Award: DE-EE0005942

Halide and Oxy-halide Eutectic Systems for High Performance High Temperature Heat Transfer Fluids

Started from Oct. 1st, 2012

University of Arizona

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Presentation outline

- Introduction to the key studies of the project
- Objectives and goals
- Approaches and the current budget period tasks
- Up-to-date key technical results and discussions
- Significance of the current results
- Challenges and barriers
- Planned future work

Introduction to the key studies of the project

- Ionic halide and covalent metal halide salts have dissimilar bonding mechanism that can be utilized to create deep eutectic systems.
- $NaCl$, KCl, $AlCl_3$, $ZnCl_2$, $FeCl_3$, are usually cheap and have large reserve.
- High boiling-point ionic halide salts in the eutectic system are expected to keep the eutectic system thermally stable at high temperatures (above 800 ^{0}C).
- Lewis acid/base additives and network forming additives will be used to tune the thermodynamics and transport properties of the eutectic system simultaneously

Table 1 Data for chloride salts

Chloride salt	Melting (°C)	Boiling (°C)
NaCl	800	1413
KCl	770	1420
LiCl	605	1382
$CaCl_2$	772	1935
$FeCl_2$	677	1023
$FeCl_3$	na	315
$MgCl_2$	714	1412
$MnCl_2$	654	1225
CuCl	426	1490
$CuCl_2$	498	993
$ZnCl_2$	293	732
$AlCl_3$	120	262

Objectives and goal

The eutectic salt will be engineered to meet the following targeted property:

	Target	Stretch Target
Thermal Stability (liquid)	≥ 800 ^oC	≥ 1300 ^oC
Melting Point	≤ 250 ^oC	≤ 0 ^oC
Heat Capacity	≥ 1.5 J/g/K	≥ 3.75 J/g/K
Vapor Pressure	≤ 1 atm	
Viscosity	≤ 0.012 Pa-s @ 300 ^oC; ≤ 0.004 Pa-s @ 600 ^oC	
Density	≤ 6,000 kg/m^3 @ 300 ^oC; ≤ 5,400 kg/m^3 @ 600 ^oC	
Thermal Conductivity	≥ 0.51 W/m/K @ 300 ^oC; ≥ 0.58 W/m/K @ 600 ^oC	
Materials Compatibility	Carbon Steel (<425 ^oC), Stainless Steel (<650 ^oC) and Nickel Alloys. Corrosion <100μm/year	
Materials Cost	≤ $1 / kg	

Approaches and budget period tasks

- The primary mechanism to modify and meet both thermodynamics and transport properties lies in the choice of ternary and quaternary systems of ionic and covalent halide salts.
- The secondary level of control of the energetics, thermal conductivity, and viscosity is offered by Lewis acid/base additives and/or network forming additives.

- Optical Combinatorial Rapid Screening (OCRS)
- Computer-Assisted Rapid screening of Eutectic (CARE)
- Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) of the Eutectic salt
- Property measurement: thermal conductivity, viscosity, density, Cp, vapor pressure, radiation.

Task 1.1: Combinatorial analysis ionic/covalent low eutectic salts (KCl-NaCl-$ZnCl_2$, KCl-NaCl-$AlCl_3$)

Task 1.2: Explore vapor pressure reduction with additives (Lewis Acid-Base, oxy-halides)

Task 1.3: Determine corrosion rates of different container/piping alloys (iron and nickel alloys) in molten salts

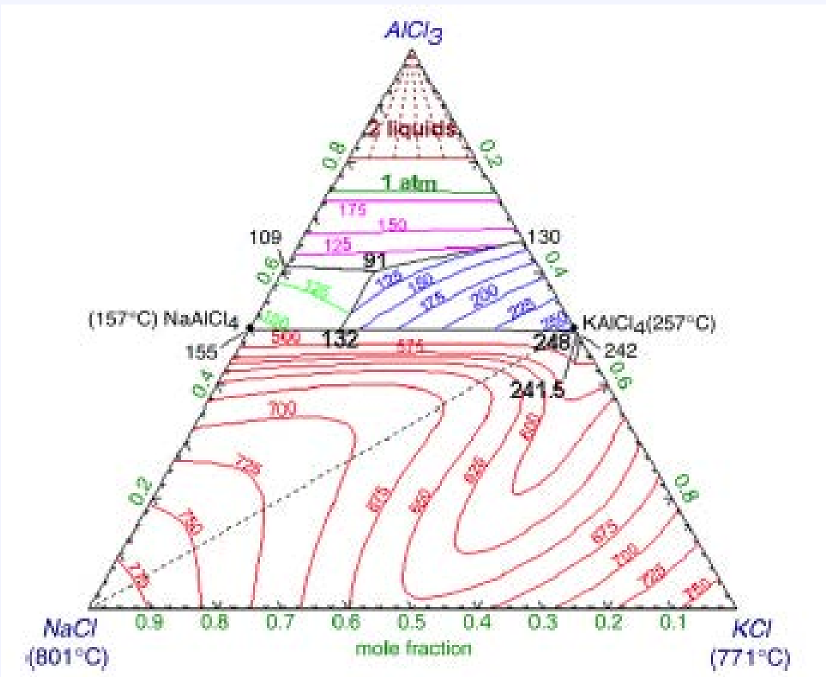
Task 1.4: Determine thermal and transport properties up to 800°C

Up-to-date key technical results and discussions

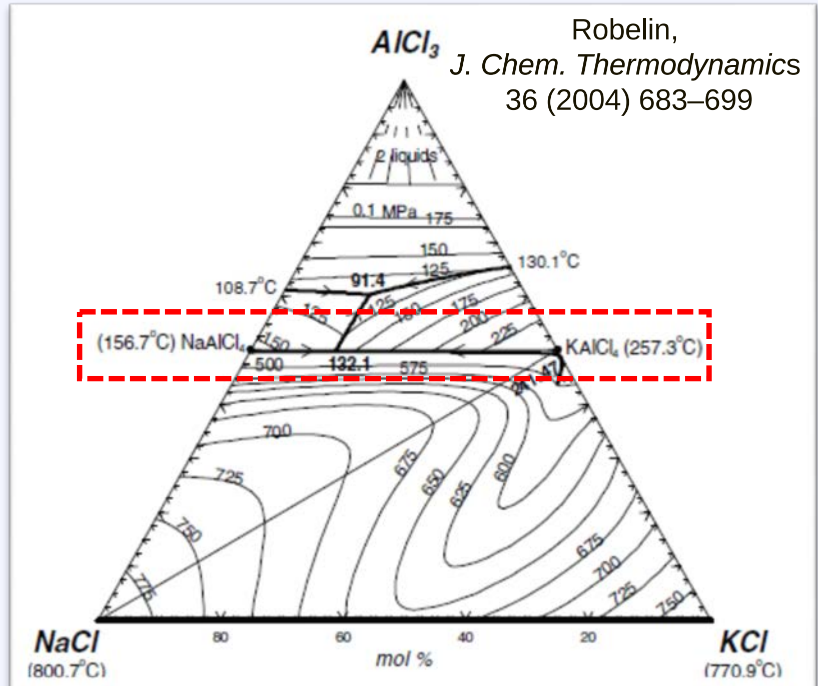
- 1) Eutectic compositions and melting
- 2) Evaporation and vapor pressure
- 3) DSC and TGA tests
- 4) Corrosion test
- 5) Properties

1) Eutectic compositions and melting

KCl-NaCl-$AlCl_3$ ternary system



CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 33 (2009) 295311



Robelin,
J. Chem. Thermodynamics
36 (2004) 683–699

T=132 ^oC at NaCl-KCl-$AlCl_3$ mole fraction of 36%-14%-50%.
T=91 ^oC at NaCl-KCl-$AlCl_3$ mole fraction of 26.25%-15%-58.75%.

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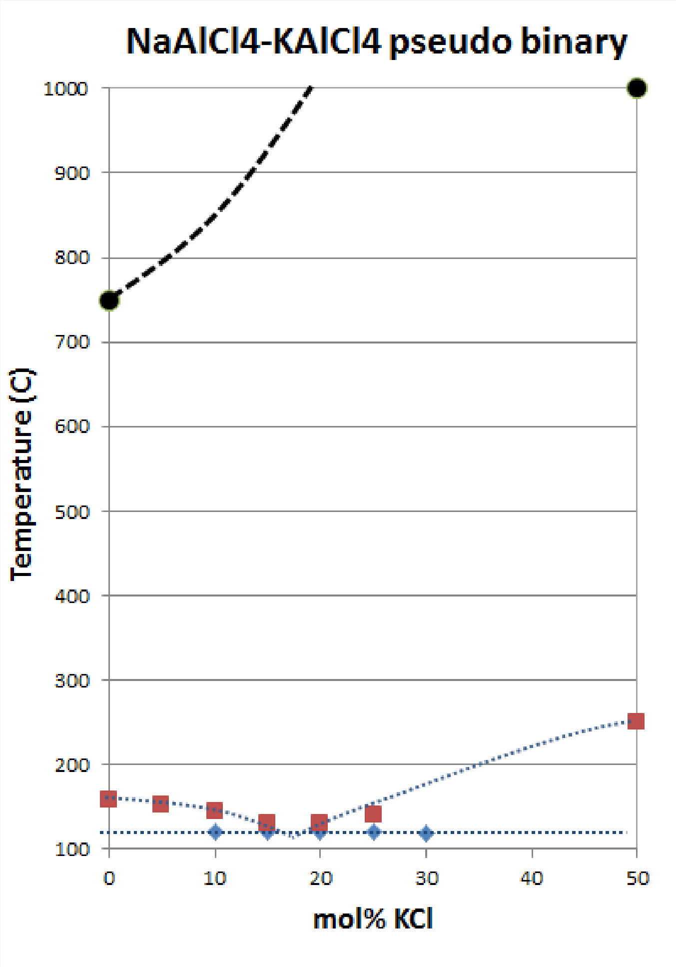
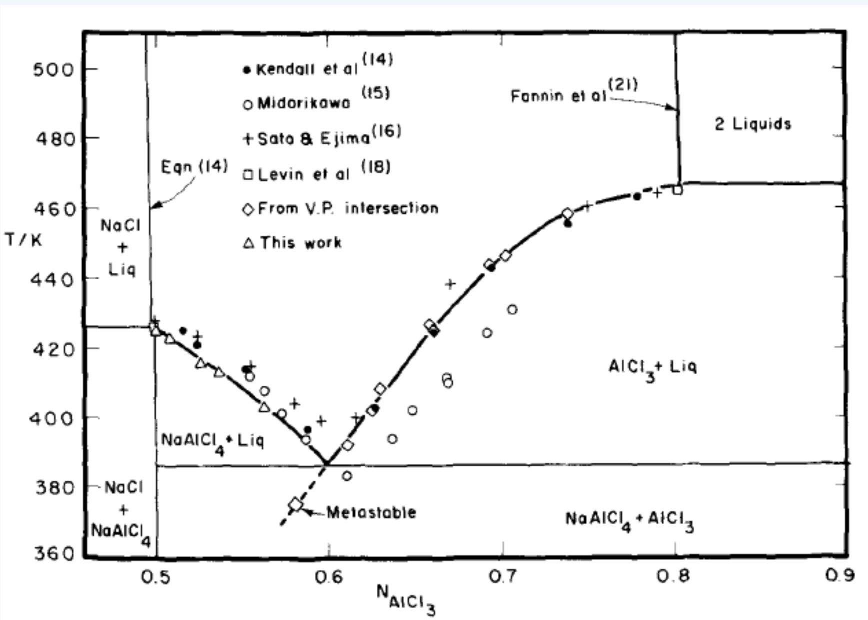
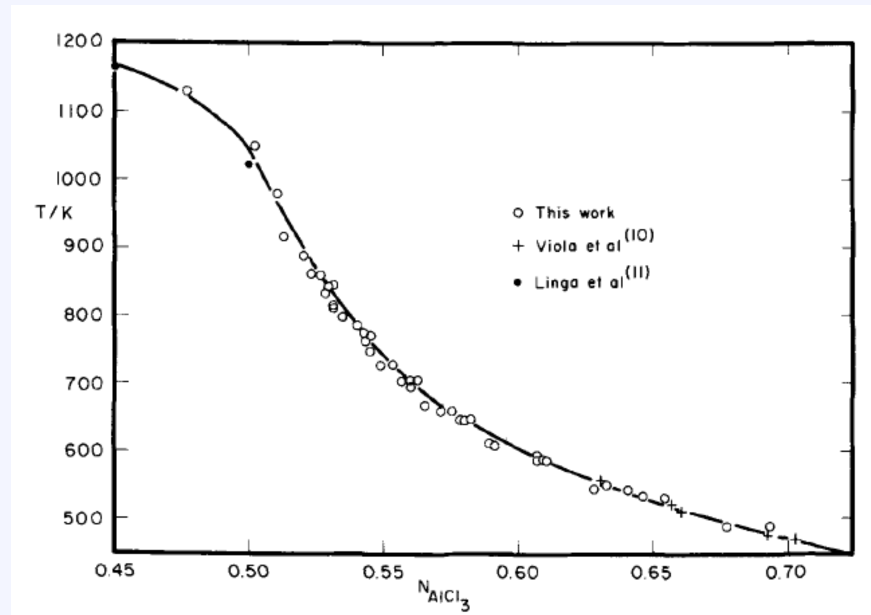
Overall, the current data from our research show that a ternary salt composition near 15KCl-35NaCl-50$AlCl_3$ will satisfy our milestone criteria of melting point <200ºC and vapor pressure <2 atm at 800ºC



