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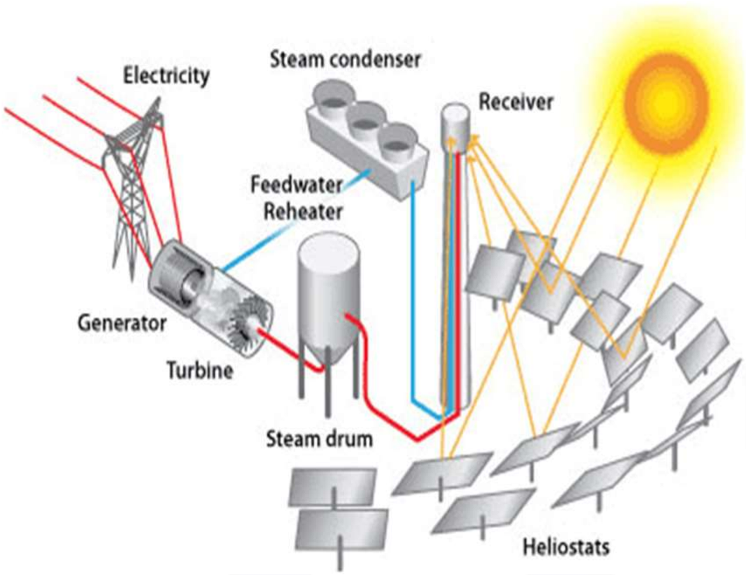

Molten Chloride Thermophysical Properties, Chemical Optimization, and Purification

Gen3 CSP Summit
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Raw Material Quality Can Differ

Major Phase

Three colored phases (white, yellow, and gray from left to right) of AC. Different moisture content and MgO content may have resulted in the color difference. Yellow is the primary phase in AC in terms of quantity.

Composition of Raw AC Measured by ICL and NREL

Salt Batch	Measurement by	Data	KCl	NaCl	$MgCl_2$
			wt%		
Jan–Dec 2018*	ICL	Average	40.6	13.9	45.3
		Stdev	0.69	0.43	0.63
Jan 2019	ICL	Average only	40.8	13.0	46.2
Aug 2019	ICL	Average only	41.4	12.8	45.9
Jan 2019**	NREL	Average	38.6	12.3	49.1
		Stdev	0.97	0.43	0.68

* Based on multiple measurements on a monthly basis

** Based on three measurements

Composition of SPK Halite Measured by Albemarle and NREL

Salt Batch	Measurement by	Data	KCl	NaCl	$CaSO_4 \cdot 2H_2O$
			wt%		
Jan 2019	Albemarle	Average only	5.96	92.5	1.41
Jan 2019	NREL	Average only	8.57	90.7	0.70

1. There are variations of raw materials even produced by the same suppliers.
2. There are variations of measurements even performed by the same entity.

Y. Zhao. 2020. *Molten Chloride Thermophysical Properties, Chemical Optimization, and Purification*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5500-78047. https://www.nrel.gov/docs/fy21osti/78047.pdf

Therefore, Final Salt Can Also Differ

Average Composition and Standard Deviation (Stdev) of Purified AC + Halite Based on ICP-AES Measurements of 10 Samples from 7 Purification Batches

	$MgCl_2$	KCl	NaCl
Composition	**wt.%**		
Average	45.31	38.70	15.99
Stdev	1.40	1.46	1.27
Composition	**mol.%**		
Average	37.51	40.92	21.57
Stdev	1.16	1.54	1.72

