TALSPEAK Chemistry in Advanced Nuclear Fuel Cycles

Mikael Nilsson and Kenneth L. Nash

Chemistry Department, Washington State University, PO Box 644630, Pullman, WA, 99164-4630
Email: knash@wsu.edu

The separation of trivalent transplutonium actinides from fission product lanthanide ions represents a challenging aspect of advanced nuclear fuel partitioning schemes. The challenge of this separation could be amplified in the context of the AFCI-UREX+1a process, as Np and Pu will accompany the minor actinides to this stage of separations. At present, the baseline lanthanide-actinide separation method is the TALSPEAK (Trivalent Actinide – Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) process. TALSPEAK was developed in the late 1960s at Oak Ridge National Laboratory and has been demonstrated at pilot scale. This process relies on the complex interaction between an organic and an aqueous phase both containing complexants for selectively separating the trivalent actinide. In this report we discuss observations on kinetic and thermodynamic features described in the prior literature and describe some results of our ongoing research on basic chemical features of this system.

INTRODUCTION

In several countries around the globe, current policy is to operate the nuclear fuel cycle without recycle. As the possibility of expanding the nuclear contribution to electricity production in some countries increases, the issue of closing the loop on the fuel cycle is being reconsidered. In the U.S., both the Advanced Fuel Cycle Initiative (AFCI) and the Global Nuclear Energy Partnership (GNEP) are programs dedicated to providing a framework for this future development. Active research programs elsewhere in the world are evaluating advanced approaches to partitioning the byproducts of fission for better waste management [1]. All of these existing programs emphasize solvent extraction as the means of partitioning the useful byproducts and managing the wastes. The AFCI/GNEP programs are evaluating options for spent fuel partitioning in a process with several options known collectively as UREX. A key feature of UREX processing is the explicit avoidance of creating a pure Pu stream at any point in the operation of the process.

The isolation of transuranics, e.g. Am and Cm, from the rest of the waste is one important step in the UREX+ concepts. Ideally, this should be done in one stage where the transuranics are separated from the total matrix of the spent fuel, although at this point no such proven process exists. However, trivalent actinides and fission product lanthanides can be selectively removed from PUREX raffinates in solvent extraction processes that take advantage of the similarity of the chemistry of these two groups. This separation is most commonly done using solvating extractants like malonamides (the DIAMEX process) [2] or phosphine oxides (the TRUEX process [3] or the TRPO process [4]).

The subsequent separation of trivalent actinides from lanthanides demands the application of a different class of reagents. The most useful hydrometallurgical methods for their mutual separation rely on the slightly greater strength of the interaction that trivalent actinides exhibit with atoms softer than oxygen. Either as a donor atom in a ligand (N, S) or as ionic media (Cl^-) [5-7]. Once the trivalent actinides and lanthanides are separated from the rest of the fission products, the separation between the two groups can be considered. A well-documented method for separation of transplutonium actinides from fission product lanthanides is to apply aqueous complexants containing soft-donor atoms, as in the TALSPEAK [8] (Trivalent Actinide Lanthanide Separation with Phosphorous-reagent Extraction from Aqueous Komplexes) or reversed TALSPEAK [9] processes. In principle, both TALSPEAK and reverse TALSPEAK are based on the extraction of lanthanides using di(2-ethylhexyl) phosphoric acid (HDEHP), or similar liquid cation exchanger, from a medium that selectively retains the actinides in the aqueous phase as complexes with polyaminopolyacetic acid complexants. In reverse TALSPEAK, the complexant solution is applied for selective stripping of actinides from a loaded organic phase. There have been attempts to implement the process in actual treatment of spent nuclear fuel, e.g., the CTH-process [10].

Working Principle of TALSPEAK

The three complexing components in the classic TALSPEAK system are shown in figure 1.

