Idaho National Engineering and Environmental Laboratory

Investigation of Polonium Removal Systems for LBE-Cooled Fast Reactors

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1st COE-INES International Symposium

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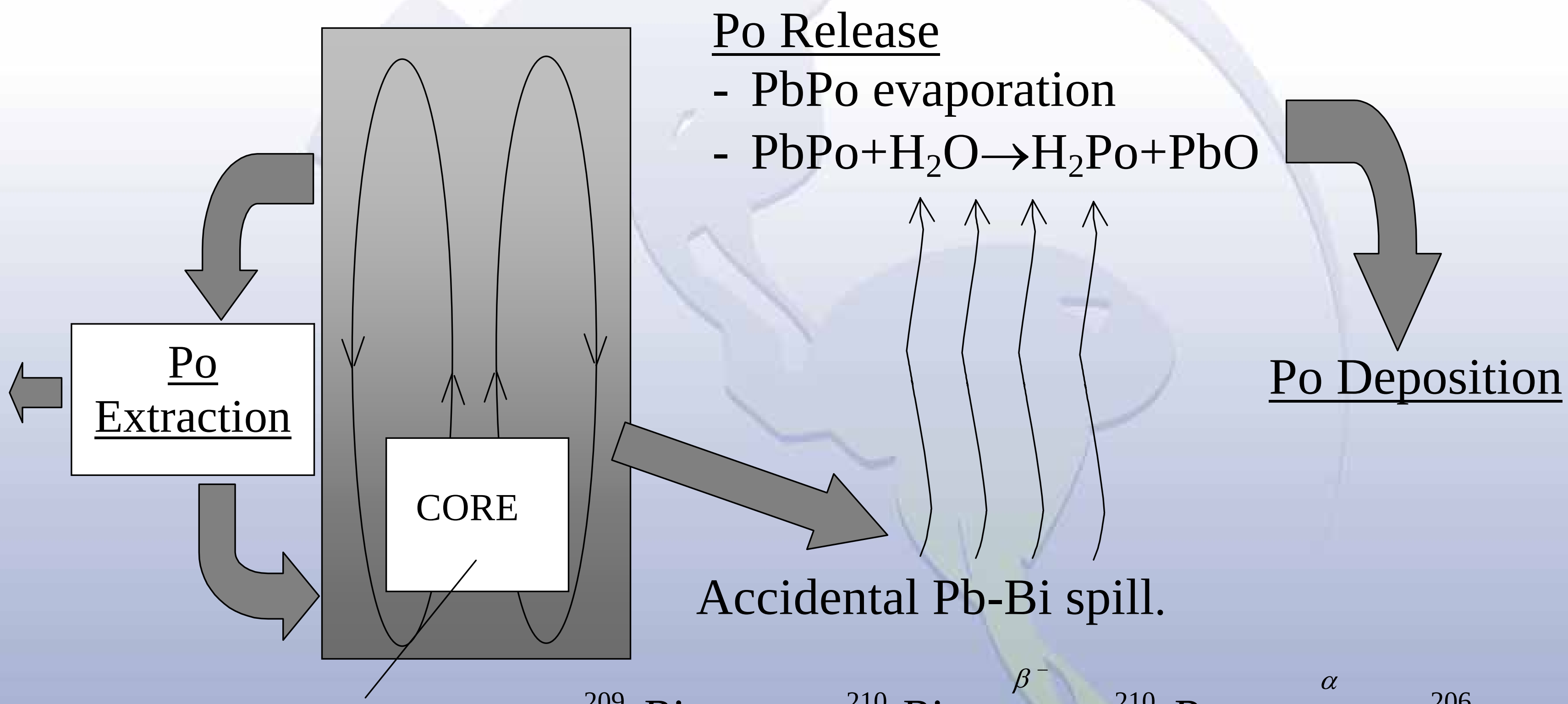
Presentation Outline

- The INEEL
- The polonium issue in lead-bismuth reactors
- Experiments at the INEEL
- Initial modeling effort
- Summary

The Polonium Issue in LBE-Cooled Reactors



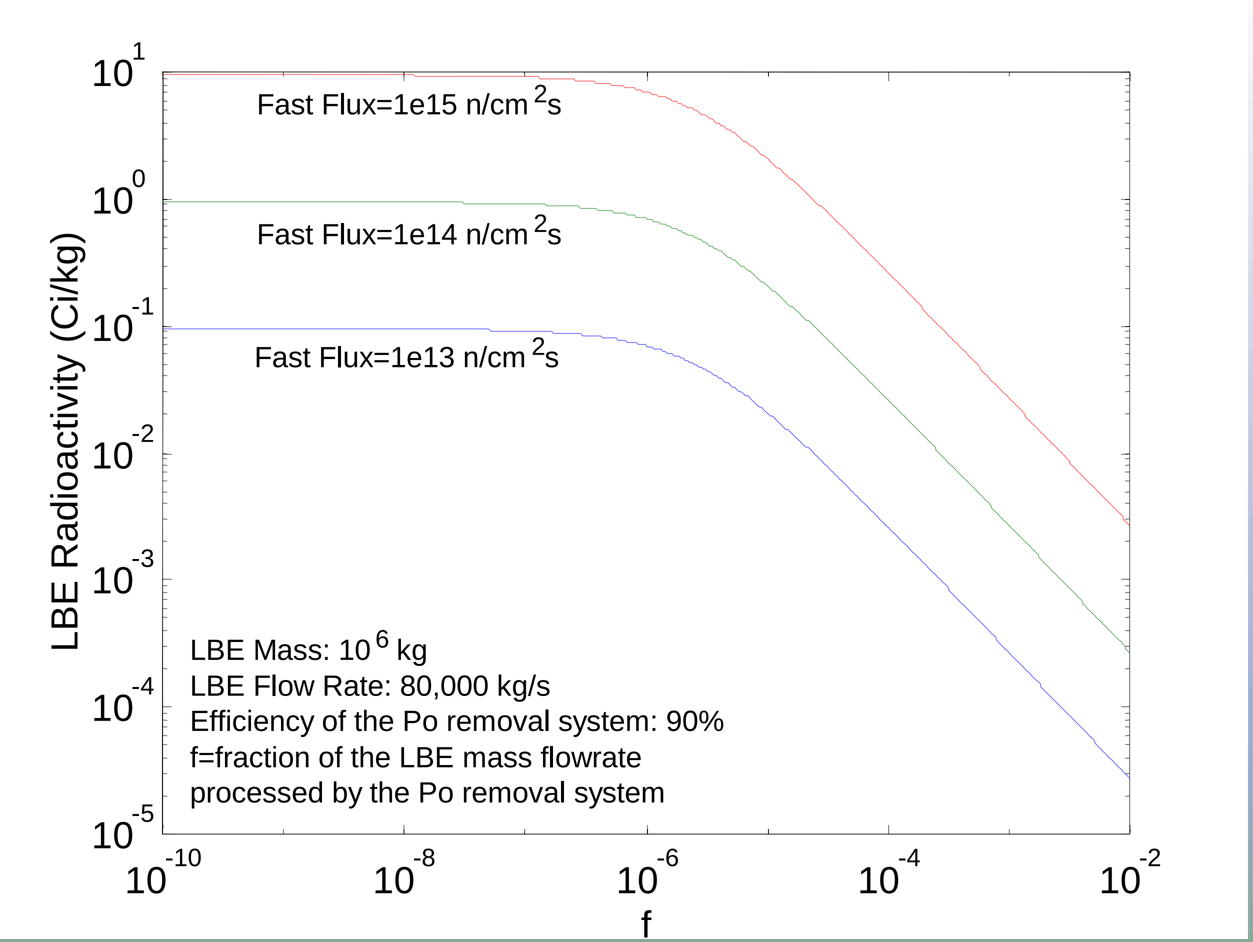
Po Production

$$^{209}Bi + n \rightarrow {}^{210}Bi \xrightarrow[t_{1/2}=5\,days]{\beta^-} {}^{210}Po \xrightarrow[t_{1/2}=138\;days]{\alpha} {}^{206}$$

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

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}Cs -	87 Ci/gram
^{60}Co -	1,130 Ci/gram
^{210}Po -	4,500 Ci gram

- Derived Air Concentrations (DAC's)

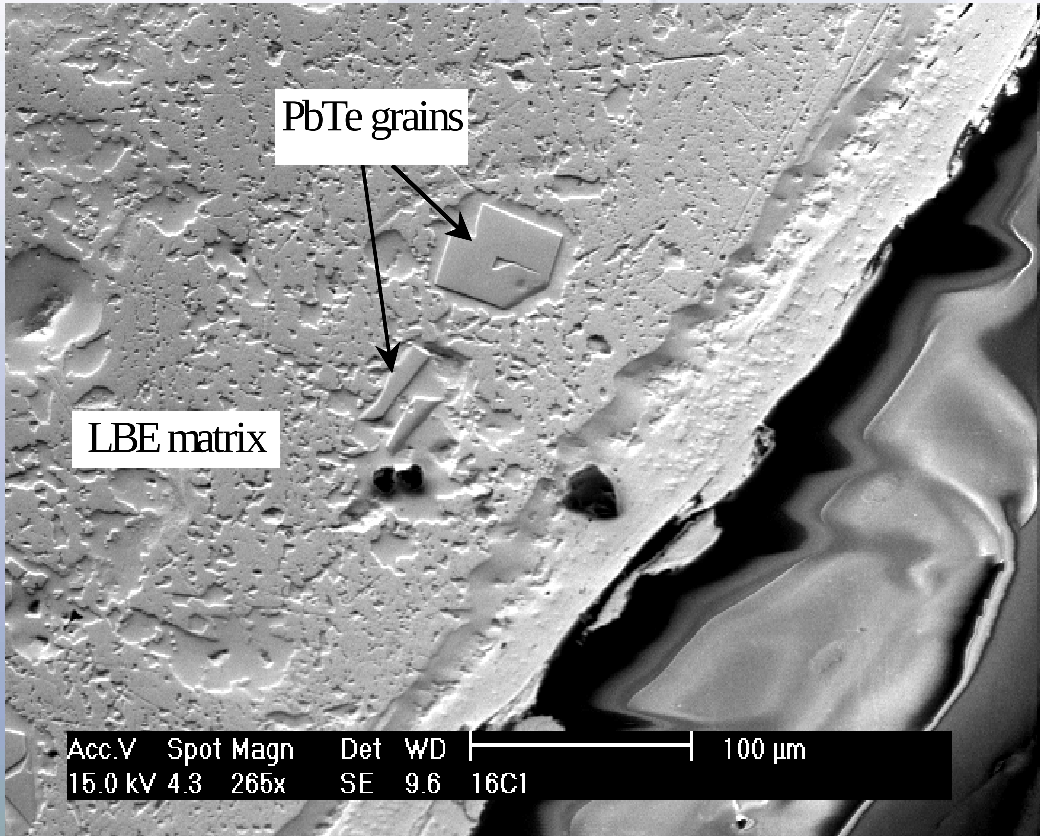
^{60}Co -	500 Bq/m^3
^{137}Cs -	200 Bq/m^3
^{210}Po -	10 Bq/m^3
^{239}Pu -	0.2 Bq/m^3

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.

