Higher Americium Oxidation State Research Roadmap

Fuel Cycle Research & Development

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SUMMARY

The partitioning of hexavalent Am from dissolved nuclear fuel requires the ability to efficiently oxidize Am(III) to Am(VI) and to maintain that oxidation state for a length of time sufficient to perform the separation. Several oxidants have been, or are being developed. Chemical oxidants include Ag-catalyzed ozone, Ag-catalyzed peroxydisulfate, Cu(III) periodate, and sodium bismuthate. Hexavalent americium has also now successfully been prepared by electrolysis, using functionalized electrodes. So-called auto-reduction rates of Am(VI) are sufficiently slow to allow for separations. However, for separations based on solvent extraction or ion exchange using organic resins, the high valence state must be maintained under the reducing conditions of the organic phase contact, and a holding oxidant is probably necessary. Until now, only Cu(III) periodate and sodium bismuthate oxidation have been successfully combined with solvent extraction separations. Bismuthate oxidation provided the higher D_{Am}, since it acts as its own holding oxidant, and a successful hot test using centrifugal contactors was performed. For the other oxidants, Ag-catalyzed peroxydisulfate will not oxidize americium in nitric acid concentrations above 0.3 M, and it is not being further investigated. Peroxydisulfate in the absence of Ag catalysis is being used to prepare Am(V) in ion exchange work, discussed below. Preliminary work with Ag-catalyzed ozone has been unsuccessful for extractions of Am(VI) from 6.5 M HNO_3, and only one attempt at extraction, also from 6.5 M HNO_3, using the electrolytic oxidation has been attempted. However, this high acid concentration was based on the highest Am extraction efficiency using the bismuthate oxidant; which is only sparingly soluble, and thus the oxidation yield is based on bismuthate solubility. Lower acid concentrations may be sufficient with alternative oxidants and work with Ag-ozone, Cu(III) and electrolysis is on-going.

Two non-solvent-extraction separations are also under investigation. The first would separate Am(VI) by co-crystallization with uranium and the other oxidizable actinides as their nitrate salts. This novel idea has been successful in lab scale testing, and merits further investigation. Similarly, success has been achieved in separations using inorganic or hybrid ion exchange materials to sorb the lanthanides and actinides, while allowing pentavalent americium to elute. This is the only technique currently investigating Am(V), despite the advantages of this oxidation state with regard to its higher stability.

The ultimate destination for this roadmap is to develop an americium separation that can be applied under process conditions, preferably affording a co-separation of the actinyl (VI) ions. Toward that end, emphasis is given here to selection of a solvent extraction flowsheet for testing in the INL centrifugal contactor hot test bed during FY16. A solvent extraction process will be tested mainly because solvent extraction separations of Am(VI) are relatively mature and the test bed currently exists in a configuration to support them. Thus, a major goal of FY16 is to select the oxidant/ligand combination to run such a test using the contactors. The only ligands under consideration are DAAP and DEHBA. This is not to say that ion exchange and co-crystallization techniques are unimportant. They merit continued investigation, but are not mature enough for hot test bed testing at this time.

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1. Introduction

The overarching goal of the Sigma Team for Advanced Actinide Recycle (STAAR), formerly named the Sigma Team for Minor Actinide Separation (STMAS), is to develop more efficient separation methods for actinides in support of the goal of sustainable fuel cycles. The STMAS was originally formed to bring together multi-disciplinary teams from across the DOE complex and academia that would work collaboratively to solve the difficult technical challenges and to develop robust and scientifically sound processes for the separation of minor actinides (MAs, taken in the present context to mean Am and Cm) from lanthanides. The original charter included a second objective to devise efficient separation of Am from Cm, but due to programmatic considerations, this goal is no longer explicitly pursued. In the past two years, a systems options study in the MRWFD program supported the merit of full actinide recycle in terms of a future sustainable fuel cycle based on fast reactors. A more recent extension of that study examined differences in U/Pu and U/TRU recycle schemes, concluding that both are of interest for future development. The study results have prompted us as of FY-16 to broaden the scope of the Sigma Team to include actinide recycle generally vs exclusive focus on recycle of the MAs, and a corresponding change in the Sigma Team name to STAAR has been adopted. Given the research momentum from the past few years in the Sigma Team, the upcoming year will maintain its primary focus on developing a more robust, more efficient actinide/lanthanide (An/Ln) separation process, though with initial venturing toward a group An separation, a theme that will likely expand in future years. This goal will be pursued by integrating hypothesis-driven research that provides sound scientific understanding with applied research that develops process concepts through bench-scale demonstrations. The overall effort is carried out within the paradigm of aqueous reprocessing of used oxide nuclear fuel dissolved in nitric acid. The prime question being addressed deals with principles of selectivity through various means, one of which is use of high valent americium to be discussed in this roadmap.

