Actinide Species in Alkaline Media

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Project Overview

The fundamental chemistry of actinide ions in representative solution and solid phases will be investigated to improve the understanding of actinide behavior during sludge washing operations

Experimental Program

Preparation and structural characterization of actinide-containing sludges from the BiPO, Redox, and PUREX processes

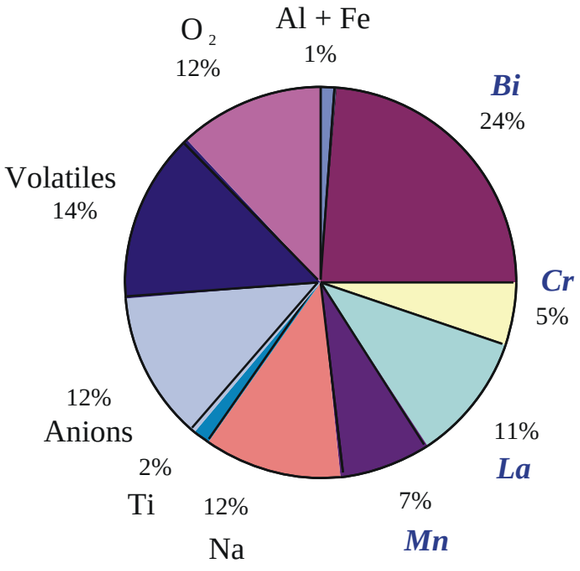
Thermodynamics and kinetics studies of complexation and redox reactions of U, Np, Pu, and Am in strongly alkaline solutions

Emphasis is on determining the influence of RADIOLYSIS, COMPLEXATION, and REDOX CHEMISTRY on actinide concentrations and speciation in alkaline solutions

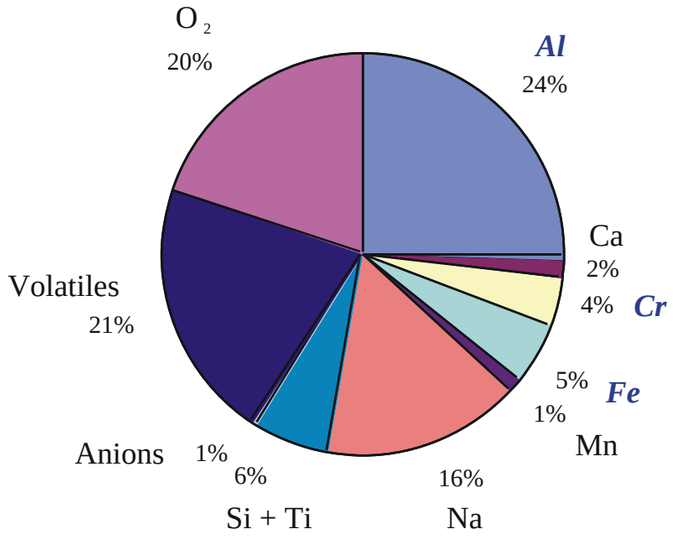
Sludge Compositions and Simulant Analyses

The bulk nonradioactive components of dried sludge materials arising from the BiPO$_4$ (Cycle 3), Redox, and PUREX processes are presented in the pie charts below. *The principal differences in the waste sludge analyses stem from the unique aspects of the separations process*; that is, BiPO$_4$ wastes are rich in Bi, La, Mn, and Cr; Redox wastes are largely Al with lesser amounts of Fe and Cr; and PUREX sludges contain mostly Fe with some Al and Mn.

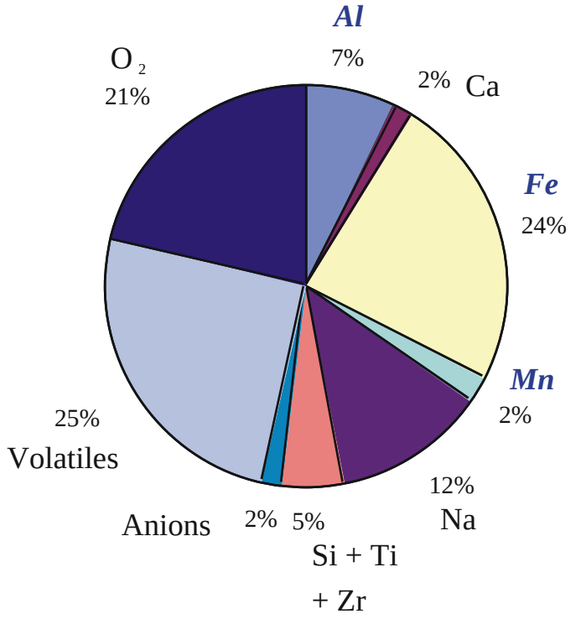
BiPO$_4$ (Cycle 3)