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PGT Bulk sample analysis      Wed Apr  3 12:14:52 2002

ZAF Method, variable-width filter

Sample /xd1/window1/#1,18C1-03.spt
Accelerating Voltage:           19.75 keV
Takeoff Angle:                  32.00 degrees
Library for system standards: /imix/spectra/system_standards.dir

Elm   Rel. K     Z     A     F    Norm wt% Atomic % Method used    Line

 Pb   0.5800   1.042 1.002 1.000   60.56   48.74   From spectrum  L line
 Cd   0.0004   0.931 1.450 0.987    0.05    0.08   From spectrum  L line
 Te   0.2998   0.982 1.315 1.000   38.69   50.56   From spectrum  L line
 W    0.0069   1.005 1.030 0.974    0.70    0.63   From spectrum  L line
 Bi   0.0000   1.041 1.001 1.000    0.00    0.00   From spectrum  L line

Total                             100.00  100.01

Goodness of fit     0.42

Sample /xd1/window1/#2,18C1-04.spt
Accelerating Voltage:           19.75 keV
Takeoff Angle:                  32.00 degrees
Library for system standards: /imix/spectra/system_standards.dir

Elm   Rel. K     Z     A     F    Norm wt% Atomic % Method used    Line

 Pb   0.5738   1.041 1.002 1.000   59.89   48.29   From spectrum  L line
 Cd   0.0056   0.931 1.450 0.988    0.75    1.11   From spectrum  L line
 Te   0.2891   0.982 1.322 1.000   37.53   49.14   From spectrum  L line
 W    0.0000   1.005 1.030 0.973    0.00    0.00   From spectrum  L line
 Bi   0.0176   1.041 1.001 1.000    1.83    1.46   From spectrum  L line

Total                             100.00  100.00

Goodness of fit     0.32
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Alkaline Extraction

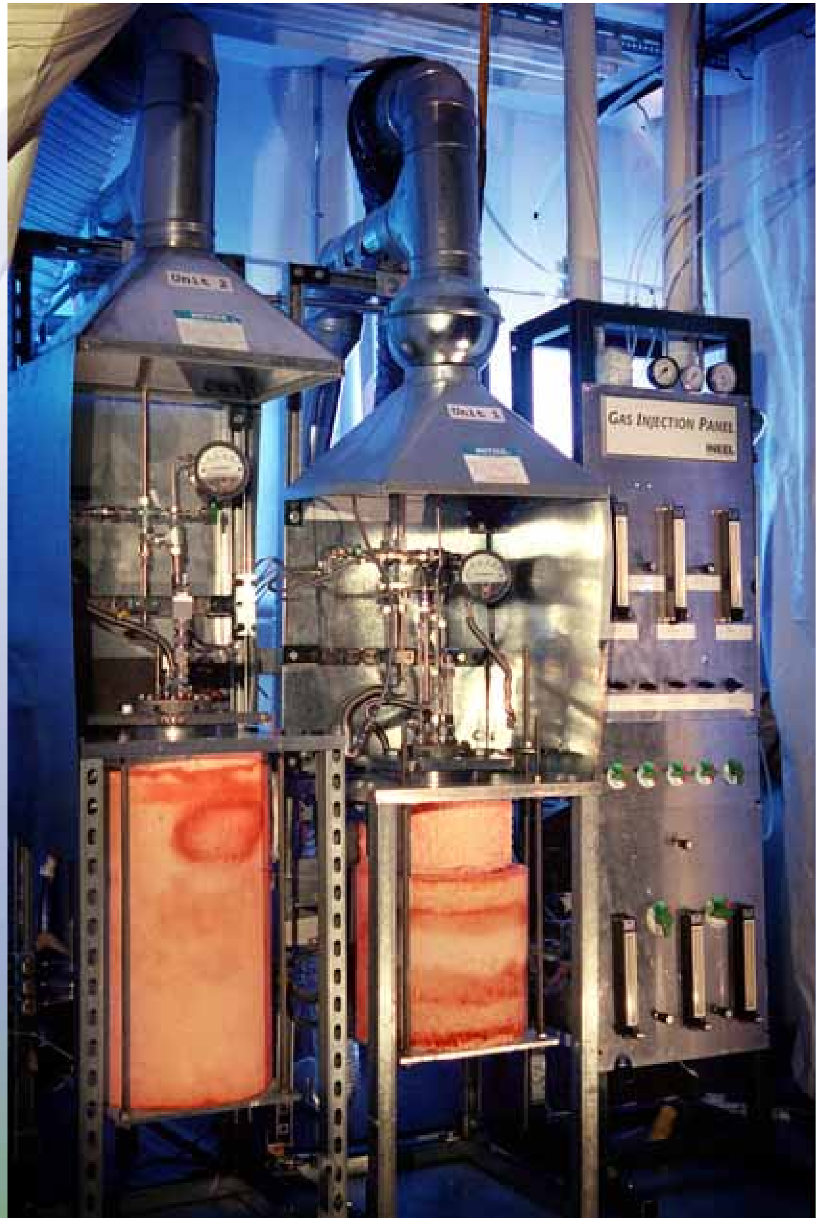
This technique was first proposed by IPPE, Russia.

- *The reaction is:*

$$PbPo + 4NaOH \leftrightarrow Na_2Po + Na_2PbO_2 + 2H_2O$$

- *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.*

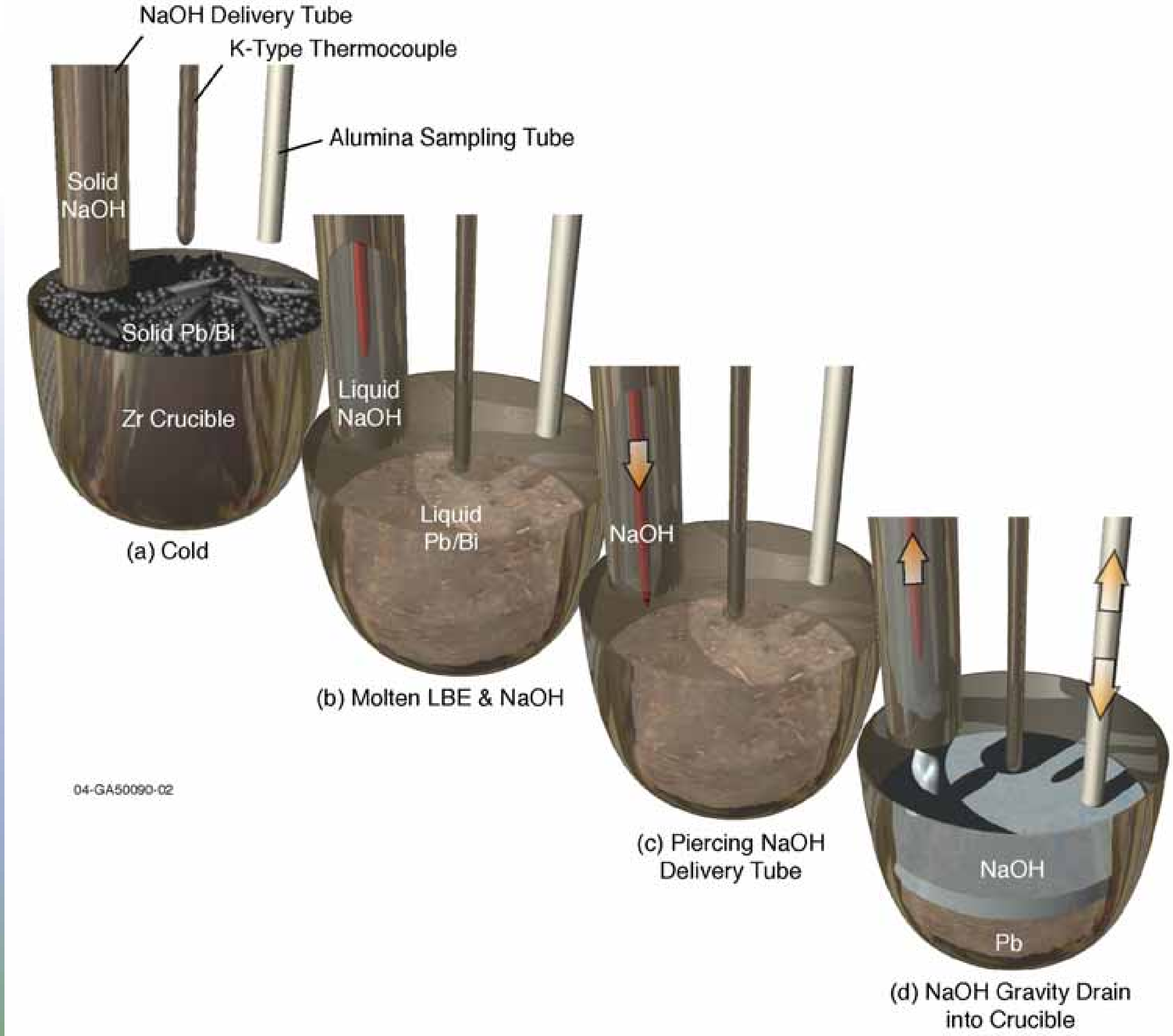
The INEEL Apparatus for Investigation of the Alkaline Extraction Mechanism