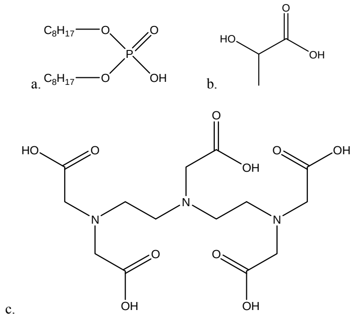

Figure 1. Structures of the different components in the TALSPEAK system;
a: di(2-ethylhexyl) phosphoric acid (HDEHP)
b: lactic acid (HL)
c: diethylenetriamine-N,N,N',N",N"-pentaacetic acid (DTPA)

HDEHP, a liquid cation exchanger that also is a chelating agent, most typically forms a tris complex with trivalent lanthanides in the organic phase, simultaneously releasing three H^+ for each trivalent metal ion transferred into the organic phase. The distribution ratios for the extraction of the lanthanides from mineral acid solutions vary by nearly 10^5 from La^{3+} to Lu^{3+} and overlap significantly with those of the trivalent actinides (Figure 2). Though separations of some individual members of the series (e.g., Am from Yb) are possible with HDEHP alone, this system is not useful for the separation of the groups. By including DTPA and lactic acid in the aqueous phase Weaver and Kappelmann found [11] that a complete group separation can be achieved with the lowest separation factor between neodymium and californium of around 10 as shown in Figure 2. The depression of the actinide distribution is most likely contributed to the stronger complexes of DTPA with trivalent actinides than lanthanides. The complexes between DTPA and Np and Pu are also stronger (depending on the oxidation state) than for the lanthanides and the separation of these two actinides should not suffer in that aspect.

The extraction mechanism for HDEHP in acidic nitrate media can shift from a chelating (ion exchange) mechanism to a solvating mechanism as the nitrate concentration is increased [12]. This is particularly true for tetra and hexavalent actinides. In the p[H^+] range used in TALSPEAK, the extraction mechanisms for trivalent lanthanides and/or trivalent actinides is predominantly of a cation exchange/chelating nature. Under most conditions, three HDEHP hydrogen-bonded dimers surround one metal ion as defined by the following reaction stoichiometry [12-15]

$$\mathrm{M}^{3+} + \overline{3(\mathrm{HA})_2} \rightleftarrows \overline{\mathrm{M(AHA)}_3} + 3\mathrm{H}^+ \quad (1)$$

where HA is the monomeric HDEHP molecule and a bar over a species denotes that it is present in the organic phase. Because several hydrogen ions are exchanged to the aqueous phase for each cation, the extraction is very sensitive to changes in p[H^+]. The extraction mechanism for tetravalent plutonium in low acidity (TALSPEAK conditions) will probably follow the same mechanism as the trivalent ions, surrounded by 4 dimers and with the release of 4 protons. The extraction mechanism of neptunium will depend on the oxidation state of neptunium. For tetravalent neptunium it will be similar to plutonium (IV). For pentavalent neptunium (NpO_2^+) it is assumed that no neptunium is extracted by HDEHP at the acidity used in TALSPEAK.

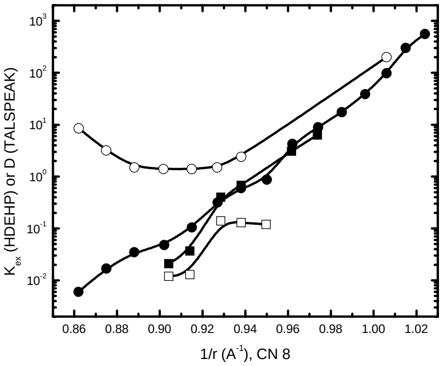

Figure 2. Extraction of trivalent actinides and lanthanides by HDEHP from mineral acid and lactate buffer media containing DTPA: (● (Ln) ■ (An)) Extraction equilibrium constants (K_{ex}) for trivalent f elements ions into HDEHP/toluene from perchloric acid solutions [16], values also shown in table 1; (○ (Ln), □ (An)) Distribution ratios (D) for trivalent f-elements in the TALSPEAK process (0.3 M HDEHP in

diisopropylbenzene, 1.0 M lactic acid, 0.05 M DTPA, pH 3) [11].

There are several examples of the determination of lanthanide and trivalent actinide HDEHP extraction equilibrium constants in the literature. The data plotted in Figure 2 are taken from Stary [16]. These equilibrium constants will be used below in several hypothetical calculations of the thermodynamic features of TALSPEAK. The calculations are discussed in greater detail in the recent review of TALSPEAK [17].

