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Corrosion Mechanisms in Chloride and Carbonate Salts

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Abstract

State of the art thermal solar power uses nitrate salts as the heat transfer fluid. In order to increase operating efficiencies high turbine inlet temperatures must be achieved. Different heat transfer fluids must be considered for this purpose. Corrosion mechanisms in chloride and carbonate based salts were reviewed to better understand the practical implications for using either salt in a solar system.

Chloride salts are susceptible to high corrosion rates in the presence of moisture and oxygen. Purification techniques are extremely important to ensure good materials performance, as formation of protective layers does not readily occur. Carbonate salts form protective oxide layers, which inhibit corrosion from the base alloy. Large amounts of work have been done for molten carbonate fuel cells, but different atmospheric conditions and temperature ($>650^{\circ}\text{C}$) will merit investigation for solar applications.

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NOMENCLATURE

S-CO ₂	Supercritical Carbon Dioxide
DOE	Department of Energy
SNL	Sandia National Laboratories
MCFC	Molten Carbonate Fuel Cell
CSP	Concentrated Solar Power
HTF	Heat Transfer Fluid
TES	Thermal Energy Storage
LMFR	Liquid Metal Fuel Reactor

1. INTRODUCTION

Current technology in CSP utilizes molten nitrates as a heat transfer fluid (HTF) and as thermal energy storage (TES) media. One of the most recent industrial scale plants, Gemasolar, which has 15 hours of TES, allowing it to produce power during the night hours [1]. In current plant configurations nitrate salts work well and several decades of experience exist both at Sandia National Laboratories and elsewhere. However, in order to increase plant efficiencies, temperatures of receivers and TES systems must be increased.

It has been well known that nitrate salts approach their limit of stability around 600°C [2]. While this realm of stability depends on many factors (i.e. pressure, temperature, presence of various cations, time at temperature, free surface available for reaction, impurity concentrations, etc.) nitrate salts will likely not be able to push toward the aggressive temperatures needed for economic viability of solar thermal. Temperatures of 700-800°C are being projected to fully utilize Advanced Supercritical Carbon Dioxide (S-CO₂) Brayton Cycles [3].

Many different alternatives for HTFs exist in this temperature regime. One major concern for the high temperature HTFs is materials compatibility. In most situations as temperature is increased the corrosive behavior of the fluid increases in an Arrhenius fashion. Mechanisms of corrosion must be well understood in order to discern and strategically focus precious time and resources available for research.

Two salt families were investigated: carbonate anions (CO₃) and chloride anions (Cl). Salts were chosen primarily due to economic considerations and for the thermal stability in the region of interest, ~700-800°C. This report will detail some of the important corrosion studies that have been done for both chloride and carbonate salts and will also discuss potential methods for purification of the salt. The report will also provide some suggested metal alloys for use in containment vessels, piping, pumps, valves, and tanks.

2. CHLORIDE SALTS

2.1. Influences of Impurities

It is well accepted that impurity levels tend to drive corrosion. One of the first experiments proving this fact investigated commercial electrode thinning (also called penciling), shown in Figure 1, in high temperature sodium-potassium chloride salt [4]. Corrosion rate increased significantly with alkalinity of the melt (oxide concentration) as shown in Figure 2. It was found that at extremely high values of oxide concentration the electrode weight loss significantly decreased due to preferential attack on the containment vessels. Chromate concentrations in the melt were found to be extremely high in these cases, where as much as 70% of the chromium from the containment vessel was dissolved into the melt [4]. As such, purity was found to be critically important for materials performance.

