

DEVELOPMENT OF BIODEGRADABLE ISOSACCHARINATE-CONTAINING FOAMS FOR DECONTAMINATION OF ACTINIDES: THERMODYNAMIC AND KINETIC REACTIONS BETWEEN ISOSACCHARINATE AND ACTINIDES ON METAL AND CONCRETE SURFACES

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RESEARCH OBJECTIVE

Actinide contamination of steel and concrete surfaces is a major problem within the DOE complex. Almost all current decontamination technologies rely on removal of the contaminated surface layer by mechanical means or by chemical methods, using harsh chemicals. Some of the technologies are ineffective. Others are expensive, labor intensive, and hazardous to workers. Still others create secondary mixed wastes that are not environmentally acceptable. This project seeks fundamental information that will lead to the development of a new and more environmentally acceptable technology for decontamination of actinides, especially Pu, on steel and concrete surfaces. The key component of this technology is isosaccharinate (ISA), a degradation product of cellulose materials that is biodegradable. Isosaccharinate will be incorporated into foams/gels for safe and easy use in decontamination of actinides from steel, concrete, and other surfaces. Thermodynamic data are being developed on the interactions of ISA with actinides and competing metals [e.g., Fe(III) and Ca(II)] under a wide range of conditions relevant to decontamination of steel and concrete. The efficiency of the ISA containing foams/gels/solutions for decontamination is also being tested. This project builds on capabilities at three different national laboratories, and represents a joint effort between PNNL, LBNL, and SNL.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes the results of nearly first two years of a three-year project. The past available data on ISA with tetravalent actinides have been very limited (limited to pH 12), empirical, and only related to determining actinide behavior in cementitious environments. The emphasis of our work has been on developing fundamental data for ISA complexes to test its use/applicability for cleaning actinide contaminated surfaces and for cleaning surfaces contaminated with other radionuclides and non-radioactive elements. Although ISA forms strong complexes with all different oxidation states of actinides, the complexes it forms especially with tetravalent actinides are of the highest interest. This is because actinides (especially Pu and Th) are expected to be present in the tetravalent state, the state at which they are extremely insoluble and need to be removed for decontamination purposes. Therefore, a major emphasis of our fundamental studies on actinides has been on the actinides in their tetravalent state. For this purpose we are developing fundamental data on 1) ISA and its complexes with tetravalent

actinides, in particular Th(IV) and Np(IV), in the entire range of pH values of environmental interest, and 2) ISA complexes with metal ions (e.g., Fe(III), Al(III), and Ca(II)) that compete with the actinides for ISA. In addition to fundamental studies, we are also conducting proof-of-principle decontamination tests and developing specifications for incorporation of ISA into decontaminating media (e.g., foams, gels). The progress made on these various research activities is briefly discussed below.

An Improved Method for Preparation of Ca(ISA)₂(c) and Isosaccharinate Solutions, and Nuclear Magnetic Resonance characterization of solution species

A common method for producing calcium isosaccharinate [Ca(ISA)₂(c)] is by the hydrolysis reaction of α -lactose using Ca(OH)₂ (Whistler and BeMiller 1958). This method, however, produces a product with significant impurities, mainly CaCO₃ and unreacted Ca(OH)₂. The product thus produced is also fairly insoluble and would have to be converted to a more soluble form for use in fundamental studies and as a decontaminating agent. Methods to produce high quality Ca(ISA)₂(c) and to convert this to a more soluble form have been developed. A method described below for purification of Ca(ISA)₂(c) has been developed that is rapid, not very labor intensive, and produces Ca(ISA)₂(c) of very high purity. The method is:

- 1) Add 0.25 moles Ca(ISA)₂ prepared by Whistler and BeMiller (1958) method to one liter of solution containing 0.35 moles Na₂CO₃ and 0.01 M NaOH
- 2) Shake mixture (typically 1 hour is sufficient). Na₂CO₃ reacts with Ca(ISA)₂ to produce solid CaCO₃(c) and NaISA solution.
- 3) Filter out CaCO₃(c) that has precipitated to separate it from the NaISA solution and residual Na₂CO₃ and NaOH solution.
- 4) Adjust pH to between 4.5 and 5.0 using HCl to get rid of excess carbonate and hydroxide to obtain NaISA solution.
- 5) Add CaCl₂ to reprecipitate Ca(ISA)₂(c)

Wash the precipitate and repeat the above steps if end product of highest quality is desired. In most cases, one time through steps 1 to 5 is adequate. The solids can be recovered by evaporation, freeze-drying, or other procedures. Freeze-drying is most efficient, and loses less material and produces a product of consistent quality.