TABLE I. Equilibrium constants for trivalent lanthanide and actinide extraction by HDEHP in toluene from nitric acid solution. [16]

Ln^{3+}	log K_{ex}	An^{3+}	Log K_{ex}
La^{3+}	-2.22		
Ce^{3+}	-1.80		
Pr^{3+}	-1.47		
Nd^{3+}	-1.35		
Pm^{3+}	-1.00		
Sm^{3+}	-0.52		
Eu^{3+}	-0.22	Am^{3+}	-1.70
Gd^{3+}	-0.10	Cm^{3+}	-1.46
Tb^{3+}	+0.63	Bk^{3+}	-
Dy^{3+}	+0.90	Cf^{3+}	-0.22
Ho^{3+}	+1.23	Fm^{3+}	+0.48
Er^{3+}	+1.52	Es^{3+}	-
Tm^{3+}	+2.00		
Yb^{3+}	+2.48		
Lu^{3+}	+2.76		

As mentioned above, the DTPA is responsible for the separation between actinides and lanthanides between the phases. DTPA has been known to complex trivalent metals either as 1:1 M:L or a 1:1:1 M:L:H complex [18].

$$M^{3+} + R^{5-} \rightleftarrows MR^{2-} \tag{2}$$

$$M^{3+} + R^{5-} + H^{+} \rightleftarrows MRH^{-} \tag{3}$$

where R^{5-} is a completely deprotonated DTPA. At the pH of TALSPEAK process operation, protonated DTPA species, most probably H_3R^{2-}, dominate speciation of the free DTPA ligand. Thus, for the metal to bind to DTPA several protons need to be displaced, making the system even more sensitive to pH. Some equilibrium constants for metal-DTPA complexation were collected in the recent review [17]. For tetravalent ions DTPA have even higher affinity than for trivalent, for Np^{4+} log β is around 30, compared to 22.9 for Am^{3+} [19]. Pentavalent and hexavalent actinyl ions may be complexed by DTPA, however the data in the open literature are scattered. On the other hand pentavalent actinyl ions are not expected to be extracted by HDEHP under TALSPEAK conditions so the net distribution should be low.

Lactic acid, being more abundant than both HDEHP and DTPA in TALSPEAK, is also known to complex metals according to equation 4 below. Even though the complexes are weak the relative abundance of lactate makes it important to consider these complexes when trying to describe the system.

$$M^{3+} + nL^{-} \rightleftarrows ML_{n}^{3-n} \tag{4}$$

where L^- is a lactate ion. The affinity for the trivalent lanthanides and actinides with lactic acid is high enough to enable the possibility of mixed complexes (e.g., Am-DTPA-lactate or $Ln(HDEHP)_2(lactate)$) being formed. In some studies of TALSPEAK chemistry [14, 20], the presence of mixed ligand complexes has been suggested, though direct observation of the existence of such species is lacking.

The different species of DTPA and lactic acid when the metal is disregarded can be described using a speciation diagram shown in Figure 3. From this figure it is clear that in the working pH range for TALSPEAK the dominating species for DTPA is H_3R^{2-} and that lactic acid and lactate ion are present in similar amounts.

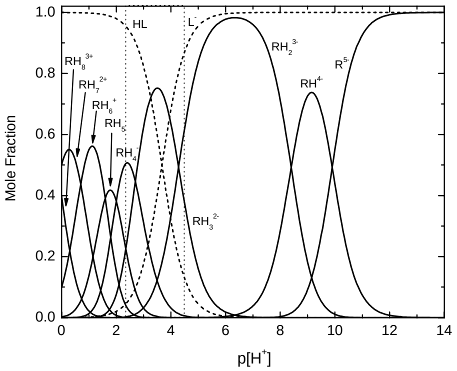

Figure 3. Speciation diagram showing DTPA and lactic acid calculated using protonation constants at 0.1 M ionic strength, 25.0°C [19]. The dotted rectangle outlines approximate working conditions for the TALSPEAK system.

Considering the pH dependency of the mechanisms involved, correct and careful control of the pH is important. There are a few reports of the pH dependency of the extraction in the TALSPEAK system, as shown in Figure 4. Those investigations all point to a decreasing trend with higher pH, both linear and non-linear trends have been observed.