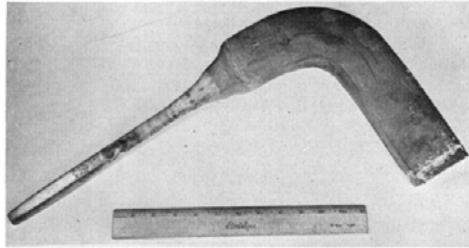


Figure 1: Electrode exhibiting thinning while immersed in high temperature Na, K //Cl [4]

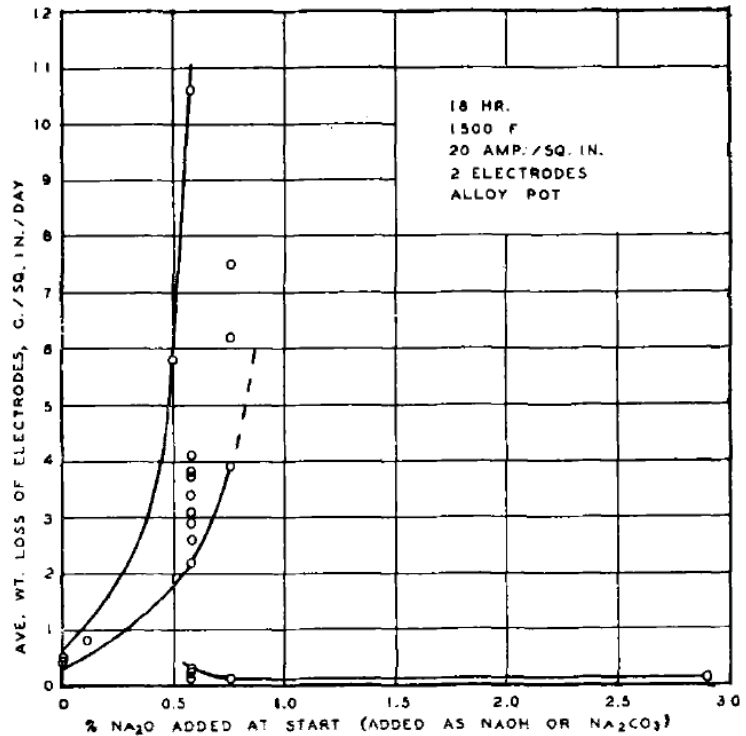


Figure 2: Dissolved oxide content tended to drive corrosion rates. Low values of weight loss corresponded to significant attack of the containment vessels, which tended to protect electrodes [4].

The mechanism for accelerated corrosion by chlorine and chloride was suggested by Grabke *et al.* [5]. They postulate that chlorine initially forms at the corrosion scale surface and, through diffusion, congregates at the corrosion scale oxide-metal interface. Formation of chlorides with alloying components form and continuously evaporate, due to the high vapor pressure of the newly formed chlorides[6]. As the metal chloride diffuses toward the outer scale surface it is oxidized to form a non-protective oxide scale. Chlorine again forms and returns partially to the

oxide-metal interface. Chlorine acts as a catalyst and, thus, accelerates oxidation rates. This process was explained specifically in reference to iron based alloys, where various oxides, such as hematite or magnetite are formed. Formation of a protective, passive layer in iron could not be maintained, even when air oxidation created a visible oxide film on iron prior to immersion in salt [7]. Nickel was not directly tested, although preliminary data indicated only slight passivity at best [7].

The Liquid Metal Fuel Reactor (LMFR) program, which sought to use salts for processing reactor fuel, went to large lengths to ensure high purity levels were achieved in chloride melts [8, 9]. Steps taken included [9]:

- Inert atmospheres of helium or argon that were purified by passage over titanium chips at 850°C
- System leak detection with helium mass spectrometer detector
- Salts were prepared by vacuum melting constituent salts and then outgassing at 500°C
- Purified salts were only handled in a dry box whenever possible.

Static, tilted table, natural convection, and forced convection corrosion tests were performed using a variety of alloys and ceramics (see Table 1). NaCl-KCl-MgCl were used in all corrosion configurations and exhibited relatively low corrosion on many of the alloys, 0-120 microns/year, with the exception being 5 Cr steel, which was estimated to corrode at 450 microns/year. Despite the fourfold rate increase this is widely regarded as good corrosion resistance [10]. No preferential corrosion was observed at welded joints. Alumina performed the best of ceramics with no cracking or spallation (mass change of -0.14% over 1000 hours), while MgO and ZrO₂ cracked and spalled. SiC had the worst performance, crumbling completely during the course of the tests. These data were found to be the most extensive in regards to breadth of alloys investigated during the course of the survey.