Dilute aqueous solutions of the Ca and Na salts of “ α ”-D-isosaccharinate (ISA⁻) have been analyzed by ¹³C and ¹H NMR spectroscopy (Cho et al. 2003). The positions of the six ¹³C ISA NMR lines show a pH dependence that can be used to infer that the most acidic proton is the one associated with the carboxylate group, with log K⁰ of -3.27 ± 0.02 for the reaction [HISA(aq) \rightleftharpoons ISA⁻ + H⁺]. In acidic solutions (pH <~4.5), NMR signals were found that could be assigned to “ α ”-D-isosaccharino-1,4-lactone (ISL), formed from dehydration of isosaccharinic acid (HISA). These data provided fundamental information about the expected isosaccharinate species important in a large range of pH values (1 to 14).

Isosaccharinate complexes with tetravalent actinides

The solubility of NpO₂(am) as a function of pH at a fixed concentration of ISA shows that the observed aqueous Np concentrations are up to several orders of magnitude higher than expected in the absence of

ISA (Fig. 1A). To further develop fundamental data, the solubility of $\text{NpO}_2(\text{am})$ was also determined as a function of ISA concentrations at a fixed pH of 12 (Fig. 1B). These data showed dramatic increases in solubility with the increase in ISA concentrations. When the solubility as a function of ISA concentrations at a fixed pH of 12 are compared with the concentrations at a fixed pH of 5 (Rai et al. 1998), the dramatic increases in Np concentrations are observed in most of the environmental range of pH values with the increase in ISA concentrations. A comprehensive thermodynamic model for system $\text{Np(IV)}\text{-Ca}^{2+}\text{-Na}^+\text{-H}^+\text{-OH}^-\text{-ISA}^-$ was developed (Rai et al. 2003) based on the data obtained in this study and those reported in the literature. The model is based on studies of 1) the solubility of $\text{Ca(ISA)}_2(\text{c})$ and NMR investigations of $\text{HISA}(\text{aq})$ (isosaccharinic acid) and $\text{ISL}(\text{aq})$ (dehydration product of $\text{HISA}(\text{aq})$) to determine the acid dissociation constant of $\text{HISA}(\text{aq})$, hydrolysis reaction of $\text{ISL}(\text{aq})$, and complexation constants of Ca^{2+} with ISA^- ; 2) $\text{NpO}_2(\text{am})$ solubility in a wide range of pH values (~ 2 to 14) and total ISA concentrations of 0.0016 *m* and 0.008 *m*, and at fixed pH values of approximately 5 and 12 with total ISA concentrations ranging from 0.0001 *m* to 0.1 *m* to determine equilibrium constants of various $\text{Np(IV)}\text{-ISA}$ complexes; and 3) solvent extraction of Np-ISA solutions, containing fixed NaClO_4 concentrations ranging from 0.103 *m* to 6.54 *m* and at fixed pC_{H^+} values ranging from 1.5 to 1.9, with dibenzoylmethane to test/extend the model to high ionic strength and acidity. Pitzer's ion-interaction approach was used to interpret the data. The isosaccharinate complexes required to explain these data included Ca(ISA)^+ , $\text{Np(OH)}_3(\text{ISA})(\text{aq})$, $\text{Np(OH)}_3(\text{ISA})_2^-$, $\text{Np(OH)}_4(\text{ISA})^-$, and $\text{Np(OH)}_4(\text{ISA})_2^{2-}$. The values of equilibrium constants for the complexes determined from these data (Table I) provided close agreement between the observed and predicted concentrations in all of the systems investigated in this study and those reported previously. The thermodynamic data developed from these studies are summarized in Table I.