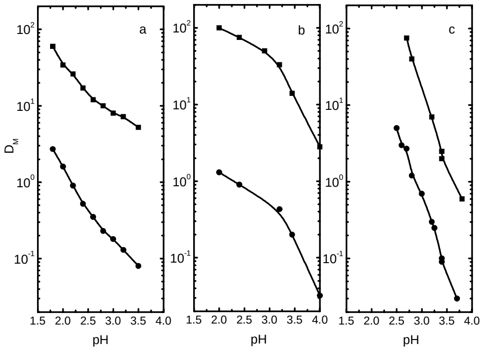

Figure 4. pH dependence of extraction of Am (●), Eu (■ a and b), Nd (■ c.) a. Organic phase: 0.5 M HDEHP in diisopropylbenzene. Aqueous phase: 1 M lactic acid and 0.05 M DTPA. Reproduced from data in [11], b. 0.5 M HDEHP in *n*-decane from 1 M lactic acid and 0.07 M DTPA versus the p[H^+] of the aqueous phase. Reproduced from data in [13], c. Organic phase: 1 M HDEHP in odorless kerosene. Aqueous phase: 1.5 M lactic acid and 0.05 M DTPA. Reproduced from data in [9].

Using relatively simple mass balances and a set of stability constants from the literature it is possible to describe the distribution ratio for a given metal as a function of [H^+]. This calculation was carried out in the previous review paper [17] and figure 5 is a reproduction from those calculations.

By comparing Figures 4 and 5 it is clear that the experimental pH dependency is not accurately described with this model, based on the mechanisms and stability constants found in the open literature. Unknown interactions between the different components of TALSPEAK, for example, the presence of mixed ligand complexes in either phase could account for the discrepancy between theoretical and experimental values. To attempt to address this question, we have investigated the effect of lactic acid on extraction equilibria and phase transfer kinetics. There are reports in the literature that lactic acid play a larger role than just an inert buffer. This work may give us clues if lactic acid remains inert or if and how it interacts in the system.

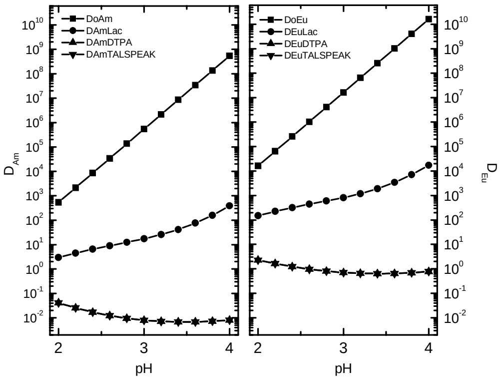

Figure 5. Calculated distribution ratios for Am^{3+} and Eu^{3+} for HDEHP extraction from mineral acid solution (■), in contact with 1 M lactic acid (●), 0.05 M DTPA (7), 0.05 M DTPA, 1.0 M lactic acid (B). Calculations based on a self-consistent set of equilibrium constants at 0.1 M ionic strength and T = 25°C obtained from [19].

EXPERIMENTAL

Chemicals and Materials Used

The HDEHP used was obtained 97% pure from Sigma-Aldrich and was purified before use by the copper precipitation method [21]; the product of purification was above 99% pure. The *n*-dodecane and 1,4-diisopropyl benzene were both obtained from Alfa Aesar with a purity of 98% and was used as received. The lanthanides used were obtained from Arris International Co. as the metal oxides (carbonate in the case of cerium) and had a purity of 99.999%. These were dissolved in nitric acid and standardized as regards to metal concentration (ICP-OES), acidity, and nitrate concentration (ion exchange and potentiometric titration). The concentrated nitric acid (69.9% w/v) and an 85% (w/v) aqueous solution of lactic acid was obtained from J.T. Baker and used as supplied. DTPA (puriss) was obtained from Fluka and used as is. Sodium hydroxide was obtained from Sigma-Aldrich in the form of 50% (w/w) solution. Sodium nitrate used was obtained from Ricca Chemical Company; a saturated solution was filtered and recrystallized to remove all impurities prior to use. The analytical grade KHP used to standardize the base in the potentiometric titrations was obtained from Sigma-Aldrich and stored in an oven at 80°C to keep it dry. The ^{241}Am tracer in 0.1 M HNO_3 solution was obtained from Pacific Northwest National Laboratory. The $^{152+154}$Eu tracer was prepared by irradiating europium oxide (99.999% pure from Arris) in the 1MW TRIGA reactor at the Nuclear Radiation Center, WSU. The activated europium oxide was dissolved in nitric acid and standardized for activity.