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



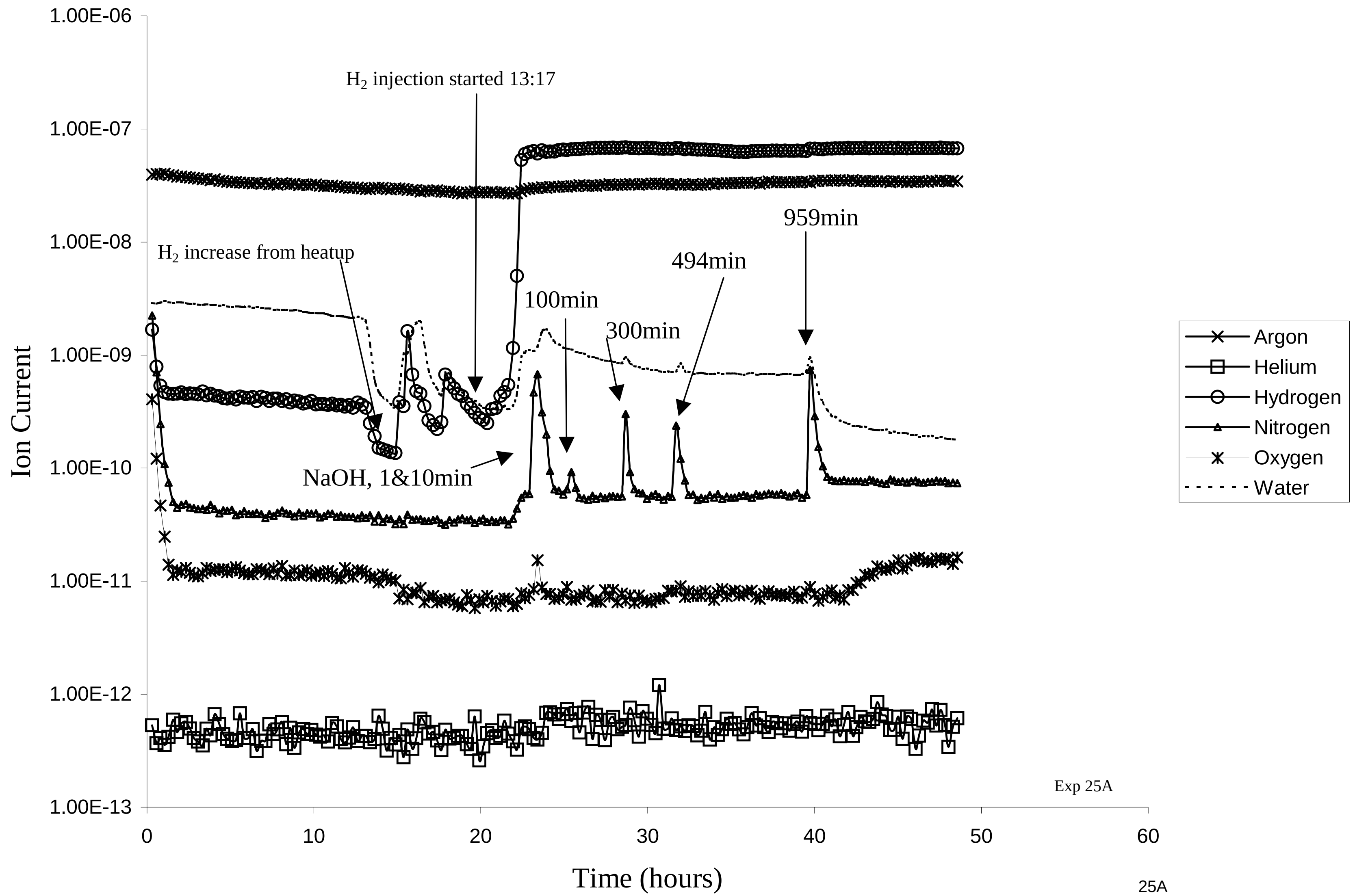
Two different NaOH sampling methods

A crucible removed from the reaction cell after cooldown

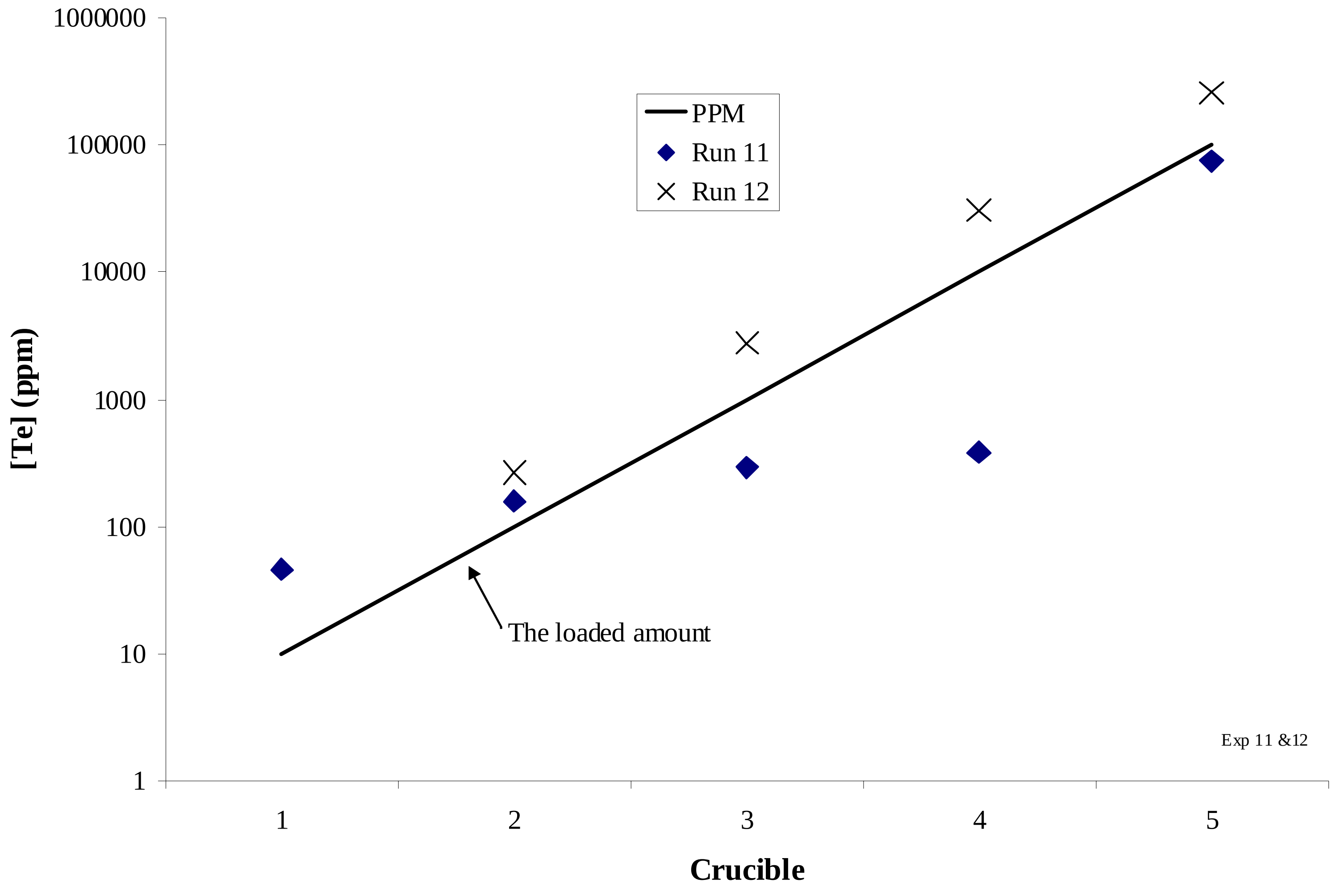
Post Experiment LBE and NaOH residual removed from crucible