To meet the overarching goals described above, STAAR is pursuing three major high valent americium approaches: 1) oxidation to Am(VI) followed by solvent co-extraction with the other hexavalent actinides; 2) oxidation to Am(VI) followed by co-crystallization with the other hexavalent actinides; 3) oxidation to Am(V) with separation from other lanthanides and actinides by ion exchange. The solvent extraction techniques have received the most attention and are thus more mature, and work towards a second hot test in a centrifugal contactor test bed will be described in this roadmap.

Specific to the oxidation of Am, research is focused on advancing the understanding of the production, stabilization, and separation of Am(VI). While it is recognized that the use of Am(V) would result in a more facile system both in ease of oxidation and subsequent high valence state stability, this option does not provide the possibility of co-extraction of U, Np, Pu and Am, all as their actinyl ions. Therefore, future research will concentrate mainly on production and partitioning of Am(VI), at least for solvent extraction purposes. Research is structured to test the hypothesis that Am(VI) can be produced and remain stable in irradiated first-cycle raffinate solution long enough to perform a separation. This STARR research in high valent Am chemistry has already lead to successful testing of tandem oxidation and extraction in a centrifugal contactor using the sodium bismuthate oxidant to prepare Am(VI). However, given the difficulty as well as the high pay-off of the desired separation several options are being concurrently investigated, and some investigation of Am(V) chemistry will continue as a contingency, especially as related to ion-exchange separations. Methods for oxidizing Am(III) will be optimized, including investigations of the potential for chemical oxidation with Cu(III), catalyzed ozone, peroxydisulfate, and electrochemistry. The stability of Am(VI) will also be characterized, and the kinetics of autoreduction will be determined. Attention will be paid to the stability of Am(VI) solutions in contact with extraction solvents, using different extractants such as diamylamylphosphonate (DAAP) and dialkylmonoamides such as diethylhexylbutyramide (DEHBA).

LANL will specifically investigate the feasibility of ozone and catalysts as chemical oxidants and the subsequent extraction of Am(VI), and will characterize the spectroscopic signatures of Am(V) and

Am(VI). PNNL will assist with Cu(III) chemistry as needed, with the Cu(III) periodate oxidizing agent being suppled either by PNNL or Colorado School of Mines. A test of oxidation-extraction will be performed in the tandem reactor-contactor hot-test rig at INL, and a decision regarding the oxidation/ligand system for that test will be made in mid-year, based on batch contact extraction results discussed above.

In techniques other than solvent extraction, ORNL will perform tests of co-crystallization of actinyl nitrate salts using uranyl nitrate as the bulk carrier for the actinyl ions. SRNL is examining ion-exchangers in combination with Am(V) as a means to achieve an Am/Ln separation.

To guide the multi-lab research, this road-map for the project addressing all research needs leading to hot testing at INL in FY16 for the appropriate solvent extraction technology and, ultimately an integrated hot test with simulated and real HLW in future years has been prepared.

2. Scope

The scope of this effort is to develop a road-map to guide research related to oxidation of Am(III) to Am(VI) and subsequent separation with other multivalent actinides. This road-map addresses research needs and schedule to 1) gather the data necessary to support testing of potential solvent extraction processes in the tandem reactor-contactor engineering-scale hot test rig at INL in FY16 and 2) enable development of potential flowsheets leading to an integrated hot testing with simulated and real HLW within the next two to five years. Additionally, risks relative to development of higher Am oxidation state separation processes are identified.

3. Higher Am Oxidation State Separation Risks

The following risks have been identified relative to the successful development of a separation process based upon higher oxidation states of americium. These risks will need to be addressed in the development of a potential process. While the number of risks associated with solvent extraction appears to be greater, this is also a reflection of the fact that more work has been done in this area to identify risks.

3.1 Solvent extraction of oxidized americium

1. The oxidation rate of Am(VI) using sodium bismuthate is slow.
2. Sodium bismuthate is a solid phase oxidant that requires filtration.
3. Alternative oxidants do not provide the high D_{Am} found with bismuthate.
4. Difficulty in obtaining a consistent oxidation yield of Am(VI).
5. Stability of Am(VI) in the presence of the organic solution and radiation.
6. Ability to re-oxidize Am in previously treated aqueous solution to increase separation efficiency.
7. Introduction of undesirable components into overall process (waste) when using chemical oxidants.

