Investigation of Polonium Removal Systems for LBE-Cooled Fast Reactors

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Presentation Outline

• The INEEL
• The polonium issue in lead-bismuth reactors
• Experiments at the INEEL
• Initial modeling effort
• Summary
The Polonium Issue in LBE-Cooled Reactors

Po Production

- $^{209}\text{Bi} + n \rightarrow ^{210}\text{Bi}$
- $^{210}\text{Bi} \rightarrow ^{210}\text{Po}$
- $^{210}\text{Po} \rightarrow ^{206}\text{Po}$

Po chemical form in LBE: 99.8% PbPo, 0.2% elementary Po

Po Release
- PbPo evaporation
- PbPo + H$_2$O $\rightarrow$ H$_2$Po + PbO

Accidental Pb-Bi spill.

Po Deposition

Po Extraction
Why Polonium Removal

Processing as low as 0.01% of the coolant mass flow rate can reduce the Po source during accidents by two orders of magnitude.
Radiological Risk of Po-210

- U.S. Nuclear Regulatory Commission
- Specific activities
  - $^{137}\text{Cs} - 87 \text{ Ci/gram}$
  - $^{60}\text{Co} - 1,130 \text{ Ci/gram}$
  - $^{210}\text{Po} - 4,500 \text{ Ci/gram}$
- Derived Air Concentrations (DAC’s)
  - $^{60}\text{Co} - 500 \text{ Bq/m}^3$
  - $^{137}\text{Cs} - 200 \text{ Bq/m}^3$
  - $^{210}\text{Po} - 10 \text{ Bq/m}^3$
  - $^{239}\text{Pu} - 0.2 \text{ Bq/m}^3$
Tellurium as a Surrogate of Polonium

- Po has no stable isotopes
- Tellurium and polonium are both Group VI elements.
- They are both solid and metallic at room temperature and pressure.
- Their most stable oxidation state is +4.
- Their atomic radii are comparable.
- There are similarities in their electrochemical behavior as indicated by their pH-potential diagrams.
- The Russians used Te as a Po surrogate for their alkaline extraction experiments.
Experimental Use of Tellurium

Like Po, Te forms a stable intermetallic compound with Pb in lead-bismuth.
Alkaline Extraction

This technique was first proposed by IPPE, Russia.

- The reaction is:

$$\text{PbPo} + 4\text{NaOH} \leftrightarrow \text{Na}_2\text{Po} + \text{Na}_2\text{PbO}_2 + 2\text{H}_2\text{O}$$

- LBE does not participate in the reaction.

- The reaction was found to be impaired by the presence of oxides in the melt. So our experiments will be carried out in a reducing environment.
The INEEL Apparatus for Investigation of the Alkaline Extraction Mechanism
Experimental Run Main Steps

- Load the LBE and tellurium into the crucible.
- Energize the heaters to melt the metals and reach the desired temperature.
- Add the NaOH.
- Hold conditions for a selected time.
- Turn off gas injection to allow for gravity separation of the NaOH from the metals.
- Extract samples from the NaOH and metal regions.
- Cooldown the apparatus.
- Analyze the samples with the ICP and SEM, as needed.
Alkaline Experimental Steps
Two different NaOH sampling methods

a) Interface Sampling

B) Bulk Sampling
A crucible removed from the reaction cell after cooldown
Post Experiment LBE and NaOH residual removed from crucible
Alkaline Extraction Experimental Results
Mass Spec data Exp. 25A
Measured Te concentration in Experiments

[Graph showing the concentration of Te in experiments with crucibles labeled 1 to 5. The x-axis represents the crucible number, and the y-axis represents the concentration in ppm. The legend indicates PPM, Run 11, and Run 12. The loaded amount is shown with a line and markers for each run.]
The solubility of Te in NaOH

