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GEN3 CSP MATERIALS: CRITICAL REVIEW OF LIMITED EXISTING AND NEW SURVEY DATA

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ABSTRACT

Novel high temperature (≥700°C) Heat Transfer Medias (HTMs, *e.g.*, molten salts) and corrosion-resistant Containment Materials (CMs, *e.g.*, metal alloys or ceramics) are necessary for concentrated solar power (CSP) given the emphasis on higher temperatures and high cycle efficiency in the 3rd generation CSP (Gen3 CSP) technologies. In early 2019, we sent out an online survey to the Gen3 CSP community to fully assess the communal needs for thermophysical properties measurements of which HTMs and CMs, and what temperature range and other testing environments would be ideal for those materials. Based on the recorded responses, seven unique HTMs and twenty-six unique CMs were identified. Since then the list has been constantly updated, following our interactions and inputs from the Gen3 CSP community, with some new materials substituting their older counterparts. Currently, there are total of ten unique HTMs and twenty-nine unique CMs that are under consideration by the Gen3 CSP community. By analyzing the available body of research to date and combining it with our survey data from within the Gen3 CSP community, this paper presents trends of what people in the CSP world are thinking regarding materials worth investigating and suggests which thermophysical property measurements are critical to advance high-temperature CSP systems.

INTRODUCTION

Many of the critical thermophysical properties (*e.g.*, thermal conductivity, thermal diffusivity, and specific heat) for those HTMs and CMs are not readily available at high temperatures with varying compositions and degrees of contaminants and corrosion. We have performed a thorough literature review and have summarized relevant thermophysical properties in Appendix Table A1. As can be readily seen, there exits large gaps in available thermophysical properties. Figure 1 summarizes the number of publications reporting thermophysical properties for a number of potential molten salts. This indicates that there is a clear need for more thermophysical property measurements, and for developing engineering models from these measurements, to enable engineering designs for realizing the Gen3 CSP systems.

This paper will focus on presenting the survey responses for the Gen3 CSP prioritized HTMs and prioritized CMs. Nonetheless, this is followed by brief discussion on our work aimed at measuring the thermophysical properties of these HTMs and CMs at those high temperatures (≥700°C) across a range of conditions with novel immersion electrothermal probe technique and modified photothermal technique, thereby providing research and support analysis for the Gen3 CSP integrated thermal system. Overall, by analyzing the available body of research to date and combining it with our survey data from within the Gen3 CSP community, we would like to leave the reader with trends of what people in the CSP world are thinking regarding materials worth investigating and which thermophysical property measurements are critical to advance high-temperature CSP systems.

GEN3 CSP SURVEY RESULTS

We began by creating a short online survey that will fully assess the needs of the Gen3 CSP awardees regarding materials of interest. This survey requested that awardees prioritize (i)

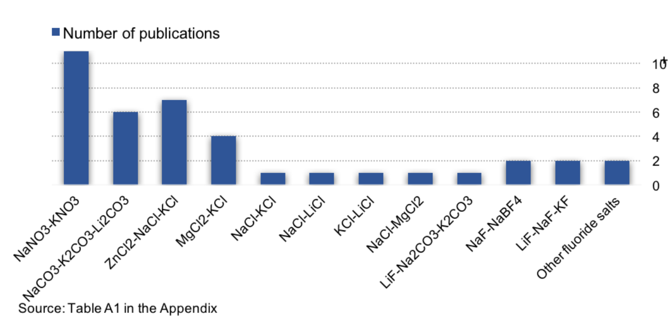

Figure 1: Number of publications on thermophysical properties data of molten salts above 700 °C. Very limited property data exits