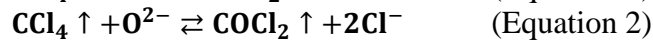
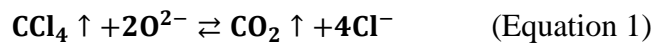
Table 1: Materials tested during LMFR research at Brookhaven National Laboratories [9]

Salts	NaCl-KCl-MgCl ₂ , LiCl-KCl	Most tests were performed at 500°C
Materials Tested		
Alloys		
1020 Mild steel	347 SS	Inor-8 (Hastelloy N)
1 ¼ Cr – ½ Mo steel	410 SS	Hastelloy C
2 ¼ Cr – 1 Mo steel	430 SS	Tantalum
5 Cr steel	16-1 Croloy	Molybdenum
304 stainless steel (SS)	446 SS	Gold
310 SS	Inconel	Stellite 90
316 SS		
Ceramics		
Al ₂ O ₃		
MgO		
ZrO ₂		
SiC (nitride bonded)		

2.2. Purification techniques available

Salt purification is critical for materials corrosion properties. Techniques to purify salts will be discussed in addition to tradeoffs related to thermal energy storage. In literature purification was accomplished by a chlorinating process (CCl_4 , HCl , or some other chlorinating compound) [6, 11, 12] or by reduction of the salt by using active metals such as Mg [13] or saturation of a salt with a liquid metal (i.e. LiCl with Li metal [14-16]) such that redox potential of the melt is lowered. Lethal Concentration (LC_{50}) will be given when applicable, which gives an indication what concentration causes death in 50% of the cases.

CCl_4 (saturated in N_2) (LC_{50} 8000ppm over 4 hours, rat) bubbling in KCl-LiCl at 800°C for 4 hours was thought to achieve very low oxygen content, $\sim 3\text{ppm}$ [6, 11]. The reactions given are:



The oxide content is consumed either as phosgene (COCl_2), which may decay into CO and Cl_2 at the elevated temperatures or carbon dioxide. If phosgene is produced in any appreciable quantity it is an extreme hazard (LC_{50} 800ppm, human) and must be controlled. Additionally, if decomposition into chlorine does occur (LC_{50} 293ppm/hour, rat) materials compatibility issues can be exacerbated [17], where exposure to chlorine gas is found to be significantly more corrosive than liquid chlorides.

Liquid Mg - 30 at.% Cd alloy was used as a reducing agent for a $\text{MgCl}_2\text{-NaCl-KCl}$ salt [18]. Several techniques were outlined depending on the purity level required and amount of salt that needed to be processed. Large tanks of salts were held at 0.03 Torr for 3 to 5 days while heating to 500°C . Once a filtration process had been performed, the salt was contacted with the alloy reducing agent and was well mixed for three weeks [18].

Caution should be used if attempting this technique for several reasons. First, a eutectic is formed around 508°C between Mg and Ni (formation at 11% Mg [at%]) [19]. This could lead to unexpected material behaviors, although authors used 304 stainless (nominal 8-11% Ni) and did not comment on any problems relating to this issue [18]. Second, this method should not be used with salts that have cations of a lower electronegativity than Mg or salts where impurities of Mg cannot be tolerated [18].

Another example of using an active metal to drive reducing condition was utilized by several authors [14, 16]. Conditions of two tests appeared nearly identical with vastly different results ([%wt], 3.5% Li_2O , 1% Li_3N in LiCl then saturated with Li metal, at 725°C for 30 days under an Argon environment). Mishra *et al.* commented that tantalum, the only repeated metal between the studies, had a “dramatic reduction in thickness” and also that “alloys showed no corrosion resistance to the salt medium” [14]. However, Indacochea observed relatively minimal corrosion with little weight loss ($<1.2\%$) [16]. The reason for this discrepancy is not clear, however, no comments were made by either author as to the initial purification of the LiCl , which is crucial for materials performance and must be included and fully characterized in future experiments.

Limitations on using liquid metals as reducing agents were realized by drastic changes in performance with modest changes in cover gas (Ar + 10% O₂)[15, 16].

