SAND2016-8201PE

CSP Gen 3 Roadmap

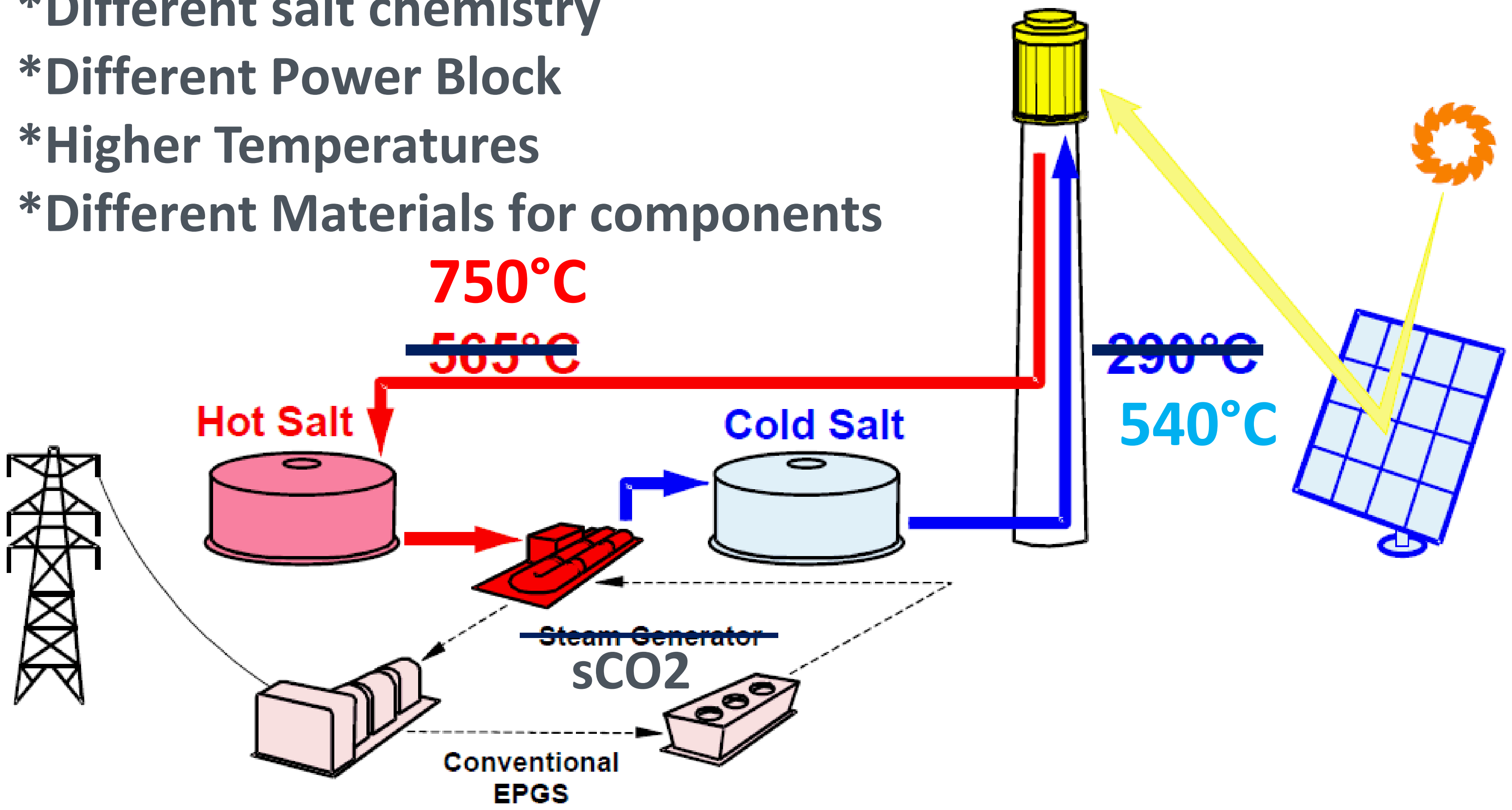
Molten Salt Technology

August 18 – 19, 2016

Chair: Judith Vidal, NREL
Co-chair: Alan Kruizenga, SNL

Distinct Differences to Solar Two

*Different salt chemistry
*Different Power Block
*Higher Temperatures
*Different Materials for components



Materials Concerns – Salt Chemistries

Salt	Melting Point (°C)	Heat Capacity (J/g-K)	Density (kg/L)	Media Cost ($/kg)	Media Cost $/kWh$_{th}$	Tank Vol. (m^3/MWh)
$NaNO_3/KNO_3$ (baseline)	220	1.5	1.7	1.1	14	7.0
$ZnCl_2/NaCl/KCl$	204	0.81	2.4	0.8	19	9.3
$MgCl_2/KCl$	426	1.15	1.66	0.5	8	9.4
$Na_2CO_3/K_2CO_3/Li_2CO_3$	398	1.6	2.4	2.5	28	4.8

Accurate Properties over thermal ranges is required for design

Salt (proponents)	Notable Advantages	Notable Disadvantages
Zn-based chloride (Halotechnics; U. Arizona)	• Lowest melting point • Corrosion control via control of melt redox potential (oxygen exclusion and possibly zero-valent metal addition) • Compatibility with CO_2?	• Measureable vapor pressure disperses $ZnCl_2$ in headspace • Very corrosive if oxygen or water exist • Lowest heat capacity • Zn plating and Cr depletion
Mg-based chloride (SRNL)	• Lowest cost per kg • Corrosion control via control of melt redox potential via zero-valent metal addition • Compatibility with CO_2?	• Highest melting point • Very corrosive if oxygen or water exist • Intergranular corrosion
Ternary carbonate (U. Wisconsin, NREL)	• Highest heat capacity and density leads to smallest required tank volume • Inherently compatible with CO_2 • Substantial carbonate salt experience from use in molten-carbonate fuel cells operating at ~650 °C.	• Highest cost per kg (unless low-lithium blends are proven effective) • High melting point

Materials Concerns

- Chlorides: Water and O2 lead to increased corrosion rates
  - $MgCl_2$/KCl
    - (SRNL): Cleaned salt by step-wise heating using Ar bubbling/Mg contact
    - (UW-Madison): Purification of (HCl/H_2)
    - (SRNL/UW-Madison): Redox control and monitoring is crucial
    - (UW-Madison and SNRL): Marked difference without purification/redox agents.
  - $ZnCl_2$/NaCl/KCl
    - (Halotechnics): $ZnCl_2$ has high vapor pressure and causes practical issues
    - (U Arizona): Low corrosion rates when O_2/H_2O free conditions
  - Chemical compatibility of chloride salts with CO_2(g)?
  - Monitoring sensor required to determine any air intrusion
- Carbonates: Does the cost out weigh the lack of purification?
  - (UW-Madison): Okay in atmospheric air/CO_2 cover gas.
  - May not require any in-plant chemical processing
  - Smaller tank size required
  - Compatible with CO_2

Corrosion Performance

- Chloride Based:
  - In Air: Relatively Poor
    - (U Arizona):Corrosion of C276 is 75x higher in air vs. argon cover at 800°C.
    - (NREL) Alumina-forming alloys are promising if oxygen is present
    - (NREL) Castable cements are diffusion barriers for metallic samples
  - Inert Cover Gas: Relatively Good
    - (SRNL): At 800°C, H230 showed no sign of intergranular attack (12 weeks)
    - (SRNL): Good corrosion resistance: 2.2 µm to 9.5 µm/yr
    - (Halotechnics):In625 & H242 had best corrosion resistance at 700°C
- Carbonate Based
  - (NREL): Ni-based coatings corrode at $<$ 46 µm/yr (700°C)
  - (UW-Madison): SS347 works well to 650 °C.