3.2 Ion exchange of oxidized americium

1. Solid phase formation requires filtration.
2. Performance of newly developed ion exchangers.

3.3 Co-crystallization of oxidized americium

1. Kinetics of the oxidation rate of Am(VI).
2. Ability to oxidize Am(III) to Am(VI) in presence of uranyl nitrate.

4. Current Status

4.1 Sodium Bismuthate Oxidation for Extraction

Sodium bismuthate is the mature americium oxidant with regard to development for process application in work performed at INL. It can be used to generate either Am(VI) or Am(V) depending on the temperature under which oxidation is performed. Unlike most of the other oxidants under investigation it is as an off-the-shelf reagent that is readily available for study. Following several years of batch contact measurements using this oxidant and DAAP as the solvent extraction ligand, a successful hot test demonstrated that Am(VI) can be generated and extracted on a process scale using centrifugal contactors. The highest D_{Am} are found in extractions from 6-7 M HNO_3, although this appears to be a function of higher Am(VI) yields in the presence of more dissolved bismuthate at these acidities, rather than a reflection of the ligand chemistry. Yields of 65-85% are obtained, although some problems in consistency have been reported. This high acidity is also required for maximum extraction efficiency when using DEHBA as the ligand for bismuthate-oxidized Am. This oxidant is successful probably because it generates its own holding oxidant due to the slow dissolution of the residual $NaBiO_3$ solids, which successfully counter-acts the reducing tendency of the organic phase. The solids are also its main disadvantage in that they must be filtered prior to the solvent extraction contact. This filtration is not insurmountable and was successfully performed during the aforementioned centrifugal contactor hot test. A second disadvantage of sodium bismuthate is that it has slow oxidation kinetics, requiring the 1-2 h oxidation to be performed batch-wise prior to the solvent extraction contact. A third disadvantage is that, as a chemical oxidant, it adds dissolved solids to the waste-stream. Despite these disadvantages, this oxidant has provided nearly all the Am(VI) solvent extraction data under this sigma team. Although not an exhaustive list, key published work includes:

1. Mincher, B.J.; Martin, L.R.; Schmitt, N.C. Tributylphosphate extraction of bismuthate-oxidized americium. Inorg Chem, 2008, 47, 6984
2. Mincher, B.J.; Schmitt, N.C.; Tillotson, R.D.; Elias, G.; White, B.M.; Law, J.D. Characterizing diamylamylphosphonate (DAAP) as an americium ligand for nuclear fuel cycle applications. Solvent Extr Ion Exch, 2014, 32, 153
3. Mincher, B.J.; Tillotson, R.D.; Garn, T.; Rutledge, V.; Law, J.; Schmitt, N.C. The solvent extraction of Am(VI) using centrifugal contactors. J Radioanal Nucl Chem, 2015, DOI 10.1007/s10967-015-4397-6.

Current research using sodium bismuthate as the oxidant is centered on measurements of the kinetics of reduction of bismuthate-oxidized americium across a range of acid and americium concentrations, examination of the effect of various sources of reagents and their associated trace reducing agents on the yield of oxidized americium, the investigation of monoamides as Am(VI) ligands, and the autoreduction rates of Am(VI) under various process conditions.

4.2 Silver/Ozone Oxidation for Extraction

Work has been performed to identify new oxidation methods as potential alternatives to bismuthate. One idea is to utilize ozone as an oxidant, as ozone is a gaseous additive which would not add to the waste stream and is well-known for forming Am(VI) in high pH carbonate solutions. While ozone alone was shown to be an insufficient oxidant in nitric acid media, the addition of a catalyst has proven effective in oxidizing Am(III) to Am(VI). It is also advantageous in that it can increase the solubility of the oxidant (which is limited by physical solubility of ozone in the uncatalyzed solution), and may act as a holding oxidant once the ozone is consumed. Silver was selected as the baseline catalyst due to its high solubility in nitric acid solutions, large redox potential, ability to act as a multi-electron oxidant, and since it is a known fission product. The use of a homogeneous catalyst has the advantage that it would eliminate the need for filtration prior to extraction in a centrifugal contactor. Neither Ag(I) or Ag(II) is extracted by DAAP, which is a major advantage that would enable silver to be recycled in an process flowsheet. The silver/ozone oxidation of Am(III) to Am(VI) has been successfully demonstrated using UV/Vis to quantify the produced high valent oxidation states, and a U.S. patent application has been filed for this technology. Quantitative oxidation to Am(VI) in 1-3 M HNO_3 has been achieved, and the results are consistent with the oxidation rates being controlled by the rate of ozone mass transfer into the nitric acid solution. The quantitative yield of Am(VI) is analogous to the well-known Ag-catalyzed oxidation of Am in dilute acid solutions using the peroxydisulfate system (discussed below). Silver (II) acts as the holding oxidant, in that Am(VI) does not reduce as long as it is present, in analogy with Bi(V). The Ag(II) stabilized at higher nitric acid concentrations. However, the yield and stability of Am(VI) actually decreases at higher acid concentrations.

In solvent extraction experiments using Ag/ozone oxidation a 15-sec contact with 1 M DAAP in 3 M HNO_3 resulted in $D_{Am} = 0.33$, consistent with Am(III) extraction by 1 M DAAP at that acidity. This means that contact with the organic solvent phase was sufficient to reduce the high valent Am, even in the presence of excess Ag(II). Further experiments with shorter contact times and alternative catalysts are in progress.

