Project # 3261 of ISTC
Cm in chlorides

Current status

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ISTC Contact Expert Group on Nuclear P&T related Projects,

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Study of curium thermodynamics in molten chlorides

Goals

•Thermodynamics of formation of oxygen curium compounds

- equilibrium constants (and Gibbs energy change) for reactions of curium oxygen compounds formation versus temperature;

- equilibrium constants (and Gibbs energy change) for reactions of curium oxygen compounds formation versus the inverse effective radius of solvent cation.

•Thermodynamics of formation of oxygen-free curium compounds

- equilibrium constants (and Gibbs energy change) for reactions of curium oxygen compounds formation versus temperature;

- equilibrium constants (and Gibbs energy change) for reactions of curium oxygen compounds formation versus the inverse effective radius of solvent cation.

•Simulation of curium behavior in molten chlorides

Pourbaix diagrams

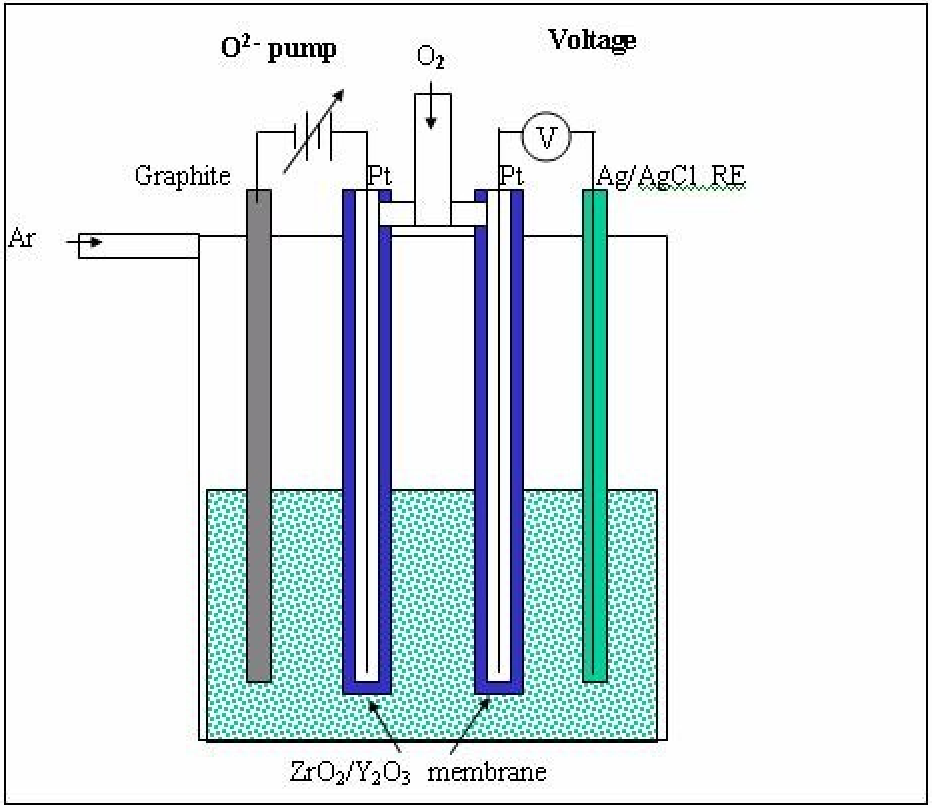
Study of Cm thermodynamics in molten chlorides

Investigation methods

•Thermodynamics of formation for oxygen Cm compounds

Potentiometric titration with oxygen pump

<u>advantage</u> - small concentration of Cm in melt



Study of Cm thermodynamics in molten chlorides

Investigation methods

- **Thermodynamics of formation of oxygen-free Cm compounds**

Method of EMF

Cyclic Voltammetry

Chroho Potentiometry

necessary request - Cm concentration in melt must be more than 3%wt
(interaction of Cm with melt is negligible)

- **Simulation of Cm behavior in molten chlorides**

Study of curium thermodynamics in molten chlorides

Conditions

Molten salts
LiCl-KCl, NaCl-CsCl, NaCl-KCl

•Temperature range
450^{o}C - 850^{o}C

•Cm content
10^{-4} – 10^{-2} mol/kg (Potentiometric titration)
(2 – 5) 10^{-1} mol/kg (EMF, Cyclic Voltammetry, ChrohoPotentiometry)