Just outside one stdev

Just outside two stdev

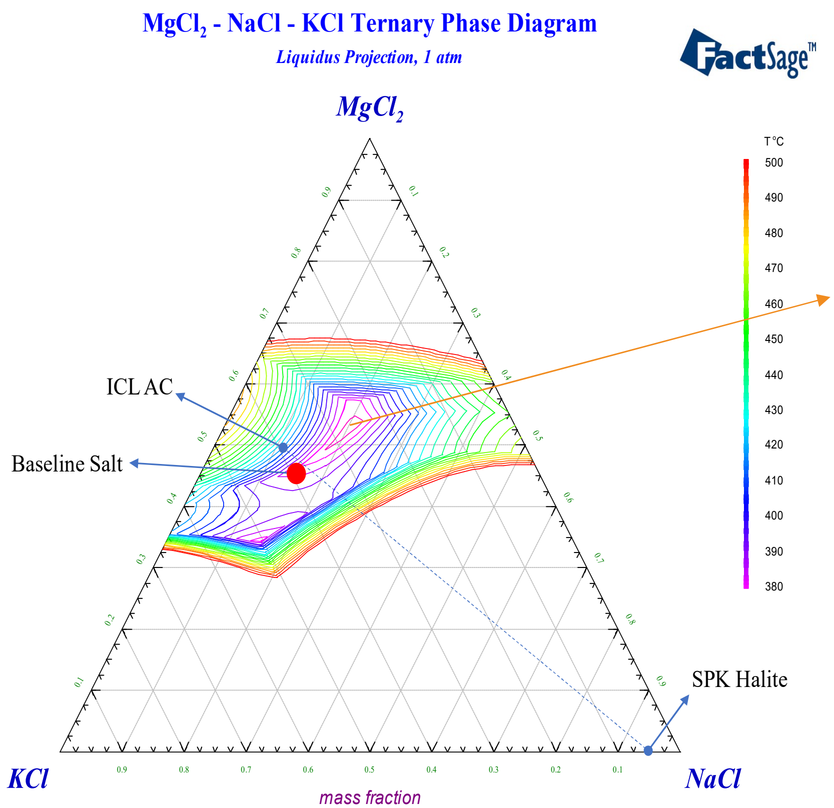
Compositions of UW-Madison's recent large-batch purifications

	$MgCl_2$	KCl	NaCl
Batch 1, wt.%	43.85	37.40	18.75
Batch 2, wt.%	43.44	38.41	18.15

It is not surprising that the final salt compositions also vary slightly. Small composition variation is acceptable because most properties are not expected to be very sensitive to composition.

Y. Zhao. 2020. *Molten Chloride Thermophysical Properties, Chemical Optimization, and Purification*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5500-78047. https://www.nrel.gov/docs/fy21osti/78047.pdf

Salt Purification/Optimization Criterion I: Minimized Melting Point



$NaCl-KCl-MgCl_2$ phase diagram calculated by FactSage showing the compositions of the purified baseline salt, AC, and SPK halite. The colored contours indicate the liquidus temperatures up to 500°C calculated by FactSage. The radius of the red dot corresponds to the highest standard deviation in composition measurement.

This is the true eutectic region. The goal was to be as close to this region as possible given our raw materials' compositions (raw ICL AC and SPK halite).

This leads to NREL's recipe of 6.5 g of SPK halite for each 100 g of ICL AC.

Y. Zhao. 2020. *Molten Chloride Thermophysical Properties, Chemical Optimization, and Purification*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5500-78047. https://www.nrel.gov/docs/fy21osti/78047.pdf

Sensitivity of Melting Point to Composition Variation

Variations of raw materials, measurements and purification procedure are not a major concern. Salt properties are not very sensitive to these variations.