Redox



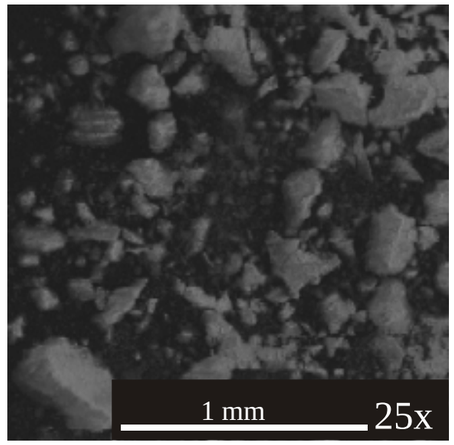
PUREX

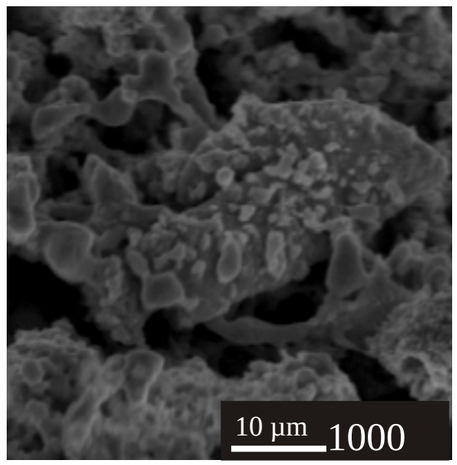


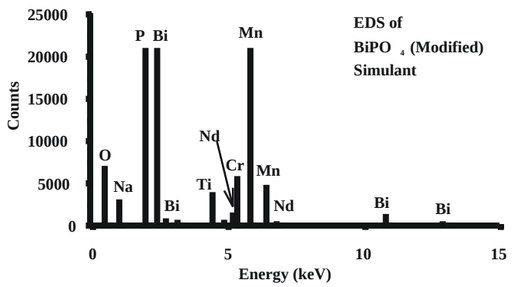
Sludge Simulant Analysis

Minor changes to the published synthesis of the two BiPO$_4$ sludge simulants were made: 100% La was substituted with 33.3% each of La, Nd, and Eu in both BiPO$_4$ simulants. Because Al, Ti, and Fe are present in actual sludge samples and because actinides are known to sorb to oxide surfaces, these elements were added to the simulant referred to as BiPO$_4$ (Modified). In general, *the energy dispersive spectroscopy (EDS) results compare favorably with the wet chemical waste analyses except that the BiPO$_4$, BiPO$_4$ (Modified), and PUREX simulants prepared here contain 3-5 times more Mn than found in the actual wastes*.

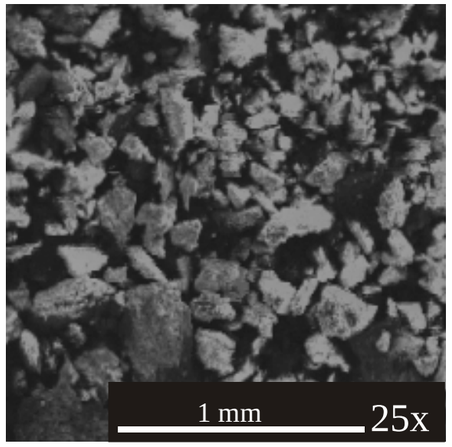
BiPO$_4$ (Modified) Simulant Dried to 120 ðC