Experimental liquid/solid phase diagram of pseudo binary system determined by DSC

Boiling point of binary systems NaCl-$AlCl_3$ at a pressure of 0.989 atm has been reported/tested.





Dewing E.W., Thermodynamics of the System NaCl-$AlCl_3$, Metallurgical Transactions B, Vol. 12B, Dec. 1981, pp.705-719.

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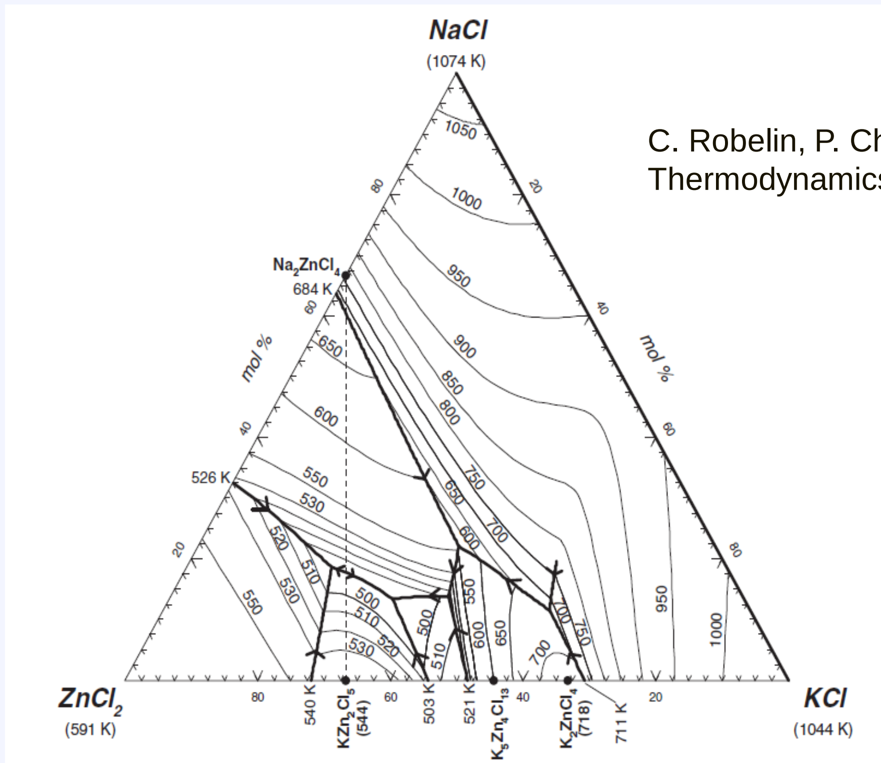
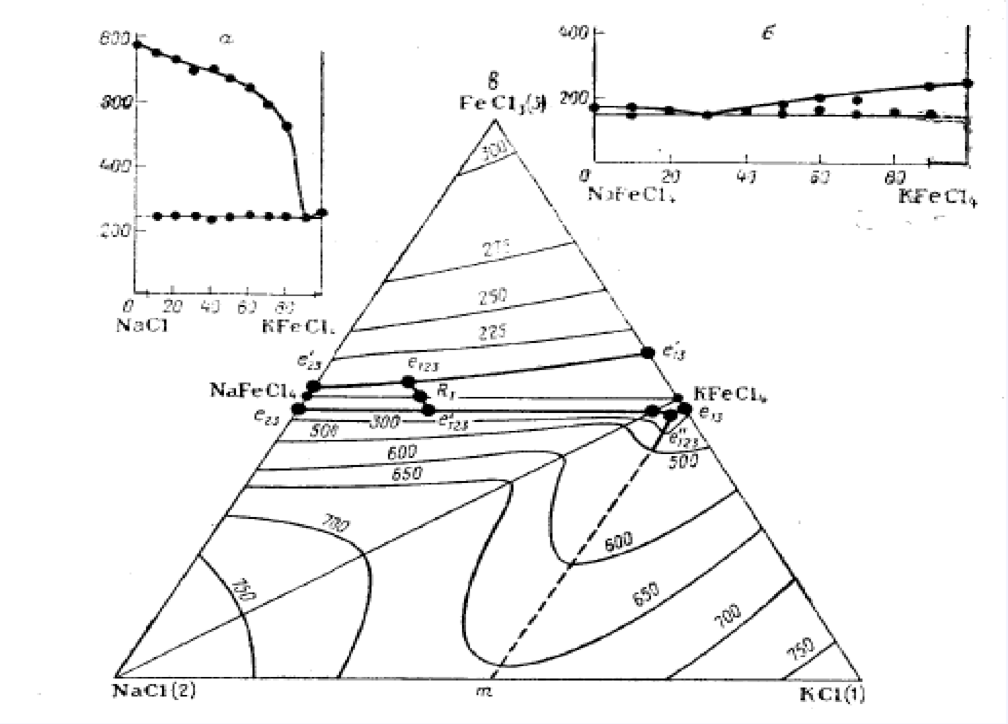
KCl-NaCl-$ZnCl_2$ ternary system



C. Robelin, P. Chartrand / J. Chem. Thermodynamics 43 (2011) 377–391

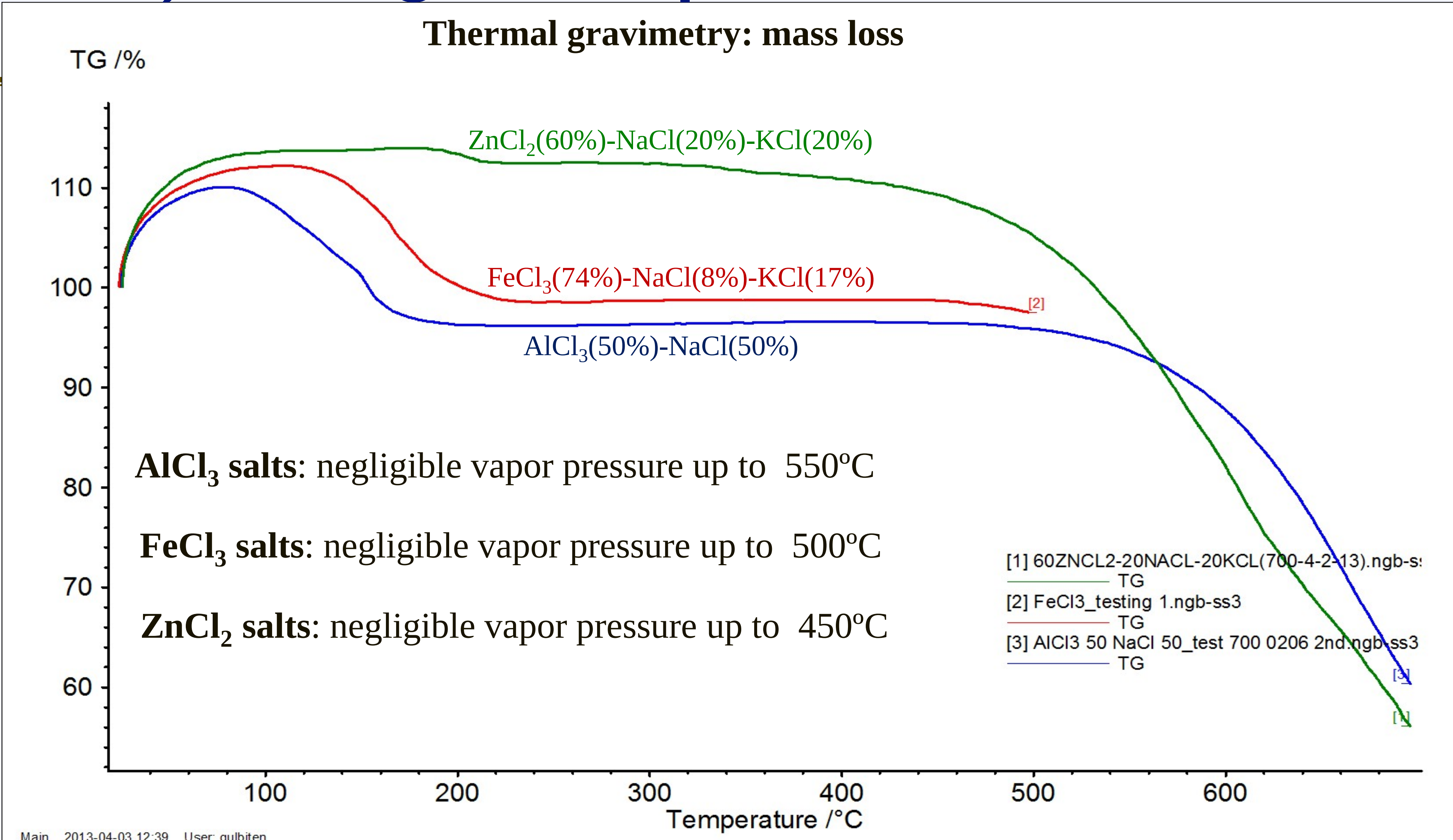
T=213 ^{o}C at NaCl-KCl-ZnCl2 mole fraction of 18.6%-21.9%-59.5%.
T=204 ^{o}C at NaCl-KCl-ZnCl2 mole fraction of 13.4%-33.7%-52.9%.
T=229 ^{o}C at NaCl-KCl-ZnCl2 mole fraction of 13.8%-41.9%-44.3%.