Common information

Duration of project	24 months
Estimated total cost	$280,000.00
Participants	RIAR

Collaborators – ITU, CIEMAT, KTH, (CEA)

Study of curium thermodynamics in molten chlorides

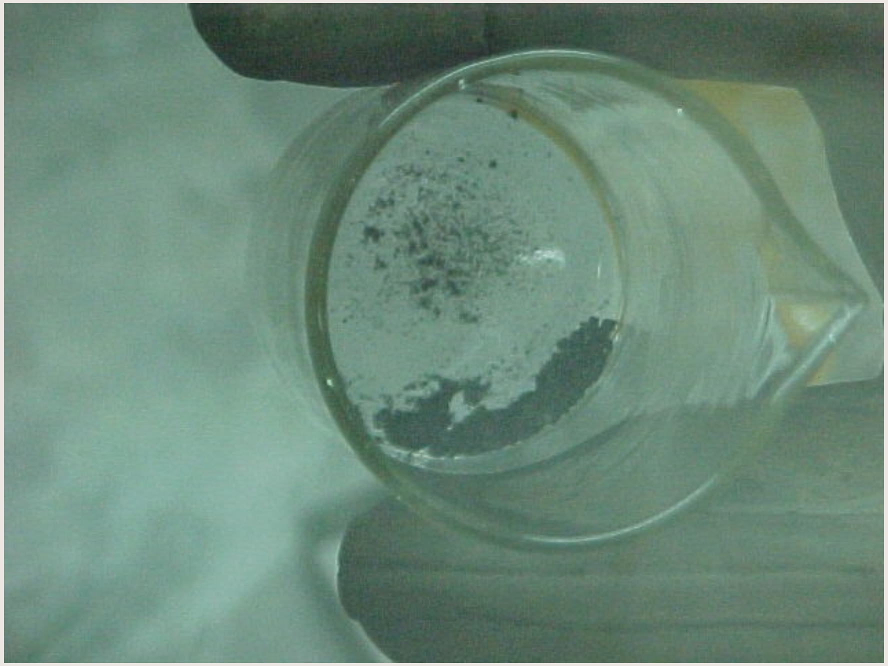
	Quarter 1	Quarter 2	Quarter 3	Quarter 4	Quarter 5	Quarter 6	Quarter 7	Quarter 8
Task 1	Quarter report on Subtasks 1.1 - 1.3	Quarter report on Ttask 1	Quarter report on Ttask 1	Chapter in the annual report on Task1, Publication				Chapter in the final report on Task 1
Sub task 1								
Sub task 2								
Sub task 3								
Sub task 4								
Sub task 5								
Task 2				Chapter in the annual report on Task 2	Quarter report on Ttask 2	Quarter report on Ttask 2	Chapter in the quarter report on Task 2, Publication	Chapter in the final report on Task 2
Sub task 1								
Sub task 2								
Sub task 3								
Task 3							Quarter report on Ttask 3	Chapter in the final report on Task 3 Presentation at a Conference
Sub task 1								
Sub task 2								

Task 1.1. Additional purification and synthesis of curium preparation

Purification of CmO2

•Initial curium reactive, wt%:

Cm	74
Pu	16
Am	0.7
non-radioactive impurities	0.5



Task 1.1. Additional purification and synthesis of curium preparation

Purification of CmO2

Curium reactive after purification, wt%:

Cm	88
Pu	<0.1
Am	0.7
non-radioactive impurities	<0.2

Purification method is shown in the book "Technology of Transplutonium Elements" by V. Nikolayev, Ye. Karelin, H. Kuznetsov, Yu. Noporov, 2000

Task 1.1. Additional purification and synthesis of curium preparation

Purification of salt after investigation

Salt contains

NaCl-2CsCl
$BaCl_2$
CmO_2, CmOCl, $CmCl_3$
Na_2SiO_3, trace of compounds of Zr, Y, Sc