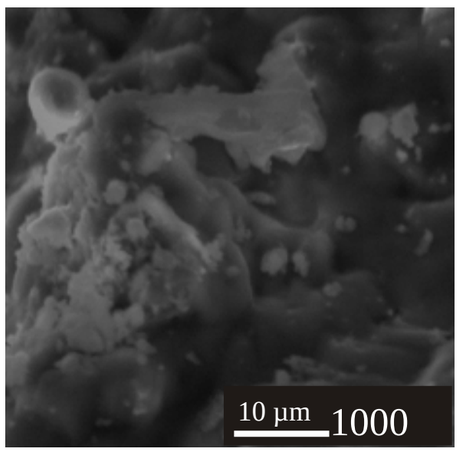


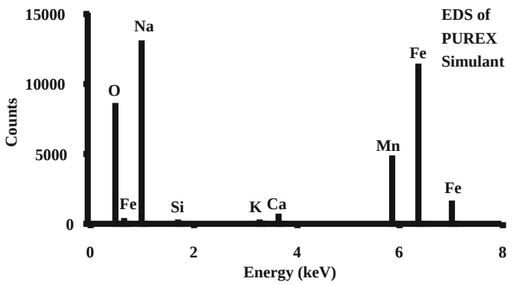




PUREX Simulant Dried to 120 ðC





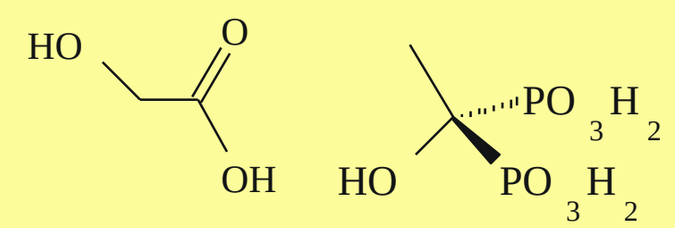


Sludge Washing Procedure

Consecutive washing of sludges was performed in order to determine if actinide ions are mobilized during the component-wise dissolution of the sludge matrix

The wash solutions become increasingly aggressive :

- 0.01 M $NaNO_2$ + 0.01 M NaOH (sluicing liquid from Hanford baseline strategy)
- 3.0 M NaOH (leachant from Hanford baseline strategy)
- HO_2
- 0.05 M Glycolic Acid + 0.10 M NaOH
- 0.10 M HNO_3
- 2.0 M HNO_3
- 0.50 M 1-Hydroxyethane-1,1-diphosphonic acid (HEDPA)