Material Concerns – Alloys

- Mechanical properties at high temperatures
  - Creep
  - Thermal fatigue
- Code qualification
- Alloys workability for building components
  - Weldability and welds performance under thermal cycling and molten salt exposure
- Thermal cycling effects
- Long-term corrosion and stress corrosion cracking
- Optimum alloy selection for hot-side vs. cold-side components

Component Hardware Concerns

Significant differences from current Solar Salt:

- Different salt chemistry
- Higher Temperatures

- Lead time exists (>1 year)
- Risk associated with design
- Design/Transient conditions
- Test validation needed!

1. Valves and Pumps – materials and design?
2. Piping and Welds – availability and performance?
3. Tank (internal insulation vs. compatible material vs. coatings) – design and vendors?
4. Receiver – design?
5. Salt-to-sCO_2 Heat Exchanger - design, operation, and vendors?
6. Sensors: flow meters, pressures, flux sensors – vendors?
7. Purification subsystem/component – what does this even entail?

Do we understand system conditions well enough for component design?

Receiver Design Experience (Example)

SolarReserve:

- Past experience includes Solar Two and Crescent Dunes
- Superalloys for tubes
  - Provide good thermal stability, oxidation resistance, high temperature strength, and low cycle fatigue (LCF)
- Creep and fatigue require adjustment to manufacturer's LCF data (usually 3 cycles/minute at isothermal conditions)
  - Non-isothermal operating conditions
  - Longer cycle time (once/day)
  - Additional safety factor
- Sandia report (SAND93-0754) provides a methodology for adjusting Low Cycle Fatigue data.

System Concerns

- Are current system models trusted enough for component design?
  - Current systems models do not have complete sCO_2 power block representation, which feeds back to component design
- System models must accurately identify working conditions of components, directly driving storage inventory
- Pilot-scale experience needed
  - “Small” salt loop (e.g., 10,000 kg)
  - Demonstrates how components work together
  - Provides operating experience
  - Test start/stop, drain, and off-design behavior
  - Develop salt handling protocols
  - Test corrosion coupons under more industrial conditions
  - Identify environmental and safety issues

Known Issues:

- Obtain/confirm property measurements at temperature
- Chloride salts: Purification is primary issue. What are subsystem costs here?
  - React with O_2/H_2O: sealed system required; seals become critical
  - Limits of O_2/H_2O
  - Will mitigation additives stay in the melt throughout loop?
- Carbonate salt: Can we allow a higher cost in view of no need of sealed and highly purified cover gas?
  - Are low-Li blends effective
  - Can alloys used at 650°C (in MOFCs) be used at 700°C+?
- Component Designs: Solar Salt system starting point, but new designs required
  - Are alloys available in the necessary forms?
  - Is code qualification required?
  - Long-term reliability in these temperatures/salts unknown
  - Select optimum alloys for hot-side and cold-side components
- System Level
  - Highest efficiency sCO2 engines have narrow input temperature range – can mean substantial storage inventory and cost.
  - Wider temperature ranges result in lower efficiency per Carnot
  - Parasitic loads need to be managed
  - Initial Melting process as a concern.
  - Purge/Blanket inert atmosphere: control and maintain over the life of the plant
  - Hardware maintenance in the future i.e. Changing out a tube
  - Will materials cost (tanks, piping, etc.) allow the system to be economically viable?

Concluding Remarks

- System concept is proven with nitrates; experience from Solar Two, Gemasolar, and Crescent Dunes help mitigate risk
- Detailed Systems Models needed for component design; Helpful for salt selection (cost comparison)
- Materials concerns must be addressed:
  - Select a salt chemistry and alloys
  - Develop industrial handling and processing methods
  - Demonstrate corrosion/salt chemistry monitoring
- Testing needed (pre-plant testing):
  - Mundane components stretch current design envelope, must be tested at scale for bankability
  - Run dynamic (thermal cycle) tests
  - Prove in components and augment design
  - Understand operational concerns
  - Validate controls and sensors

Workshop Objectives

- Identify risks and knowledge gap areas
- Outline and prioritize R&D required to address risks
- Identify possible show stoppers if not addressed (i.e. vendor availability, lead times, etc.)

Scope and Ground Rules

Goal of Session: To identify (less-detailed) what issues need to be addressed to enable a "Solar Three" project.

- Time is limited: let's put down the major needs/issues.
  - Less discussion; more about getting issues written down
  - We will vote at the end of Session 2
- Breadth over depth: Keep the goal in mind – identify issues!
- Capture final thoughts: Name, Idea/Specific Issue
  - Give to Amanda!

CSP Gen 3 Roadmap

Molten Salt Technology

Salts and Materials Compatibility (40 min)

August 18 – 19, 2016

Chair: Judith Vidal, NREL

Co-chair: Alan Kruizenga, SNL

Salt Chemistries

- Chlorides
  - Compatibility with CO_2(g)?
  - Oxygen and moisture level allowed?
  - Mg-chloride system
    - Mg saturation at 550 °C or lower to avoid Mg plating
    - MgO precipitation → clogging?
    - Mg- corrosion mitigation at 550 °C
    - Other active metals evaluations to mitigate corrosion
    - Cost of purification process
  - Zn-chloride system
    - Zn plating and Cr depletion at what temperature?
    - Localized corrosion?
    - Cost of purification process

Salt Chemistries

- Carbonates
  - Compatibility with CO_2(g) → Extend thermal stability
  - Oxygen and moisture level allowed?
  - Cost of ternary eutectic
    - New mixtures low in Li-carbonate with NaOH, KOH to lower melting point
      - Thermal properties, thermal stability and corrosivity.
  - Uniform corrosion? Corrosion rates?
  - Handling, atmosphere?
  - Corrosion mitigation approaches
- Accurate salt properties for tank volume determination → cost of TES including cost of salt and alloy

Materials Compatibility

- Mechanical properties requirements (thermal fatigue, creep, strength)
  - Hot-side (750°C)
    - Tank and piping
    - Receiver (hot spots to 800 °C)
    - Heat Exchanger (750 ° C, 25 MPa – sCO_2 side)
  - Cold-side (550°C)
    - Tank and piping
- Available alloys (code qualified?)
  - Hot-side: H230, IN625
  - Cold-side: SS310, SS347, In800H, HR224, HR120
  - Need heat treatments?
  - Data available for oxidation in air, corrosion resistance
- Workability
  - Weldability and weldments behavior in molten salts

Key Concerns - Summary

- Thermophysical properties at the temperature range
- Oxygen and moisture level
- Cost of salt purification process
- Cost of materials (salts and alloys for volume needed)
- Clogging (salt freezing, corrosion products, plating, etc.)
- Corrosion mechanisms; do we understand them enough?
- Are cost-effective alloys available?
- Workability, welding, piping, etc......
- Does mechanical degradation occur due to chemical interaction?
- What are we missing?

CSP Gen 3 Roadmap

Molten Salt Technology
Pipe/Heat Trace/Insulation/Tank (30 min)

August 18 – 19, 2016

Chair: Judith Vidal, NREL
Co-chair: Alan Kruizenga, SNL

Piping/Heat Trace

- Piping
  - Seamless or welded
  - Code qualification
  - Thickness concerns
  - Joints: welding or flanges/gaskets
  - Flow → corrosion rate under flow conditions
- Heat Trace for freezing control
  - Installation methods due to extreme temperature
  - Material of construction

Tanks/Insulation

- Tanks
  - Alloys for cold and hot sides
  - Welding processes
  - Gas phase vs. liquid phase exposure
  - Cover gas and oxygen/water control
  - If internal insulation/refractory is used, cheep alloys may be able to be used
  - Pressure vessel concerns?
  - Level sensors
- Internal Insulation
  - Refractories
  - Castable cements (not for carbonates due to binders)
- Use of coatings?