4.3 Copper Periodate Oxidation for Extraction

The copper (III) periodate oxidation of Am to Am(VI) has been shown using UV/Vis observation of the produced high valent oxidation state at PNNL. In contrast to sodium bismuthate, Cu(III) has the advantages that the oxidation is rapid and that the highest Am(VI) yields of 98-99 % occur in $\leq$ 3 M HNO_3. These results are similar to those described for Ag/ozone above. In work that was performed at INL, the extraction of Cu(III)-oxidized Am(VI) using DAAP shows maximum distribution ratios of slightly < 2 in the nitric acid concentration range 2-3 M, consistent with the reported maximum high valent americium yields reported by PNNL at that acid concentration. Although the D_{Am} is marginal, this convincingly demonstrates that some fraction of Am was extracted as Am(VI). The oxidation for these extractions was conducted using a 10-sec, 20 mg/mL Cu(III) periodate treatment, and a 5-sec extraction contact time. Longer extraction contacts reduced the $D_{Am} < 1$, probably due to the absence of a holding oxidant while in contact with the organic phase. The key publication describing the use of Cu(III) as an Am(VI) oxidizing reagent is:

1. Sinkhov, S.I.; Lumetta, G.J. Americium(III) oxidation by copper(III) periodate in nitric acid solution as compared with the action of Bi(V) compounds of sodium, lithium, and potassium. Radiochim Acta, 2015, 103, 541

Current research using this oxidant is related to increasing the batch extraction data-set using DAAP and DEHBA extractants, and the use added sodium periodate as a potential holding oxidant, as suggested by McCann et al, *Reduction of copper and silver in unconventional oxidation states*, (Actinide Separations Conference presentation, 2015). This compound is only periodically available for study.

4.4 Electrochemistry for Extraction

The electrochemical oxidation of Am to Am(VI) has been demonstrated using UV/Vis observation of the high valent oxidation state at INL. This is the first reported successful electrochemical oxidation of Am in a non-complexing medium, and was achieved using surface functionalized electrodes developed at UNC that bind Am to facilitate the oxidation. Depending on the applied potential, various ratios of Am(III), Am(V) and Am(VI) are obtained. Until now, this work has been performed in 0.1 M HNO_3, adjusted to 1 M in total nitrate. The degradation of electrodes at higher acidities may be a disadvantage of this approach, although work is on-going. Initial attempts at solvent extraction have recently been performed by adjustment of the acidity of oxidized solutions, followed by 5-sec, 1 M DAAP contacts. A D_{Am} of ~ 1 was obtained in a single experiment using a 2-sec contact. If this can be repeated it suggests extraction of Am(VI). For longer contacts, extraction efficiency consistent with the extraction of Am(III) have so far been obtained, again illustrating the need for a holding oxidant. The key publication describing the electrochemical oxidation of Am in nitric acid solution is:

Dares, C.J.; Lapides, A.M.; Mincher, B.J.; Meyer, T.J. Low potential electrochemical oxidation of ^{243}Am(III) in nitric acid by a derivatized, high surface area metal oxide electrode. Science, 2015, 350, 652

4.5 Peroxydisulfate (with or without Silver) Oxidation for Extraction or Ion Exchange

The peroxydisulfate oxidation system is the traditional Am oxidizing method used in analytical chemistry, and has been successful with or without Ag catalysis. Similarly to bismuthate it is an off-the-shelf reagent, and it can be used as an Am(V) or Am(VI) oxidizing agent under appropriate conditions, with the addition of Ag often used to favor the hexavalent oxidation state. Its disadvantage is that it is only effective in dilute acid, although successful batch contacts for Am(V) have been performed by oxidizing the Am in dilute nitric acid, followed by acidity adjustments and subsequent solvent extraction. The use of sodium peroxydisulfate as an oxidant has provided some solvent extraction data for this Sigma Team, and is the main oxidant under study for ion exchange purposes. Its use in solvent extraction was discouraged by the program due to concerns about introducing sulfates into the final waste form. The key publication is:

1) Mincher, B.J.; Schmitt, N.C.; Schuetz, B.K.; Shehee T.C.; Hobbs, D.T. Recent advances in *f*-element separations based on a new method for the production of pentavalent americium in acidic solution. RSC Advances, 2015, 5, 27205.