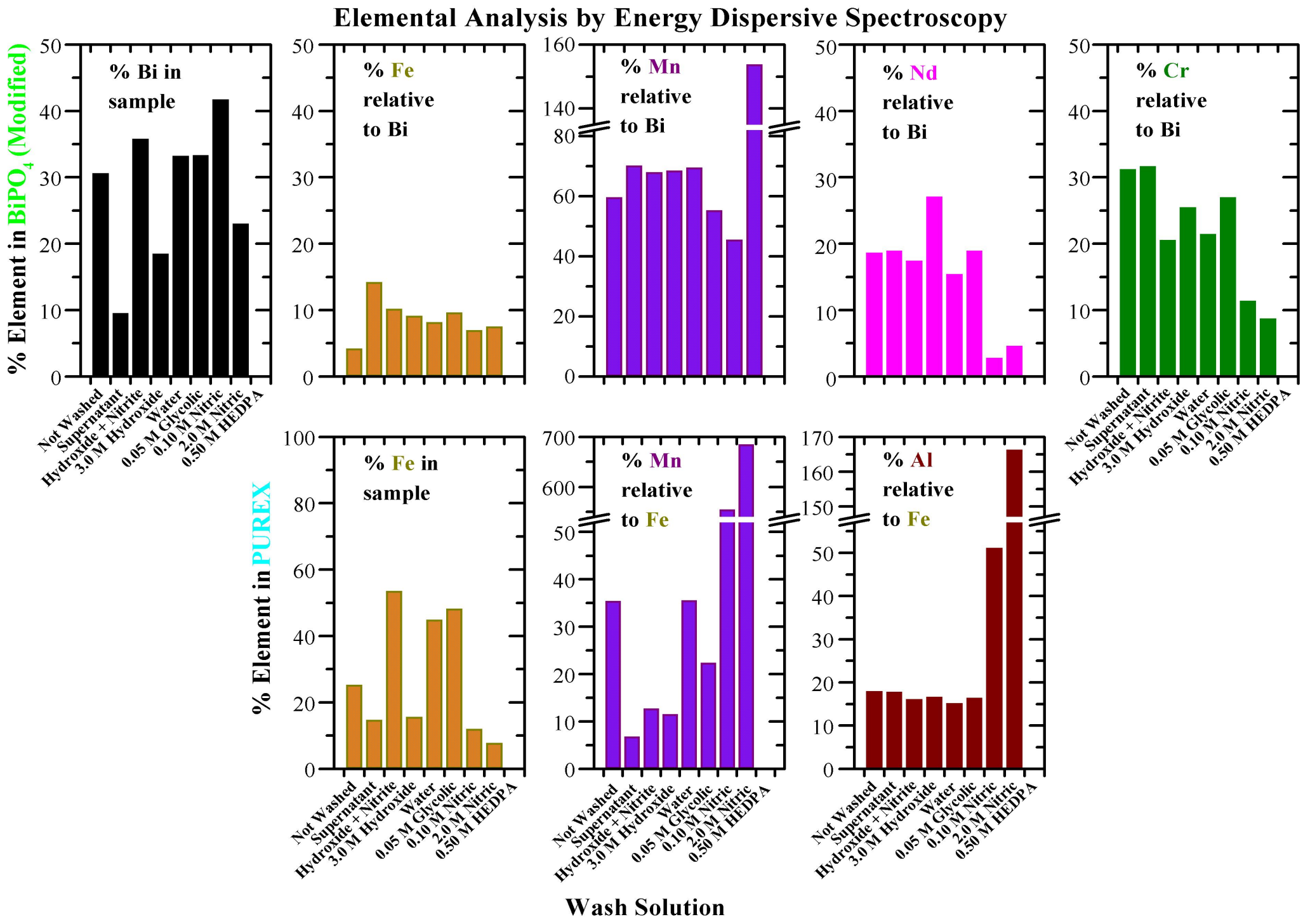
Glycolic Acid **HEDPA**

Pu(III + IV), Pu(VI), and Np(V) (also containing Pa(V)) were quantitatively sorbed to sludges from pH ² 9.5(5) solution, exposed to a simplified supernatant (0.10 M $NaCO_3$ + 0.50 M $NaOH_2$ + 1.0 M $NaNO_3$) for 22 h, and consecutively contacted with each wash solution for 0.5 h each

Filtered and unfiltered samples were assayed radiometrically

Energy Dispersive Spectroscopy

The major trends in the depletion of Fe, Nd, and Cr during washing of the $BiPO_4$ (Modified) simulant match the solution spectroscopic data and lead to an increase in Mn content, as the latter is not dissolved until the 0.50 M HEDPA wash. *The depletion of Fe from the PUREX simulant gives rise to an increase in both the Mn and Al contents of the residual solids*, which indicates that these elements are present in highly intractable forms.



Acknowledgments

The kinetics experiments were performed by James Sullivan (ANL) and Melissa Baird (student participant), the electrochemistry by Artem Gelis (ANL), and the U sludge washing experiments by Alexander Garnov (LBNL).

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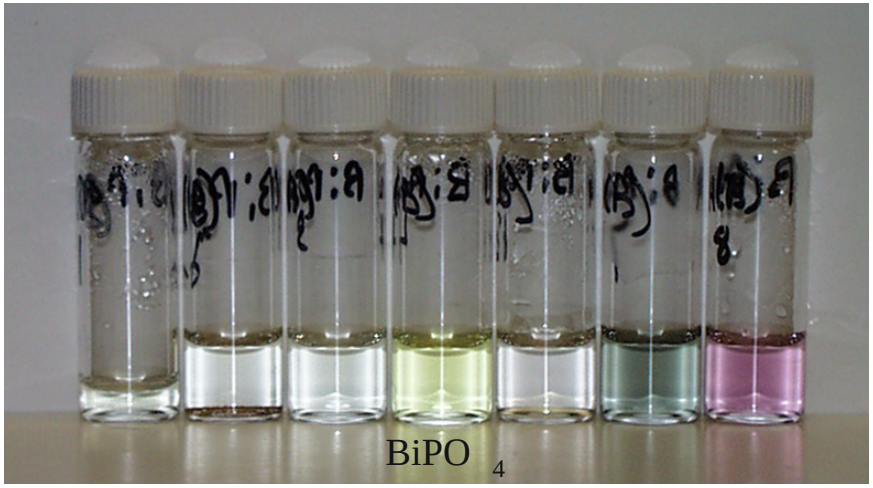
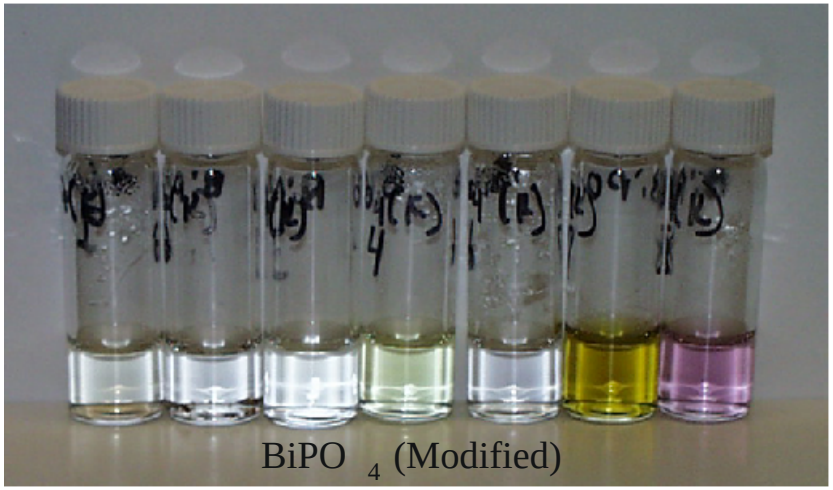
Transition Metals are Released During Sludge Washing