KCl-NaCl-$FeCl_3$ ternary system



T=139 °C at NaCl-KCl-$FeCl_3$ mole fraction of 34%-13%-53%.
T=141 °C at NaCl-KCl-$FeCl_3$ mole fraction of 35%-17%-48%.
T=240 °C at NaCl-KCl-$FeCl_3$ mole fraction of 2%-51%-47%.

2) Melting and evaporation



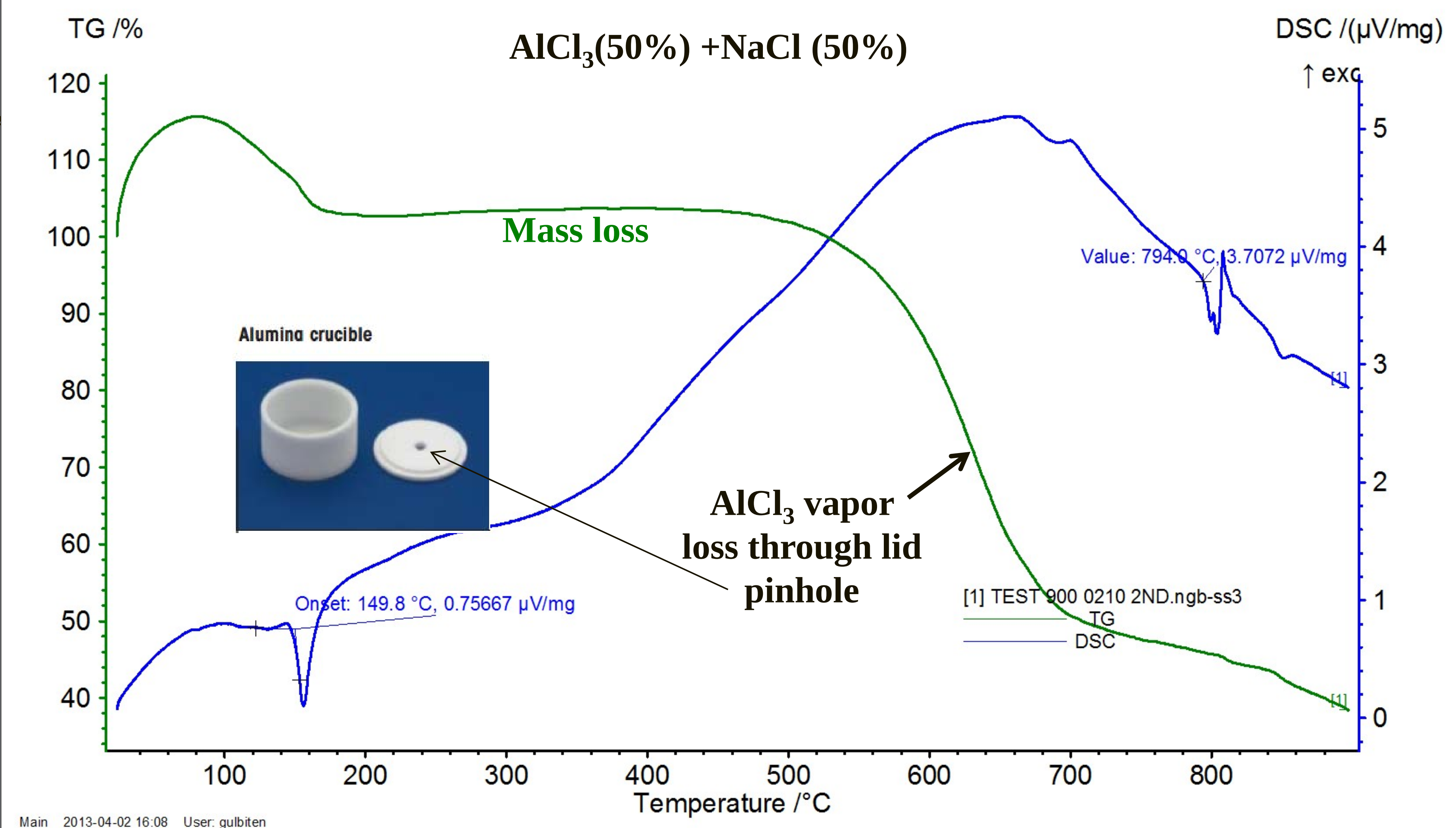
$AlCl_3$ salts: negligible vapor pressure up to 550°C

$FeCl_3$ salts: negligible vapor pressure up to 500°C

$ZnCl_2$ salts: negligible vapor pressure up to 450°C

[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 449F3	60ZNCL2-20NACL-20KCL(700-4-2-13).ngb-ss3	2013-04-02	Al2O3_ZnCl2	xu	3.4	1/1	25/10.0(K/min)/ 700	N2, 100.0ml/min / N2, 20.0ml/min	---
[2] STA 449F3	FeCl3_testing 1.ngb-ss3	2013-02-22	Fe comp.	GHazal	4.4	1/1	25/20.0(K/min)/ 500	N2, 100.0ml/min / N2, 20.0ml/min	---
[3] STA 449F3	AlCl3 50 NaCl 50_test 700 0206 2nd.ngb-ss3	2013-02-07	test 700 0206 2nd	Lucas	4.4	1/1	25/10.0(K/min)/ 700	N2, 100.0ml/min / N2, 20.0ml/min	---

Created with NETZSCH Proteus software



Instrument : NETZSCH STA 449F3 STA449F3A-0825-M **File :** C:\NETZSCH\Proteus6\data\TEST_AlCl3_high T\TEST 900 0210 2ND.ngb-ss3

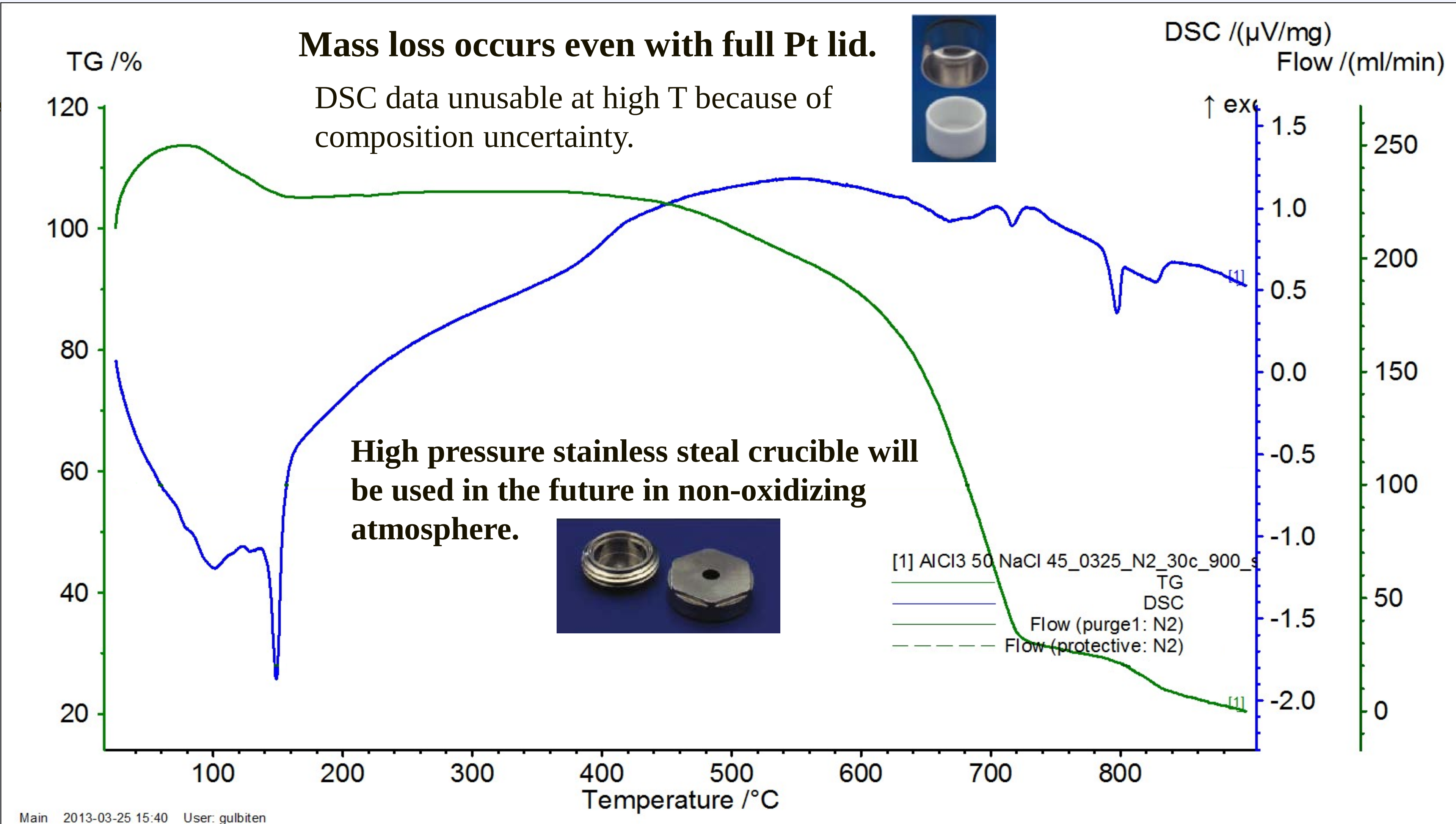
Project :	**Sample :** Lucas, 2.9 mg	**Sample car./TC :** DSC/TG Cp S / S	**TG corr./m. range :** 000/35000 mg
Identity : TEST 900 0210 2ND	**Material :**	**Mode/type of meas. :** DSC-TG / Sample	**DSC corr./m. range :** 000/5000 µV
Date/time : 2/10/2013 3:10:03 PM	**Correction file :**	**Segments :** 1/1	**Pre Mment Cycles :** 3xVac
Laboratory :	**Temp.Cal./Sens. Files :** TCALZERO.TCX / SENSZERO.EXX	**Crucible :** DSC/TG pan Al2O3	
Operator :	**Range :** 25/10.0(K/min)/ 900	**Atmosphere :** N2 / N2	

Created with NETZSCH Proteus software

Mass loss occurs even with full Pt lid.