CSP Gen 3 Roadmap

Molten Salt Technology

Receivers (20 min)

August 18 – 19, 2016

Chair: Judith Vidal, NREL

Co-chair: Alan Kruizenga, SNL

Receiver Design Experience

- Solar Two and Crescent Dunes serve as design points
- Superalloys and/or ceramics for tubes?
  - Thermal stability, oxidation resistance, high temperature strength, and low cycle fatigue (LCF)
  - Protection needed from falling objects? (i.e. big tools)
  - Is there an advantage to go with ceramics?
- Creep and fatigue lifetime prediction due to LCF
  - Non-isothermal operating conditions
  - Longer cycle time (once/day)
  - Additional safety factor
  - Sandia report (SAND93-0754) provides a methodology for adjusting Low Cycle Fatigue data.
- Uncertainty requirements on molten salt properties for design?

Receiver Needs?

- What experiments/tests are needed to prove out design?
  - Start up / Shut down
  - Recovery
  - Others?
- Is a systems model needed?
  - How robust of a systems model is needed?
- What are the maintenance needs?
- What else are we missing here?

CSP Gen 3 Roadmap

Molten Salt Technology

Pumps, Valves, and Sensors (30 min)

August 18 – 19, 2016

Chair: Judith Vidal, NREL

Co-chair: Alan Kruizenga, SNL

Pumps, Valves

- Pumps and Valves:
  - Is materials selection the biggest issue?
  - Pumps and valves require significant engineering:
    - Design is part, but also how it is tied to system
    - Points to understanding system as a whole
- Pumps:
  - CTE will need to be managed effectively
  - Design will have to account for any bearing materials (if needed)
- Valves:
  - What is the best choice: bellows or packed?
  - Trace heat is critical for bellows
- What facilities are needed to prove in operating and develop lessons learned?
- What are the maintenance issues?
- What else are we missing here?

Sensors

- Flow monitoring:
  - Will ultrasonic meters work at the higher temperatures?
  - Are other technologies of interest?
- Real-time flux monitoring: feedback for flow control
  - Pump speeds/valve operation controlled from energy input
- Pressure measurements:
  - Is this an vendor availability issue vs. a design issue?
- Other sensors we need to develop?
  - Level Indicators, etc.

CSP Gen 3 Roadmap

Molten Salt Technology

Primary Heat Exchanger (15 min)

August 18 – 19, 2016

Chair: Judith Vidal, NREL

Co-chair: Alan Kruizenga, SNL

Technical Concerns

- Harsh conditions for HX molten salt to sCO_2
- Design for high temperature (750 °C) and pressure (250 bars for sCO_2 side and ~25 bars for molten salt side)
- Fabrication?
- Welding
  - Conventional
  - Solid state
- Performance evaluation?
  - Heat transfer

CSP Gen 3 Roadmap

Molten Salt Technology

Systems Level (15 min)

August 18 – 19, 2016

Chair: Judith Vidal, NREL

Co-chair: Alan Kruizenga, SNL

Systems View

- Components cannot be considered without a systems context
  - Model
- System must accommodate off-design operation that may impact design
  - Startup
  - Fault recovery
  - Weather
  - Commissioning
- BOP stuff may fall in cracks
  - Maintenance Procedures
  - Maintenance of purity
  - Repair procedures

Areas of Consideration for R&D

- Systems Model
  - What needs to be known for salt system design?
    - Temperatures, heat loads, flux levels on RX
  - What new features are needed (SAM?)
  - Operational modes (is turbine always full power or off?)
  - What key elements of the salt system must feed back to the systems model (i.e., flux limitations)
- Operational issues
  - What needs development testing?
    - Startup sequences
    - Off-design operation
    - Freeze/thaw operations
    - Initial salt melt and loading
  - What facilities are needed
    - Test loops (MSTL-like?)
    - Need tower for receivers
    - Static/dynamic environments
- Installation and build
  - What unique skills or tools are needed?
  - What new hazards are presented and how mitigated?
  - Repair and replacement processes?

CSP Gen 3 Roadmap

Molten Salt Technology
Prioritization Assessment (30 min)

August 18 – 19, 2016

Chair: Judith Vidal, NREL
Co-chair: Alan Kruizenga, SNL

Process/Logistics

1. Take 5-10 minutes to cast votes
   - See next slide
   - Generate a separate list of show stoppers
2. Count the votes (5 minutes)
3. Extract general theme(s)
4. Closing Discussions
5. End Session 2

Ballot: What are the top three areas of greatest concern?

1. Salt Chemistry/Compatibility
2. Piping/Tanks
3. Heat Trace/Insulation
4. Receivers
5. Pumps/Valves
6. Balance of plant sensors
7. Primary Heat Exchanger
8. System

Priority	Area
1	
2	
3	

From this vote we will use the numbers to provide a semi-quantitative assessment

Show Stoppers (List your top five)	
1	2
3	4
5	

Supporting Slides

Current state MS technology

- Summary of the state of current research
  - MURI
  - SRNL
  - NREL
- Summary of the state of molten salt handling and operation
  - UW – Madison
  - SolarReserve
- Plans for commercialization
- System integration progress

Na-K-Zn chloride salts properties

(a) Melting point (°C)

x_t Salt	$\bar{x}$
# 1	199.3
# 2	198.7
# 3	210.3

(b) Heat of fusion (kJ/kg)

x_t Salt	$\bar{x}$
# 1	67.71
# 2	71.06
# 3	73.89

(c) Heat capacity (kJ/kg K)

x_t Salt	$\bar{x}$
# 1	0.917
# 2	0.913
# 3	0.900

(d) Vapor pressure P(kPa), T(K)

$$P = B_0 + B_1T + B_2T^2 + B_3T^3 + B_4T^4 + B_5T^5 \quad \text{kPa}$$

Coefficients	Salt #1	Salt #2	Salt #3
B_0	-224.9590465714	-74.0696572754	705.6109360679
B_1	1.8021497506	0.8324072573	-3.7301343209
B_2	-0.0054603724639	-0.003648540878	0.006709306701
B_3	8.0546319542E-6	7.7315167538E-6	-3.7954279864E-6
B_4	-5.7740359473E-9	-7.6753149819E-9	-1.2697693384E-9
B_5	1.6379805946E-12	2.8738713547E-12	1.4153293535E-12
Uncertainty @ confidence of 95%	±0.54 (kPa)	±1.1 (kPa)	±0.42 (kPa)

(e) Viscosity (Pa·s), T(K)

$$\mu = A\exp(-T/T_1) + B\exp(-T/T_2) + \mu_0 \quad (\text{Pa}\cdot\text{s})$$

Coefficients	Salt #1	Salt #2	Salt #3
μ_0 (Pa·s)	2.97E-3	4.46E-3	3.41E-3
A (Pa·s)	152.3679	131.0731	0.12055
B (Pa·s)	0.05994	0	497613.0848
T_1 (K)	56.03143	62.36328	204.70939
T_2 (K)	235.78682	-	29.9169
Uncertainty @ confidence of 95%	±1.31E-05 (Pa·s)	±2.04E-05 (Pa·s)	±2.68E-05 (Pa·s)

(f) Density ρ (kg/m^3), T(K)

$$\rho = A_0 + A_1T \quad (\text{kg/m}^3)$$

	Salt #1	Salt #2	Salt #3
A_0	2.5417368449E3	2.5810897805E3	2.8783243363E3
A_1	-0.53018137763	-0.43205969697	-0.92630377059
Uncertainty @ confidence of 95%	±13.507 (kg/m^3)	±6.1726 (kg/m^3)	±20.2500 (kg/m^3)