2.3. Ullage gas effects on system and chemistry

Effects of ullage gas chemistry are, as expected, intimately related to system performance. Introduction of oxygen and moisture have deleterious effects as discussed earlier. Studies will be discussed contrasting additions of oxygen [15, 16], wet and dry O₂ streams [20, 21], and use of chlorine in situ above the salt [17].

Corrosion tests were performed with a LiCl saturated with Li metal for 30 days at 725°C. Straight line extrapolation rates, using Ar as the ullage gas, found maximum rates to be 730 $\mu\text{m}/\text{year}$ (Table 2). However, modifying the ullage to 10% O₂/Ar mixture resulted in corrosion as shown in Figure 3 [16]. Literally no analysis could be performed due to the excessive corrosion. Similar tests were performed later at 650°C for six days. 316L with O₂ mixture lost 75 times more mass than earlier studies, despite the reductions in temperature and duration. The best alloy in this study (In600) would equate to a linear extrapolation of 1886 $\mu\text{m}/\text{year}$ (characterized as poor performing). It should be noted that use of linear extrapolations to determine yearly wastage from short duration tests are extremely rough estimates, but the author wanted to provide a quantitative estimate of increased corrosion when oxygen is added to the system. These data indicate that an inert, oxygen free atmosphere must be obtained. The second influence of water will be discussed.

Table 2: Weight loss and thickness reduction comparisons for different ullage gases [15, 16].

Alloy	Ar only as cover (725°C, 30 days)		90%Ar-10%O ₂ (650°C, 6 days)	
	Weight Loss [%]	Thickness Reduction [mm]	Weight Loss [%]	Thickness Reduction [%]
316L (welded)	0.18	0.03	13.5	3.3
316L (welded /aluminized)	0.28	0.03	11.5	7.2
In600	-	-	2.2	0.9
In625	-	-	56.4	39
Ta (annealed)	1.2	0.04	-	-



Figure 3: Excessive corrosion after 30 day test at 725°C with Ar-10% O₂ as the ullage gas [16].

Presence of moisture is both an oxygen source and will drive hydrolysis [12] by:



This reaction is also expected to be further confirmed by changes in the current-potential behavior [20] and is shown in Figure 4. The influence of moisture results in a twofold effect: introduction of oxygen for worsening corrosion and evolving HCl, which will act to exacerbate corrosion in the head space. During experiments with chloride salts, an observed continually evolved fuming was observed causing further corrosion of metal near the crucible where tests took place [21]. The partial pressure of water during tests was estimated to be 0.1-1% and half of alloys tested disintegrated after six days of exposure under these conditions (900°C, NaCl-MgCl₂) [21].