DSC data unusable at high T because of composition uncertainty.

High pressure stainless steal crucible will be used in the future in non-oxidizing atmosphere.

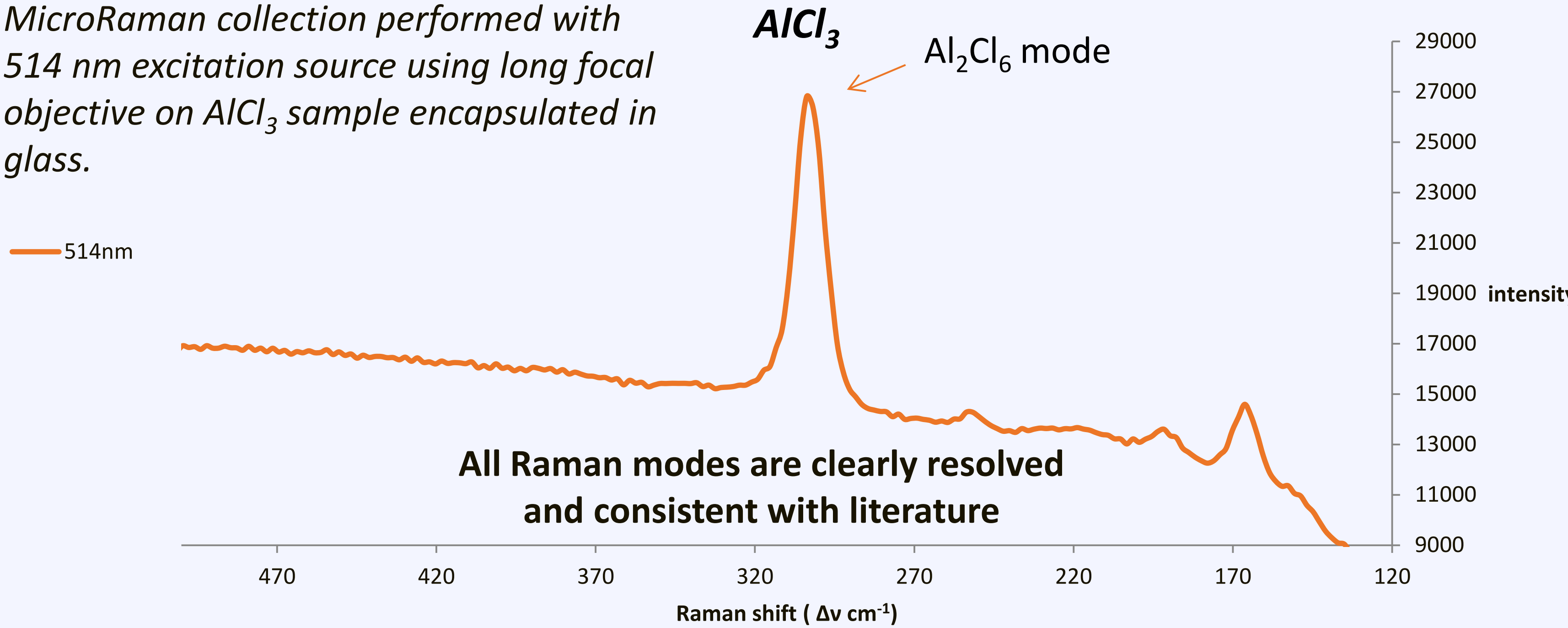


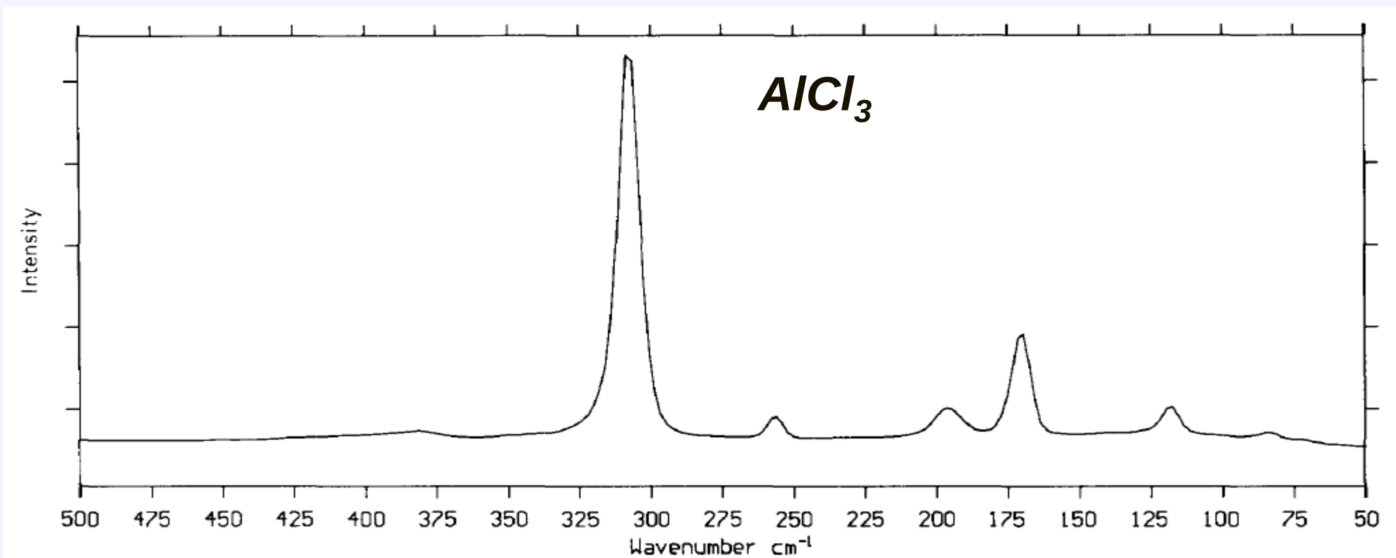
Instrument : NETZSCH STA 449F3 STA449F3A-0825-M **File :** C:\NETZSCH\Proteus6\data\AlCl3 50%\AlCl3 50 NaCl 45_0325_N2_30c_900_second time_first run.ngb-ss3

Project :	MOLTEN SALTS	**Sample :**	xu, 2.9 mg	**Sample car./TC :**	DSC/TG Cp S / S	**TG corr./m. range :**	000/35000 mg
Identity :	new method_N2	**Material :**	AlCl3	**Mode/type of meas. :**	DSC-TG / Sample	**DSC corr./m. range :**	000/5000 µV
Date/time :	3/25/2013 11:47:53 AM	**Correction file :**		**Segments :**	1/1	**Pre Mment Cycles :**	3xVac
Laboratory :	DRLUCAS	**Temp.Cal./Sens. Files :**	TCALZERO.TCX / SENSZERO.EXX	**Crucible :**	DSC/TG pan Al2O3		
Operator :	xu	**Range :**	25/10.0(K/min)/ 900	**Atmosphere :**	N2 / N2		

Created with NETZSCH Proteus software

MicroRaman collection performed with 514 nm excitation source using long focal objective on $AlCl_3$ sample encapsulated in glass.





H.G.M. Edwards et al./Journal of Molecular Structure 344 (1995) 37–44

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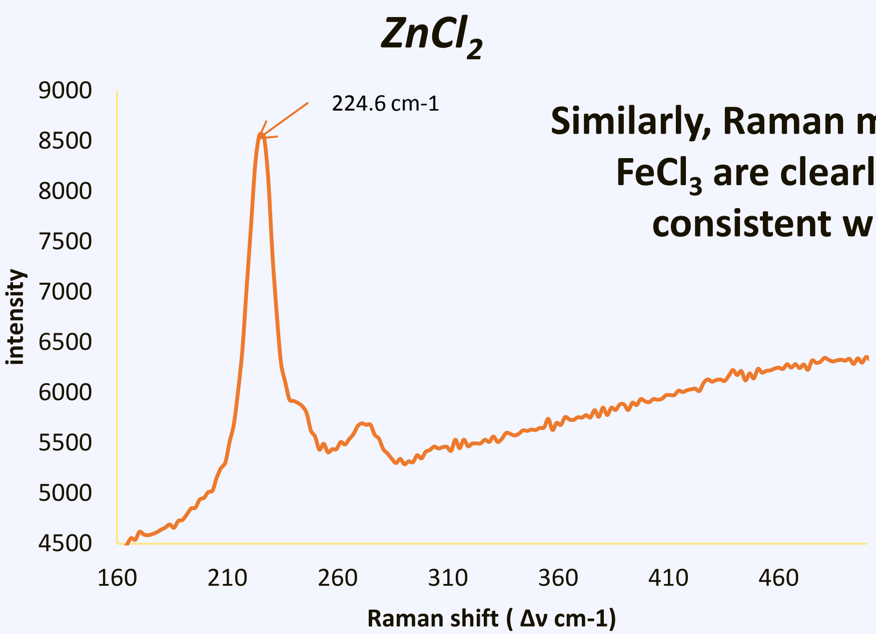
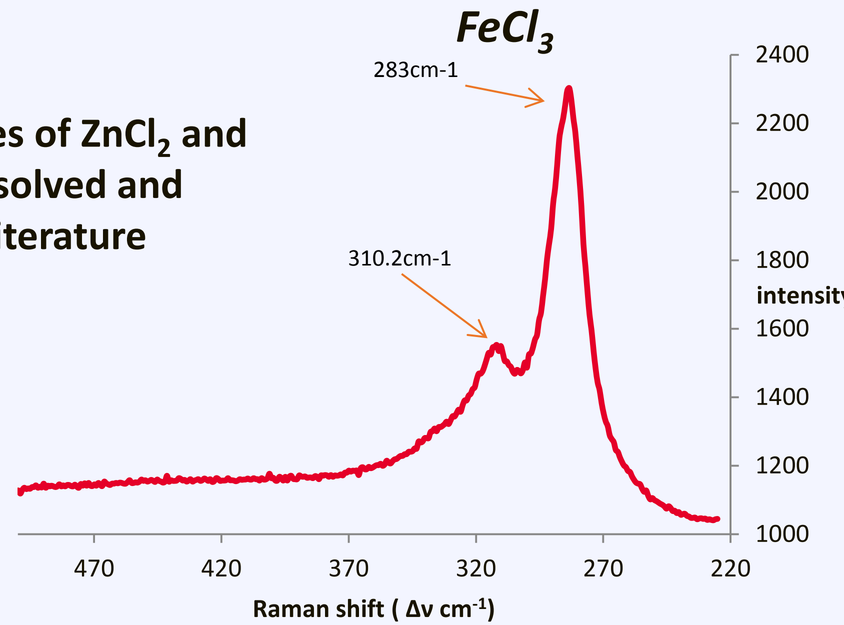
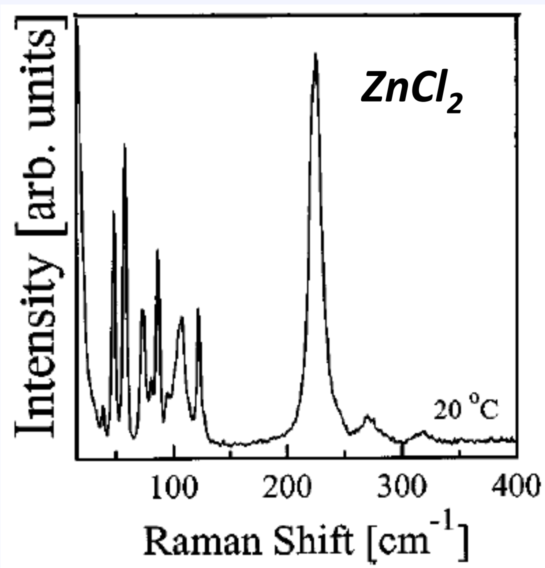
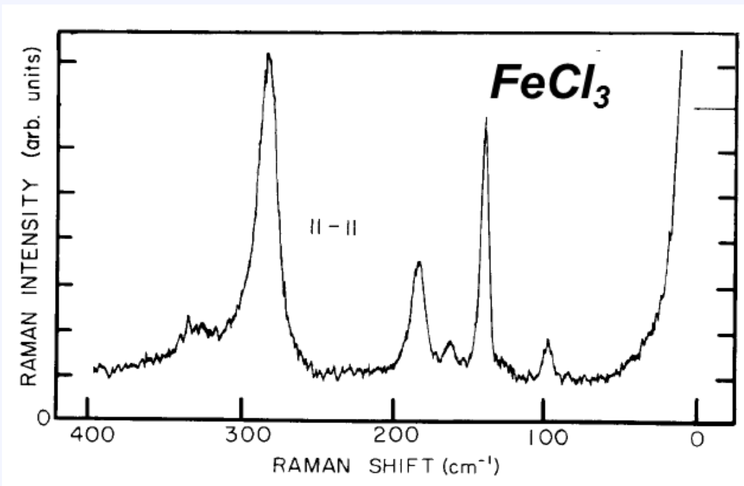