- Exp. 14, 550C
- Exp. 15, 550C
- Exp. 16, 450C
- Exp. 17, 450C

Loaded to [Te] = 1,200 ppm

Loaded to [Te] = 120 ppm
Experiment 24 Te concentration plotted as a function of time
First Order Modeling

\[ \frac{dc}{dt} = -k_1 c \]

\[ \int_{[Te]_0}^{[Te]_t} \frac{dc}{c} = -k_1 \int_0^t dt \]

\[ -(\ln[Te]_t - \ln[Te]_0) = k_1 t \]

\[ \ln \left( \frac{[Te]_t}{[Te]_0} \right) = -k_1 t \]
Second Order Modeling

\[-\frac{d[Te]}{dt} = k_2[Te]^2\]

\[\left(\frac{1}{[Te]_t} - \frac{1}{[Te]_o}\right) = k_2 t\]
A linear plot for a first and second-order fit of Te extraction data. All time step data from Experiment 24 was used in the fit.
A linear plot for a first- and second-order fit of Te extraction data

**First order fit**

\[ y = 0.0007x + 0.006 \]

\[ R^2 = 0.996 \]

**Second order fit**

\[ y = 0.0218x + 0.8105 \]

\[ R^2 = 0.9997 \]
Second order rate constants compared to loaded Te concentration

![Graph showing second order rate constants compared to Te concentrations (ppm).]
Second order rate constants compared to LBE oxygen potential

![Graph showing the relationship between second order rate constants and LBE oxygen potential. The x-axis represents LBE Oxygen Potential (atm) with values ranging from 1.00E-26 to 1.00E-19, and the y-axis represents the rate constant (sec⁻¹) with values ranging from 0.01 to 0.00001.]
Arrhenius rate law

\[ k = s e^{-\frac{E_a}{RT}} \]

\[ \log k = \frac{-E_a}{2.3R} \frac{1}{T} + \log s \]
Log k versus 1/T to determine $E_a$
Back Reaction

\[ \text{PbTe} + 4\text{NaOH} \xrightleftharpoons[k_c]{k_r} \text{Na}_2\text{Te} + \text{Na}_2\text{PbO} + \text{H}_2\text{O} \]

\[
\frac{d(c_{PbTe})}{dt} = -k_f (c_{PbTe}) + k_r (\text{Na}_2\text{Te})
\]

\[
\frac{(\text{Na}_2\text{Te})_{eq}}{(\text{PbTe})_{eq}} = \frac{(c_{PbTe})_0 - (c_{PbTe})_{eq}}{(c_{PbTe})_{eq}} = \frac{k_f}{k_r} = K
\]
Gibbs-Helmholtz equation

\[ \frac{\delta(\Delta G^\circ / T)}{\delta T} = -\frac{\Delta H^\circ}{T^2} \]

\[ \frac{\delta(\Delta G^\circ / T)}{\delta (1/T)} = \Delta H^\circ \]

\[ \frac{\delta(\ln K_p)}{\delta T} = \frac{\Delta H^\circ}{RT^2} \]

\[ \Delta G = -RT \ln K_p \]

\[ \ln K_p = 2.303 \log K_p = \frac{-\Delta H^\circ}{RT} + C \]

-55 kJ/mole
Log $K$ versus $1/T$ to determine heat of reaction
Research products

• Fruitful collaboration between JNC and INEEL.
• Validation of the alkaline extraction process;
• NaOH delivery and sampling techniques for future experiments with Po;
• Rate constants for extraction of Te from LBE as for temperature, Te concentration, and oxygen potential;
• Validation of the Arrhenius empirical equation for Na₂Te;
• Activation energy for the formation determined;
• Electro-deposition appears that Te will migrate.
• Three ICONE, one Nuclear Technology and one future (submittal planned in two months) publications
Thank You.

We sincerely wish to acknowledge JNC for providing the funding to perform this fruitful research.
Electro-Deposition Experiments
ELECTRODEPOSITION EXPERIMENTS
Electrodes and thermocouple after cooldown
Electrodes used in the electro-deposition experiments
SEM Analysis of Mo Screen
SEM Analysis of LBE Experiment 34
SEM Analysis of Cathode, No LBE Deposition
SEM Analysis of Anode Showing LBE Deposition