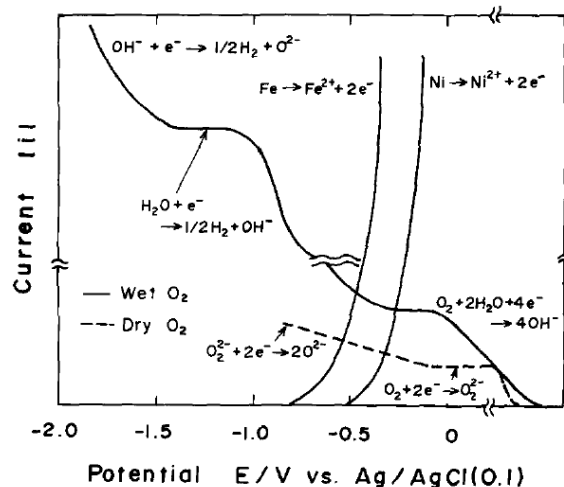
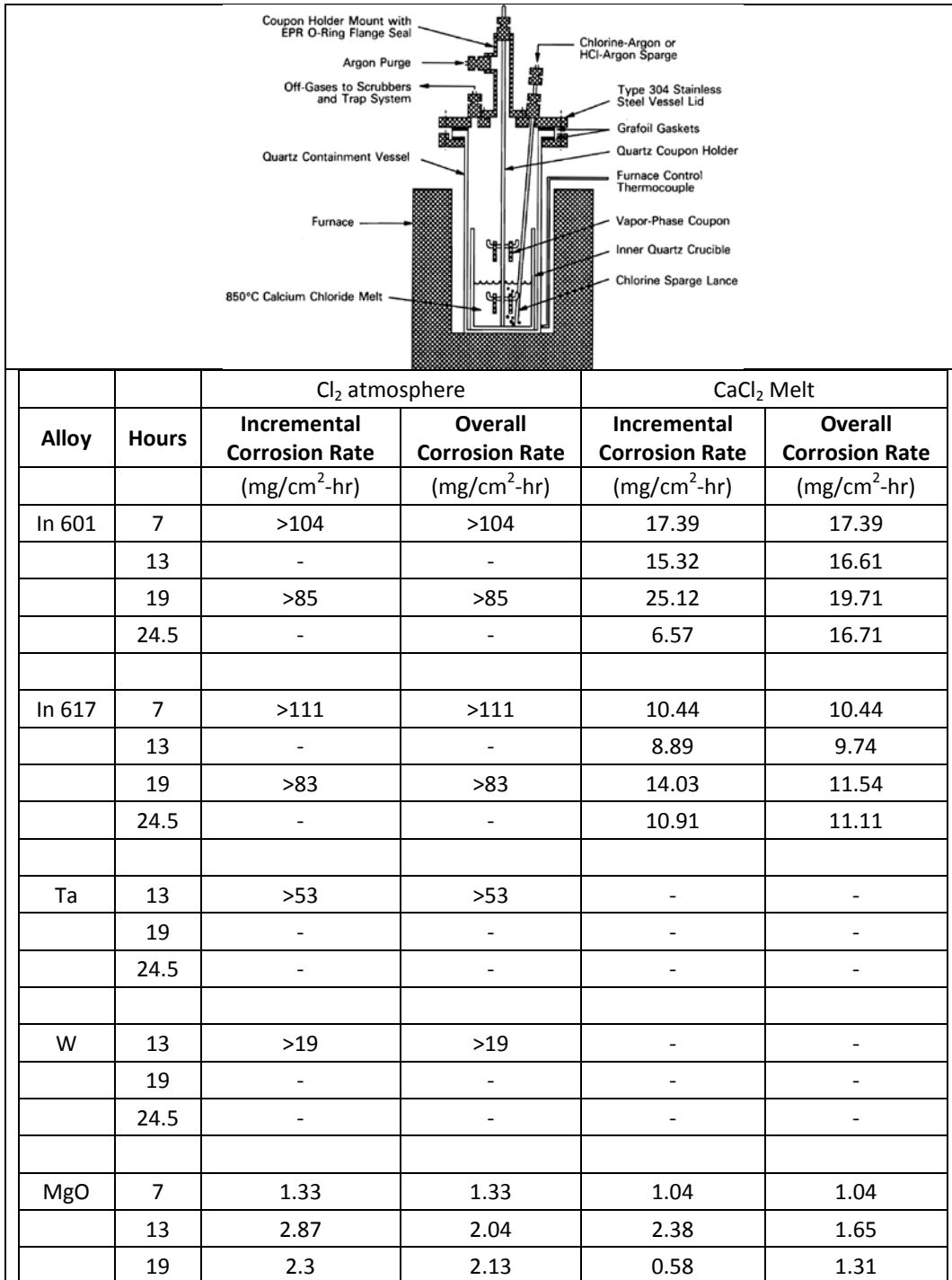


Figure 4: Influence of water on current-potential [20]

Experiments were performed investigating corrosion of alloys and ceramics exposed to a molten chloride with a Cl₂-Ar sparge, which simulated conditions used for a reconversion of CaO to CaCl₂ necessary in a pyrochemical process for plutonium recovery. In general, as shown in Figure 5, Cl₂ was much more aggressive with corrosion rates exceeding 100 mg/cm²-hr for Inconel alloys, while molten salts tended to be an order of magnitude lower (10-20 mg/cm²-hr)[17]. These data indicate use of an *in-situ* chlorinating process to purify liquid salts would need to be done in a ceramic vessel and should not be performed in typical nickel based alloys.