Similarly, Raman modes of $ZnCl_2$ and $FeCl_3$ are clearly resolved and consistent with literature



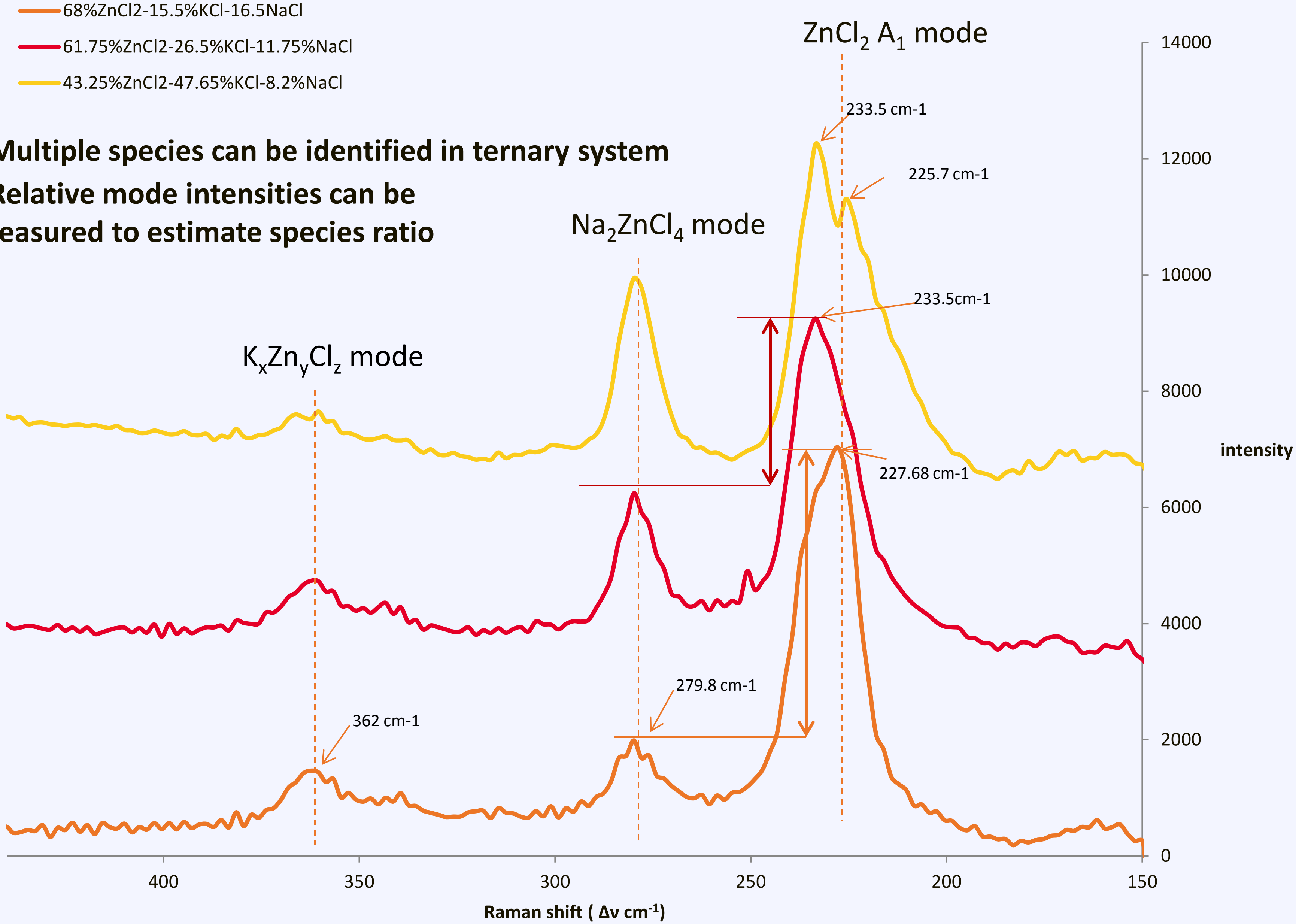




Normalized Raman spectra of $ZnCl_2$-NaCl-KCl salts

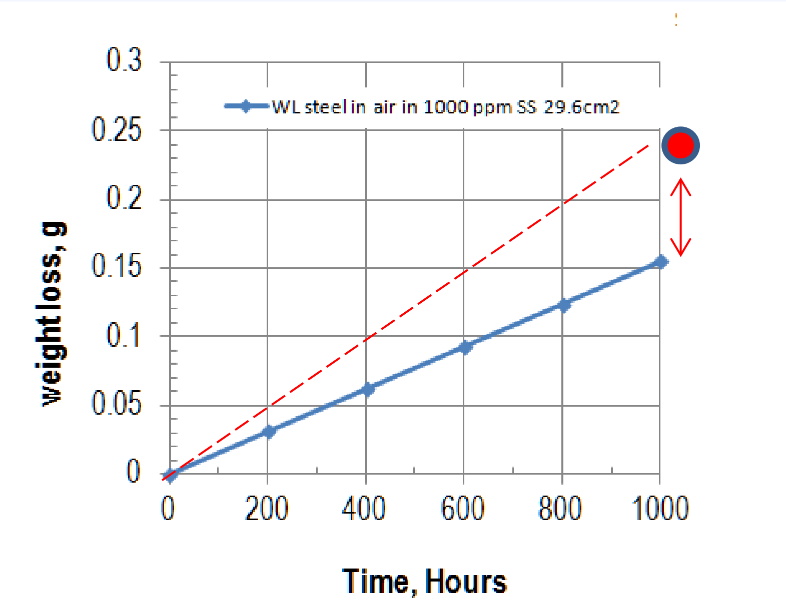
. **Multiple species can be identified in ternary system**

. **Relative mode intensities can be measured to estimate species ratio**



4) Corrosion testing

Gravimetry and Electrochemistry



Weight loss of 1008 steel in aerated water with 1000 ppm sodium sulfate in time. Measured by the

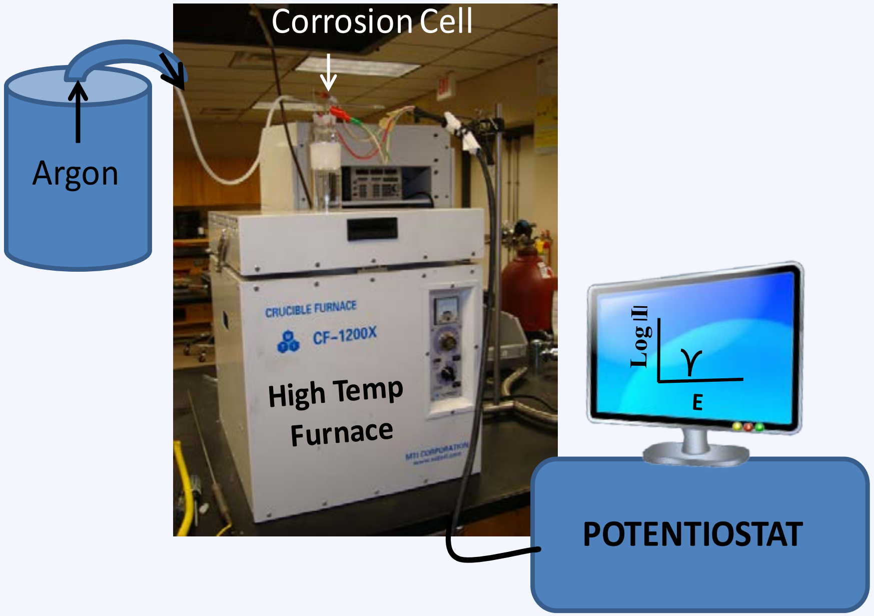
1. **gravimetric method (red line)**
2. **electrochemical method (blue line).**

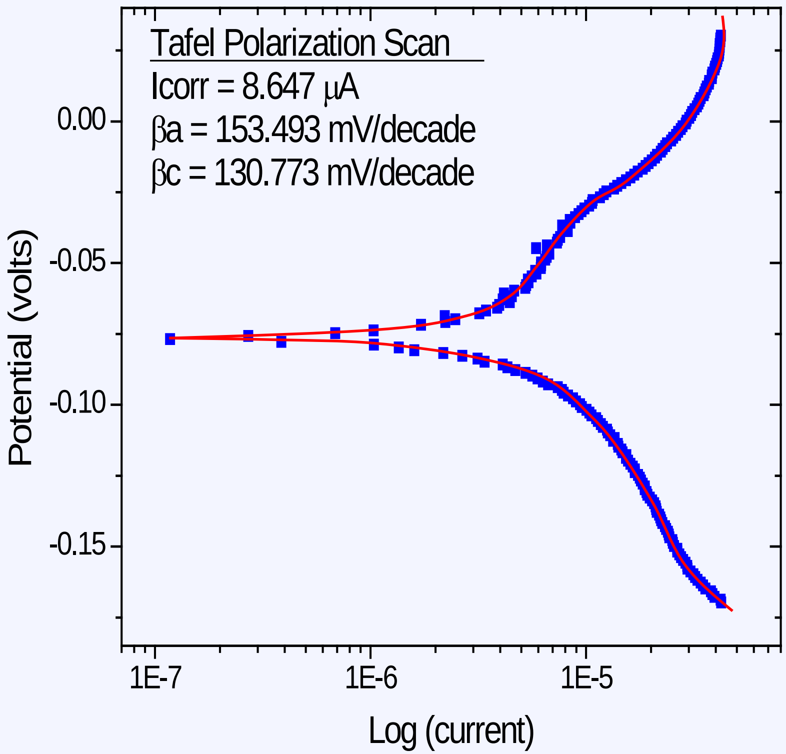
- **Gravimetric method is slow but accurate:** The weight loss by the gravimetric method is corrected for weight loss during surface preparation, e.g., from exposure to the sulfuric acid soak so the higher value using gravimetric method is not an artifact.