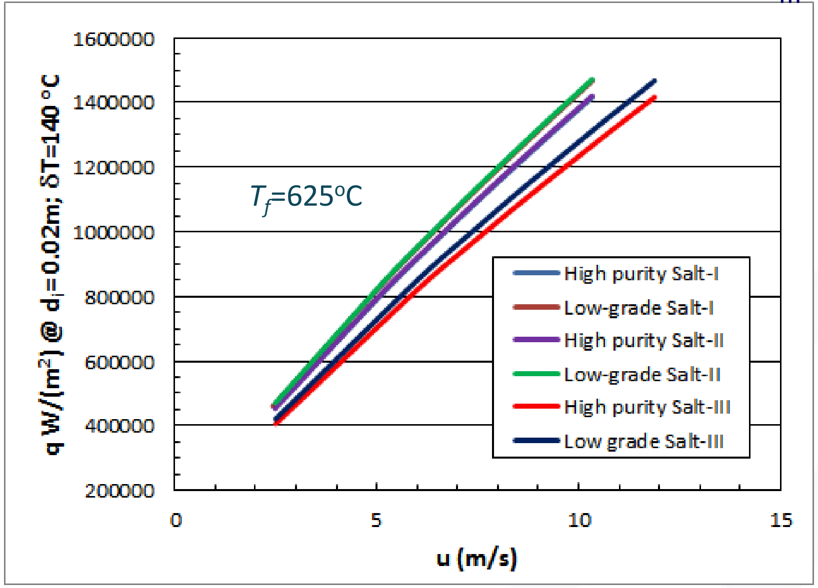
(g) Thermal conductivity k (W/m·K), T(K)

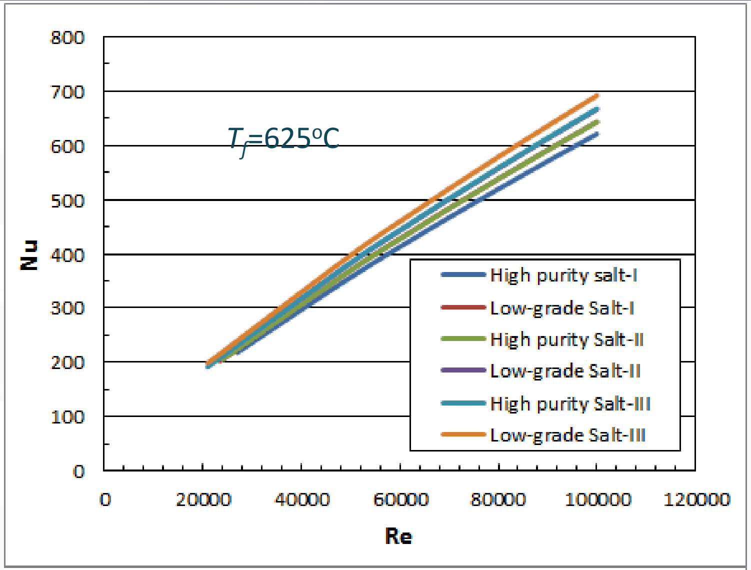
$$k = k_0 + k_1T \quad (\text{W/m}\cdot\text{K})$$

Coefficients in Eq. (4)	Salt #1	Salt #2	Salt #3
k_0	0.43719611446	0.38948756456	0.51447164399
k_1	-1.2300724988E-4	-8.1685567308E-5	-2.3308636401E-4
Uncertainty @ confidence of 95%	±8.892E-3 (W/m·K)	±7.073E-3 (W/m·K)	±9.883E-3 (W/m·K)

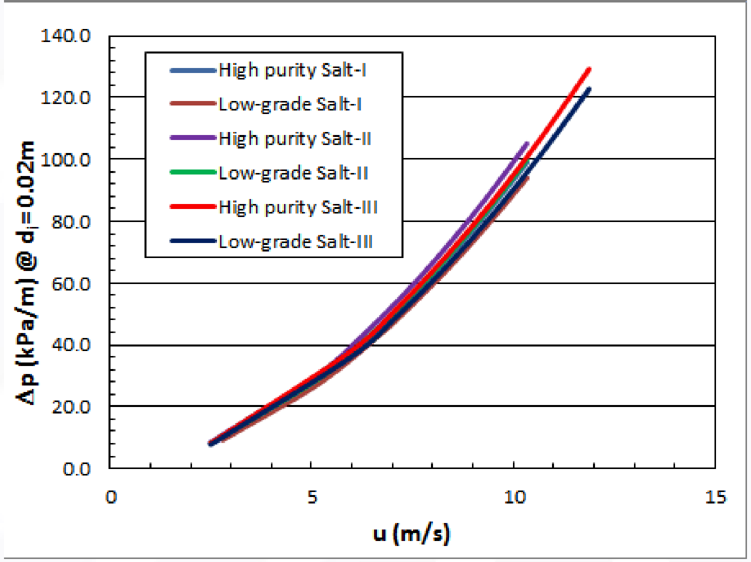
Heat transfer and pressure loss in tubes for tower receiver

800 °C for wall, inlet 500 °C, outlet 750 °C, ΔT_m = 140 °C





	NaCl	KCl	$ZnCl_2$	NaCl	KCl	$ZnCl_2$	Total Price
#1 Molar Fraction	13.08%	41.90%	44.30%	$ / 1kg total molten salt			$ / 1kg total molten salt
#1 Mass Fraction	8.09%	31.33%	60.58%	0.0065	0.1488	0.48464	0.6399295
	NaCl	KCl	$ZnCl_2$				
#2 Molar Fraction	18.60%	21.90%	59.50%				
#2 Mass Fraction	10.04%	15.07%	74.89%	0.008	0.0716	0.59912	0.6787345
	NaCl	KCl	$ZnCl_2$				
#3 Molar Fraction	13.40%	33.70%	52.90%				
#3 Mass Fraction	7.45%	23.91%	68.63%	0.006	0.1136	0.54904	0.6685725
	NaCl	KCl	$ZnCl_2$				
Relative high price ($/kg)	0.115	0.8	1.1	Price searching from			
Relative low price ($/kg)	0.045	0.15	0.5	www.alibaba.com			
Average price ($/kg)	0.08	0.475	0.8				



Corrosion of $ZnCl_2$-NaCl-KCl

Corrosion rates for Hastelloy C 276 in ternary Na K Zn chloride salt

equilibrated with aerobic and anaerobic atmospheres & found by the Electrochemical Stern-Geary Method

Temperature (°C) / Atmosphere	Surface area for WE / CE (cm^2)	Corrosion potential, E_{corr} (V)	Corrosion current density, I_{corr} ($\mu A/cm^2$)	Corrosion rate, (μm/year)
300 ... Air	18 / 27	-0.1	5	50
500 ... Air	18 / 27	0.08	44	430
800 ... Air	18 / 27	0.29	240	2400
300 ... Argon	14 / 25	-0.1	0.80	7.9
500 ... Argon	14 / 25	-0.06	1.9	19
800 ... Argon	14 / 25	0.17	3.2	32

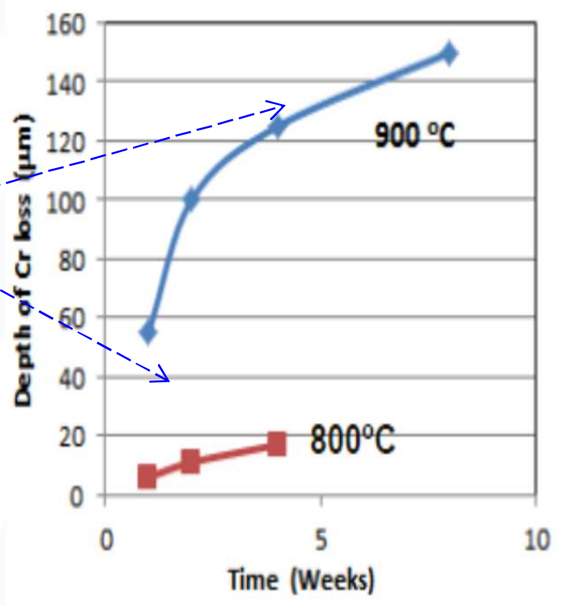
Note: as temperature increases, transport of oxygen, E_{corr} and CR increase.