Lactic Acid Extraction Dependency

Aqueous solutions were prepared by weighing suitable amounts of the different reagents into graduated glassware and diluting to the required volume. All aqueous solutions were prepared in a similar way; 1.0 mM total metal concentration with equal amounts of each lanthanide and yttrium, 0.05 M of DTPA, varying concentration of lactic acid, pH adjusted to desired value by addition of NaOH or HNO_3, and the final concentration of Na^+ adjusted to 1.0 M by adding $NaNO_3$ after final pH adjustments. The organic phase consisted of 0.3 M HDEHP in *n*-dodecane. Before extraction the aqueous and organic phases were pre-equilibrated. All experiments were carried out in triplicate. Similar experiments were carried out in parallel where one set of triplicates were spiked with trace amounts of ^{241}Am. Gamma analysis of samples containing americium were performed on a NaI(Tl) solid scintillation counter (Packard Cobra 5003). For the samples containing only non-radioactive metals, the organic phase was removed and only the aqueous phase was analyzed by ICP-MS. The aqueous phase was sampled prior to contact to observe any change in aqueous concentration due to extraction of the metal. All aqueous phases were finally checked for p[H^+] by measuring the potential with a combination glass electrode calibrated for [H^+] vs. mV.

Phase Transfer Kinetics

All solutions were prepared by weighing suitable amounts of different reagents and diluting to required volume. Organic phase consisted of 1,4-DIPB with 5g/L PPO and 0.5 M HDEHP. Aqueous solutions consisted of 0.01 M HNO_3 and 0.99 M $NaNO_3$ with different amounts of lactic acid. The experiments were carried out using a Beckman LS 6500. liquid scintillation counter. 1 mL of aqueous phase was added to a glass scintillation vial, tracer amounts of $^{152+154}$Eu was added to the aqueous phase. Three mL of organic phase was carefully placed on top of the aqueous phase and a timer was started. As soon as possible, without agitating the phases, the scintillation vial was placed in the LSC and was counted for 100 times at a certain time interval, normally between 1 and 3 minutes. As the europium is extracted into the organic phase the count rate from the LSC will increase due to an increase in the excitation of PPO from the radioactive europium isotopes. Care must be taken to compensate with appropriate backgrounds due to shine from the aqueous phase into the organic. These experiments result in datasets of counts rates in the LSC as a function of time which can be converted to concentration of europium in either phase as a function of time, see below. The technique used in this work is an adaptation of work carried out previously in phase transfer kinetics of thorium and americium extraction using HDEHP [22].

RESULTS AND DISCUSSION

Lactic Acid Extraction Dependency

The results for the extraction across the lanthanide series is shown in figure 6.

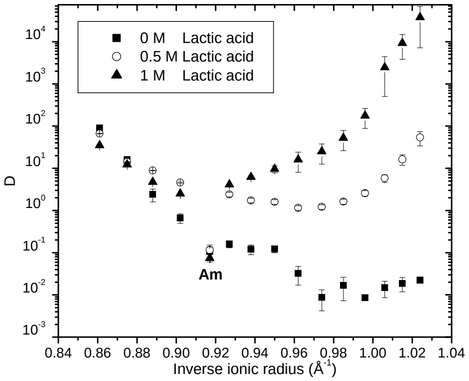

Figure 6. Extraction of lanthanides and americium using 0.3 M HDEHP in 1,4-DIBP as organic phase. Aqueous phase consisted of 0.05 M DTPA, 1 mM total lanthanides and varying concentrations of lactic acid, pH adjusted to 3.5. Contact time was 30 min at room temperature. Values for the ionic radius are taken from [23] and correspond to a coordination number of 8.

For the light lanthanides and Am^{3+}, the introduction of higher concentrations of buffered (pH 3.5) lactate has minimal impact on the partitioning of the metal ion between the HDEHP and DTPA phases. From Sm^{3+} to Lu^{3+} the introduction of 0.5 M buffered lactate increases the extraction of the lanthanide ions by a factor of 10-1000 (increasing from Sm to Lu). Doubling the lactate concentration results in an extraction increase from 10 to 10^6 from Sm to Lu. The general shape of the curve for 1 M lactic acid is similar to that shown in Figure 2 for the original TALSPEAK system.