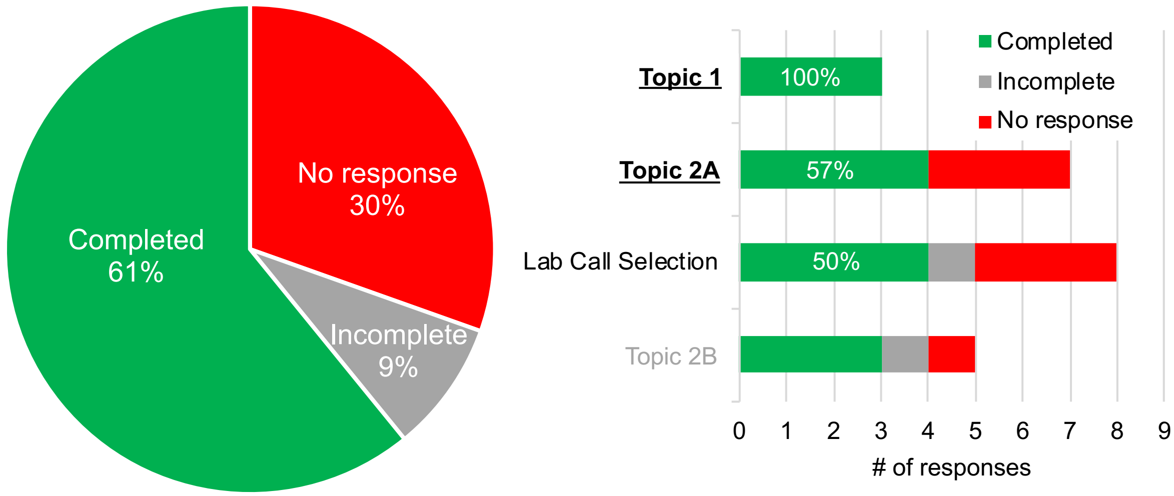

Figure 2: Response rate from twenty-three online surveys that were sent out

which heat transfer medias (HTMs) and containment materials (CMs) they want tested, (ii) what temperature range and other testing environments would be ideal for their specific materials, and (iii) which thermophysical property measurements are critical to advance the high-temperature CSP systems. The survey had gone through an internal review by our team and received final approval by the U.S. Department of Energy (DOE) before sending to the target awardees. The online survey was emailed to twenty-three awardees. Sixteen awardees initiated responses, but only fourteen completed the survey (Fig. 2).

The awardees were first asked to list the heat transfer media (HTMs) that need to be tested in terms of descending priority. Sixteen responses were recorded. And from the sixteen responses, seven unique HTMs can be distinguished. Based on the assigned priority, then the total number of responses a specific HTM received (see Fig. 3), we created a list of prioritized HTMs to be measured in terms of descending priority are (1 = most important HTM for us to analyze):

1. NaCl-MgCl2-KCl molten salt
2. CARBO HSP 40 – 70 mesh
3. Calcined Flint
4. Silica Sand
5. CO2
6. Zn- and Mg- based chloride molten salt
7. Na (100%)

The awardees were also asked to list the containment materials (CMs) that need to be tested in terms of descending priority. More (thirty-three) responses were recorded, and from these responses twenty-six unique CMs can be distinguished.

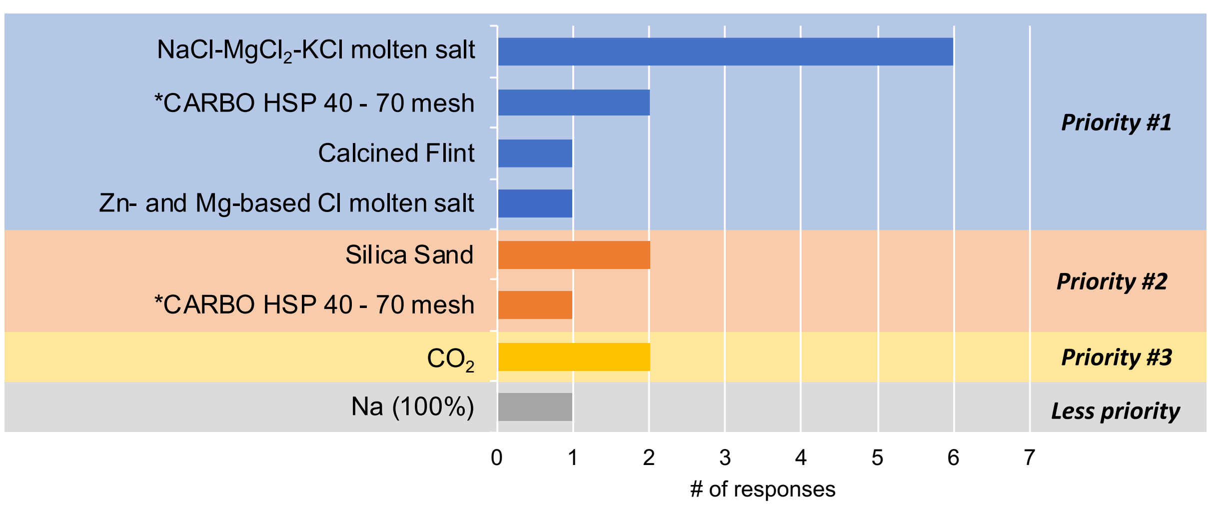

Figure 3: Survey responses for the prioritized heat transfer medias (HTMs). Asterix (*) indicates the same HTM