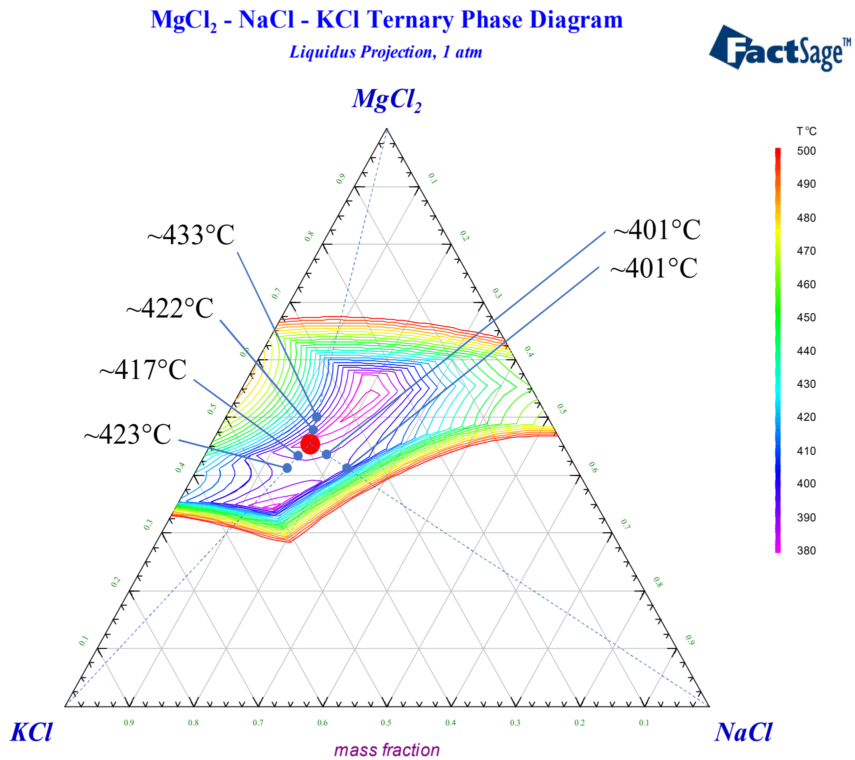
Summary of Phase Transition Temperatures During Heating for Six Salt Compositions

Orange cells indicate solidus temperatures and green cells indicate liquidus temperatures. Empty cells indicate that no clear transitions have been observed.

Added Salt	Added Amount	Transition Temperature During 1st Heating (°C)		Transition Temperature During 2nd Heating (°C)	
$MgCl_2$	5 wt.%	400–410	422.7	400–410	421.5
KCl		400.5		400.4	417.5
NaCl		400.7		400.6	
$MgCl_2$	10 wt.%	400–410	433.1	400–410	433.6
KCl		400.7		400.5	424.3
NaCl		400.7		400.4	

Additional component added on purpose

Resulting liquidus temperatures



NaCl-KCl-$MgCl_2$ phase diagram showing the locations of the baseline salt (red dot) and the six off-baseline compositions (blue dots) with their approximate liquidus temperature based on DSC measurements. The colored contours indicate the liquidus temperatures calculated by FactSage.

Y. Zhao. 2020. *Molten Chloride Thermophysical Properties, Chemical Optimization, and Purification*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5500-78047. https://www.nrel.gov/docs/fy21osti/78047.pdf

Salt Purification/Optimization Criterion II: Minimized MgOHCl

- $MgCl_2$ dehydration and hydrolysis

$$MgCl_2 \cdot 6H_2O = MgCl_2 \cdot 4H_2O + 2H_2O \text{ at } 96°\text{–}117°C$$
$$MgCl_2 \cdot 4H_2O = MgCl_2 \cdot 2H_2O + 2H_2O \text{ at } 107°\text{–}180°C$$
$$MgCl_2 \cdot 2H_2O = MgCl_2 \cdot H_2O + H_2O \text{ at } 153°\text{–}242°C$$
$$MgCl_2 \cdot H_2O = MgCl_2 + H_2O \text{ at } 304°\text{–}400°C$$
$$MgCl_2 \cdot 2H_2O = MgOHCl + HCl(g) + H_2O \text{ at } 193°\text{–}240°C$$

Dehydration

$$MgCl_2 + H_2O = MgOHCl + HCl(g) \text{ at } 210°\text{–}445°C$$

Hydrolysis

Origin of all troubles: Dehydration and hydrolysis compete in the same temperature range