Corrosion of $ZnCl_2$-NaCl-KCl

Corrosion layer thickness (Cr depletion layer) versus time for three Ni alloys in anerobic Na-K-Zn-Cl_4 salt (m.p. = 204 °C) at 800 and 900 °C

Salt #2	800 °C	900 °C		
	Hastelloy C-276	Hastelloy C-276	Haynes 230	Haynes 556
1 week	6 µm	55 µm	110 µm	115 µm
2 weeks	11 µm	100 µm	140 µm	160 µm
4 weeks	17 µm	125 µm	195 µm	270 µm
8 weeks	NA	150 µm	250 µm	370 µm

EDS cross section shows that rate of depletion of Cr (corrosion layer growth) decreased to a minimum level after a few weeks



THE UNIVERSITY OF ARIZONA

Corrosion of Haynes 230 in $MgCl_2$-KCl/(Mg or Zr)

- System with reasonable cost
- Corrosion mitigation using active metals such as Mg or Zr
- Main issue is keeping salt away from moisture and oxygen
- Salt has been tested with purities indicated to be available at low cost based on internet sources
- Salt purification by step-wise heating with Ar bubbling and Mg contact

Salt Constituents	Melting Point (°C)	Normal Boiling Point (°C)	900°C Vapor Pressure (mmHg)	Viscosity (cP)	Volumetric Heat Capacity (cal/cm^3 °C)	Heat Transfer Ranking at 700°C: Natural Convection: Laminar	Heat Transfer Ranking at 700°C: Natural Convection: Turbulent	Heat Transfer Ranking at 700°C: Turbulent Force: Pumping Factor	Heat Transfer Ranking at 700°C: Turbulent Force: Area Factor	Raw Material Cost ($/kg)	Cost/Volume at 700°C ($/L)
LiF-NaF-KF	454	1570	0.5	2.9	0.91	6.61	13.3	1.13	21.6	7.82	15.79
KCl-$MgCl_2$	426	1418	< 2.0	1.4	0.46	7.74	21.08	5.66	39.7	0.21	0.35
$NaNO_3$-$NaNO_2$-KNO_3	142	Decomp > 538		1.2	0.63					1.65	2.85

[1]: Williams, D., Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop, ORNL/TM-2006/69.
[2]: HITEC Heat Transfer Salt, Coastal Chemical Co., LLC.
[3] Singh, J., Heat Transfer Fluids and Systems for Process and Energy Applications, p. 223-227, 1985

Corrosion of Haynes 230 in $MgCl_2$/KCl/(Mg or Zr)

- *Operational needs:*
  - dry, inert gas blanketing;
  - corrosion monitoring for risk mitigation;
  - tailoring of salt composition to achieve melting point and ensure operation over the entire design temperature range
- *Gaps identified:*
  - definition of operating temperature range and performance constraints to ensure salt can be tailored,
  - optimize corrosion mitigation scheme to make it more robust and fault tolerant (e.g. –buffering),
  - verification of performance using salt from an industrial supplier with the tailored characteristics,
  - testing and mitigation strategy in a molten salt flow loop,
  - quantifying the impact of impurities on corrosion,
- *Practical issues:*
  - Industrial handling and processing (e.g. separation of MgO)

Corrosion in Molten Salts

Selection of molten salts:

- 46.18 wt% K_2CO_3 – 53.82 wt% Na_2CO_3
  (T_m = 709ºC; C_p(l) = 1.7 J/g.K; ΔH_m = 200 J/g)
- 34.42 wt% NaCl – 65.58 w.% LiCl
  (T_m = 554ºC; C_p(l) = 1.4 J/g.K; ΔH_m = 399 J/g)
- 53.82 wt% $ZnCl_2$ – 46.18 wt% KCl
  (T_m = 230ºC; C_p(l) = 0.7 J/g.K)
- 44.53 wt% NaCl – 55.47 wt% KCl
  (T_m = 657ºC; C_p(l) = 1.1 J/g.K; ΔH_m = 417 J/g)
- 33.31 wt% Na_2CO_3 – 34.55 wt% K_2CO_3 – 32.14 wt% Li_2CO_3
  (T_m = 398ºC; C_p(l) = 1.9 J/g.K)
- 35.59 wt% $MgCl_2$ – 64.41 wt% KCl
  (T_m = 423ºC; C_p(l) = 1.2 J/g.K; ΔH_m = 351 J/g)

Corrosion in Molten Salts

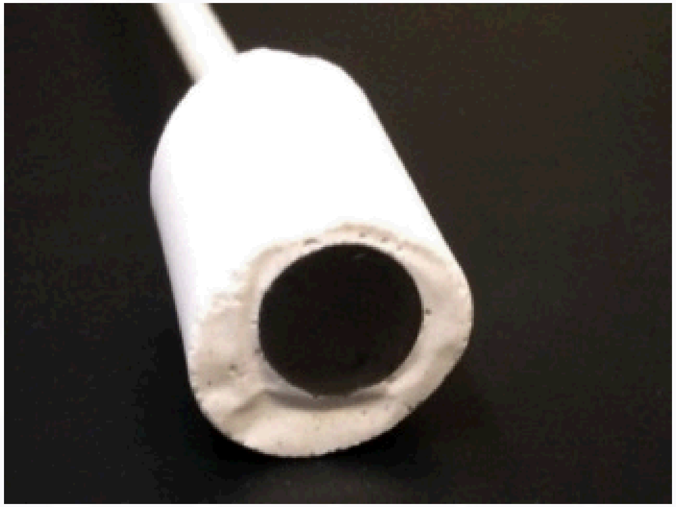
Selection of alloys:

- Stainless steels:
  - AISI 347 (347SS),
  - AISI 310 (310SS),
  - AISI 321 (321SS)
  - Incoloy 800H (In800H),
- Nickel Superalloys:
  - Inconel 625 (IN625)
- Alumina Forming Austenitic:
  - AFA-OC6
- Alumina Forming Alloys:
  - Haynes 224 (HR224),
  - Kanthal APMT (APMT)
  - Inconel 702 (IN702),

Corrosion in Molten Salts

Castable Cements:

- The cements were not chemically stable in molten carbonates
- The most chemically stable cement in molten chlorides was Aremco 645-N with BN (paint or spray).
- BN films did block the porosity of the cement and significantly reduced the salt permeability through the pores.