Alkaline Extraction Experimental Results

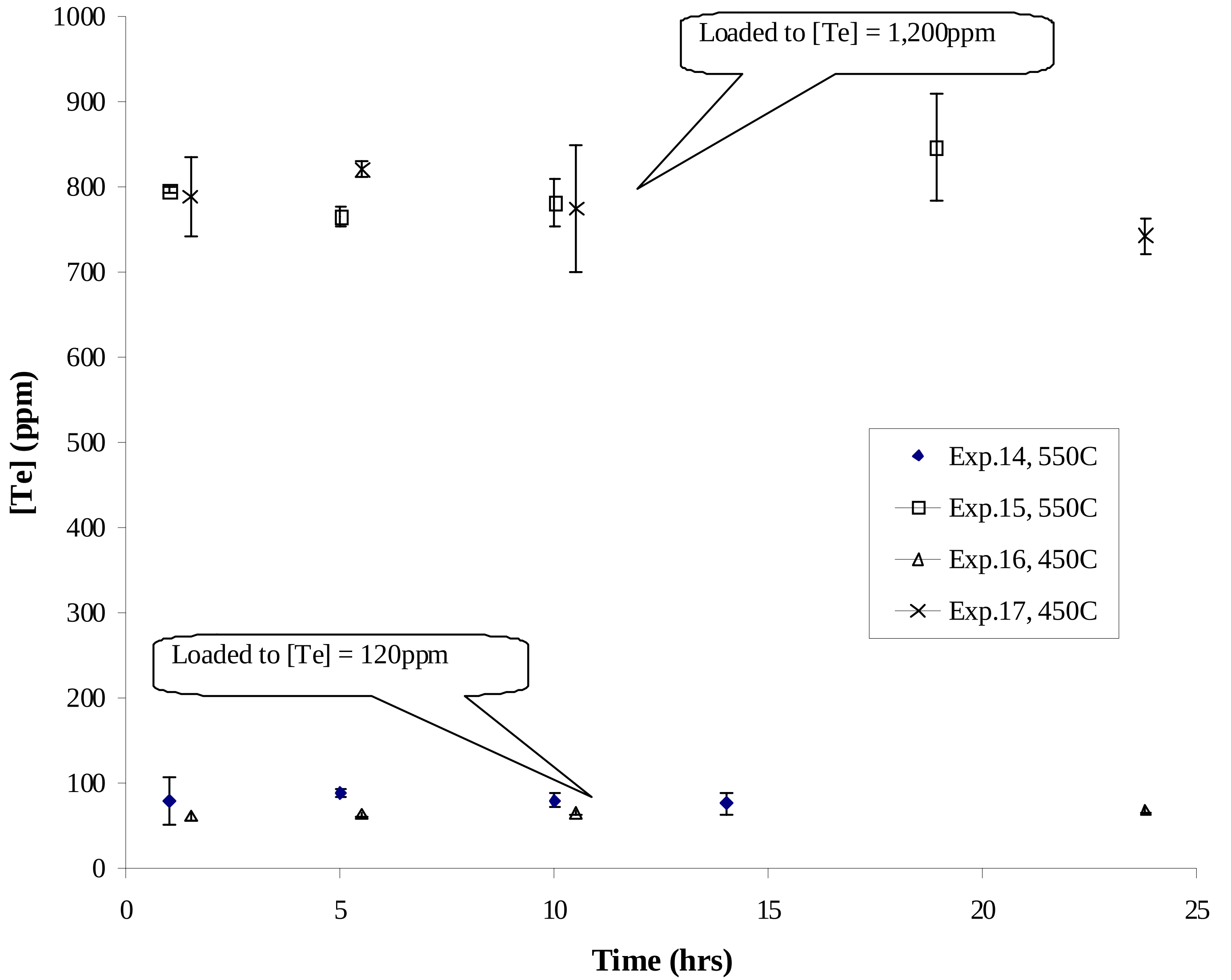
Mass Spec data Exp. 25A



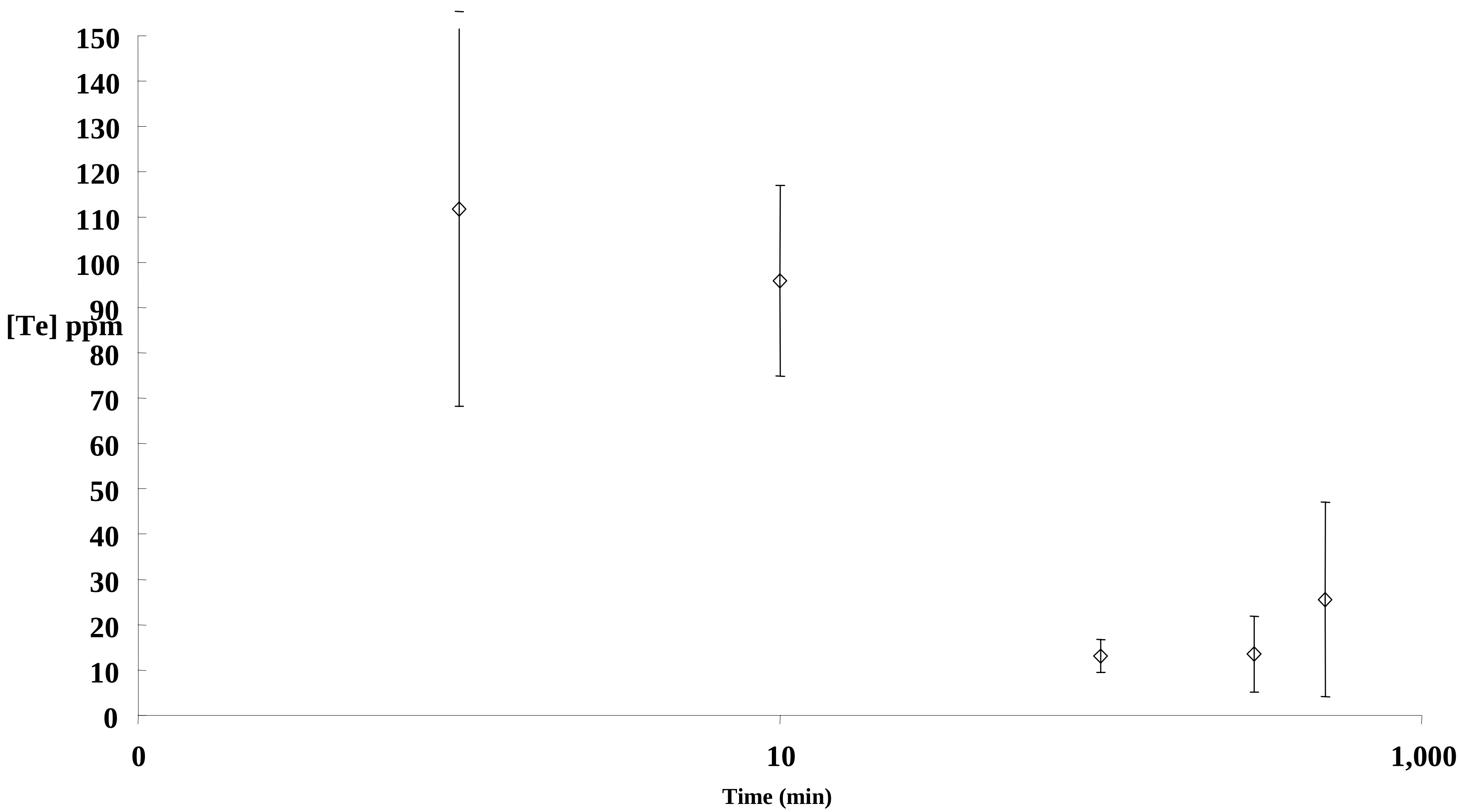
Measured Te concentration in Experiments



The solubility of Te in NaOH



Experiment 24 Te concentration plotted as a function of time



First Order Modeling

$$\frac{dc}{dt} = -k_1 c$$

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

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

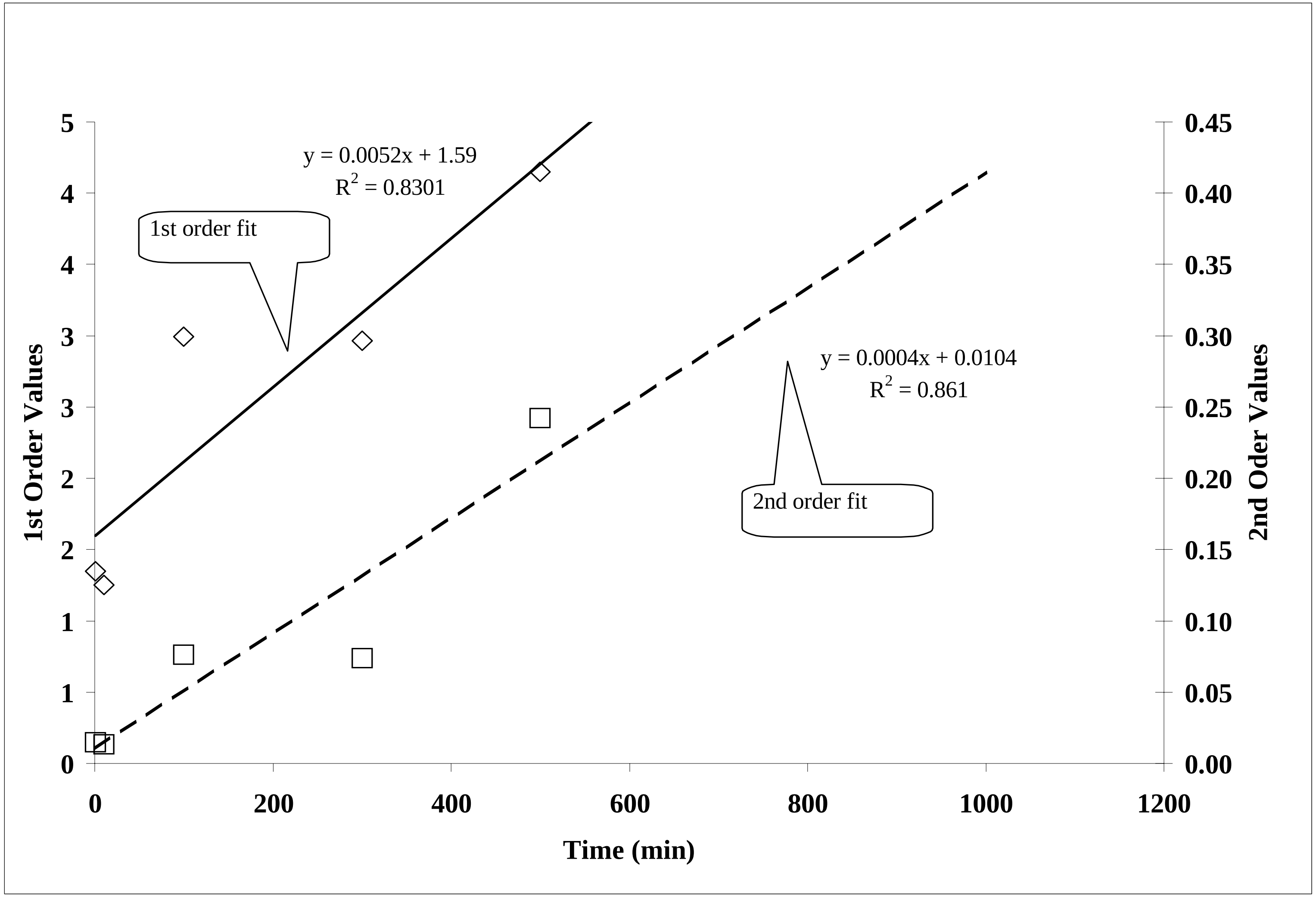
$$\ln\left(\frac{[Te]_t}{[Te]_o}\right) = -k_1 t$$