- **Electrochemical method is quick, precise but ~ 35% inaccurate:** The error in the electrochemical method arises from the assumptions used when applying Faraday's Law of electrolysis to convert charge to mass when finding the weight loss.
  - Faraday's Law of electrolysis is m = (Q/F) (M/z) in which *m* is the mass of the substance liberated from electrode in grams; *Q* is the total electric charge passed; *F* = 96,485 C mol^{-1} is the Faraday constant; *M* is the molar mass of the substance and *z* is the number of electrons transferred per mole during the rate limiting step.
  - The only arbitrary assumption is that metal forms metal ions by the loss of 2 electrons (i.e., z=2). Although reasonable, this may not be - and appears not to be - exactly true.

- **Gravimetric method used to correct an Electrochemical sensor:** The time-dependent gravimetric and electrochemical weight-loss lines are straight.
  - The slopes of these lines differ by a constant, k., and k can be used to correct the electrochemically-determined weight loss.
  - Finding k for each metal in each salt composition is an important task.
  - Knowing this constant, k, for a specific metal in a specific molten salt, allows use of the electrochemical method to quickly and *accurately* monitor the rate of corrosion of metal.

Polarization curves in molten salt





Electrochemical measurement set-up connected to the corrosion cell in the high temperature furnace. Right panel shows the blown-up view of the corrosion cell and the connecting wires going to the electrodes

Polarization curve (Log_{10} |I| versus E) for a stainless steel electrode in 13.4NaCl- 33.7KCl- 52.9$ZnCl_2$ eutectic molten salt at 250^{o}C.

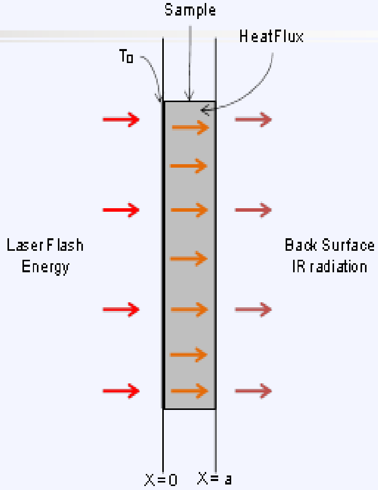
Summary of corrosion data in molten salts

Sample #	Alloy Sample	Salt Composition	Temperature & Atmosphere	Corrosion Rate (µm/yr)	E_{corr} (mV)		
					ocv (before)	cusp	ocv (after)
1	Stainless Steel (430)	1M NaCl aqueous solution	RT/Air	10	n/a	-229	-222
2	Stainless Steel (430)	$NaCl-ZnCl_2$ (40-60)	300 ^oC/Air	12	n/a	9	27
3	Stainless Steel (430)	$NaCl-KCl-ZnCl_2$ (13.4- 33.7- 52.9)	250 ^oC/Air	45	n/a	-76	n/a
4	Hastelloy (C 276)	$NaCl-KCl-ZnCl_2$ (13.4- 33.7- 52.9)	250 ^oC/Air	12	-39	-25	-37

5. Thermal and Transport Properties

Thermal conductivity by Ga-Tech.
Density, Cp, viscosity, radiation by UA

Indirect measurement - Laser Flash Diffusivity method

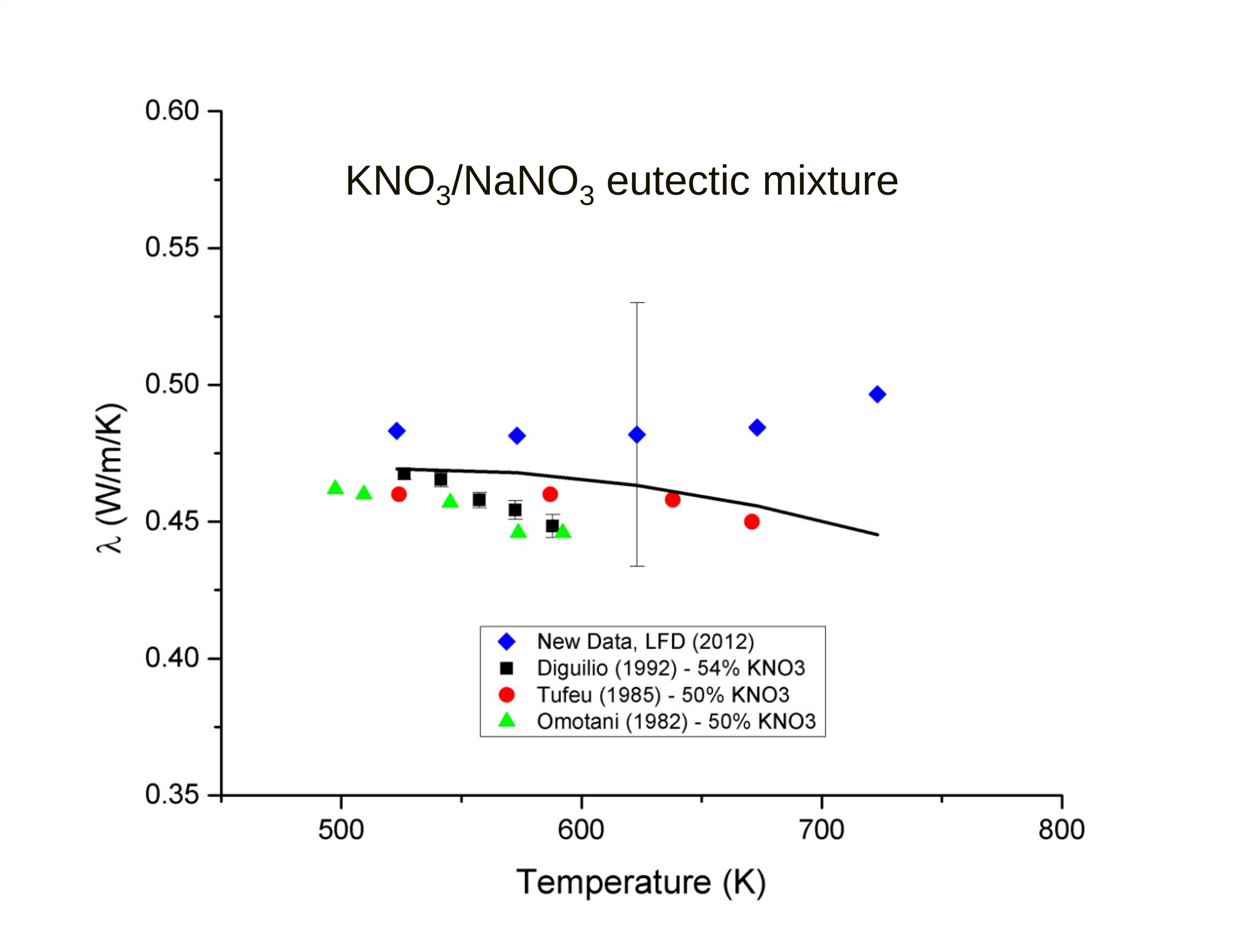


- $\lambda = \rho \, \alpha \, C_p$
  - ρ : Density → literature or measured (UA)
  - α : Thermal diffusivity → measured by LFD
  - C_p : Specific heat → measured by DSC (UA)

- Test mixture measurements by Netzsch Instruments Application Laboratory, Burlington, MA
  - $KNO_3/NaNO_3$ eutectic mixture (54 % mol KNO_3)
  - Temp. Range: 523 K-723 K
  - Reported error: 10-15%

- **Collaboration with Oak Ridge National Lab (ORNL)**
  - Will require re-design of the sample holder for high temperatures