	24.5	2.55	2.25	1.3	1.42
SiN	7	0.05	0.05	0.02	0.02
	13	0.07	0.06	-0.02	0
	19	0.07	0.06	0.04	0.01
	24.5	0.02	0.05	0	0.01

Figure 5: Experimental set up and results from simultaneous molten chloride and chlorine corrosion at 850°C [17]

2.4. Influence of alloying elements

Nickel based alloys were investigated by changing chromium, molybdenum, tungsten and cobalt (for actual compositions see Figure 6) [22]. Cobalt, along with other refractories, tended to increase the resistance to corrosion. This fact can be readily explained by the solubility of chromium into the chloride salt. When no refractory metals or cobalt was used, the Cr content in the salt was 0.1-0.2%. However, alloying 12% refractory metals or 18% cobalt yielded 10-20 times less Cr in the salt. Stable spinel formations of refractories or of cobalt act as a barrier, slowing the diffusion of Cr out of the base alloy and inhibiting diffusion of oxide ions into the alloy, thus nickel alloys with Mo, W, and Co is recommended [22]. Ta, another refractory metal, was found to exhibit passivation in chloride salts [23]. This passivation was due to the formation of a poorly soluble compound of Cr(II) and Ta(V) chloride. It is difficult to ascertain the role Cr plays in the overall performance of the alloy [6], though recent spectroscopic measurements indicate Cr and Mn are prevalent in anodic dissolution [24].

Group 1	Alloy Element Content [%]			Group 2	Alloy Element Content [%]			Group 3	Alloy Element Content [%]		
	Mo	W	Co		Mo	W	Co		Mo	W	Co
Ni+10%Cr	0.5	1	-	Ni+18%Cr	1.5	1.5	-	Ni+25%Cr	4	-	-
	1.5	1.5	-		3	3	-		8	-	-
	4	5	-		4	4	-		10	-	-
	0.5	1	5		4	5	-		12	-	-
	5	5	5		6	6	-		13	-	-
					3	3	4		2	2	-
					3	3	7		4	5	-
					3	3	10		6	6	-
					3	3	13		7	7	-
					3	3	18		3	4	3
				3	3	5	3	4	7		
				5	5	5	3	4	10		
							3	4	14		
							3	4	18		

Figure 6: Alloys investigated in high temperature molten chloride mixtures [22].

Protective layers of alumina, Al_2O_3 , were investigated in a LiCl-NaCl salt. It was found that, despite best efforts, small amounts of moisture reacted to form HCl. HCl was found to quickly react, and oxidize Al, forming hydrogen (detected) and AlCl. All reactions occurred at defects in the alumina film particularly at cracks. While the exact reaction pathways are not fully understood, deposits of alumina formed from the AlCl (or AlCl_3) reacting with water were observed [25].

2.5. Alloys to consider for chloride salts:

Haynes 242

Cr	Mo	Ni	Mn	Si	C	Fe	Co	Al	B	Cu
7 - 9	24 - 26	65	0.8	0.8	0.03	2	2.5	0.5	0.006	0.5

Reasoning: Alloy was designed for resistance to halides in general, due to the low Cr content and elevated Mo content. It is close in composition to Hastelloy N, but is available, while Hastelloy N is currently not available.

Inconel 600

Cr	Ni	Mn	S	Si	C	Fe	Cu
15.5	72	1	0.015	0.5	0.15	8	0.5

Reasoning: Low Cr content may aide in corrosion performance. Outperformed In625 (20-25%Cr) in high temperature tests [15].

HR 224

Cr	Ni	Fe	Al
20	48.7	27.5	3.8

Reasoning: High Al content may help to provide resistance by formation of stable alumina oxide.

HA 214

Cr	Ni	Mn	Si	C	Fe	Al	B	Zr	Y
16	75	0.5	0.2	0.05	3	4.5	0.001	0.1	0.01

Reasoning: High Al content may help to provide resistance by formation of stable alumina oxide. This alloy also has lower Cr and Fe content, which were found to dissolve preferentially more readily than Ni [24].

