Ion Dynamics in Radioactive Environments and Materials (IDREAM)
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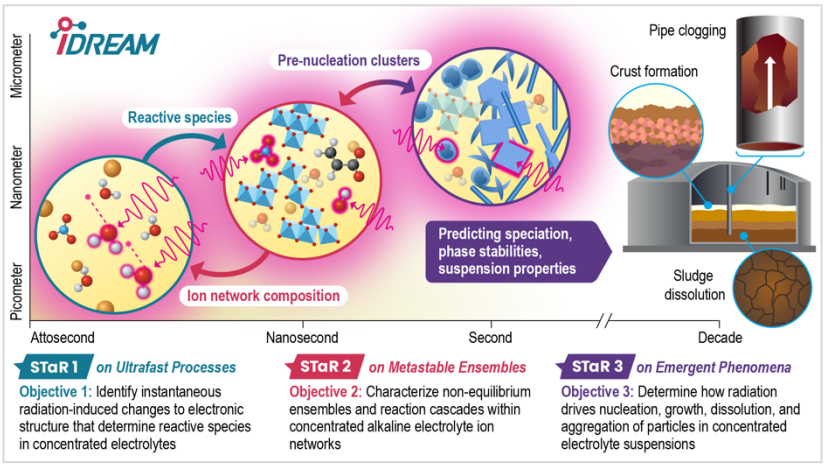
Mission Statement*: To master the cascade of radiation chemistry that drives far from equilibrium speciation and reactivity in chemically complex environments, linking attosecond timescales to decadal processes.*



Plutonium production at the Department of Energy's Hanford Site has resulted in the most challenging environmental cleanup in history. Retrieval of 200 million liters of waste containing 170 million curies of radioactivity from underground storage tanks will take billions of dollars and decades of time. Waste cleanup challenges stem primarily from supernatant, salts, and sludges containing high concentrations of sodium hydroxide, aluminate, nitrate, and nitrite, with co-disposed organics, phosphate, and trace metals. The extreme alkalinity, low water content, and continuous production of transient reactive species by ionizing radiation from radionuclides in the waste drives chemistry far from equilibrium, as indicated by a plethora of oxidized and reduced species that exist simultaneously. The extreme conditions also result in poorly predictable dissolution and reprecipitation behavior of the aluminum (oxy)hydroxides that form the bulk of the waste solids.

This is a critical moment for the tank waste cleanup mission, with the start-up of the Waste Treatment and Immobilization Plant to vitrify low-activity liquid waste. Sludge processing is not expected to start for 10 years. Given the long timeframe, a fundamental understanding of how the radiation environment changes waste speciation and reactivity is essential for developing effective and efficient processing strategies. With waste retrieval contractors, IDREAM identified where continuous radiation-induced creation of reactive species has an important influence on tank waste evolution: (1) radiolysis of water, organics, and nitrogen species, resulting in changes in pH, and creation of flammable and/or toxic gases; (2) initiation of redox reactions that convert nitrate to nitrite and affect technetium, iron, and chromium speciation; and (3) changes to mineral dissolution and precipitation rates. The advent of powerful attosecond and femtosecond X-ray pulses synchronized with a variety of ultrafast probes ushers in a new era for radiation chemistry to help unravel the complexities of Hanford Site tank waste.

Previous accomplishments uniquely position IDREAM to now focus on how radiation has driven solution speciation and precipitation to yield the complex phase assemblages at the heart of the waste processing challenge. IDREAM research already has made specific, tangible impacts on the Hanford Site cleanup mission by advancing fundamental knowledge in understanding and controlling chemical and physical processes at interfaces. For example, it is now known that gibbsite supersaturation in tank waste is related to the presence of ion networks in solution.

By addressing our project objectives with combined experimental and computational expertise, IDREAM research will transcend many orders of magnitude of spatiotemporal resolution to tackle the problems

related to far from equilibrium conditions that result from the interplay between high ionic strength and radiation-induced metastability in radioactive tank waste.

These four-year project objectives will elucidate the radiation-driven evolution of reactive species and precipitates that emerge from complex ion networks across three SpatioTemporal Regimes (STaRs) to:

1. Identify the instantaneous, radiation-induced changes to electronic structure that determine reactive species in concentrated electrolytes. STaR1 on Ultrafast Processes (attoseconds, picometers) will reveal the key reactive species that form upon irradiation of ion networks and follow their local evolution with ultrafast spectroscopies including sub-femtosecond X-ray snapshots.
2. Characterize nonequilibrium ensembles and reaction cascades within concentrated alkaline electrolyte ion networks. STaR2 on Metastable Ensembles (nanoseconds, nanometers) will elucidate the ion-network response to radiation-induced reactive species identified in STaR1 and the role of solution heterogeneity in the formation of metastable ensembles of species that ultimately transition to suspensions and precipitates examined in STaR3.
3. Determine how radiation drives nucleation, growth, dissolution, and aggregation of particles in concentrated electrolyte suspensions. STaR3 on Emergent Phenomena (seconds, micrometers) focuses on radiation-driven phase transformation processes and outcomes that dominate mesoscale observables relevant to tank waste over long time periods, including the composition, physical characteristics, and stabilities of particle suspensions and solids.

The broader scientific impact of IDREAM research will reveal mechanisms by which properties of matter emerge from complex chemical systems in far from equilibrium radioactive environments. For the first time, we will show how limited water and key solutes influence the generation of short-lived transient reactive species in concentrated electrolytes, then how these reactive species govern ion-pair formation, oligomerization, long-range ordering, and the pre-nucleation species that lead to the precipitation of new phases. Our work to understand radiation-induced mechanisms of crystallization will result in innovations in nucleation and crystal growth. Our discovery of impurity effects on critical cluster formation will inform environmental remediation. Beyond radioactive tank waste, our distinctive capabilities, including ultrafast spectroscopy to study radiolysis and multiscale-simulation tools, will have a broad and foundational impact on chemical and materials sciences.

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