4.6 Ion Exchange Separations

Inorganic and unconventional metal-organic framework (UMOF) ion-exchange materials have been evaluated to provide effective separations of minor actinides (Am, Cm), lanthanides, and other fission products. Previous work has established that a number of inorganic and UMOF ion-exchange materials exhibit varying affinities for actinides and lanthanides, which may be exploited for effective separations. The following concepts have emerged as the leading, but not exclusive, candidates for effective ion-exchange separations, (1) oxidation of Am(III) to Am(V) followed by ion exchange, (2) ion-exchange of Am(III) and fission products (lanthanides, Cs, Sr, Tc) followed by recovery of the Am using an oxidizing eluent, (3) ion-exchange of actinyl ions followed by the recovery of the Am as Am(III) using a reducing eluent, and (4) chromatographic separation. It is envisioned that the feed solution for ion-exchange separations would be the raffinate from a COEX™ or UREX type processes or fuel dissolver solution prior to any separation. Select publications describing the current understanding of the actinide/lanthanide ion exchange separation system include:

1. Shehee, T. C and Hobbs, D. T. Oxidation of metal ions by peroxydisulfate in dilute nitric acid, *submitted to* Radiochim Acta, July 2015
2. Mincher, B. J.; Schmitt, N. C.; Schuetz, B. K.; Shehee, T.; Hobbs, D. Recent advances in f-element separations based on a new method for the production of pentavalent americium in acidic solution. RSC Advances, 2015, 5, 27205
3. Burns, J. D.; Shehee, T. C.; Clearfield, A.; Hobbs, D. T. Separation of americium from curium by oxidation and ion exchange. Anal Chem, 2012, 84, 6930

4.7 Co-crystallization

The first ever demonstration of Am(VI) co-crystallization with $UO_2(NO_3)_2 \cdot 6H_2O$ has been achieved, opening the door to a whole new paradigm of used nuclear fuel recycling, where the bulk of the U, Np, Pu, and Am can all be removed from the waste stream together, without any organic solvent waste being generated. The hexavalent dioxo cations of Np, Pu, and Am have all been co-crystallized with $UO_2(NO_3)_2 \cdot 6H_2O$ in near proportion by a simple reduction in temperature, while the tri- and tetravalent states are only slightly removed from solution. In the co-crystallized form, the Am(VI) shows a much greater stability, with no reduction observed after 13 days, while in solution over 50% reduces after only 10 days. The ability to remove and stabilize hexavalent actinides from solution, especially Am(VI), is not only scientifically interesting, but could have significant implication on future nuclear fuel recycling. The key publication is:

1. Burns, J. D. and Moyer, B. A. Co-crystallization of hexavalent transuranic actinyl ions through americyl with uranyl nitrate hexahydrate in nitric acid. *Submitted* to Journal of the American Chemical Society, November 2015.

5. FY 2016 Research Plan

5.1 Data Gaps Relative to Hot Test at INL

5.1.1 Sodium Bismuthate Oxidation for Extraction

Although the previous hot test was successful at demonstrating Am(VI) extraction, data gaps were revealed. Post-extraction Am reduction and stripping were not as successful as anticipated. This is a surprising result since most effort has been focused on prevention of Am(VI) reduction. However, during the hot test Am(VI) was not adequately reduced for stripping purposes. This was attributed to the short contact times between the phases in the centrifugal contactors. This may possibly be remedied by increasing the concentration of the H_2O_2 reducing agent used in the strip stage, or by building in a delay to allow the organic phase itself to reduce the loaded Am. The Am distribution ratio in the extraction stage was also lower than anticipated (< 2), although it was consistent with preliminary batch contacts using the same reagents. An effort to identify the source of the occasional low D_{Am} (which was attributed to low oxidation yield due to an unknown reducing impurity associated with one of the reagents) is underway. The sources of the sodium bismuthate and 1 M DAAP currently available at INL are consistently providing D_{Am} of 3-4 in batch contacts from nitric acid solution. Slightly higher D_{Am} values ~ 5 are obtained using 1 M DEHBA as the ligand, although D_{Am} was ~ 2 for DEHBA co-extractions in the presence of U, Np, and Pu. New batch contact data will be acquired upon receipt of the baseline raffinate simulant solution currently being prepared at PNNL.

Finally, re-oxidation of a previously treated aqueous phase appears to be more difficult than the initial oxidation, which is important to the design of a multi-stage extraction. The reason for this is not understood, although various aqueous phase clean-up steps are being tested.

Thus, to be prepared for a sodium bismuthate hot test, the main data needs are to measure D_{Am} from the new simulant, using the two ligands over a range of acid concentrations, and to increase the reductant concentration in the strip stage.