Second Order Modeling

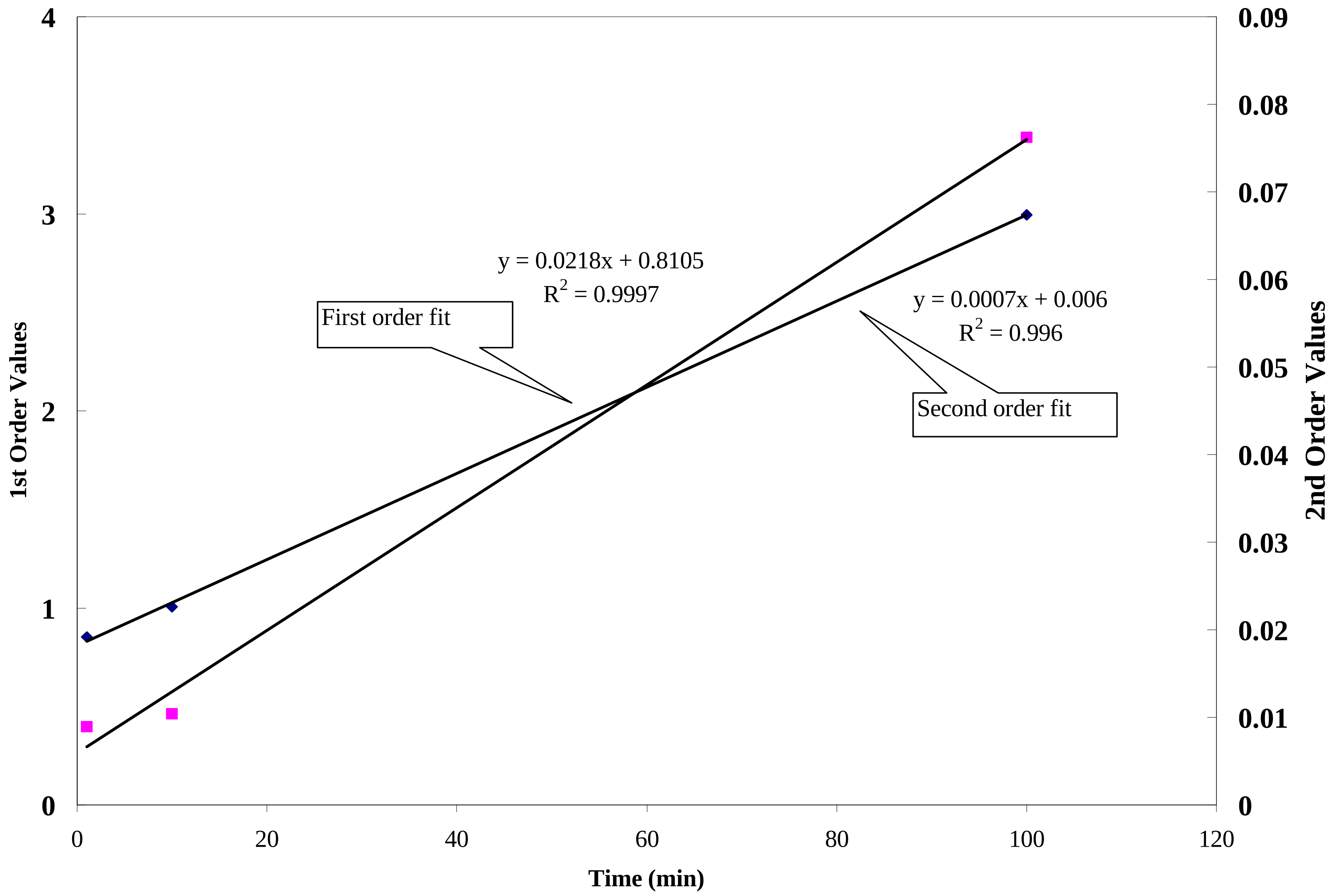
$$\frac{-d[Te]}{dt} = k_2[Te]^2$$

$$\left(\frac{1}{[Te]_t} - \frac{1}{[Te]_o}\right) = k_2 t$$

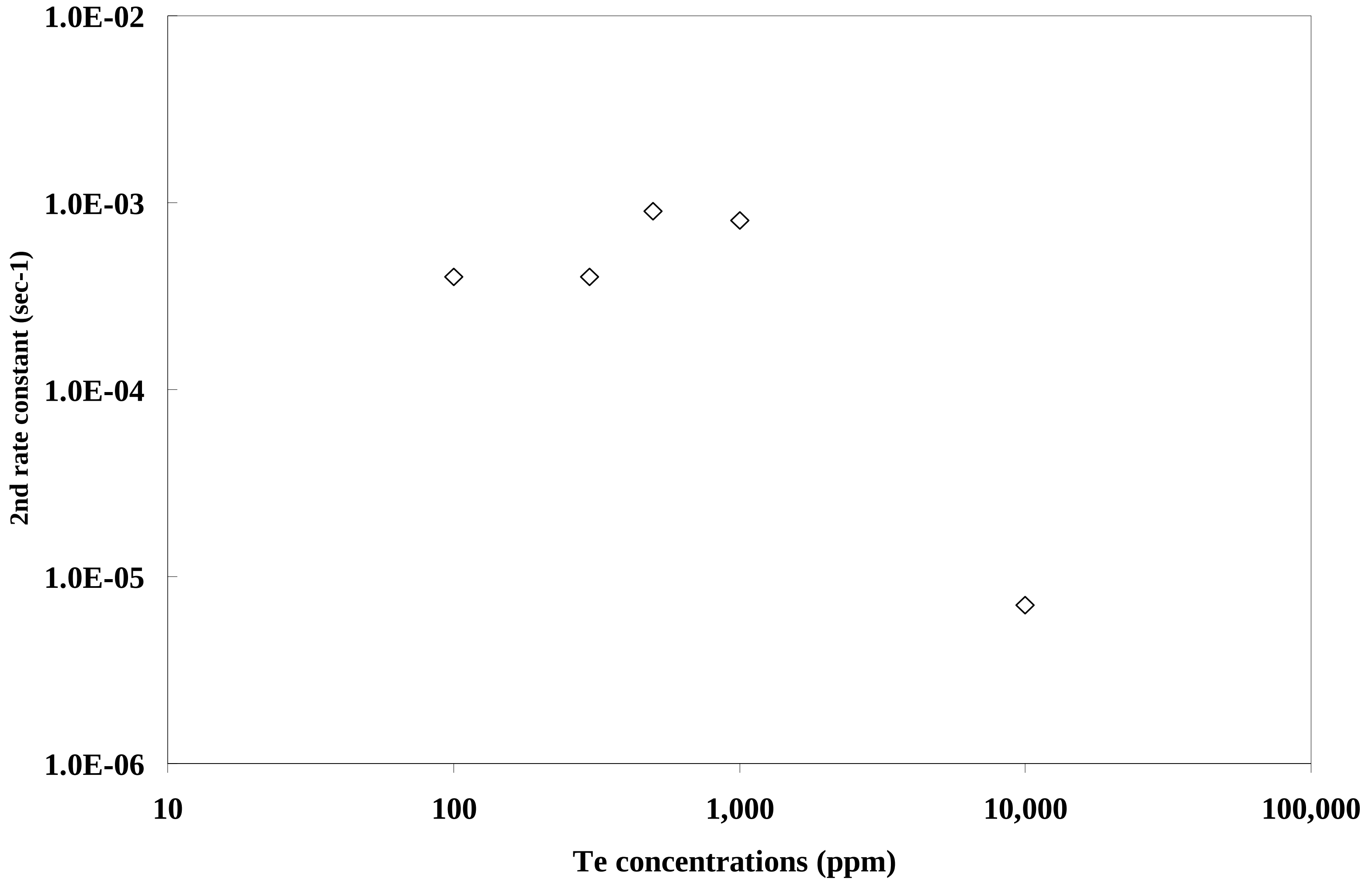
A linear plot for a first and second –order fit of Te extraction data All time step data from Experiment 24 was used in the fit.



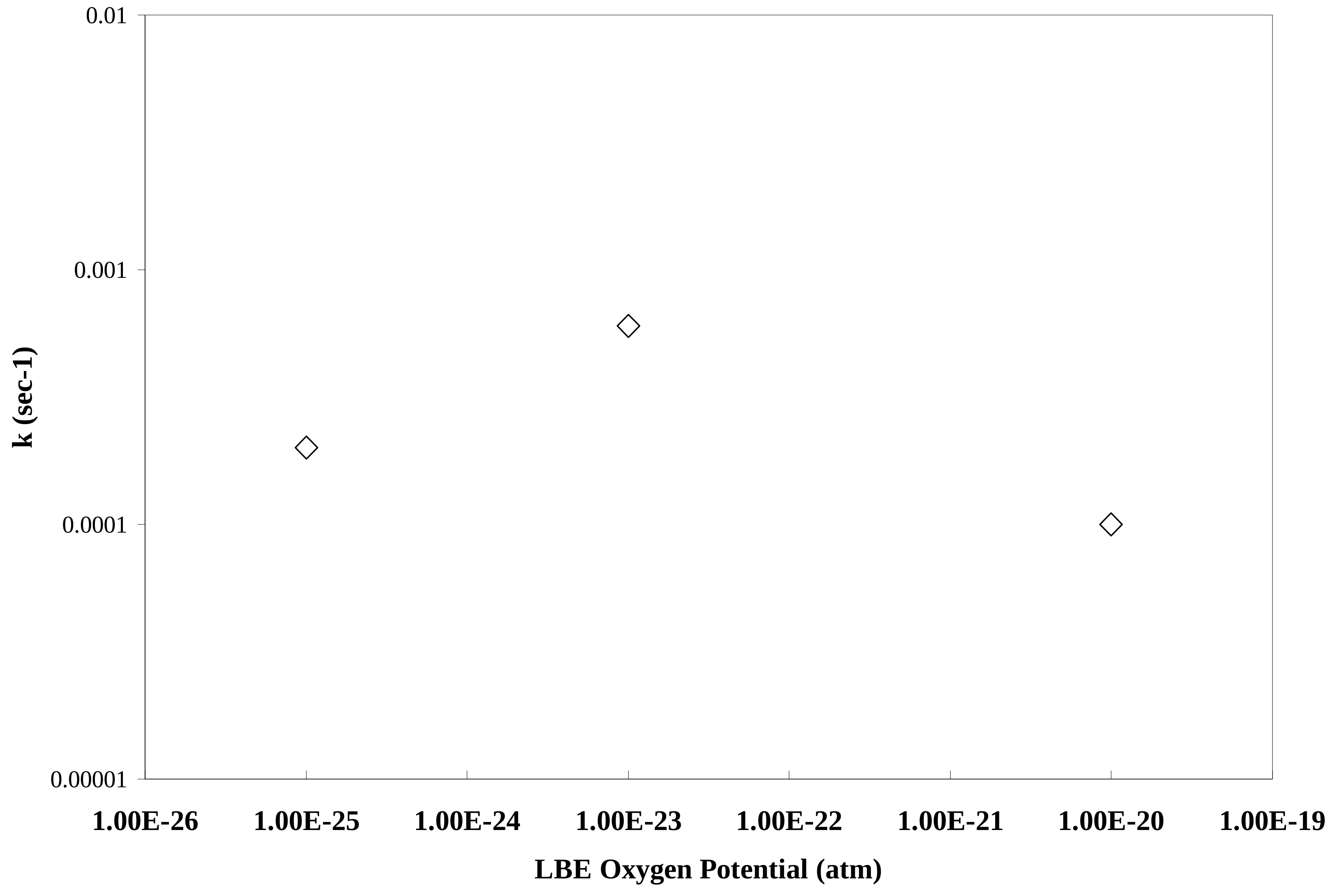
A linear plot for a first- and second-order fit of Te extraction data