Task 1.1. Additional purification and synthesis of curium preparation

Purification operations

1) Removing of Na, Cs, Cl, Si

dissolution of salt in nitric acid at heating;
adding of the solution obtained from washing the equipment and electrochemical cell to the above solution;
evaporation of the solution to dryness to remove the excessive quantity of nitric acid;
dissolution of the evaporated residue in nitric acid;
precipitation of the oxalic acid on heating curium and barium oxalates;
filtration of the solution containing sodium, cesium and chlorine compounds

2) Removing of Ba

decomposition of the oxalate precipitate containing curium and barium;
dissolution of curium and barium oxides in nitric acid;
precipitation of barium iodate by adding potassium iodate;
filtration of the solution containing curium

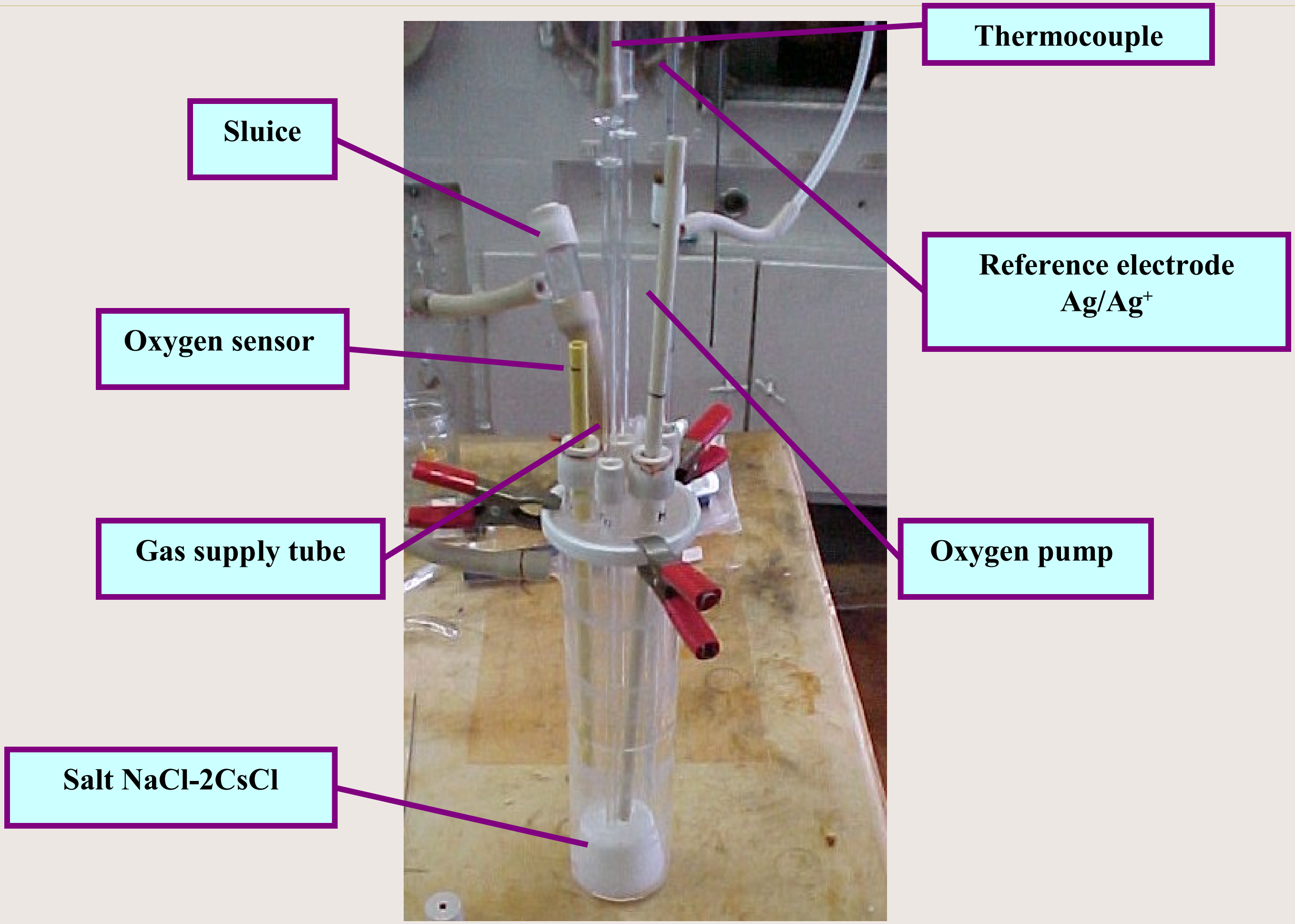
3) Preparation of CmO2

precipitation of curium oxalate from the solution by oxalic acid;
oxalate calcination to curium oxide in air at high temperature.