5.1.2 Silver/Ozone Oxidation for Extraction

A system design was prepared to enable batch Ag/ozone oxidation of Am solutions prior to feeding them into the centrifugal contactor hot test bed for extraction. The main modification to the current test bed was to design a system to introduce the ozone into the batch oxidation reactor. Its utility is speculative in the absence of batch contact data. To date, only scoping experiments have been performed for batch extractions using DAAP, which has limited the information for suggesting the feed conditions or the solvent systems to be used for a hot test bed demonstration. Continued batch contact experiments to demonstrate successful extraction of Am(VI) using this oxidant are necessary. Preliminary extraction data indicates that both Ag(II) and Am(VI) are nearly instantaneously reduced by DAAP, which has prevented the extraction of Am(VI). The purity of DAAP has been confirmed via NMR, and pre-treatment methods for destroying trace impurities are being explored to help increase the extraction yields. Alternatively, other homogeneous catalysts are being explored, including Co which has exhibited significantly more stability when contacted with the DAAP extractant. While experiments have indicated that oxidation rates are dependent on the rate of ozone mass transfer, these experiments have been performed at small-scale (1-3 mL). Additional experiments will need to be performed to adapt the oxidation techniques to the scaled up conditions required for the hot test bed experiments.

5.1.3 Copper Periodate Oxidation for Extraction

The Cu(III) periodate system has been examined for use in Am(VI) DAAP extraction in repetitive experiments in which oxidant concentrations, oxidation times and contact times have been varied. Short contact times favor higher D_{Am}, however, the current 5 sec contact time is about as low as practicably achievable for batch contact experimental measurements. The resulting optimum D_{Am} of ~ 1.7 is marginal for a hot test, especially given that it is likely be lower for extractions from the raffinate simulant. However, as Cu(III) periodate becomes available, elevated periodate concentrations in conjunction with the Cu(III) periodate oxidizing agent will be examined as a potential holding oxidant during the batch contact extraction experiments in an attempt to improve these extraction efficiencies. This is the second-most successful oxidizing agent to date, and the easiest to migrate to the existing hot test bed. However, a set of batch contacts over a range of acidities from the baseline raffinate will be required. If this oxidant is selected for the FY16 hot test, approximately 80 g of Cu(III) periodate will be required. This is an order of magnitude more material than has ever been prepared in the past.

5.1.4 Electrochemistry for Extraction

Although very promising, this technology requires significant development before it can be suggested for hot testing. Among the data gaps are the development of electrodes robust enough to support oxidation in highly acidic solution, enhancement of electrode surface areas to perform bulk solution oxidation, an investigation of oxidation in the presence of the other metals in the raffinate, and continued batch contact experiments to discover the conditions that better maintain the Am(VI) oxidation state during the extraction.

5.1.5 Peroxydisulfate (with or without silver) oxidation for extraction or ion exchange

Peroxydisulfate is not under consideration as an oxidant for solvent extraction purposes at this time. Its use in ion exchange is discussed in the next section.

5.1.6 Ion Exchange Separations

The ion exchange approach is fundamentally different than the solvent extraction approach that the INL test bed is currently designed to support. However, an ion exchange test bed could be designed. Testing in support of new ion-exchange flowsheet concepts would use a conventional ion-exchange column and resin that exhibits high affinity for more highly charged ions such as the Ln(III) and actinides (Am, Cm) and +4 metals (Zr). New unconventional metal-organic framework materials are being developed by A. Clearfield's group at TAMU which is funded by NEUP. New materials prepared and characterized for lanthanide affinities will be sent to SRNL and tested for affinity towards the transuranic elements (Am, Pu, Np). A new variety of hybrid ion exchangers ($M(O_3PC_6H_4PO_3 \cdot nH_2O$; $M = Zr^{4+}$ or Sn^{4+}) has been shown to perform better than the previous generation, especially with regard to uptake of Am/Cm at pH = 1.17. A K_d value of ~6000 mL/g for Cm(III) was achieved. Additional new materials prepared by W. Lin's group at UC and other materials reported in the literature that show promise for minor actinide/lanthanide separations may be tested as well.

Batch contact experiments will measure the separation factors by inorganic and hybrid ion-exchange materials. A surrogate raffinate will serve as the feed solution to the ion-exchange processes. The feed solution will include actinides, fission products and other key components (e.g., Zr) that would be present from reprocessing of irradiated nuclear fuels. Testing will determine conditions that prevent the precipitation of lanthanum sulfates and evaluate solid/liquid separation techniques (e.g., filtration) if precipitated solids cannot be prevented.

5.1.7 Co-crystallization

The research into group separation of the hexavalent actinides by co-crystallization was only initiated in the past year. While the results of this investigation show great promise, additional data is needed to better understand the system. Single metal (Np(VI), Pu(VI), or Am(VI)) co-crystallizations with $UO_2(NO_3)_2 \cdot 6H_2O$ have been demonstrated, but data gaps exist for mixed metal co-crystallization to achieve a bulk separation. Other data gaps include experimental parameters of acidity, uranium concentration, and temperature on the crystallization process which will be need to be addressed. The aim will be to mimic the process conditions of fuel dissolutions, making it advantageous to implement this technology at the front-end of the fuel cycle in production scale.