Second order rate constants compared to loaded Te concentration



Second order rate constants compared to LBE oxygen potential

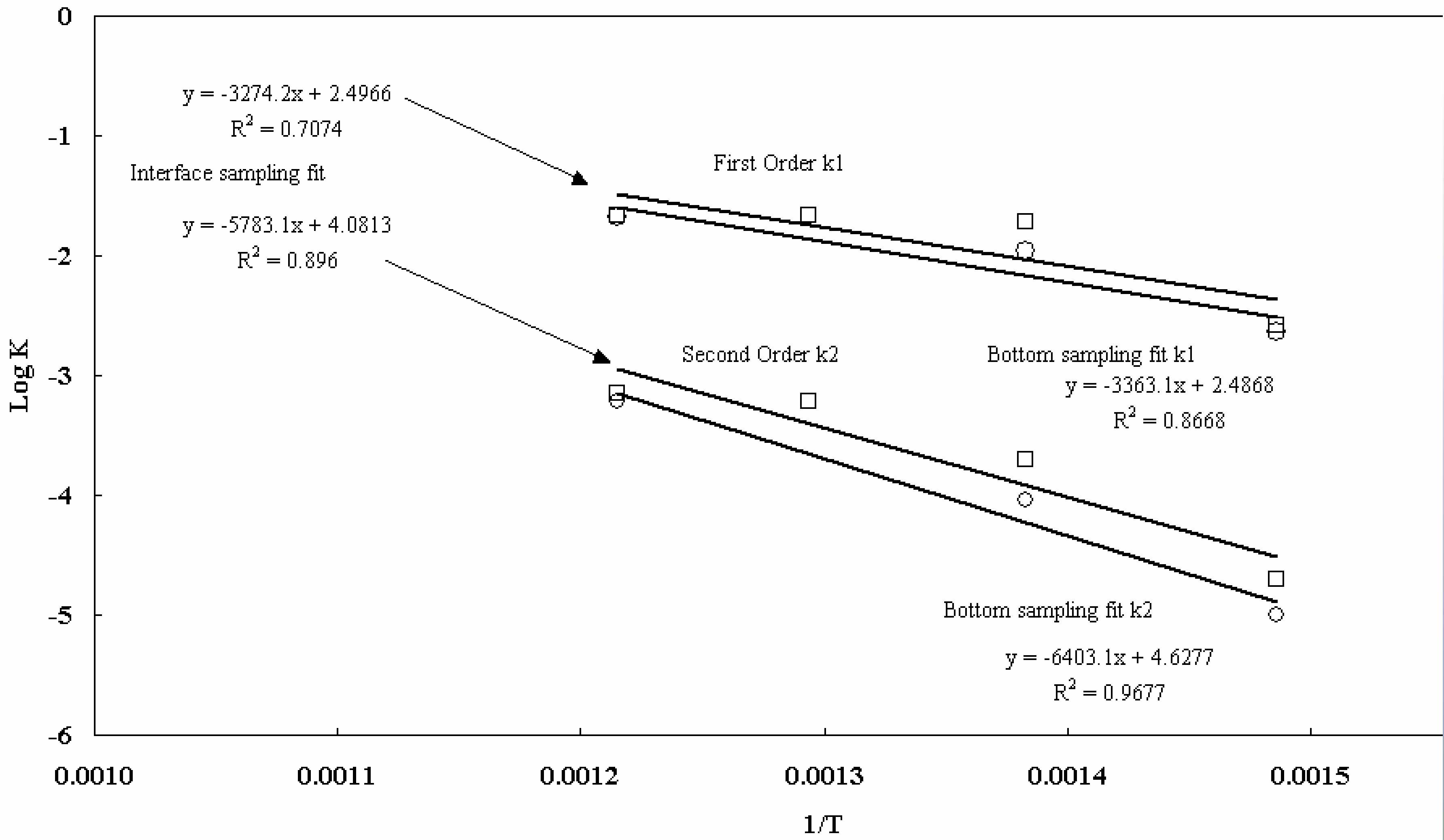


Arrhenius rate law

$$k = se^{-E_a/RT}$$

$$\log k = \frac{-E_a}{2.3R}\frac{1}{T} + \log s$$

Log k versus 1/T to determine E_a



Back Reaction

$$PbTe + 4NaOH \underset{k_r}{\overset{k_c}{\rightleftarrows}} Na_2Te + Na_2PbO + H_2O$$

$$\frac{d(c_{PbTe})}{dt} = -k_f(c_{PbTe}) + k_r(Na_2Te)$$

$$\frac{(Na_2Te)_{eq}}{(PbTe)_{eq}} = \frac{(c_{PbTe})_0 - (c_{PbTe})_{eq}}{(c_{PbTe})_{eq}} = \frac{k_f}{k_r} = K$$