The final product is curium oxide CmO2 (Cm-88wt%).

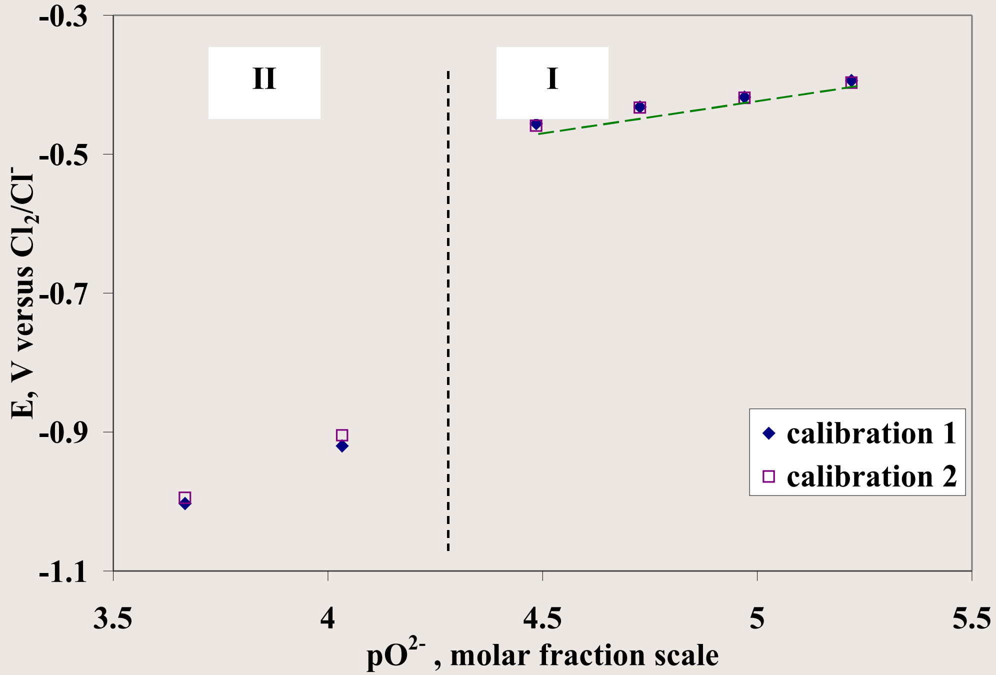
Task 1.2. Hot experiments using the potentiometric titration method.

Calibration of oxygen sensors



Task 1.2. Hot experiments using the potentiometric titration method.

Calibration of oxygen sensors



Dependence of oxygen sensor potential upon concentration of oxide ions in molten NaCl-2CsCl at 550oC

Calibration #1 - by oxygen pump

Calibration #2 - by BaO

Task 1.2. Hot experiments using the potentiometric titration method.

Calibration of oxygen sensors

Parameters of calibration curves for Section I, mole fraction scale

Temperature, K	A	B(experimental)	B(theoretical)
823	-0.823±0.001	0.0817±0.0001	0.0817
873	-0.855±0.001	0.0889±0.0023	0.0867
923	-0.852±0.001	0.0922±0.0008	0.0916

Task 1.2. Hot experiments using the potentiometric titration method.

Study of curium thermodynamics in NaCl-2CsCl

Fragment of the NaCl-2CsCl + 3wt%$CmCl_3$ salt ingot

Task 1.2. Hot experiments using the potentiometric titration method.

Study of curium thermodynamics in NaCl-2CsCl

Electrochemical cell for oxide barium titration

Task 1.2. Hot experiments using the potentiometric titration method.