5.2 FY 2016 R&D Plans and Schedule

The milestone (FT-16IN03010302) for the recommendation of an oxidant/ligand combination for the next hot test at INL is due on May 1, 2016.

5.2.1 Sodium Bismuthate Oxidation for Extraction

The following tasks will be performed in FY16, in continued development of the sodium bismuthate oxidant in preparation for a potential second hot test.

1. Complete the evaluation of reagent purity as a source of the variability in oxidation yield. Until now, bismuthate particle size, water quality and nitric acid quality have been examined and are

found to yield consistently high D_{Am}, when varied. Different sources of DAAP have not yet been tested. This is expected to be complete by the end of February 2016.

2. Measure D_{Am} for DAAP extractions for oxidations performed in batch tests using the baseline raffinate simulant composition being provided by PNNL. This is expected to be complete by the end of February 2016.
3. Measure D_{Am} for DEHBA extractions for oxidations performed in batch tests using the baseline raffinate simulant composition being provided by PNNL. This is expected to be complete by the end of March 2016.
4. Make a recommendation for the parameters for a potential hot test using sodium bismuthate as the oxidant, based on the above. Complete by end of April, 2016.

Related tasks not specifically leading up to the hot test will also be conducted, as detailed in the INL white paper for FY16. These tasks include measurements of the stability of Am(VI) under realistic solvent extraction conditions, including in the presence of other redox active constituents of the feed, and high radiation dose rates. Work will also continue with the examination of monoamides as Am(VI) solvent extraction ligands, including BAMA, to be studied in collaboration with JAEA.

5.2.2 Silver/Ozone Oxidation for Extraction

The following tasks will be performed in FY16, in preparation for a potential hot test with the catalytic ozone oxidant system.

1. Determine the compatibility of Ag(II) with DAAP, and if deemed incompatible identify alternative oxidants which are compatible that can still oxidize Am(III) to Am(VI) in nitric acid.
2. Test pre-treatment protocols for DAAP to try to improve the stability of Ag(II) during extractions. If DAAP is still incompatible with Ag(II), test other extractants such as the amides being developed at INL for improved stability.
3. Optimize oxidation conditions (flowrates, catalyst concentration, etc.) and perform necessary experiments for proper scale-up during a hot test.
4. Develop batch distribution ratios for Am using the optimum catalyst system.
5. Provide input for the recommendation of using catalytic ozone system in a potential hot test during the summer of FY16.

5.2.3 Copper Periodate Oxidation for Extraction

Batch contact data sufficient to support an initial proposed hot test will be prioritized, using the optimized conditions from the preliminary testing described in Section 5.1.3. The two main tasks are:

1. Measure D_{Am} for DAAP extractions for oxidations performed in batch tests using the baseline raffinate simulant composition being provided by PNNL. This is expected to be complete by the end of February 2016.
2. Measure D_{Am} for DEHBA extractions for oxidations performed in batch tests using the baseline raffinate simulant composition being provided by PNNL. This is expected to be complete by the end of March 2016.
3. Make a recommendation for the parameters for a potential hot test using copper periodate as the oxidant, based on the above. Complete by end of April, 2016.

5.2.4 Electrochemistry for Extraction

Continued electrochemistry research will concentrate on the development of electrodes that operate under conditions of higher acidity, maximizing production of the Am(VI) oxidation state, and on solvent extraction batch contacts of electrolytically-prepared Am(VI). This technology is not mature enough to consider for the 2016 hot test.

5.2.5 Peroxydisulfate (with or without silver) oxidation for extraction or ion exchange

This solvent extraction option is not being pursued for hot testing at this time. Ion exchange is discussed in the next section.

5.2.6 Ion Exchange Separations

This technology is not being considered for the FY16 hot test. However, the following tasks will be performed in FY16, in continued development of the ion exchange flowsheet for a potential future hot test.

1. Perform batch contact tests to determine feasibility of oxidative strip of americium from ion-exchange materials. This task is expected to be complete by the end of March 2016.
2. Perform batch contact tests of ion-exchange flowsheet concepts. This task is expected to be complete by the end of August 2016.

5.2.7 Co-crystallization

This technology is not being considered for the FY16 hot test. However, co-crystallization of the oxidized actinides with $UO_2(NO_3)_2{\cdot}6H_2O$ will continue to be investigated and the following tasks will be performed in FY16.

1. Perform tests of co-crystallization of actinyl nitrate salts as a group U-Am. This task is expected to be complete by the end of March 2016.
2. Perform tests of co-crystallization of An(VI) in the presence of key fission products like representative lanthanides, Cs, and Sr. This task is expected to be complete by the end of July 2016.

Other plans are to increase the temperature of the initial solution up to *ca*. 50-60°C to increase the concentration of UO_2^{2+} in solution, in so doing, increase the percent precipitation after cooling. This approach will resemble the process conditions of fuel dissolutions and make it advantageous to implement on a production scale.