In the same manner, based on (first) the assigned priority and (secondly) the total number of responses a specific CM received (see Fig. 4), we created the list of prioritized CMs to be measured in terms of descending priority are (1 = most important CM for us to analyze):

1. Inconel 740H
2. Inconel 625
3. High Purity Alumina Refractory SR-99
4. Westmoreland® WAM-BLG
5. Graphite
6. Cermet ZrC/W 0.6/0.4-vol%
7. NiWC3
8. Haynes 230

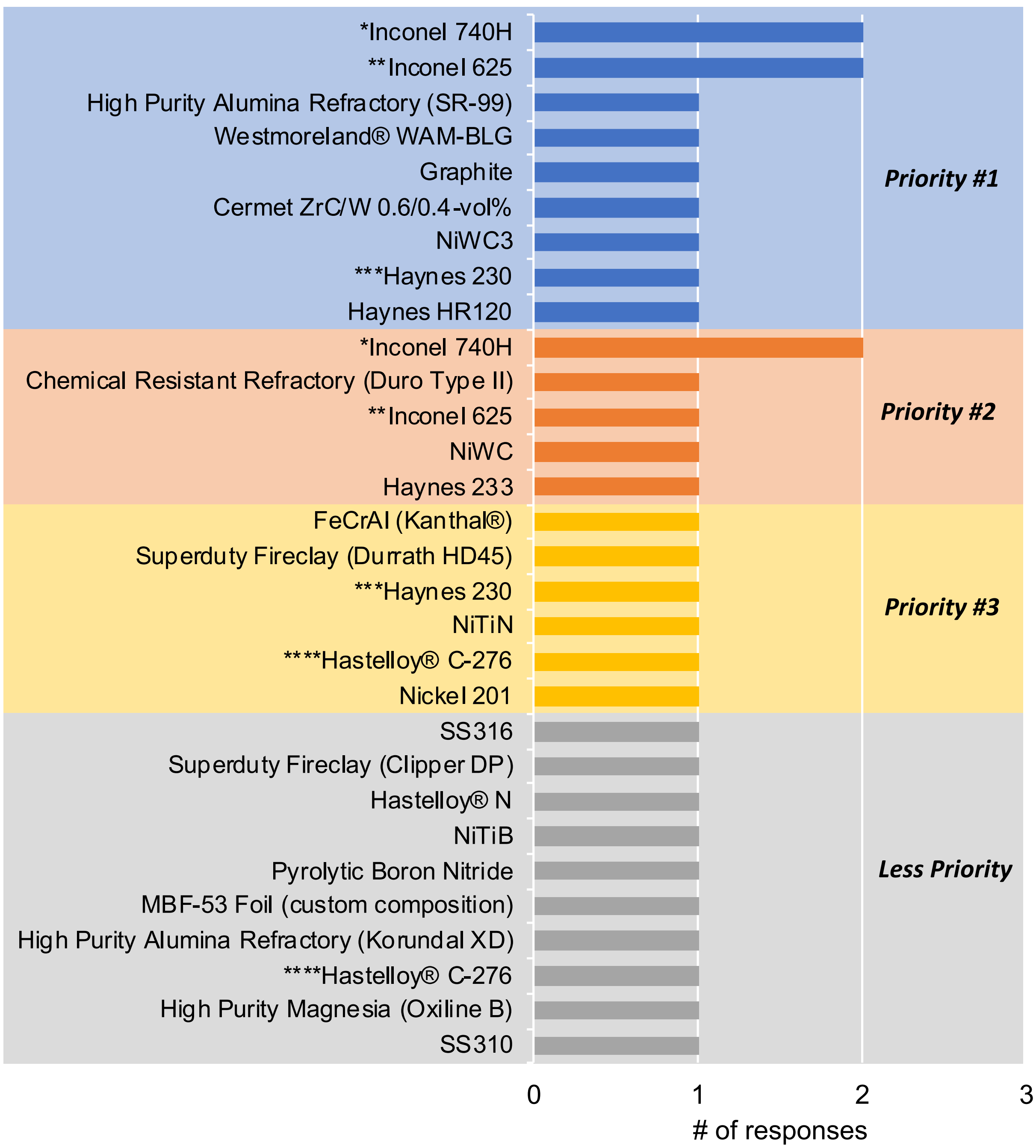

Figure 4: Survey responses for the prioritized containment materials (CMs). Asterixis (*//***/****) indicate the same CMs**