Study of curium thermodynamics in NaCl-2CsCl

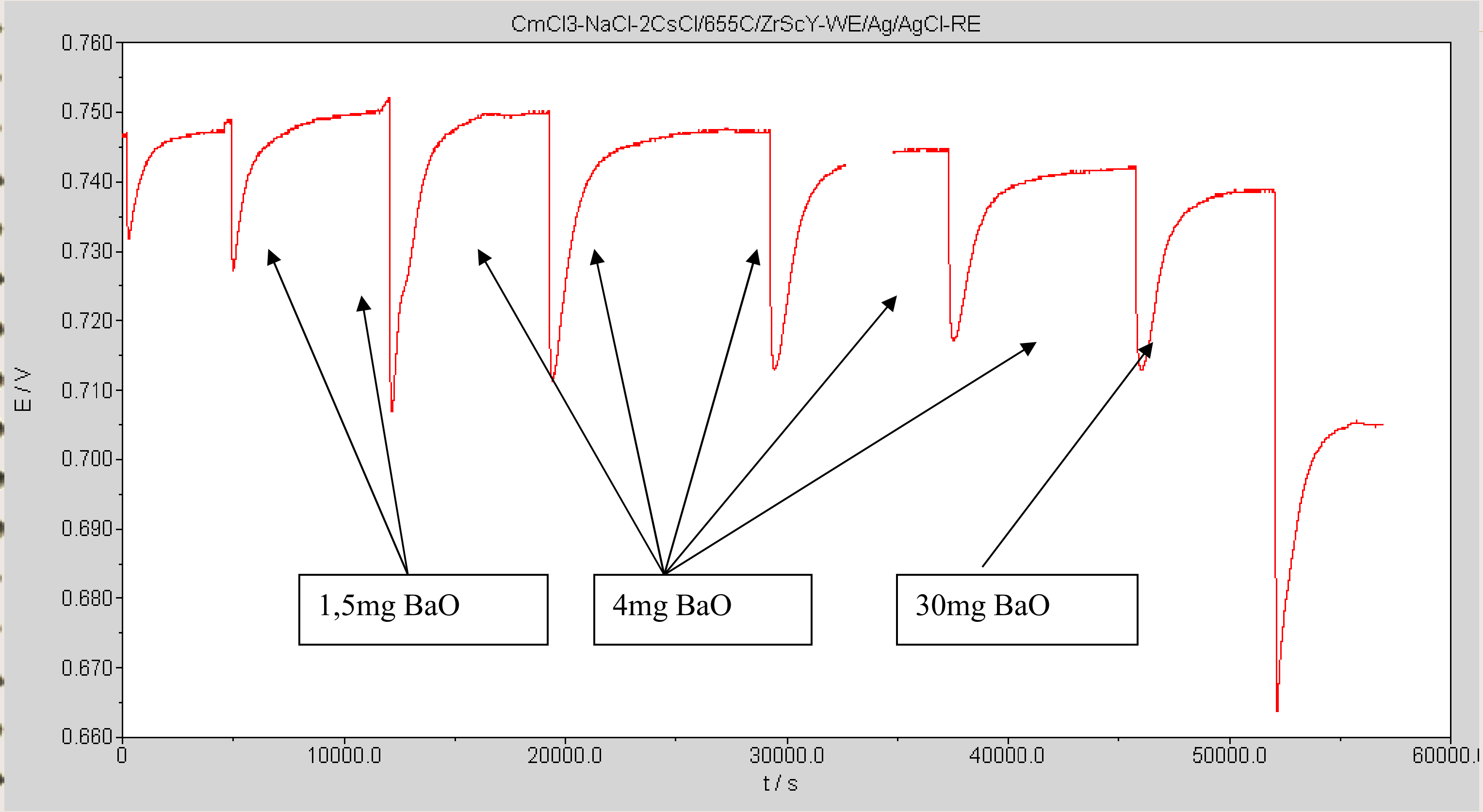
Potentiometric titration of curium-containing melt was made by the combined method:

1*10E-5 moles of oxide ions
were added into the melt on passing of the 1mA current
through the "oxygen pump
of zirconium-yttrium ceramics (8 mm in diameter)
– "auxiliary electrode" electric circuit;

then different number of 1-30mg oxide barium batches was used.

Task 1.2. Hot experiments using the potentiometric titration method.

