.
10. Treatment of waste streams generated for storage and final disposal.

This option is the baseline process being integrated into the SHINE pre-conceptual design.

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