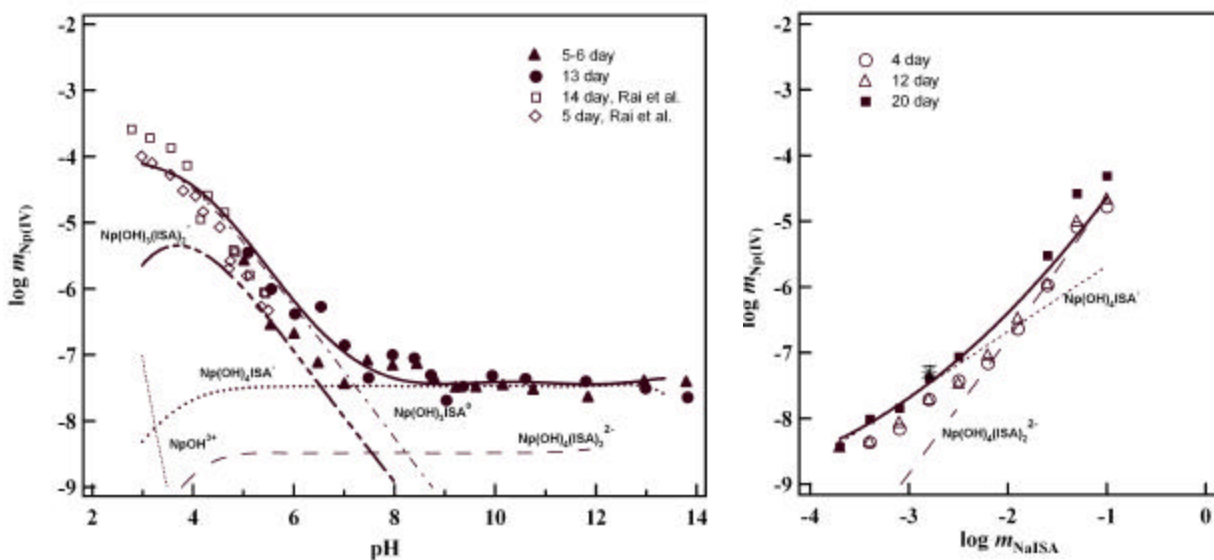


Fig 1. Aqueous Np(IV) concentrations in equilibrium with $\text{NpO}_2(\text{am})$. A(left) -- at a fixed total ISA concentration of 0.0016 *m*. B (right) -- at a fixed pH of ~ 12 . Solid line represents total concentrations, while other lines represent concentrations of different species, as identified, predicted using modeling parameters reported in Table I.

Table I. Important Chemical Reactions Included in the Model.

Reaction	log K ^o	Reference
Ca(ISA) ₂ (c) Ca ²⁺ + 2ISA ⁻	-6.26± 0.07	This Project
	-6.54	Van loon et al. (1999)
	-7.62	Rai et al. (1998a)
	-6.36± 0.10	Vercammen et al. (1999)
Ca ²⁺ + ISA ⁻ CaISA ⁺	1.44± 0.07	This Project
	1.70	Van loon et al. (1999)
	1.7	Vercammen et al. (1999)
Ca ²⁺ + 2ISA ⁻ Ca(ISA)(aq)	NN	This Project ^a
	5.4	Rai et al. (1998a)
ISL(aq) + H ₂ O ISA ⁻ + H ⁺	-3.64 ± 0.07	This Project
HISA(aq) ISA ⁻ + H ⁺	-3.27 ± 0.02	This Project ^b
	-4.46	Rai et al. (1998a)
Np ⁴⁺ + H ₂ O NpOH ³⁺ + H ⁺	-0.5	Rai et al. (1999)
NpO ₂ (am) + ISA ⁻ + H ⁺ + H ₂ O	2.57 ± 0.37	This Project
Np(OH) ₃ ISA(aq)	2.76	Rai et al. (1998b)
NpO ₂ (am) + 2ISA ⁻ + H ⁺ + H ₂ O	4.68 ± 0.37	This Project
Np(OH) ₃ (ISA) ₂ ⁻		
NpO ₂ (am) + ISA ⁻ + 2H ₂ O Np(OH) ₄ ISA ⁻	-4.76 ± 0.37	This Project
NpO ₂ (am) + 2ISA ⁻ + 2H ₂ O Np(OH) ₄ (ISA) ₂ ²⁻	-2.90 ± 0.37	This Project

^a This project in this column refers to the data presented in Rai et al. (2003), and NN = not needed.

^b Based on our NMR studies (Cho et al. 2003) and consistent with the solubility studies on Ca(ISA)₂(c) (Rai et al. 2003).

Studies, similar to those described above for Np, were also conducted on the solubility of ThO₂(am) as a function of pH at a fixed ISA concentrations, and as a function of ISA concentrations at different fixed pH values. These fundamental data on Np(IV) and studies with Th are helping to develop a fundamental understanding of the ISA reactions in an environmentally important range of pH values and as a function of ISA concentrations such that chemical conditions necessary for foams and other media containing ISA for cleaning purposes can be well established based on scientific grounds.

Isosaccharinate complexes with important metal ions present in matrix of contaminated materials such as steel and concrete

In order to determine the influence of metal ions (e.g., Fe(III) and Ca(II)) on the extractability of actinides from contaminated surfaces, comprehensive thermodynamic data for ISA complexes with metal ions are required. We have developed comprehensive data for the Ca system, and have reported those results above. No data on ISA complexation with Fe(III) are available in the literature. Therefore, we have initiated studies with the Fe(III)-ISA system. We have preliminary data on the solubility of Fe(OH)₃ (2-lie ferrihydrite) in the absence and presence of 0.001 M ISA as a function of pH. These data show that ISA increases the solubility of Fe(III). Additional studies in this system are planned to be able to develop a comprehensive thermodynamic model for this system.