6. FY 2017 – 2020 Research and Schedule

6.1 Solvent Extraction Systems

It is desirable to select one oxidant/solvent system for continued development and this should be a priority for FY17. The following discussion assumes that the choice to work with Am(VI) as opposed to Am(V) is established for solvent extraction. Under this scenario the parameters remaining are the choice of oxidant and the choice of the solvent extraction ligand. Although all oxidants will have both advantages and disadvantages, the difficulty of the desired separation demands that a realistic selection be based upon the Am(VI) oxidation yield and the persistence of Am(VI) during the actual separation, in priority to other concerns. It has been shown that once produced, Am(VI) is inherently stable enough in nitric acid to perform separations, however, contact with the organic phase and high radiation doses cause accelerated reduction beyond the so-called autoreduction rates. The reduction rates under these realistic conditions must be evaluated, and a mechanistic understanding of the reduction mechanisms would be beneficial in that it may suggest ways to mitigate their effects, if necessary. The likely reducing agents are the organic ligand, radiolytically-produced HNO_2 and H_2O_2, and possibly redox-active metal ions in the dissolved fuel solution. The effects of these species on Am(VI) stability can be investigated in tandem with selection of the preferred oxidant and ligand. These data will enable development of potential flowsheets leading to an integrated hot test with simulated and real HLW within the next two to five years.

6.2 Ion Exchange Systems

Following on work from other STAAR researchers, once a standard oxidation system has been determined, the ion-exchange systems still face challenges. As has been demonstrated by work at SRNL for FY15, precipitates form during the oxidation of americium in more complex surrogate systems when peroxydisulfate is utilized. Should the use of peroxydisulfate or sodium bismuthate be chosen as the oxidant of choice, a filtration step will be necessary. An integrated test of Am(III) oxidation followed by filtration (if necessary) and ion-exchange separation in a column-configuration is the next logical step. The filtration step likely would not be needed if using the silver catalyzed ozone or Cu(III) periodate oxidation systems can be adopted. These oxidants may be more applicable in this system, which is probably less reducing than are organic solvent systems. The currently used ion exchangers have a small particle size that does not readily lend them to a column type configuration. However, recent work at SRNL has investigated modifying the synthesis of sodium titanates to produce larger particles that are suitable for use in conventional ion-exchange columns. Further development is needed to ensure that the larger particles are mechanically robust. Similar development efforts will be needed for the non-conventional MOF materials.

6.3 Co-crystallization Systems

The group separation by co-crystallization is still in the very early stages of development. More experiments are needed to investigate group oxidation in dissolved fuel solution. This will greatly dependent on the success of other STAAR researchers in their objectives to identify a suitable oxidation system. Once again, oxidants may be applicable here that are unsuitable for organic solvent systems. The behavior of fission products and their impact on the co-crystallization process will need to be evaluated. In addition to the chemistry concerns, there will also be engineering challenges to address, crystallization rector design, filtration methods, number of recrystallizations performed, to name a few. As with any technology, scale up in not always linear and larger batch experiments will be needed before flow sheet development and pilot testing can begin. Despite these challenges, the early success of this new line of research warrants a thorough investigation of this option.

7. Conclusions

This roadmap has summarized a disparate variety of approaches to Am partitioning, within the common theme of the oxidation of Am to valence states above Am(III). During the history of this sigma team, the partitioning of Am(VI) by solvent extraction has progressed from merely a dubious idea to the optimization of the conditions to be used in centrifugal contactor-based separations. Three chemical oxidation systems of varying levels of maturity, for which the pros and cons were discussed here, are now under consideration for further solvent extraction hot testing. These are sodium bismuthate, Cu(III) periodate, and Ag/ozone as oxidants. Based on success with batch extraction contact measurements, one of these will be selected for the second hot test in the summer of FY16. Also, due to research performed under this sigma team, the electrochemical oxidation of Am in nitric acid solution is now possible for the first time. However, this is a recent breakthrough, which will require further development before hot testing with this oxidation technique can be proposed.

High valent Am partitioning technologies are being investigated in addition to solvent extraction. These may have advantages in that Am(V), a much more stable valence state than Am(VI), can be used in ion exchange separations, while both inorganic ion exchangers and co-crystallization techniques can exploit separations without the need to resort to organic reagents with their reducing tendencies. These novel techniques are not ready for testing, but deserve continued attention.

Finally, there are some investigations that are so fundamental that they will support any and all of the technologies being developed. The stability of high valent Am, once it is produced, is of equal importance to the initial oxidation yield. Thus, the effects of radiolysis products such as H_2O_2 and HNO_2, fuel dissolution components such as fission products or other metal ions, and the utility of holding oxidants during separations will remain important topics in successful process design.