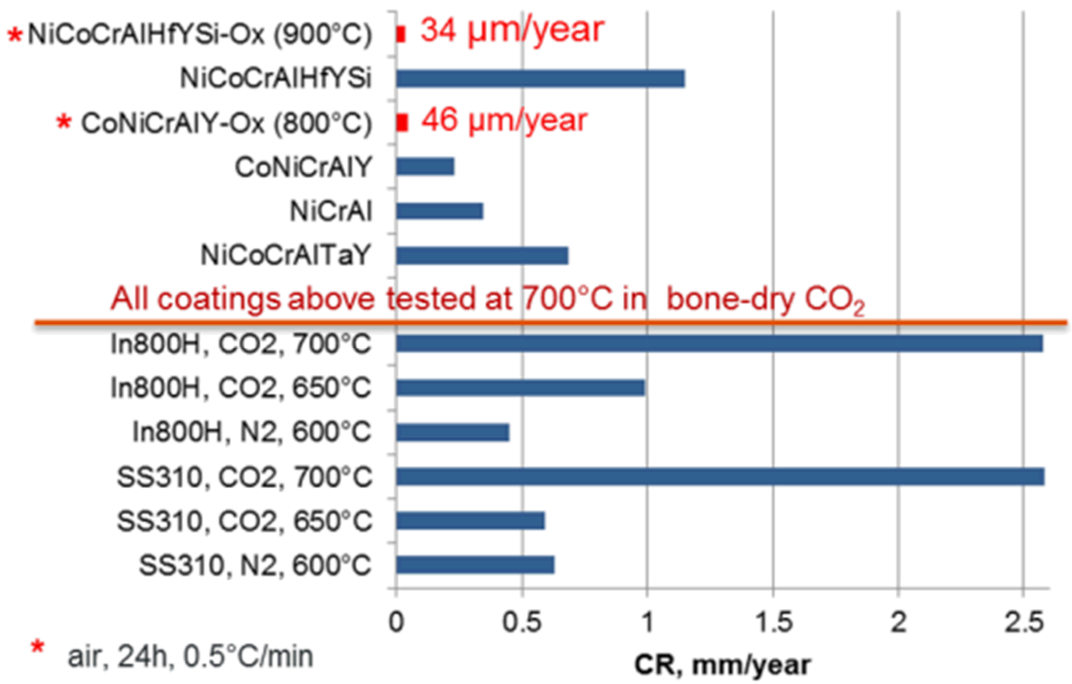


Encapsulated 347SS cylinder

- J.C. Gomez-Vidal and E. Morton, Castable cements to prevent corrosion of metals in molten salts. *Solar Energy Materials & Solar Cells* **153** (2016) 44–51.

Corrosion in Molten Salts - Coatings

Corrosion rates of bare and coated alloys in Na_2CO_3 – 34.55 wt% K_2CO_3 – 32.14 wt% Li_2CO_3 in bone-dry CO_2 and nitrogen atmospheres.

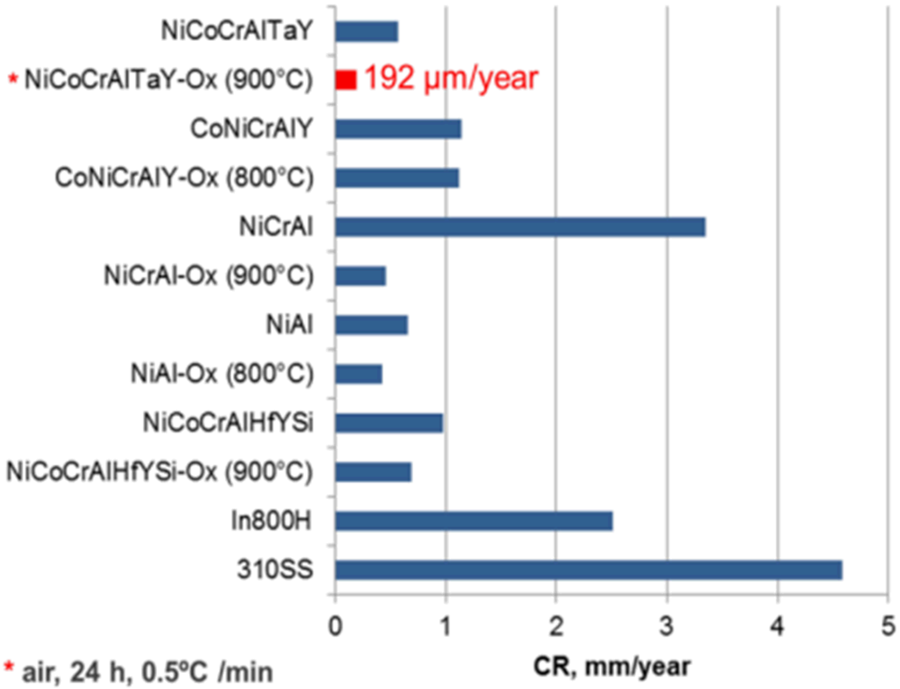


Substrate/ Deposition/Coating	Condition	CR_{alloy}, µm/year
In800H	N_2(g), 600°C	451 ± 156
	bone dry-CO_2(g), 650°C	990 ± 82
	bone dry-CO_2(g), 700°C	2,577 ± 273
310SS	N_2(g), 600°C	632 ± 20
	bone dry-CO_2(g), 650°C	589 ± 29
	bone dry-CO_2(g), 700°C	2,456
310SS / HVOF / A9	bone dry-CO_2(g), 700°C, as-deposited	687 ± 152
	bone dry-CO_2(g), 700°C, Ox: air, 800°C, 24 h, 0.5°C/min	512
310SS / HVOF / A5	bone dry-CO_2(g), 700°C, as-deposited	344 ± 124
310SS / HVOF / D4	bone dry-CO_2(g), 700°C, as-deposited	228 ± 9
	bone dry-CO_2(g), 700°C, Ox: air, 800°C, 24 h, 0.5°C/min	46
In800H/APS/ SPM4	bone dry-CO_2(g), 700°C, as-deposited	1,150 ± 42
	bone dry-CO_2(g), 700°C, Ox: air, 900°C, 24 h, 0.5°C/min	34

J. C. Gomez-Vidal, J. Noel, and J. Weber. Corrosion evaluation of alloys and MCrAlX coatings in molten carbonates for thermal solar applications, *Solar Energy Materials & Solar Cells* **157** (2016) 517–525.

Corrosion in Molten Salts - Coatings

Corrosion rates of bare and coated alloys in NaCl – KCl at 700ºC in N_2(g)