Study of curium thermodynamics in NaCl-2CsCl



Oxygen sensor potential vs time on adding the BaO batches. Batches No. 11-18.

Melt	**NaCl-2CsCl**
Melt temperature	**650oC**
Initial curium content in experiment	**0,3%**

Task 1.3. Processing and analysis of the obtained data in order to determine the optimum curium concentration for the experiments on determination of thermodynamic parameters of insoluble curium compounds

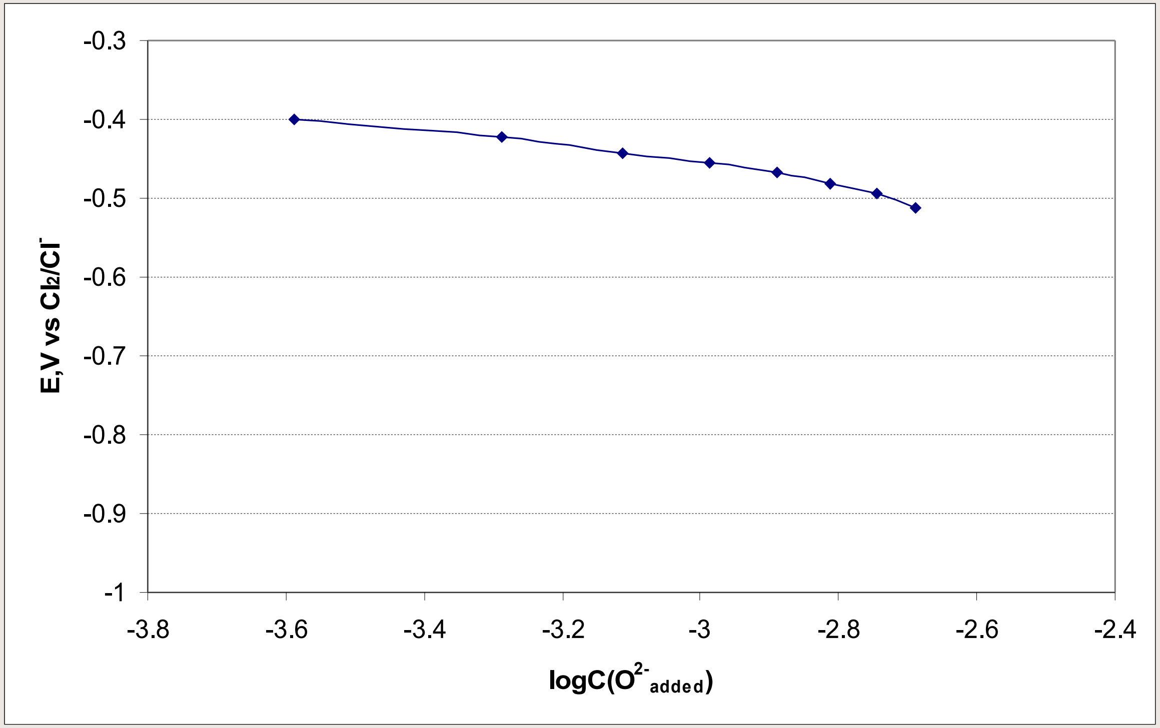
Equilibrium constant
for CmO^+ and CmOCl
were calculated and
data for calculation of conditions of Cm_2O_3 study were obtained from experimental curve

After treatment of experimental curve conditions for precipitation of Cm_2O_3 was calculated as the following:

content of curium in the melt is more than 1wt%
mass of the barium oxide batch is 30 mg.

Task 1.2. Hot experiments using the potentiometric titration method.

Study of curium thermodynamics in NaCl-2CsCl



The “oxygen sensor potential – oxide ion concentration” dependence at titration of molten BaO at 550oC

Melt	**NaCl-2CsCl**
Initial curium content in experiment	**0,3%**

Study of curium thermodynamics in NaCl-2CsCl

The dependence of the reaction formation constants of the soluble oxichloride, insoluble oxichloride and insoluble curium oxide on temperature for the NaCl-2CsCl melt will be calculated upon potentiometric titration at 750oC using a new type of the silver reference electrode in the third quarter

ISTC Project # 3261 is under continuation