9. Haynes HR120
10. Chemical Resistant Refractory (Duro Type II)
11. NiWC
12. Haynes 233
13. FeCrAl (Kanthal®)
14. Superduty Fireclay (Durrath HD45)
15. NiTiN
16. Hastelloy® C-276
17. Nickel 201
18. SS316
19. Superduty Fireclay (Clipper DP)
20. Hastelloy® N
21. NiTiB
22. Pyrolytic Boron Nitride
23. MBF-53 Foil (custom composition)
24. High Purity Alumina Refractory (Korundal XD)
25. High Purity Magnesia (Oxiline B)
26. SS310

Since then the list has been constantly updated, following our interactions and inputs from all Gen3 CSP community, with some new materials substituting their older counterparts. At the time of writing this paper, there are total of ten unique HTMs and twenty-nine unique CMs that are under consideration by the Gen3 CSP community. We expect that this list will not stop growing in the near future, therefore, we will present the updated list during our presentation at the conference.

IMMERSION ELECTROTHERMAL PROBE AND MODIFIED PHOTOTHERMAL TECHNIQUES

To measure thermophysical properties of HTM (*e.g.*, the molten salts), the most common technique is a transient hot wire approach. In this approach, a current is passed through a wire and the temporal temperature response of the wire is monitored. Using heat transfer models the thermal conductivity of the HTM can be determined. This approach has several limitations and is not the most accurate approach for measuring thermophysical properties. Specifically, this approach is confounded by natural convection and has a reduced degree of accuracy and sensitivity due to having a solid metal core resulting in a high axial effusivity. Our innovative immersion electrothermal approach is an improvement over the transient hotwire technique. The immersion electrothermal probe that we will develop will be used in conjunction with the 3-omega technique to simultaneously measure the thermal conductivity, thermal diffusivity, and heat capacity of the HTM. While the 3-omega technique is conventionally used to measure thermal conductivity of thin-films and bulk solids [1], the modified metal-coated fiber geometry used as heater-thermometers allows us to accurately measure thermal conductivities of liquids, gases, and powders [2].

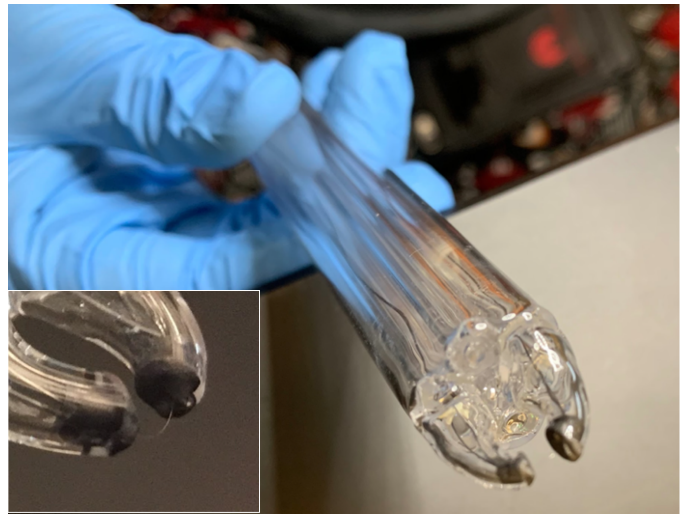

Figure 5: The electrochemical immersion probe. The inset shows Pt-coated single ceramic fiber connected with high-temperature carbon paste on to four tungsten wires, to create four-point electrical connection

The immersion probe, depicted in Fig. 5, will consist of a metal-coated fiber connected in a four-probe configuration. The sensor utilizes an electrically insulating ceramic core of diameter ~50 µm coated with ~100 nm platinum, which serves as the metal heater-thermometer for 3-omega measurements. The core is made from ceramics due to the low thermal conductivity (~1 W/m-K) and ability to withstand high temperatures. The sensor is subsequently coated with a corrosion resistant insulating layer using sputtering in a custom rotary lathe. The fiber is then flexed into a U-shape, and four-point electrical connections are achieved. The probe is designed such that only the fiber is exposed, while the electrical leads are covered in a high temperature corrosion resistant sheath (*i.e.* quartz) which is capable of withstanding temperatures up to 1200°C.