Haynes 230

Cr	Mo	Ni	Mn	Si	C	Fe	Co	W	Al	B	La
22	2	57	0.5	0.4	0.1	3	5	14	0.3	0.015	0.02

Reasoning: High alloying with refractory materials, in the presence of Ni/Cr alloys, were found to provide better resistance to corrosion [22].

HA 556

Cr	Mo	Ni	Mn	Si	C	N	Fe	Co	W	Al	Ta	La	Zr
22	3	20	1	0.4	0.1	0.2	31	18	2.5	0.2	0.6	0.02	0.02

Reasoning: (5.5%Mo+W, 18%Co) may indicate better performance [22], despite the high concentration of Fe.

HR-120

Cr	Mo	Ni	Mn	Si	C	N	Fe	Co	W	Al	B	Cb
25	2.5	37	0.7	0.6	0.05	0.2	33	3	2.5	0.1	0.004	0.7

Reasoning: (5.0 % Mo+W, 3% Co) may indicate better performance [22], despite the high concentration of Fe.

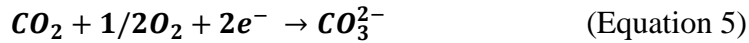
3. CARBONATE SALT

3.1. Carbonate Salt Chemistry

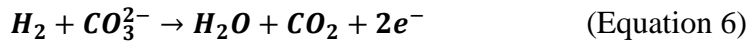
An important parameter in understanding carbonates is the basicity of the melt, which is defined on the basis of the Lux-Flood model (akin to pH in an aqueous system), where an acid is an oxide (O^{2-}) acceptor and where a base is defined as the oxide donor [20]. Therefore, the activity of oxide ions in the melt is extremely important to understanding the fundamental behavior of the melt. The electrode potential, as suggested by [20], can be calculated as:

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{CO_2} P_{O_2}^{1/2}}{a_{CO_3^{2-}}} \right) \quad (\text{Equation 4})$$

Most systems were studied under Molten Carbonate Fuel Cell (MCFC) conditions, where $P_{CO_2} = P_{O_2}^{1/2} = 0.3 \text{ atm}$ and E^0 is calculated to be nearly zero. T is temperature, F is Faraday's constant and R is the gas constant. There have been numerous electrochemical studies performed to gain a thermodynamic understanding of the system [20, 26-28]. MCFC conditions will not be typical of thermal energy storage [TES] conditions for several reasons. First, MCFC require a mixture of oxygen and carbon dioxide for the cathodic electrode in order to sustain the following reaction [29]:



Whereas the anode requires hydrogen to sustain [26]:



Thus, the anode will experience a mixture of hydrogen, moisture and carbon dioxide atmospheres. Many of the works reported in this survey were found to be under either a representative anodic or cathodic atmosphere.

Second, the MCFC is set up as an electrochemical cell with a galvanic couple. TES will not intentionally have a driven electrochemical cell where preferential reactions are taking place. The exception of this is if a anodic or cathodic corrosion protection scheme utilized, similar to what is done in many other industries [10]. Despite both of the differences identified insight into typical chemistry processes, influences of alloying, and identifiable impurities will be discussed.

3.2. Ullage gas effects (Atmosphere, Anode gases, cathode gases)

Ullage gas chemistry has been shown to be important for the corrosion of alloys in carbonate salts. Results indicate that under varying conditions the partial pressure of CO_2 and O_2 are important for performance issues. The corrosion processes were identified to be in five major steps: (i) gas oxidant (O_2/CO_2) dissolved into carbonate melt, (ii) oxidant transport in the melt, (iii) corrosion reactions at salt/alloy surface, (iv) chemical dissolution of oxide scale, (v)

preferential dissolution of soluble products [30]. Ullage gas diffusion into the melt is said to be the first step in major corrosion process for the carbonate system. Confirmation of this has been shown in many data.