- MgOHCl thermal decomposition

$$MgOHCl = MgO + HCl(g) \text{ at } 500°\text{–}568°C,$$

One mechanism to reduce MgOHCl, <u>but at the expense of producing HCl</u>

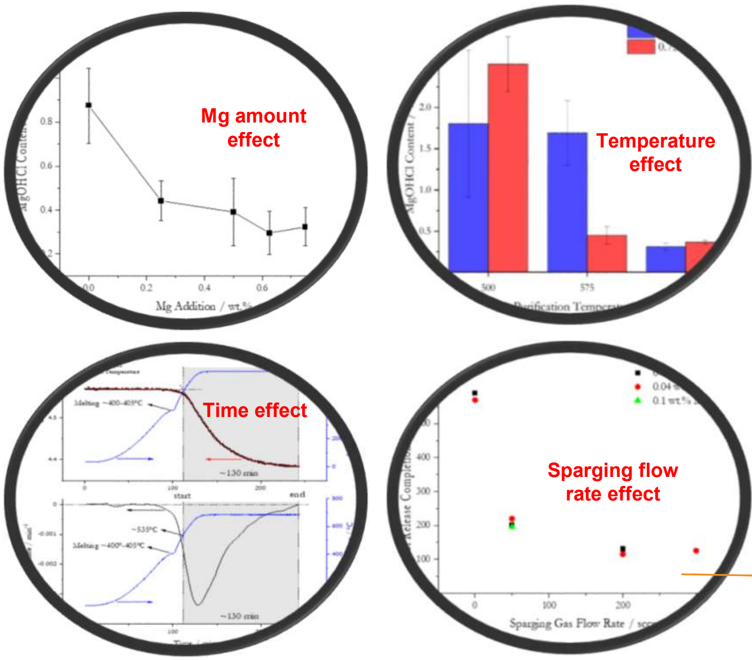
- MgOHCl reduction by Mg

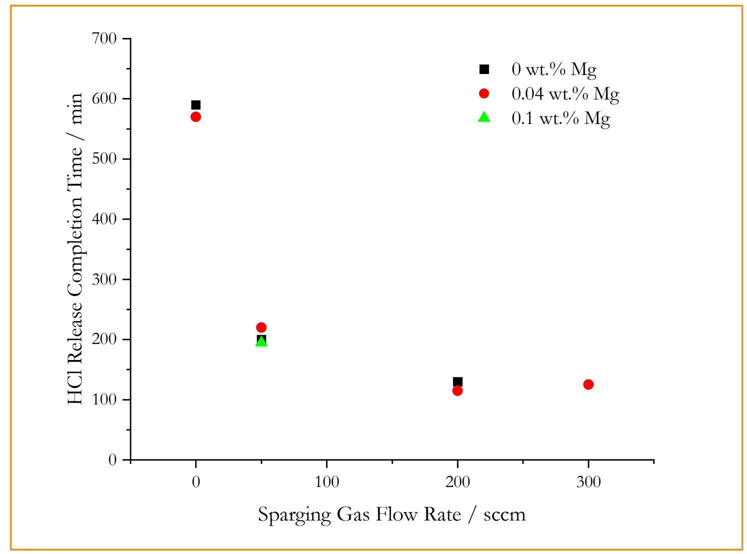
$$2MgOHCl + Mg = 2MgO + MgCl_2 + H_2$$

The other mechanism to reduce MgOHCl, <u>but at the expense of producing H_2</u>

Y. Zhao. 2020. *Molten Chloride Thermophysical Properties, Chemical Optimization, and Purification*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5500-78047. https://www.nrel.gov/docs/fy21osti/78047.pdf

Results in a Laboratory Setting





Variation of HCl release time (or purification time needed) at 670°C as a function of inert gas sparging rate with different levels of Mg addition

Fundamental engineering parameters for purification design:

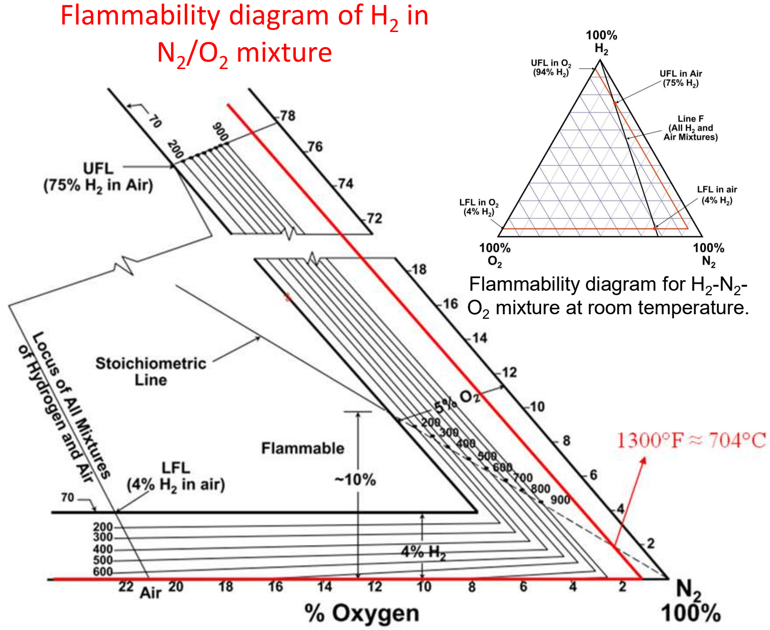
1. Mg amount
2. Purification temperature
3. Sparging gas flow rate
4. Purification time

Y. Zhao and J. Vidal, "Potential Scalability of A Cost-effective Purification Method for MgCl2-Containing Salts for Next-generation Concentrating Solar Power Technologies," Sol. Energy Mater. Sol. Cells, vol. 215, no. June, p. 110663, 2020

Transferring Science to Engineering – Example

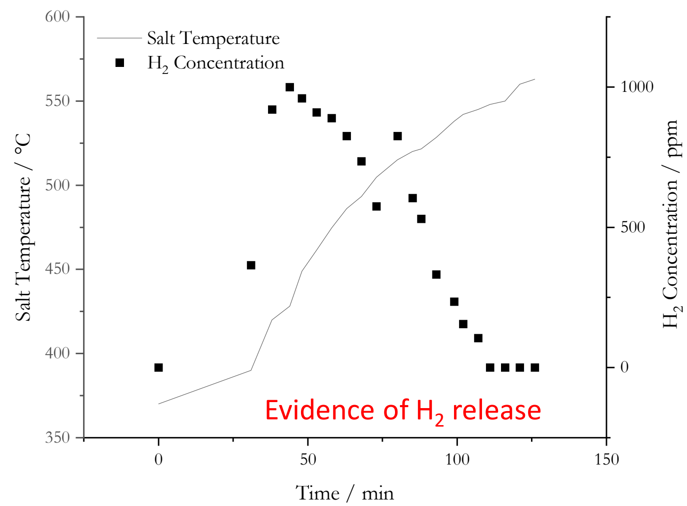
Mg and H_2 concerns
$$\begin{cases} Mg \text{ (or other reactive metals)} + 2HCl = MgCl_2 + H_2 \\ 2MgOHCl + Mg = 2MgO + MgCl_2 + H_2 \end{cases}$$

Flammability diagram of H_2 in N_2/O_2 mixture



Flammability diagram for H_2-N_2-O_2 mixture at room temperature.

Flammability diagram of N_2-rich H_2-N_2-O_2 mixture **at elevated temperatures**. Note that the temperatures in the diagram are in Fahrenheit. The area bounded by the red lines is the flammability region at about 704°C.



Hydrogen gas sensing during salt purification with a 10-g Mg piece added at the beginning. The H_2 concentration data were collected manually.

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Transferring Science to Engineering – Example

- Engineering solution: Salt Melter needs to be designed accordingly to minimize H_2 risk.
- Ideally, separate melter chambers are needed, each with unique function.

