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Development and Characterization of (Semi-)Clathrate Hydrates for Capture and Separation of ^{85}Kr and Xe from Nuclear Reactor Off-Gas Streams

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ABSTRACT:

The overarching goal is to develop and characterize novel clathrate and semi-clathrate hydrate compounds for efficient capture and separation of ^{85}Kr and Xe from off-gas streams generated as fission products during nuclear reactor irradiation. We will execute this research in an iterative manner using a combination of various experimental as well as modeling methods. First, Kr and Xe hydrate samples will be synthesized at moderately high-pressure (P) and/or low-temperature (T) conditions. Crystal structure, chemical bonding, thermodynamics and kinetics of hydrate formation will then be characterized using a suite of *in situ* real-time experimental techniques including X-ray/neutron diffraction, Raman spectroscopy, inelastic neutron scattering coupled with molecular dynamics simulations, and calorimetry. The systematic studies will reveal fundamental relations among chemical composition, crystal structure, coordination chemistry, thermodynamic stability, and formation kinetics of Kr- and Xe-bearing hydrates at relevant P-T conditions. Lastly, based on the obtained *chemistry-structure-stability* relations, we will modify the hydrate compositions by doping thermodynamic promoters (organic molecules or salts) and thus develop novel (semi-)clathrate compounds that can be stabilized at mild P-T (close to ambient) conditions while potentially incorporating other volatile radionuclides, especially ^{129}I.

This research will fill critical knowledge gaps in fundamental understanding of the relationships among chemistry, structure, and formation thermodynamics/kinetics of Kr/Xe-bearing (semi-)clathrate hydrates at relevant P-T conditions. By doing so, we will develop novel (semi-)clathrate hydrate compounds: 1) with optimal phase stability at close-to-ambient conditions (e.g., >280 K, <1 MPa); and 2) tailored for capturing and separating ^{85}Kr and Xe from nuclear reactor off-gas streams that also contain $^{129}I_2$ and $^{14}CO_2$. These developed hydrate phases will be unique for nuclear energy applications, as, currently, no structures of known materials can incorporate all the major volatile radionuclides (^{85}Kr, ^{129}I, ^{14}C, ^{3}H) from nuclear reactor off-gas streams. To achieve this goal, we will address the following key questions:

- How do the different sizes of Xe and Kr control the framework types of clathrate hydrates?
- What are the structural effects of the large guest molecules as a clathrate stabilizer, and how do they change as a function of temperature and pressure?
- Is there an optimum for the amount of the loaded Xe/Kr and of the guest molecule stabilizer?
- How does the presence of other species in nuclear reactor off-gas streams, especially $^{129}I_2$ and $^{14}CO_2$, affect the incorporation of ^{85}Kr and Xe into a given (semi-)clathrate framework?
- Is the (semi-)clathrate hydrate radiation resistant?
- What are the principles that control the structure and stability of (semi-)clathrate hydrates?

Our specific deliverables include: 1) Synthesis of Kr- and Xe-bearing clathrate hydrates w/wo a clathrate stabilizer; 2) Establishment of the *chemistry-structure-stability* relationship; 3) Synthesis of Kr- and Xe-bearing semi-clathrate hydrates in the presence of I_2 and CO_2; 4) Proof-of-concept design of a hydrate-based technology for efficient capture, separation and storage of ^{85}Kr/Xe, $^{129}I_2$ and $^{14}CO_2$ at the benchtop scale. The results will lay the foundation for a viable clathrate hydrate-based technology for capture and separation of ^{85}Kr and Xe from nuclear reactor off-gas streams.