We have solved the radial heat diffusion equation and developed analytical thermal transfer functions for multi-layered metal-coated fiber that can be used to obtain thermal conductivity (k), thermal diffusivity (α), and volumetric heat capacity (C) from the experimental 3-omega data. Thus, fitting the experimental data to theoretical models in select frequency windows will simultaneously yield both the k and C, for which we can then compute the α. In this configuration, the technique is less sensitive to the thermal properties of the metal and outer insulating layer compared to that of the salt. This enables us to choose the metal and the insulating layer based primarily on chemical compatibility with the molten salt environment, and demonstrates the versatility of the proposed technique.

The photothermal technique is a modified Xenon flash diffusivity method suited to measure thermal conductivity, specific heat, and thermal diffusivity of containment materials, which accommodates the high temperature and corrosive chemistry requirements. This specific thermometry method and the most recent experimental results are discussed in another paper, which is also presented and published in this conference proceeding.[3] The flash method can measure wide ranges of thermal conductivity (0.1-4000 W/m-K) and thermal diffusivity (0.01-2000 mm^2/s), with measurement uncertainties smaller than 5%. A custom designed furnace integrated with the sample chamber allows for measurements under high vacuum (~10^{-4} mbar) and temperatures up to 1250°C. The customized sample holders allow us to measure thermophysical properties of liquids, anisotropic solids, thin films/lamellae structures, and materials under mechanical pressure.

The internal pump integrated with the instrument supports defined atmospheres in the sample chamber over the entire temperature range. This allows for in situ monitoring of thermophysical properties in the presence of reactive gases, and water and oxygen contaminants. Furthermore, the containment materials will be exposed to the different molten salt chemistries of interest for extended periods of time, and the effect of aging on thermophysical properties will be quantified. The data analysis software can account for multi-dimensional heat loss from the sample, multilayered structures, porosity, transparency, translucency and roughness of sample. By accounting for these features, errors as big as 15% can be avoided. Furthermore, this broadens the class of materials that can be reliably measured.

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APPENDIX

Table A1. Literature review of thermophysical properties of molten salts above 700 °C. Blue fonts indicated thermophysical properties data of candidate molten-salt heat-transfer fluids that was recommended by U.S. Department of Energy in the CSP Gen3 Demonstration Roadmap (Table 8 in Mehos et al.[4]). Legend: for materials under column "Alloy", H indicates Hastelloy, In Inconel, and SS Stainless-Steel

Type	Salt	Composition By Wt.	Properties											Ref
			T_{melt}	Stability Limit	$T_{reference}$	k	α	c_p	Corrosion (target: **<50 um/yr.**)			Density	Absolute Viscosity	
			(°C)	(°C)	(°C)	(W/m-K)	(mm²/s)	(J/g-K)	@ T (°C)	Rate (um/yr.)	Alloy	(kg/m³)	(mPa-sec)	
Solar Salt (baseline)	$NaNO_3$	0.6			260	0.492	-	1.488				1924.6	4.343	
	KNO_3	0.4			288	0.498	-	1.492				1907	3.558	
					316	0.503	-	1.497				1889.3	2.929	
					343	0.508	-	1.502				1871.6	2.436	
					371	0.514	-	1.507				1854	2.062	
					399	0.519	-	1.512				1836.3	1.786	
			220	-	427	0.524	-	1.516	-	-	-	1818.6	1.589	[5]
					454	0.529	-	1.521				1801	1.454	
					482	0.535	-	1.526				1783.3	1.361	
					510	0.54	-	1.531				1765.6	1.29	
					538	0.545	-	1.535				1748	1.223	
					566	0.55	-	1.540				1730.3	1.142	
					593	0.556	-	1.545				1712.6	1.026	
Carbonate Salt	Na_2CO_3	0.334	398	800-850	-	-	-	1.4-1.5	900	<1000	In600	2000	4.3 (800 °C)	[6]
	K_2CO_3	0.345	-	-	450	0.454	0.136	1.612	-	-	-	2071	TBD	[7]
	Li_2CO_3	0.321	-	-	500	0.458	0.139	1.612	-	-	-	2045	TBD	
			-	-	550	0.470	0.144	1.612	-	-	-	2023	TBD	
			-	-	600	0.492	0.152	1.612	-	-	-	2007	TBD	
			398-417	850	-	-	-	2.205	-	-	-	-	-	[8]
			-	-	-	-	-	-	-	-	-	-	-	[9]