Pilot-scale salt melter layout showing the salt transfer line (red) to the hot tank and sparge-gas transfer line (purple) heading to the scrubber (not shown) [1]

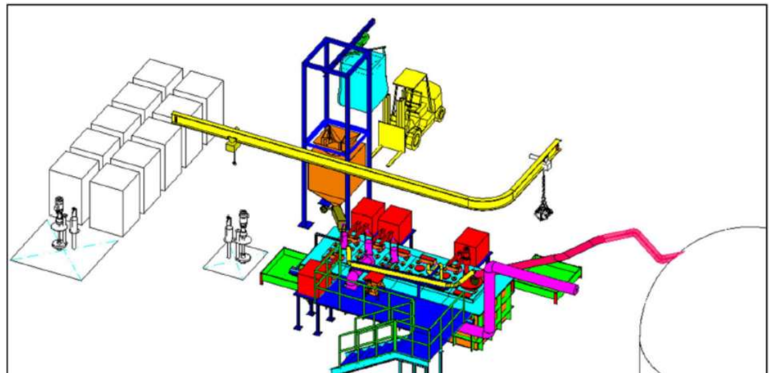


Image courtesy of Hatch

Delivered Salt
- Anhydrous carnallite: 49% $MgCl_2$, 38% KCl, 12% NaCl, < 1.5% H_2O by wt.
- Halite: NaCl

Dehydration and hydrolysis — 117° to 400 °C
$$MgCl_2 \cdot xH_2O \rightarrow MgOHCl + HCl(g)$$
→ Remove moisture and hydrates <u>w/o Mg</u>

Thermal decomposition of MgOHCl — > 550 °C
$$MgOHCl \rightarrow MgO(s) + HCl(g)$$
→ Reduce MgOHCl <u>w/o Mg</u>

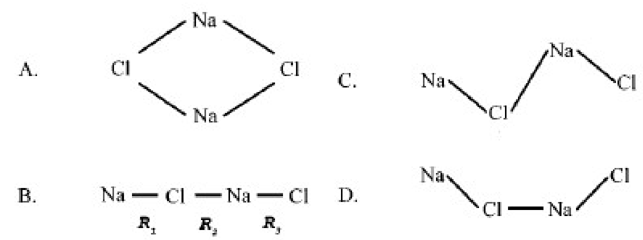
Chemical purification — > 650 °C
$$2\,MgOHCl + Mg \rightarrow 2\,MgO(s) + MgCl_2 + H_2(g)$$
→ Reduce other impurities and more MgOHCl <u>w/ Mg</u>

Settling of MgO and other impurities — MgO, Fe, … ↓
→ Remove particulates, or sludge

[1] C. Turchi, S. Gage, J. Martinek et al. 2021. CSP Gen3: Liquid-Phase Pathway to SunShot. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5700-79323. https://www.nrel.gov/docs/fy21osti/79323.pdf.

Remaining Unknown: Salt Vapor Composition

- Salt vapor pressure measured by University of Arizona [1] is significantly higher than thermodynamic software prediction (> 30x difference).
- Salt vapor can be complicated. For example, vapor above NaCl can be NaCl monomers, Na_2Cl_2 dimers, or even Na_3Cl_3 trimers [2].



Different forms of polymeric Na_xCl_x vapor [2]

We don’t know:
1. Exact phases in the vapor – complex polymeric K-Na-Mg-Cl?
2. Vapor condensation kinetics.

Hence, there are potential issues with:
- Design of TES tank ullage gas system,
- Clogging of TES tank vents and other components,
- Plugging of porous thermal insulation,
- Weight gain of tank ceiling refractory

[1] X. Wang, J. Del Rincon, P. Li, Y. Zhao, and J. Vidal, “Thermophysical Properties Experimentally Tested for NaCl-KCl-MgCl2 Eutectic Molten Salt as a Next-Generation High-Temperature Heat Transfer Fluids in Concentrated Solar Power Systems,” J. Sol. Energy Eng., vol. 143, no. 4, pp. 1–8, 2021, doi: 10.1115/1.4049253.
[2] J. Berkowitz and W. A. Chupka, “Polymeric gaseous molecules in the vaporization of alkali halides,” *J. Chem. Phys.*, vol. 29, no. 3, pp. 653–657, 1958, doi: 10.1063/1.1744555