Study of Chemical Separation Methods for the Treatment of a Uranium Containing Process Effluent

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1. Introduction

A chemically-complex solid uranium waste awaits a management and disposal strategy. A process has been proposed for the treatment of such a waste.[1] However, owing to the chosen treatment process, a large volume of secondary liquid waste is generated. The treatment of this secondary waste forms the focus of this study.

The effluent contains approximately 400 ppm uranium which must be removed to below free release level. The effluent also contains a range of impurities, the most significant of which is Si at 24,000 ppm. The difference in solubility between silicon and uranium complexes could be used for the mutual separation of silicon from solution by precipitation as silica (SiO_2). Separation of the in-active silicon would reduce the final volume of secondary wastes requiring final disposal. A second removal step for the removal of residual uranium contained in the liquid waste from the first stage is also required. The addition of peroxide to form insoluble uranium peroxide precipitates offers promise. If UO_4 precipitation can be used to effectively remove uranium from the process effluent to less than 1 ppm, then the effluent can be safely discharged.

2. Materials and Methods

2.1 Si-U Separation experiment.

All experiments were conducted with samples of the real process effluent. For the purpose of selective silicon precipitation uranium was retained in solution as the soluble uranyl-peroxo carbonate ($UO_2(O_2)(CO_3)_2^{4-}$) species.[2] Sodium carbonate solution was added to the effluent before pH adjustment by H_2SO_4 to pH 12. Hydrogen peroxide was then injected in excess; this was followed by the further addition of H_2SO_4 in-order to reduce the pH to below 9 thus inducing selective silicon precipitation as SiO_2. The precipitates were separated from solution, washed and then dried for 24hrs. Residual uranium activity was analyzed using gamma and alpha spectrometry. In the event of a uranium activity higher than the free release level, the silica was re-dissolved and re-precipitated.

2.2 Uranium peroxide precipitation experiment

Initially a simulated process effluent solution was used. A volume of uranium solution, uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$; UNH) was added to a sodium nitrate solution resulting in uranium concentrations of 1000 ~ 10 ppm. Hydrogen peroxide (H_2O_2, 30%) was injected into the simulated solution to reach a 1M followed by pH adjustment to 3~4. Optimized process conditions were applied to the real effluent. Uranium concentrations were analyzed by ICP-MS and UV-spectrophotometry. Solid analysis was done using SEM, TEM-EDS and XRD.

3. Result and discussion

3.1 Si-U separation experiment

Fig. 1 shows the residual radioactivity of the silica. A single purification step reduces the activity by 46% to below 1Bq/g. Additional purification steps reduces the activity further, however, achieving only an additional 20% reduction after five purification cycles is not deemed economical.

In order to reduce the residual activity further, while limiting the number of purification cycles, different washing conditions were tested to remove residual uranyl ions from the silica surface. If an acidic solution is used for washing, the residual activity is reduced to levels akin to four purification cycles (Fig. 1 & 2). This is credited to a change of the silica surface zeta potential as H^+ concentration rises releasing bound UO_2^{2+}.
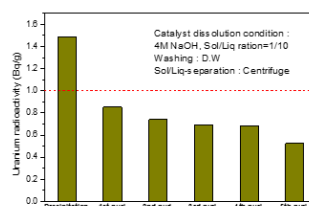

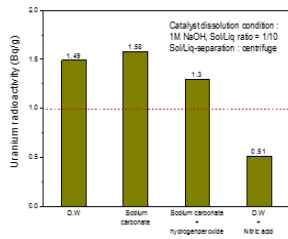Fig. 1. Uranium radioactivity of precipitates after application of existing method.

Fig. 2. Uranium radioactivity of precipitates with different washing solution.

3.2 Uranium peroxide precipitation experiment.

Fig. 3 shows the change in uranium concentration with and without mixing after setting initial uranium concentrations in the simulated effluent. The higher initial uranium concentration, the faster UO_4 precipitated. The residual uranium concentration in solution was confirmed to be less than 1 ppm. However, at lower initial uranium concentrations, about 10ppm, the precipitation of UO_4 hardly occurred. At every concentration tested the precipitation rate was faster while stirring. When the initial concentration is high or the solution is mixed, the number of particle collisions increases, so nucleation rapidly occurs leading to particle growth and thus effective removal of uranium.
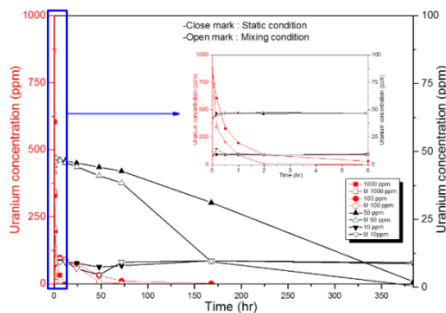

Fig. 3. Variation of residual uranium concentration with different initial concentrations.

The uranium concentration in the real process effluent was about 100 ppm. Impurities such as Si, Sb, Fe were measured at several ppm. The rate of UO_4 precipitation from the real process effluent was 2~3 times faster than simulated experiment. Fig. 4 shows the results of solid phase and particle size analysis of the formed particles using SEM-EDS and a particle size analyzer. The pure UO_4 precipitate formed spherical and very small particles, but UO_4 particles formed in the real process effluent were larger and not perfectly spherical. In addition, the result of EDS analysis showed that Si, Fe, Sb and other impurities in solution were co-precipitated together with UO_4 particles. Thus the particle size and precipitation rate were affected by the presence of the impurities.
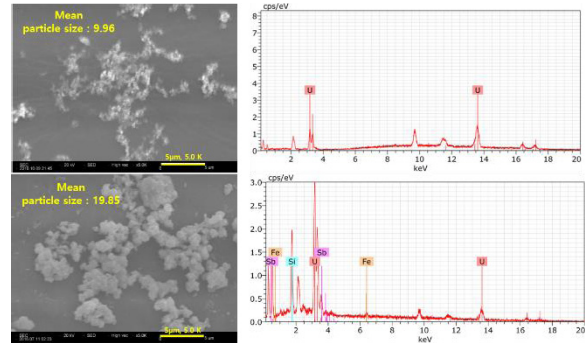

Fig. 4. PSA and SEM-EDS results of precipitated UO_4 particles.

4. Conclusion

This study has established the feasibility of chemical separation methods for the treatment of a uranium containing effluent. Separation of inactive silicon reduces the final volume of secondary wastes requiring disposal. A single purification cycle followed by acid washing reduces residual activity to below environmental release level. A second step by peroxide addition, leading to the formation of insoluble uranium peroxide, is shown to effectively remove uranium from the process effluent allowing discharge the environment.

5. Acknowledgement

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