Netzsch Results and Comparisons



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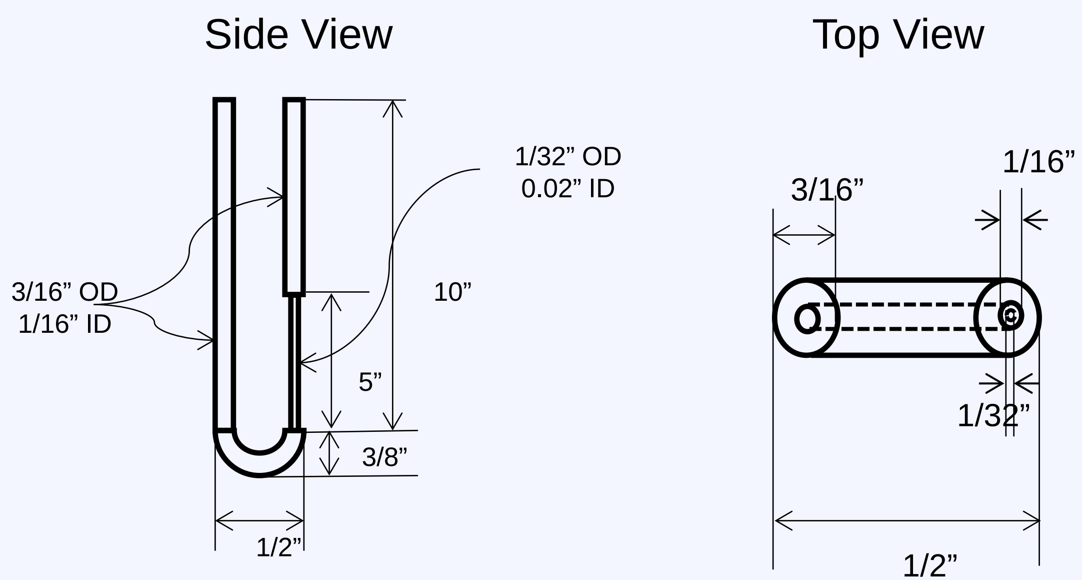
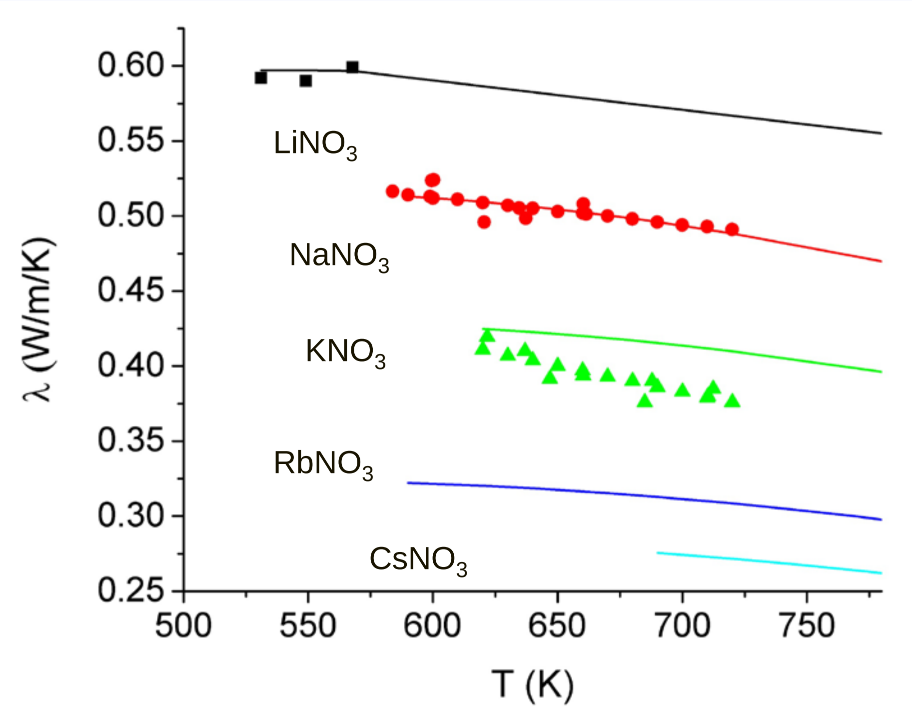
Transient Hot Wire apparatus improvements

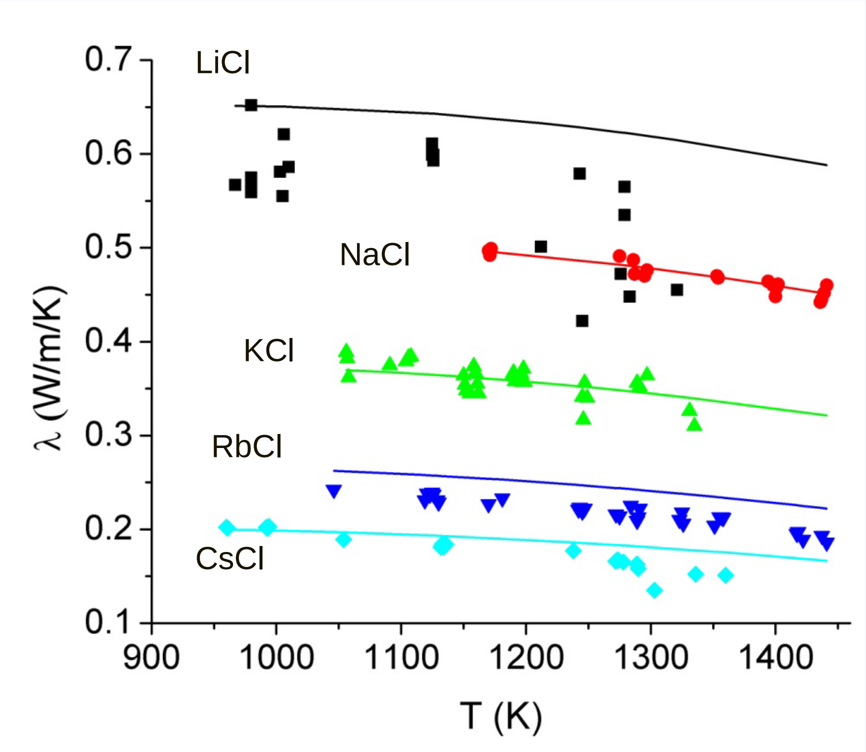
- **Existing system**
  - Mercury filled glass capillary (suitable upto 523 K)
- **Proposed set up**
  - Alumina sample holder and cell
  - Capillary filled with gallium



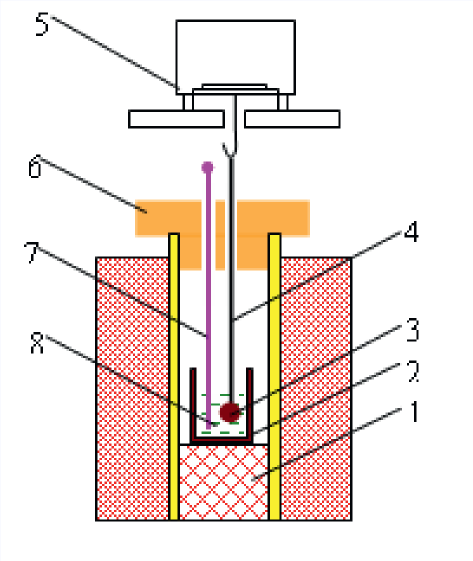
Model Development

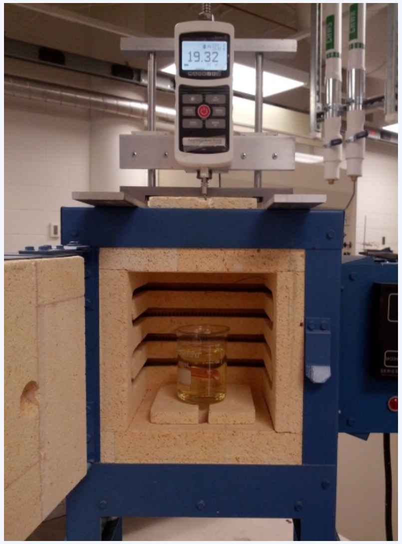
- **Thermal conductivity correlation and prediction**
  - alkali-nitrates from $NaNO_3$ data
  - alkali-chlorides from NaCl data





High temperature HTF density (UA)





(a) (b)

(a) Schematic diagram of the test apparatus.
(b) Actual setup.

Future work (calibration with NaCl and KCl up to 1200 C, with nickel block as the weight rather than Cu for now).

High temperature HTF density (UA)

- Oxidation of nickel weight at high temperatures
  - Nickel rod: 99.98% from Good Fellow

- Color turns green during NaCl calibration
- Ni will be oxidized above 400 ^{o}C to form NiO (even before dipping into NaCl melted at 800 ^{o}C)

- Deposit 100 nm Pt on Ni rod
- Less NiO still forms after taking out

High temperature HTF density (UA)

- NaCl calibration result
- Nickel:
  - Linear thermal expansion coefficient α(T) from *Phys. Rev. B* **16**, 4872–4881 (1977)
  - Volume expansion ß(T)≈3α(T)
  - 4.19% volume expansion from 25 to 800 °C
- NaCl density at 800-850 °C
  - 1610 kg/m^3, 3.47% higher than literature value
  - It may be due to slight surface oxidation on Ni rod

Challenges and barriers

- All three ternary eutectic systems showed a vaporization at temperature about 500 C in ambient pressure. Before we find the proper quaternary system or additives to reduce the vapor pressure, we face challenges in conducting tests of thermal and transport properties under pressure. This requires equipment to hold pressures of up to 2.0 atm as expected.

Planned future work

- Pressurized test of vaporization-temperatures.
- Quaternary system and vapor pressure reduction
- Additives ($POCl_3$, B_2O_3) to reduce vapor pressure
- Property measurement at high temperatures.

Thank you!

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Backup slides for questions and discussions

Gravimetric Method

- Prepare metal surface
- Weigh metal
- Expose metal to molten salt
- Reweigh metal

Gravimetric corrosion rate is weight difference of sample before and after exposure to molten salt

Advantage

- Absolute measurement of corrosion

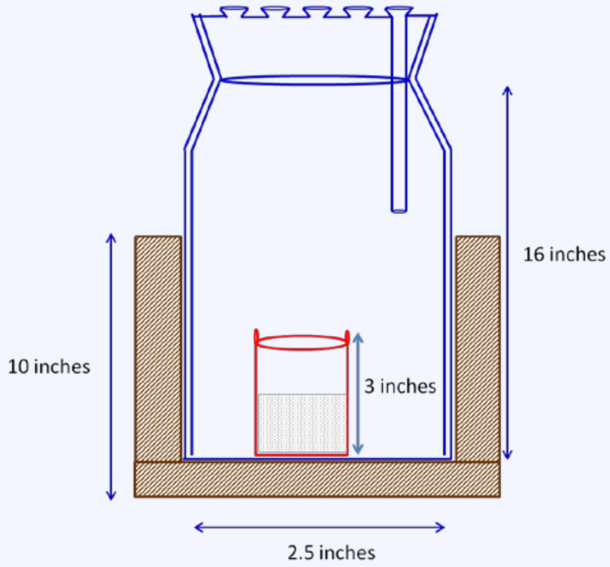
Disadvantage

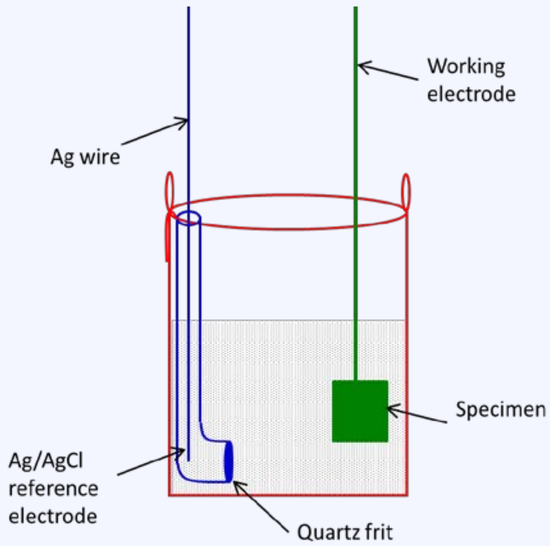
- Slow (weeks to months)
- Can only give average corrosion rate (ACR in grams per year, gpy, converted to microns per year, mpy, using density and metal area) over the long intervals of time needed to obtain data so there is a loss of information, that is rate of corrosion due to quick changes in environment

Electrochemical method

The test cell for obtaining an I/V plot is

- a working electrode (WE) made of the metal in molten salt of interest
- metal potential, E_{WE}, is obtained by measuring the voltage of the working electrode versus the potential of a silver/silver-chloride reference electrode, E_{ref}
- current is passed from working electrode to an inert counter electrode.





Left—High temperature corrosion cell with brown shaded area showing the dimensions of the high temperature furnace.