Gibbs-Helmholtz equation

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

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

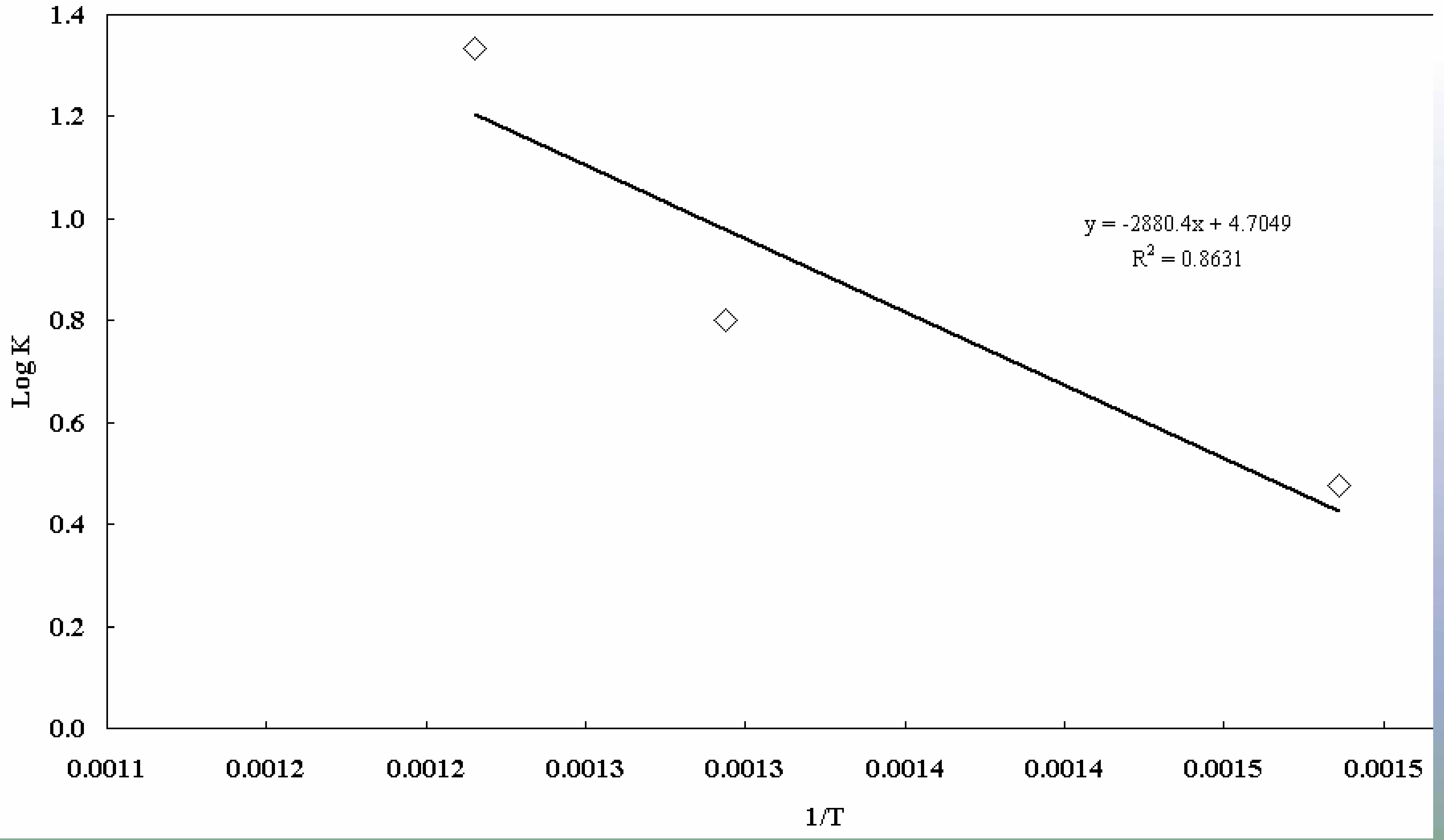
$$\Delta G = -RT \ln K_p$$

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

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

-55 kJ/mole

Log K versus 1/T to determine heat of reaction



Research products

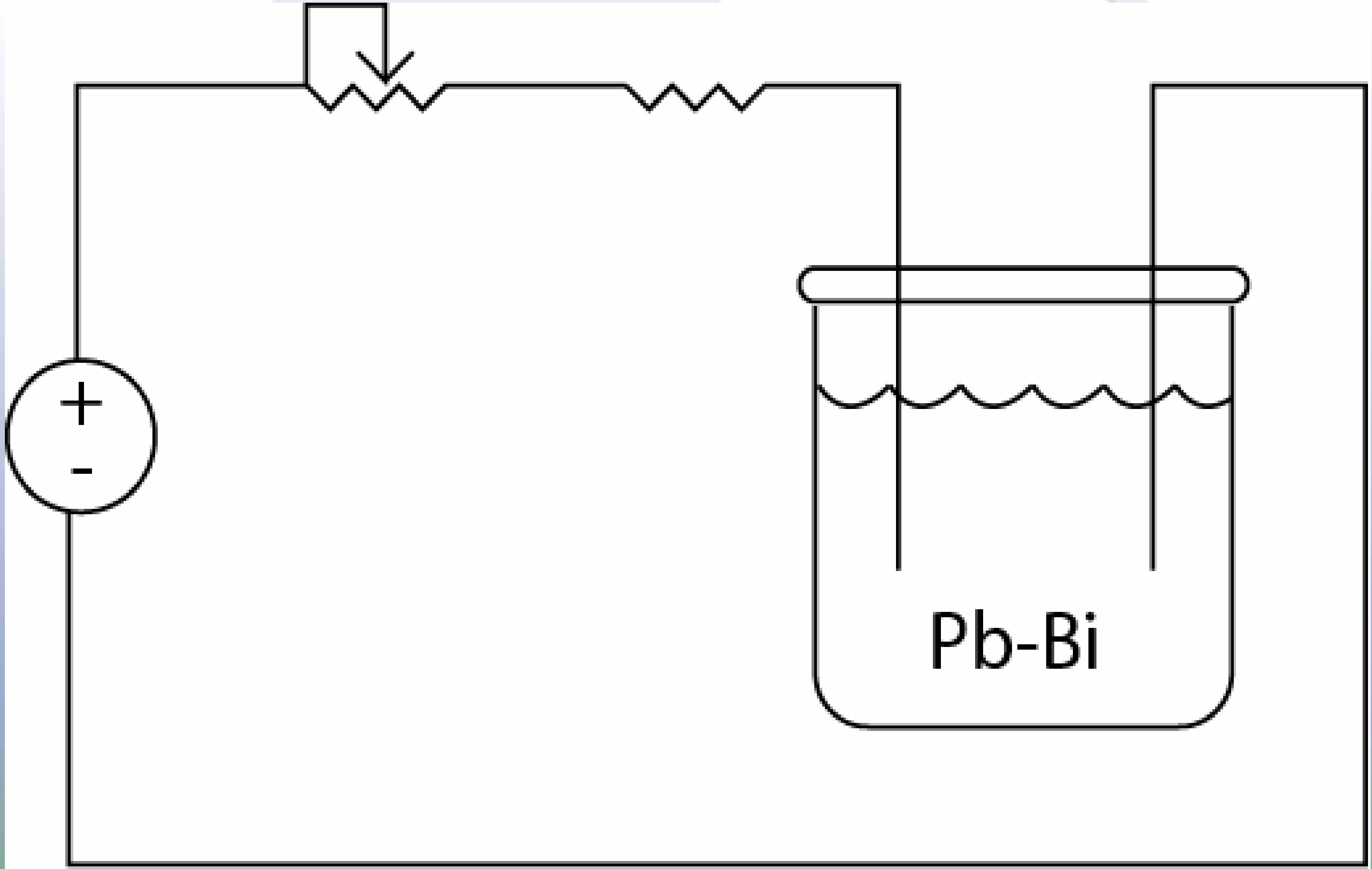
- *Fruitful collaboration between JNC and INEEL.*
- *Validation of the alkaline extraction process;*
- *NaOH delivery and sampling techniques for future experiments with Po;*
- *Rate constants for extraction of Te from LBE as for temperature, Te concentration, and oxygen potential;*
- *Validation of the Arrhenius empirical equation for Na_2Te;*
- *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.