			401	700 (in Ar)	-	-	-	-	-	-	-	-	-	[10]
			405	670 (in Air)	-	-	-	-	-	-	-	-	-	
			405	1000 (in CO_2)	-	-	-	-	-	-	-	-	-	
			-	-	-	-	-	-	-	-	-	-	18.66 (497 °C)	[11]
			-	-	-	-	-	-	-	-	-	-	6.36 (697 °C)	
			-	-	-	-	-	-	-	-	-	-	3.14 (897 °C)	
Chloride Salts	$ZnCl_2$ NaCl KCl	0.685 0.075 0.239	204	-	-	-	-	0.810 (300-600 °C)	-	-	-	2400	-	[6]
		0.529 0.134 0.337		850	300	0.325	- - -	- - -	800 (in the absence of air)	<10 ~25 ~150	HC-276 HC-22 SS304	- - -	4.0 (600-800 °C)	
				-	-	-	-	-	700	-	SS304	-	-	[12]
				-	-	-	-	-	700	-	SS316	-	-	
				-	-	-	-	-	700	-	SS309	-	-	
				-	-	-	-	-	250, 500	10, 40	HC-276	-	-	[13]
				-	-	-	-	-	500	~30	HC-22	-	-	
				-	-	-	-	-	500	>150	H-N	-	-	
			204	-	-	-	-	-	800 (in the absence of air)	-20.46 -7.36	H-230 HC-276	-	-	[14]
				-	250-800	~0.514	-	~0.900 (230-350 °C)	-	-	-	~2878	~3.41	[7, 15]
		0.443 0.138	229	-		~0.437	-	~0.917 (230-350 oC)	-	-	-	~2542	~2.97	

		0.419												
		0.595 0.186 0.219	213	-		~0.389	-	~0.913 (230-350 oC)	-	-	-	~2581	~4.46	
		6 variations	-	-	250-800	0.35-0.6	-	-	-	-	-	-	-	[16]
	$MgCl_2$ KCl	0.375 0.625	426	-	-	-	-	1.150		-		1660	-	[17]
		-	426	-	700	0.400	-	1.159	-	-	-	1660	-	[18]
		0.320 0.680	540	-	-	-	-	-	800 (in the absence of air)	16.14 10.03 -	H-230 HC-276 -	-	-	[14]
		0.434 0.566	424	-	427-832	0.37-0.45	-	0.999	800	- -	H-230 HC-276	1440-1750	< 3	[19]
	NaCl KCl	0.3442 0.5547	657	-	-	-	-	-	700 (in Nitrogen)	2500 690-980 (depend on coating treatments) 4520 190-3340 (depend on coating treatments)	In800H (bare) In800H (coated) SS310 (bare) SS310 (coated)	-	-	[20]
	NaCl	0.3442	-	-	-	-	-	-	650	7490	SS347	-	-	
	LiCl	0.6558	-	-	-	-	-	-	650	6420	SS310	-	-	
			-	-	-	-	-	-	650	5940	In800H	-	-	
			-	-	-	-	-	-	650	2800	In625	-	-	[21]

			- -	- -	- -	- -	- -	- -	700 700	12450 14310	SS310 In800H	- -	- -	
	KCl LiCl		355	-	700	0.420	-	1.197	-	-	-	1520	1.15	[18]
	NaCl $MgCl_2$		445	-	700	0.500	-	1.096	-	-	-	1680	1.36	[18]
Fluoride Salts	LiF Na_2CO_3 K_2CO_3	0.177 0.281 0.542	~400	~900	400	1.170	-	-	465	8-12	SS316L	-	-	[6]
	NaF $NaBF_4$	0.080 0.920	385	850	700	0.500		1.510	-	-	-	1750	-	[18, 22]
	LiF NaF KF	0.465 0.115 0.420	454	850	700	~0.6-1.0	-	1.890	-	-	-	2020	-	
	Other fluoride salts		385-510	-	700	0.28-0.92	-	1.090-1.460	-	-	-	1700-3140	-	