$BiPO_4$



$BiPO_4$ (Modified)

Hydroxide + Nitrite

3.0 M NaOH

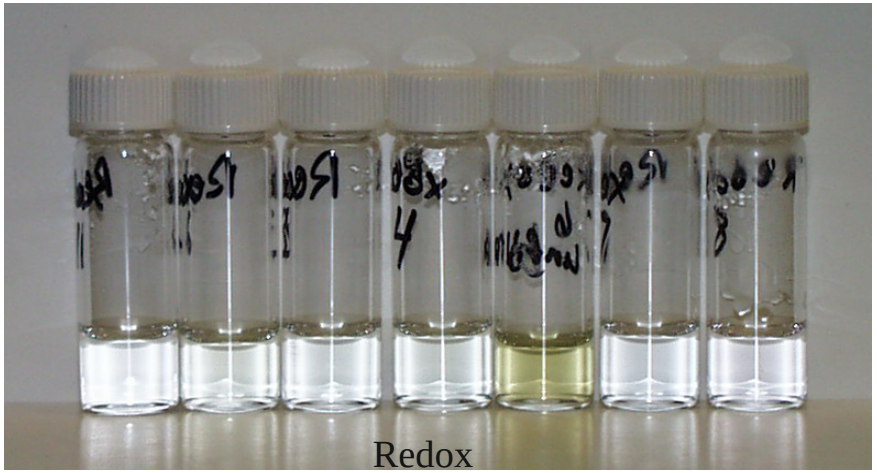
HO_2

0.05 M Glycolic

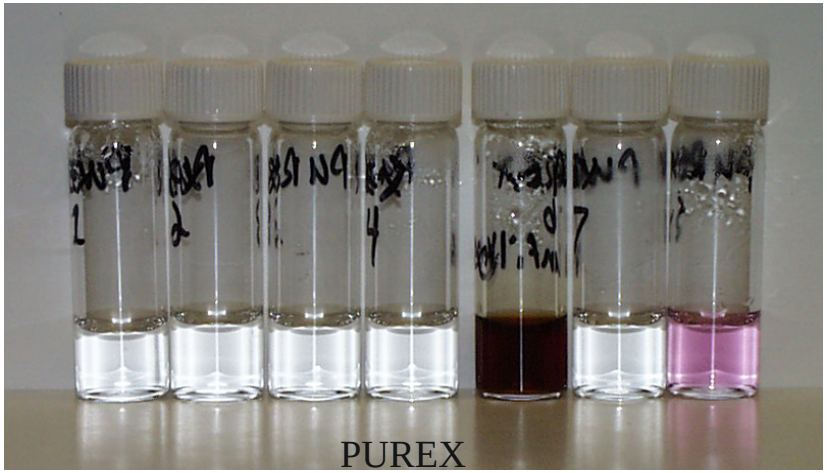
0.10 M HNO_3

2.0 M HNO_3

0.50 M HEDPA



Redox



PUREX