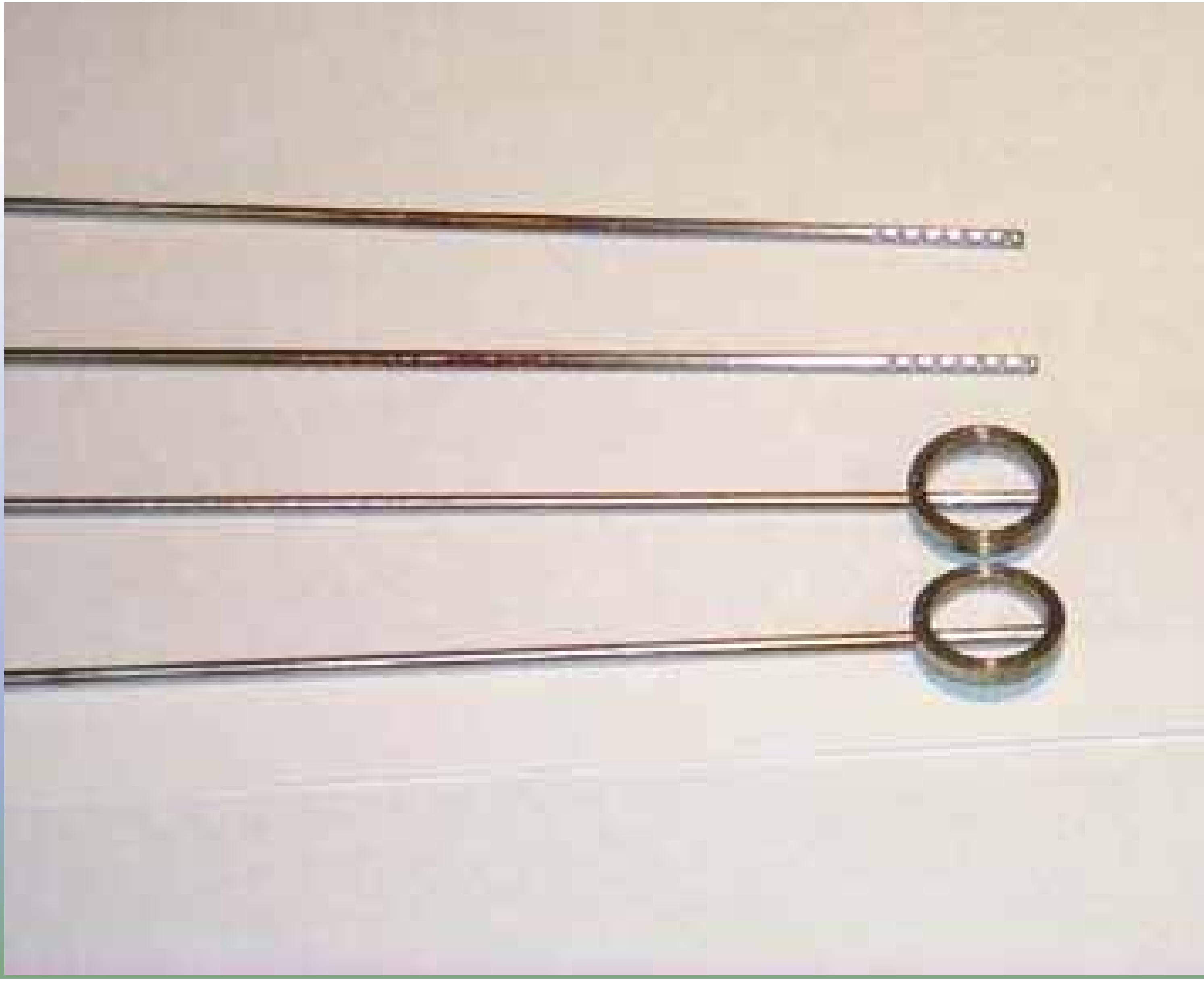
Electro-Deposition Experiments

ELECTRODEPOSITION EXPERIMENTS

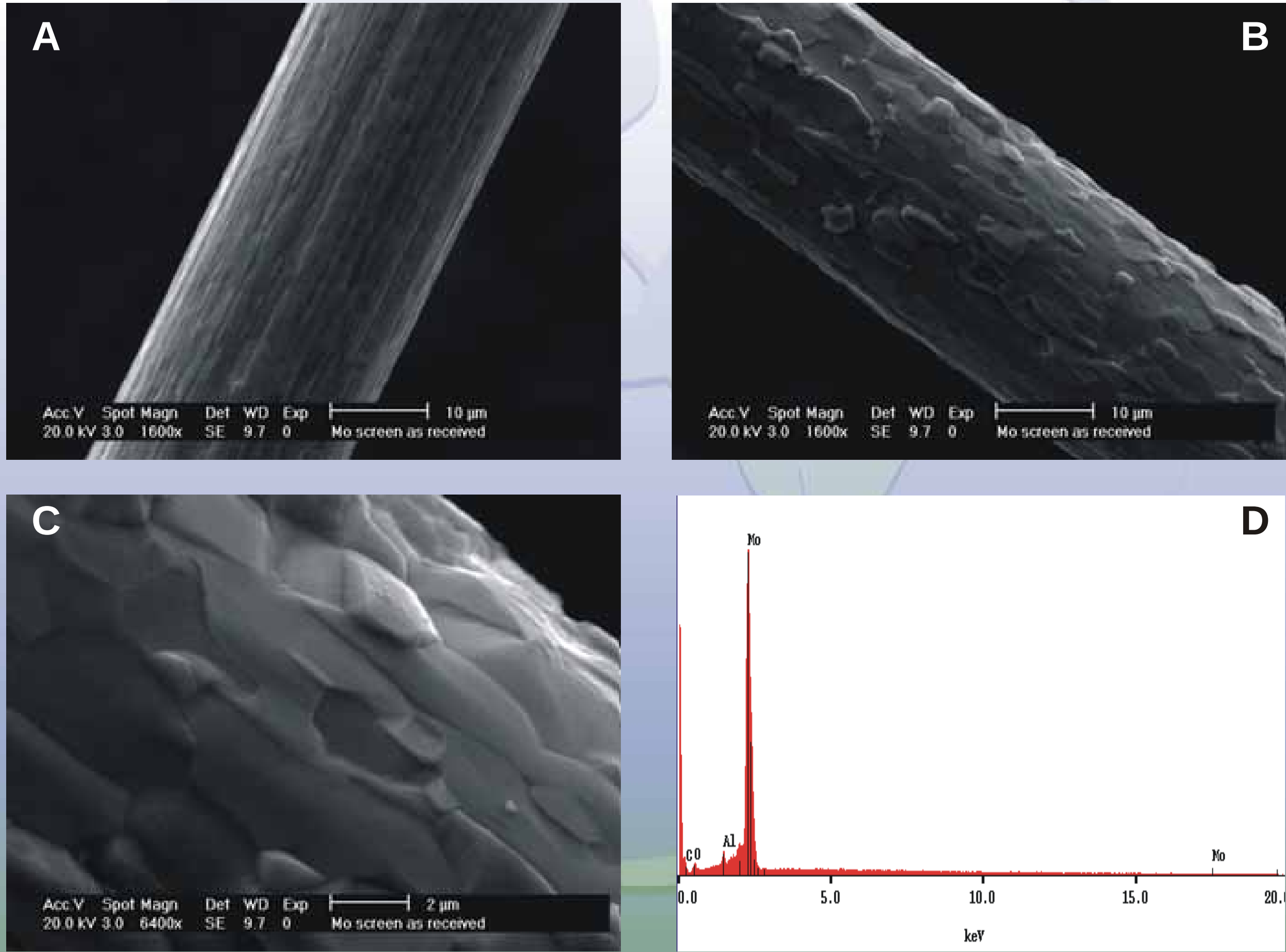


Electrodes and thermocouple after cooldown

Electrodes used in the electro-deposition experiments



SEM Analysis of Mo Screen



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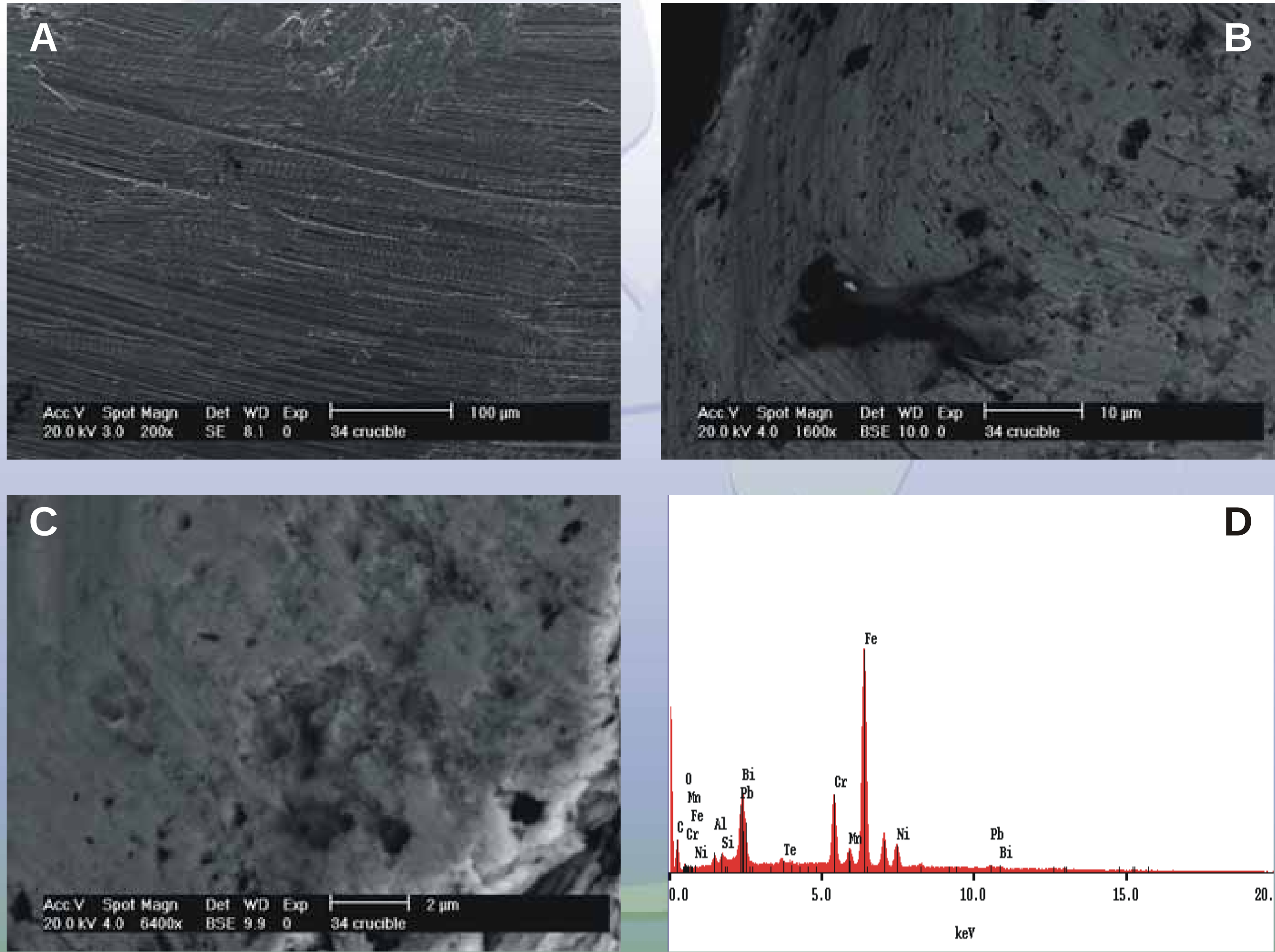
SEM Analysis of LBE Experiment 34



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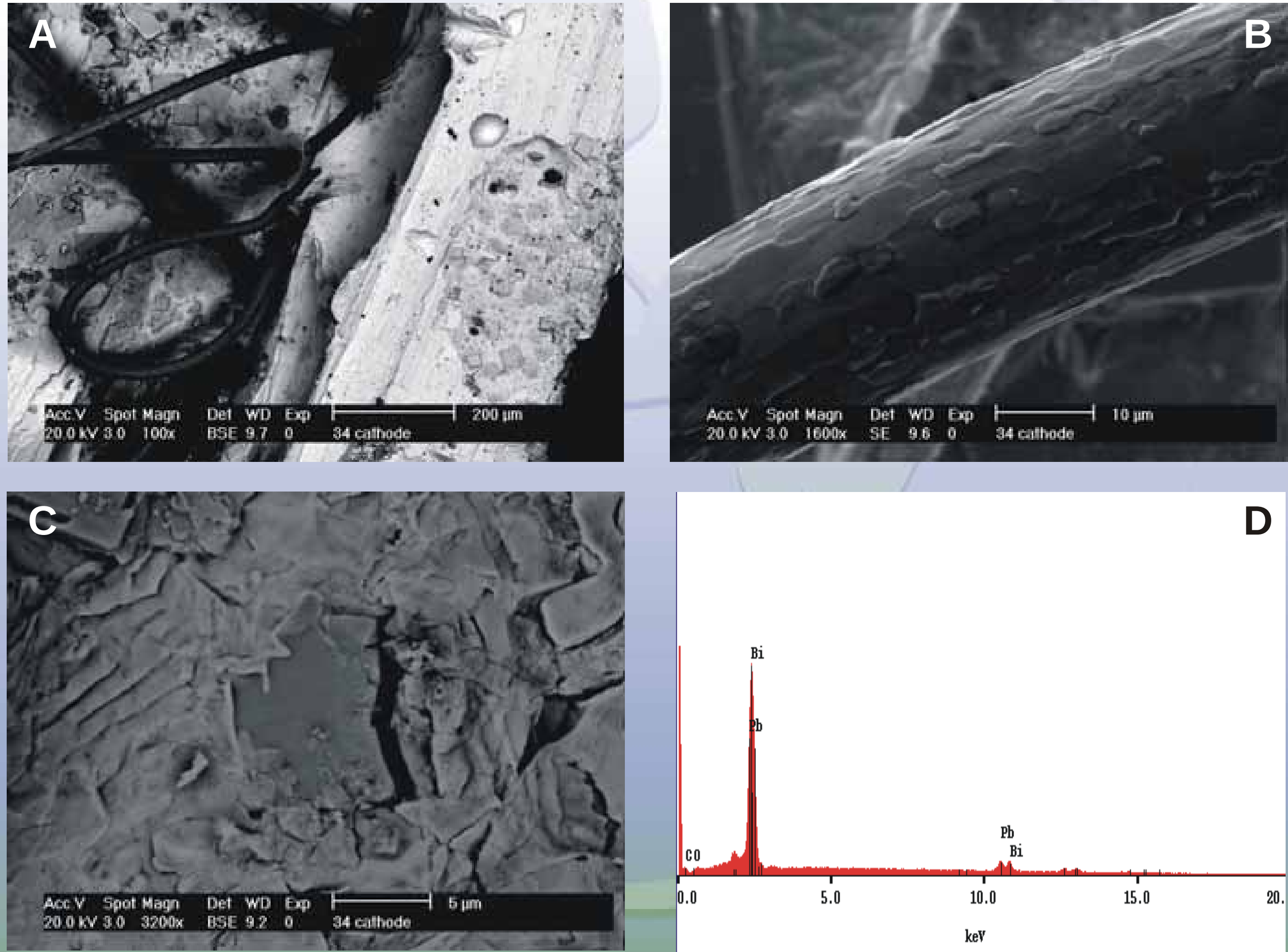
SEM Analysis of Cathode, No LBE Deposition



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SEM Analysis of Anode Showing LBE Deposition