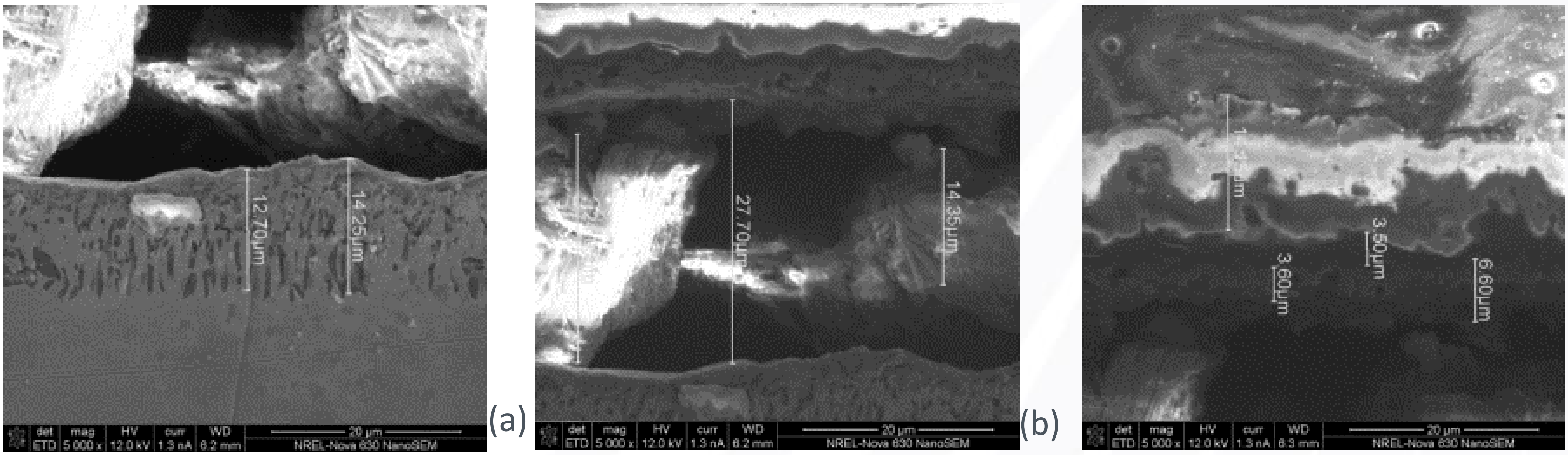


Substrate / Coating	Condition		CR, [µm/year]
310SS	bare, no coating		4,589
310SS / HVOF–A9	As deposited		570
	Ox: air, 900°C, 24 h		192
	Ox: air, 1000°C, 4 h		2,145
310SS / HVOF–D4	As deposited		1,134
	Ox: air, 800°C, 20 h		1,118
310SS / HVOF–A5	As deposited	1st polarization	3,343
		2nd polarization	598
	Ox: air, 800°C, 20 h		698
	Ox: air, 900°C, 24 h		454
310SS / HVOF–D4NS	As deposited		657
	Ox: air, 800°C, 20 h		417
In800H	bare, no coating		2,504
In800H / APS–SPM4	As deposited		978
	Ox: air, 800°C, 24 h		881
	Ox: air, 900°C, 24 h		686

- A 50ºC increase in temperature produced a dramatic increase in the corrosion rate in chloride molten salts —tripling the rate for 310SS and doubling the rate for In800H.

J.C. Gomez, J Noel, and W. Huddleston. Molten chloride corrosion resistance of MCrAlX coatings, submitted to *Solar Energy Materials & Solar Cells.*

Corrosion in Molten Salts – Al-FA



FESEM of In702 (ZA, 1050ºC, 4 h) corroded in molten chloride during 185 h under thermal-cycling condition from 550ºC to 700ºC in static ZA atmosphere: (a) alumina region (~13 µm average); (b) void space ~28 µm with solidified KCl, and (c) above void space MgO (~14.15 µm) and Cr_2O_3 (~4 µm).

- J.C. Gomez-Vidal, A.G. Fernandez, R. Tirawat, C. Turchi, and W. Huddleston. Corrosion resistance of alumina forming alloys against molten chlorides for energy production. I: Pre-oxidation treatment and isothermal corrosion tests, submitted to *Solar Energy Materials & Solar Cells.*
- J.C. Gomez-Vidal, A.G. Fernandez, R. Tirawat, C. Turchi, and W. Huddleston. Corrosion resistance of alumina forming alloys against molten chlorides for energy production. II: Electrochemical impedance spectroscopy under thermal cycling conditions, to be submitted.

R&D in MS technology

***Chlorides:* $MgCl_2$-KCl (426 ºC), $MgCl_2$-NaCl (550 ºC), $ZnCl_2$-NaCl-KCl, etc.**

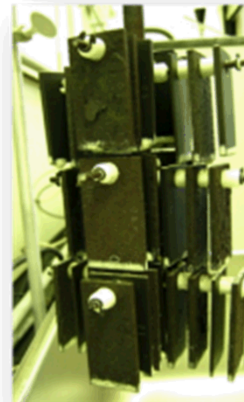
- Chemistry, redox control and monitoring is crucial. Fine tuning is required, excessive redox can lead to attack on graphite and other material.
- No oxygen and water to avoid severe corrosion with Cl_2 off-gas.
- Issues with gas space and the salt vapor leaks exposed to air.
- High nickel content alloys to 750 ºC (if salt chemistry is controlled).
- Purification with HCl/H_2 followed by redox control with Mg.
- Marked difference with and without purification/redox agents.

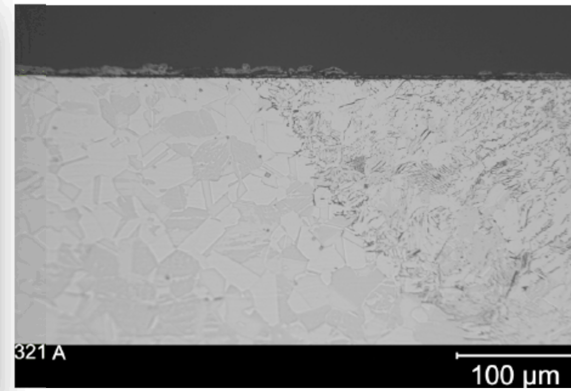
***Carbonates:* Li_2CO_3-Na_2CO_3-K_2CO_3**

- Work well in atmospheric air and CO_2 cover gas.
- Stainless alloys such as 347 to 650 ºC.

Corrosion Testing Apparatus

- Corrosion test of stainless and carbon steels, and nickel-based alloys immersed 3000 h (500 h intervals) up to 700 °C
- Post test analysis:
  - Cross section analysis
  - Weight loss
  - Microscopy imaging
  - Ion analysis of salt





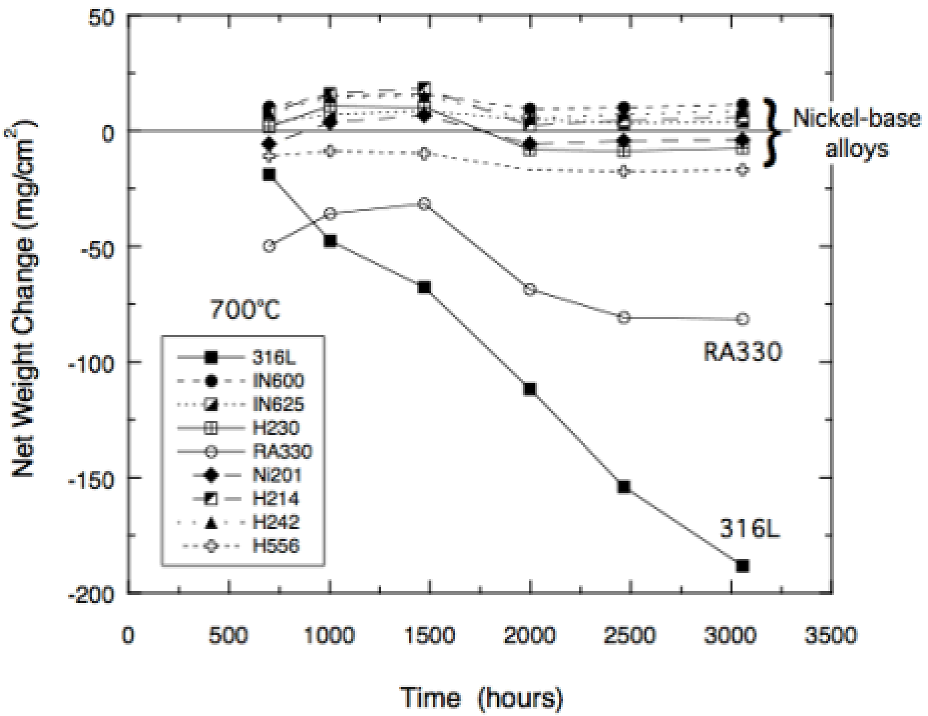
- In625 and H242 demonstrated the best corrosion resistance
- $ZnCl_2$ is too expensive and exhibits high vapor pressure at 700 °C

Results of NaCl-KCl-$ZnCl_2$ testing

Metal losses of alloys in NaCl-KCl-$ZnCl_2$ at 700°C after 3055 h and estimates of annual metal losses.

Alloy	Metal Loss (descaled), mg/cm²	Annual Loss, mils/yr	*T, °C*	*Annual Loss, mils/yr*
Nickel 201	7.3	0.83		
Inconel 600	2.2	0.25		
Inconel 625	2.6	0.30	*600*	*0.66*
Haynes 230	15.0	1.69	*600*	*0.93*
Haynes 214	---	---		
Haynes 242	10.8	1.22		
Haynes 556	36.6	4.13	*600*	*0.81*
RA330	167	18.9	*600*	*0.63*
316L SS	271	30.7	*565*	*0.62*

Work done at Halotechnics by Bob Bradshaw, John Vaugh, and Tom Roark



Net weight changes of alloys tested in NaCl-KCl-$ZnCl_2$ at 700°C.