Proof-of-Principle Decontamination Tests Using ISA

In addition to the fundamental studies described above that are being carried out at PNNL and LBNL, studies at SNL are focused on testing isosaccharinate for its effectiveness in removing actinides from contaminated surfaces and for preparing different formulations, such as foams and gels, for effective delivery of ISA to the contaminated surfaces. In a preliminary test of proof of principle, uranium as U(IV) or U(VI) in solution was deposited on the steel surface by placing a drop of U solution on the steel coupons. The concentration of U in each solution was 1×10^{-6} M at a pH of 6. The solutions were allowed to dry on the surface and sit for 3 weeks prior to decontamination with deionized water, 0.04 M ISA solution, or a 0.04 M citrate solution. The coupons were placed in 50 ml. of the decontamination solutions and gently shaken. The results showed that ISA is much superior to citrate or plain water for removing uranium from the steel surfaces (Fig. 2).

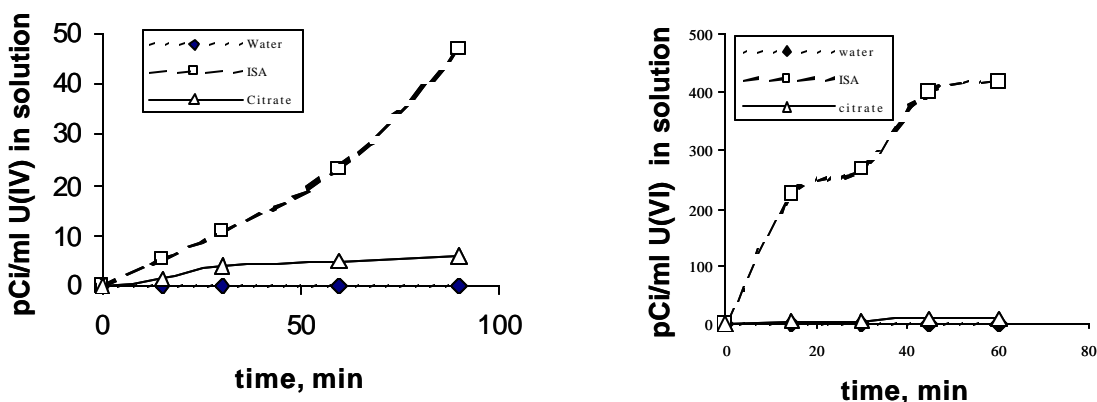


Fig 2. Decontamination of U(IV) and U(VI) contaminated steel coupons using water, citrate solution and ISA solution

PLANNED ACTIVITIES

The main outputs from this project will be 1) fundamental data to evaluate the effectiveness of isosaccharinate for decontamination of actinides from steel and concrete surfaces and 2) the development and testing of isosaccharinate containing foams/gels for worker safety and ease in decontamination. Some of the specific future technical goals/accomplishments/activities are listed below.

- Complete studies with Th(IV) complexes with ISA and prepare a journal article
 - Conduct studies to obtain fundamental data for Pu(IV)-ISA complexes
 - Conduct studies to obtain fundamental data for U(VI), Np(V), and Pu(III) complexes with ISA to cover a spectrum of oxidation states of actinide elements
 - Conduct studies on Fe and Al to determine the effect of competing ions on the complexation of actinides with ISA
 - Formulate foams containing ISA, and test ISA solutions and ISA containing foams for their effectiveness to decontaminate actinides from metal surfaces and concrete
 - Complete studies with Th(IV) complexes with ISA and prepare a journal article
 - Report these findings in open literature publications
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- Develop fundamental data over a wide range in pH values on the types of aqueous complexes and complexation constants of ISA with actinides and with metals such as Fe and Ca that compete with actinides for ISA complexation. Develop both the equilibrium and kinetic data for these important reactions.
 - Formulate foams containing ISA. Test ISA solutions and ISA-containing foams for their effectiveness to decontaminate actinides from metal surfaces and concrete.

INFORMATION ACCESS

Based on the research conducted under this project, following two manuscripts were prepared and have been submitted for publication in *Journal of Solution Chemistry*.

Rai, Dhanpat, N. J. Hess, Y. Xia, L. Rao, H. M. Cho, R. C. Moore, L. R. Van Loon. 2003. Comprehensive Thermodynamic Model Applicable to Highly Acidic to Basic Conditions for Isosaccharinate Reactions with Ca(II) and Np(IV). *Journal of Solution Chemistry* (submitted).

Cho, H. M., Dhanpat. Rai, N. J. Hess, Y. Xia, L. Rao. 2003. Acidity and Structure of Isosaccharinate in Aqueous Solution: A Nuclear Magnetic Resonance Study. *Journal of Solution Chemistry* (submitted).

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