Right—A blown-up of the cell with working electrode reference electrode in tube terminating with quartz-frit made at Technical Glass Products, Ohio.

Electrochemical method (cont.)

Method

The instantaneous corrosion rate (ICR in microns per year) is estimated from interpreting a polarization (current/voltage or I/V) curve. ICR is

$$ICR = M\,B \,/\, (A\,F\,z\,\rho\,R_p)$$

- *M* is average molecular weight of the metal or metal alloy (g/mol),
- *A* is the surface area (cm^2),
- *F* is the Faraday constant [96 485 coulomb/(mol e-)],
- *z* is the average charge of the metal [(mol e-)/mol],
- ρ is the density of the metal (g/cm^3)
- *B* is the Stern-Geary constant (volt)
- polarization resistance, R_p, where R_p is estimated by measuring:
  - the slope, β, of a linear plot of the I/E curve, measured for the anodic (β_a)and cathodic (β_c) branches within 50 mV of the rest potential ($E_{rest} = E_{corr}$)
  - the I_{corr}, the value extrapolated to the I axis from E_{corr} at the intersection of the anodic and cathodic linear interpolation of the log I versus V plot

$$R_p = \boldsymbol{\beta_a\beta_c} / [2.303\, I_{corr}(\boldsymbol{\beta_a+\beta_c})]$$
$$= B/ I_{corr} \quad \text{where B = the Stern Geary coefficient} = \beta_a\beta_c/[2.303(\beta_a+\beta_c)]$$

Advantage

Quick (minutes), allows interrogation of changing corrosive environmentals/conditions

Disadvantages

Needs to be normalized by gravimetric data due to uncertainty in z

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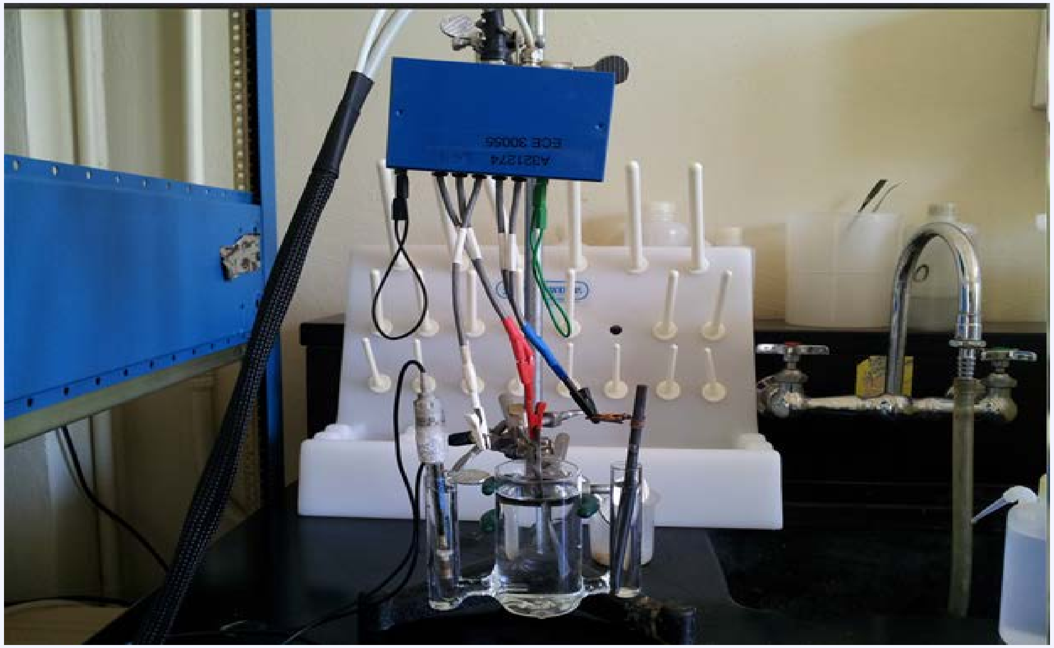
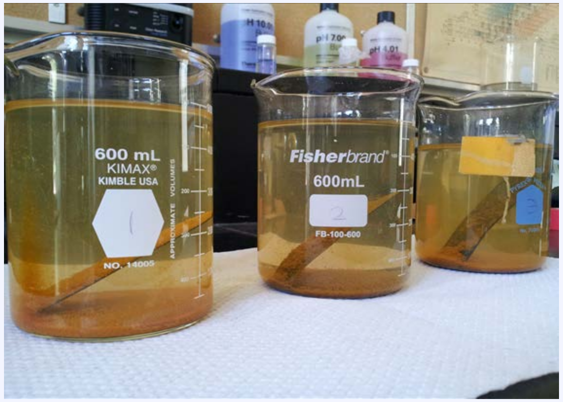
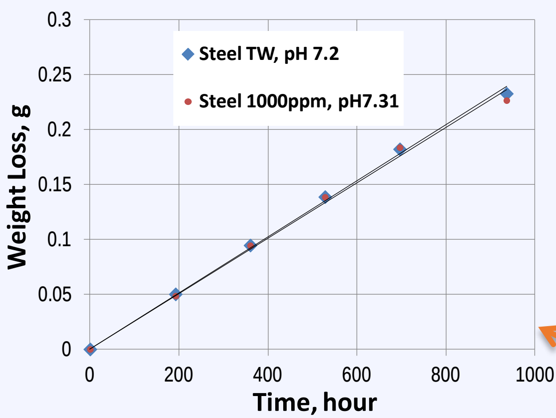


Glass cell used for electrochemical determination of corrosion rate of 1008 steel in water

Gravimetric method for corrosion test



Bench top test for determining the weight loss of metal in water in air.



Plot of weight loss of steel in time for Tucson tap water (TW) and in ultra pure water with 1000ppm sodium sulfate.

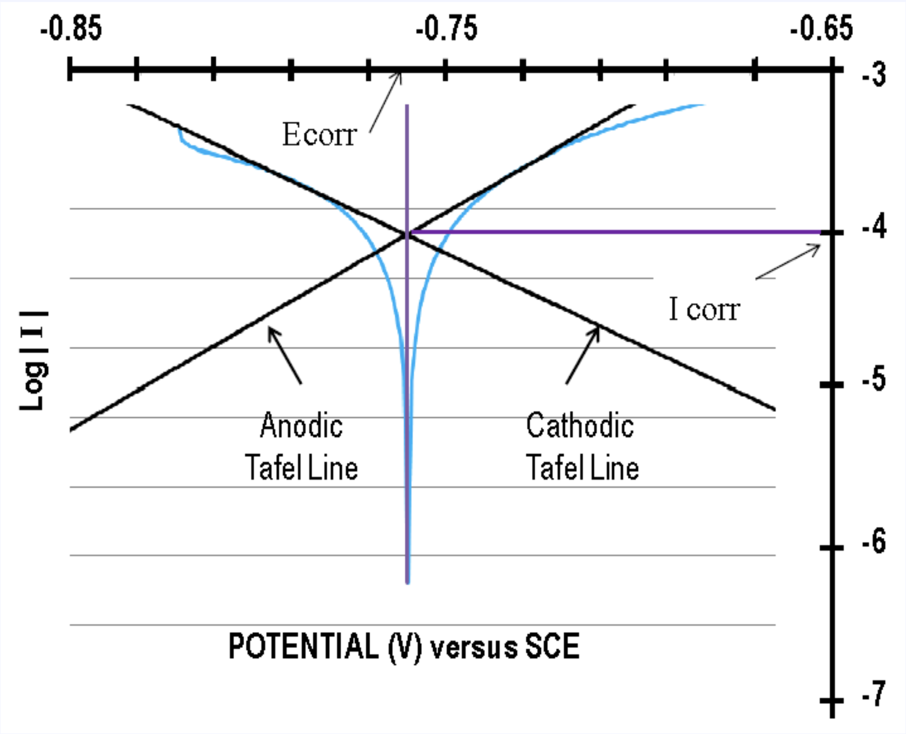
Initially, the metal is abraded with 600 grit silicon carbide paper; soaked in 1M aqueous sulfuric acid for 1 minute, rinsed with acetone, dried at room temperature and weighed.

This pre-weighed sample is then exposed to water of known composition and open to the air as shown.

The corroded metal is soaked in acid to remove corrosion products, rinsed with acetone, dried and reweighed to find the net weight loss.

A graphical summary of the gravimetric weight loss results for the steel exposed to water in time.

Electrochemical polarization resistance method



Polarization (I/V) curve for steel in aerobic water. With1000ppm sodium sulfate. WE=steel, CE=graphite, RE= SCE. T = 22C; P = 1 atm in air.

- The $\log_{10}$ of the absolute value of the steady state current, |I|, is plotted versus metal electrode potential.
- The Tafel region is the linear region of the I/V curve within 50 mV of Ecorr.
  - β_A is slope of the of the I/V curve during oxidation of metal
  - β_c is slope of the curve for oxygen reduction.
- I_{corr} , the corrosion current, is determined by extrapolating the intersection of the Tafel lines to the current axis at Ecorr.

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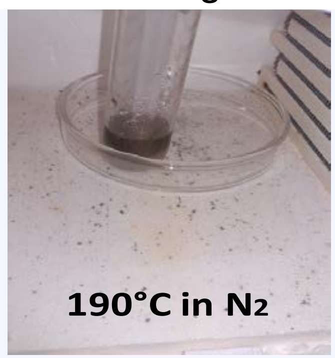
Special handling of eutectics formed from aluminum chloride

Aluminum chloride fumes in moist air forming aluminum-oxides and oxy halides.

An aluminum eutectic (50% AlCl3-15% KCl-35% NaCl) melts at 190^{o}C and appears stable for use as heat transfer fluids, if prepared properly.

Salt mixture heated at 190°C in N_2. No fumes or weight loss



Once formed under N_2 melt is stable in air with no fumes or weight loss at 190°C in air.

Preparation of the eutectic must be done in an inert atmosphere (N_2).The $AlCl_3$ is placed in a test tube; then covered by a layer of KCl and then NaCl. When $AlCl_3$ melts all are stirred and heated until this mixture melts at 190^{o}C.

The eutectic cooled to RT (22 ^{o}C) is stable in air at RT and when re-heated in air to the highest temperature tested to date, 300^{o}C.

316 stainless steel was added to the molten aluminum eutectic in air. The metal did not disturb the eutectic's stability in air, and no weight change was found for the 316 stainless steel when immersed in the eutectic in air for 100 hours.

High temperature HTF density (UA)

Future improvement

– N_2 protection for the current setup (building a home-made enclosure to purge with N_2) in case salts also react with air

– Quartz weight ordered to replace Ni

- Measure volume expansion directly (alternative way)

Vacuum sealed at the end

Take photo of the liquid level through the observation window of the furnace

Bulb (volume measured before use)

Piston dilatometry:

- The liquid level change here is transferred through a piston to a dial gauge
- Providing seal also with a piston