Recommended salt candidate

- Eutectic mixture with $MgCl_2$ is low cost with m.p. = 385 °C and thermal stability exceeding 750 °C.
- No lithium! ~$0.28/kg or $4.40/kWh for 540 – 750 °C.
- Know-how from the Mg metal industry can be leveraged. Decades of experience with compatible refractories and electrolysis cell designs.

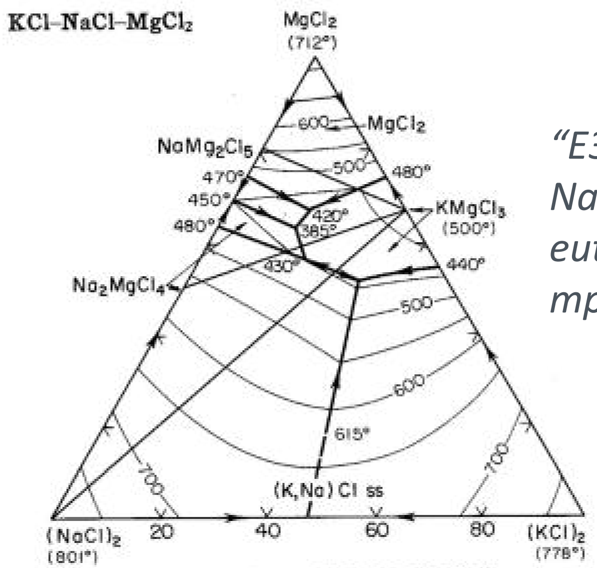
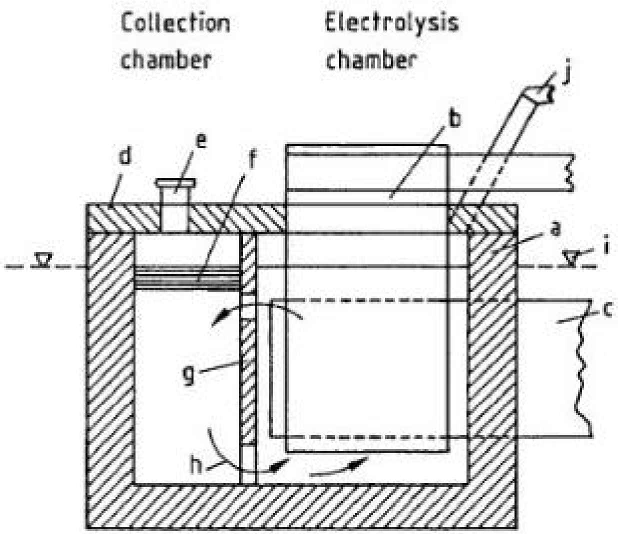


Fig. 3262.—System K_2Cl_2–Na_2Cl_2–$MgCl_2$.
Ernst Jänecke, *Z. Anorg. Allgem. Chem.*, 261, 218 (1950).

"E385"
NaCl-KCl-$MgCl_2$
eutectic 14-18-68 wt%
mp 385 °C



Electrolysis cell for magnesium production at 750 °C

Technical risks must be addressed

- $MgCl_2$ requires inert atmosphere
  - Manufacturing anhydrous $MgCl_2$ is difficult; very hygroscopic and tends to hydrolyze. Best practice is using HCl atmosphere,
  - Transportation, initial melting procedure, and operations at CSP plant must avoid exposure to water.
- Internally insulated tank, lined with compatible refractories
- Piping, valves, and pumps with nickel alloys will be costly
- Complete system costs must be understood holistically, not just salt alone: solar field, tower, TES, power block

Hydrolysis reaction:

$MgCl_2 + H_2O \rightarrow MgOHCl + HCl$

R&D in molten chloride

KCl – 32mol% $MgCl_2$ (m.p. 435 °C) tests in the lab

- Useful operating range 485 to > 900 °C
- Suitable for highly recuperative thermodynamic cycles with cold salt storage temperature (> 500 °C)
- High cold-temp for sCO_2
  - → cheap salts (lower m.p. is less relevant)
- Salt pre-treatment
  - Bubble Ar through salt at 700 °C for 1 h
  - Five cycles of Ar filling to 1 atm and pulling vacuum
  - Small amounts of residual water react with alloy' surface
- Corrosion of H230 at 800 °C (anaerobic) during 12 weeks
  - No sign of intergranular attack (2.2 µm → 9.5 µm /yr)
- Need to scale process to commercial-size

SOLARRESERVE®

Receiver design experience

- Past experience includes Solar Two and Crescent Dunes
- Superalloys for tubes
  - Provide good thermal stability, oxidation resistance, high temperature strength, and low cycle fatigue (LCF)
- Creep and fatigue require adjustment to manufacturer's LCF data (usually 3 cycles/minute at isothermal conditions)
  - Non-isothermal operating conditions
  - Longer cycle time (once/day)
  - Additional safety factor
- Sandia report (SAND93-0754) provides a methodology for adjusting LCF data.

Recommendations for Commercial Scale CSP with TES

- Scaled-up process (with moisture and air elimination) needs to be demonstrated on moderate sized MS system
- Focus on meeting market need at lowest cost
  - Less expensive materials, than H230, need to be screened to confirm low corrosion in anaerobic conditions. Example: widely available are SS347H (cold salt), and In625 (hot salt)
- Focus on obtaining high quality thermo-physical and transport property measurements between 500 to 750 °C
- Focus on means and methods for monitoring and removing moisture and oxygen on a large plant scale
- Could use similar non-nuclear components used with Na (l)
- Current CSP-MS has many similar technology challenges

Recommendations for Commercial Scale CSP with TES

- Rapidly screen corrosion rate of common materials of construction available for molten salt pumps, valves, and instrumentation
- Test commercially available equipment (pumps, valves, and instrumentation) at modest scale (~10,000 gpm) and high temperature (750°C)
  - Establish Center-of-Excellence for testing and maintaining property data and best practices
  - Provide facilities for measuring thermo-physical and transport properties for molten salts
  - Expand component test loops for testing pumps, valves, and instruments (flow, temperature, pressure, level) up to 750°C and incorporate salt corrosion control features

Challenges

- Corrosion
- Cost of materials
- Compatibility with CO_2(g)
- Pre-melting conditions
- Cover gas
- Tests under flow conditions
- Salt or vapor leaks
- Know-how-to design and operate components and instrumentation

Gaps and Concerns

- Problems with high vapor pressure due to clogging
- Salt vapor egress and precipitation on cold spots ("snow")
- Vapor phase exposed surfaces if little oxygen/n present

- Effect of salt impurities and hydrocarbons
- Air and moisture ingress with chlorides
- Purification of chlorides is needed but for carbonates
- Carbonates are easier to handle than chlorides
- Industry standards to mitigate risks and assure SAFETY
- Cost controls to assure ROI

Gaps and Concerns

- Valves and instrumentation with chlorides have shown to be worse in chlorides in particular at higher temperatures
- Trace heat and freezing is an issue with carbonates, similar issues with the high melting point chlorides
- Problems with tubing less than ½ inch diameter --- once clogged very difficult to unfreeze
- Pumps, valves and system monitoring
- Salt freezing and distortion
- High-temperature testing facilities needed
  - Flow loop to test components (valves, pumps, flowmeters, pressure transmitters, piping, flanges), evaluated flow assisted corrosion for hot/cold points, and clogging