The 30 minutes equilibration time for these experiments would argue against a kinetic explanation. None of the available thermodynamic data in this system, used to perform the model calculations shown in Figure 5, predict an increase in the extraction of heavy lanthanides as the concentration of lactate increases. Two possible explanations for this observation come to mind: 1) complexes of the form $Ln(lac)_n(AHA)_{3-n}$ are formed that are more strongly partitioned into the organic phase than $Ln(AHA)_3$ or 2) the high concentrations of buffered lactate sufficiently alter the structure of the aqueous medium to increase the magnitude of the $Ln(AHA)_3$ partitioning coefficient (K_d). Some indirect observations from the prior TALSPEAK literature suggest a tendency for partitioning of lactate into the organic phase. This aspect of the TALSPEAK system is under continuing investigation in our laboratories.

Phase Transfer Kinetics

The results of several of the phase transfer kinetics experiments are shown in figure 7. The rate data were fit using a model that includes two parallel first order reactions. It is clear from the plots that the first is a rapid reaction governing the rate of transfer that becomes unimportant after the first few minutes. Under some conditions, the second, slower reaction dominates in the longer time frame. This treatment is similar to what was reported in a previous report [24] on kinetics of calcium extraction using HDEHP. In that report, it was explained that the fast reaction correlated with the consumption of all the reagents in the phase boundary at the start of the experiment and the slower reaction, governing most of the transfer, represents the diffusion of reagents from the bulk to the phase boundary.

It can be seen that for small additions of lactic acid, 0.01-0.05 M, the kinetics of phase transfer in the unstirred system decreases. In contrast, at 0.5 M total lactate, the rate increases markedly. It appears likely that the pattern observed indicates two different kinetic regimes. At low lactic acid concentration, it is suggested that lactate decreases the rate of diffusion of europium to the phase boundary due to the formation of complexes in the aqueous medium. The rate of complexation and decomplexation for these species has not been reported, but can be expected in general to be fast enough to not limit the rate of phase transfer. However, diffusion of $Eu(lac)_n^{3-n}$ complexes toward the phase boundary must be slower than that of the hydrated cation $Eu(H_2O)_{8\text{-}9}^{3+}$.due to the increased bulk of the complexes and the reduced lability of the ligands (relative to the fast exchanging water molecules). We suggest that the high concentration of lactate in the aqueous medium significantly alters the structure of the aqueous medium and thus reduces the energetic barrier to diffusion of the cation and/or its complexes; in effect, high lactate concentration lowers water activity and thus makes transport to the interface easier. It is also possible that lactate ions (lac^-) or lactic acid (Hlac) may also be interphase active and thereby alter structure of the aqueous side of the biphasic boundary increasing the rate of europium extraction.

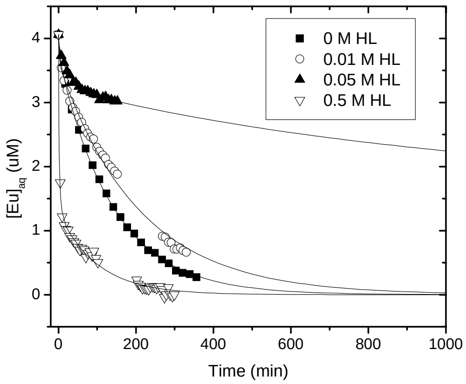

Figure 7. Extraction of europium as a function of time at different HL concentrations in an unstirred system. Organic phase was 0.5 HDEHP in 1,4-DIPM with 5g/L of PPO. Aqueous phase was 0.01 M HNO_3 with 0.99 M $NaNO_3$, trace concentration of $^{152+154}Eu$ with different additions of lactic acid. Experiments carried out at room temperature. To improve clarity, only every 5th data point is plotted in the figure. Data also exist for longer measurements, t_∞. Lines in the figure are the fitted curves to the data assuming two parallel first order reactions.

CONCLUSIONS

The information presented indicates that the lactic acid buffer participate sin the net operation of the TALSPEAK process in a manner that is not explained by existing information on the thermodynamic features of the known Eu(III)-lactate species. The results to date are suggestive of the influence of both medium effects and the presence of previously unreported metal lactate complexes in this system. Additional thermodynamic and kinetic studies are in progress in an effort to shed additional light on these complex reactions. Our objective is to reach a deeper understanding of the mechanisms that drive and limit the performance of the TALSPEAK system.

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