Thermogravimetric (TGA) data indicated that corrosion of pure iron was primarily determined by O_2 content and CO_2 had little influence on this behavior [31]. Similar gravimetric studies were performed for using Ni with Cr additions [32]. Conclusions indicated that O_2 was the main driver in oxidation processes. It was also observed that insufficient O_2 in the ullage impaired the growth of a protective oxide layer, which exacerbated corrosion (See Figure 7). Similar TGA experiments confirm behaviors are observed for 316L (i.e. alloys of Fe, Ni, and Cr). Corrosion was found to be more severe at $550^\circ C$ vs. $650^\circ C$, which indicates a change in passivation layer due to thermodynamics [33]. Below $580^\circ C$ the formation of a porous $LiFe_5O_8$ was present, while at higher temperature $LiFeO_2$ was formed and acts as a protective barrier [34].

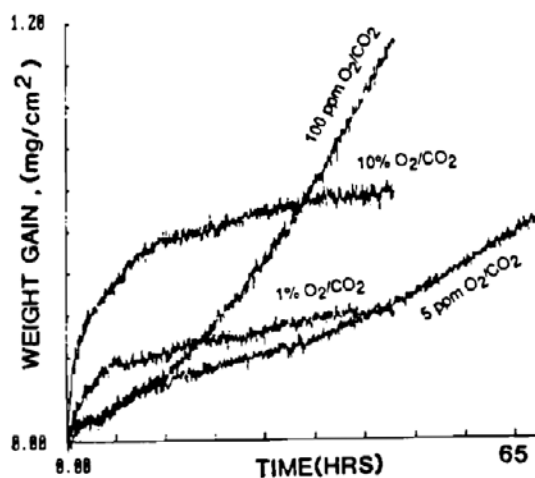


Figure 7: Weight gain curve from [32] at $650^\circ C$ with a Li_2CO_3/K_2CO_3 salt. Partial pressure of CO_2 fixed at 1atm.

Numerous electrochemical studies were utilized to discuss and identify relevant redox mechanisms that would be present in the melt under given atmospheres [20, 26-28, 34-37]. Cyclic voltammetry studies were used to discern possible mechanisms that may be of interest in nickel [26] and chromium [27]. Studies provided information on potentials needed for passivation conditions and, also, suggested reaction pathways that may be important in such systems. The reader is referred to references for further information. Corrosion estimates using Tafel extrapolation, chronoamperometry and microscopy found that Tafel values were too large when subjected to cathodic conditions and too small when subjected to anodic environments, thus the use of chronoamperometry was recommended [28].

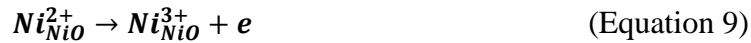
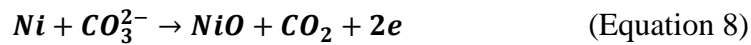
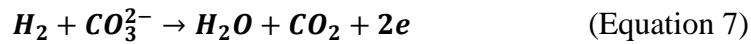
Moisture in the salt was observed to significantly promote Cr dissolution [38]. Unfortunately, the qualitative nature of the absorption measurements did not allow rate determinations. Further literature reviews of moisture in CO_2 environments did indicate that small amounts of moisture, even at the ppm levels [39]. Corrosion tests at $900^\circ C$ for carbonates, chlorides and hydroxide salts qualitatively indicate that moisture is less of an issue of relative importance as compared to chloride salts, however this would need to be investigated further [21].

3.3. Effects of alloying elements

This section will provide a brief summary of alloying elements that have been investigated and their relative effects on corrosion performance. Elements of Ni, Fe, Cr, Mo, Al, Ti, Zr, Mn, La (and other rare earths) will be included in discussions. Specific reaction pathways and thermodynamics will not be addressed in any substantial depth, though readers are referred to various works for further detail [20, 26, 27, 40, 41].

Base alloys of iron and nickel were investigated predominately throughout studies. Iron was found to form FeO, Fe₃O₄ and LiFeO₂ in the presence of anode gases [28, 31] or FeO, LiFe₅O₈, and LiFeO₂ (lithium ferrite is the conversion of Fe₂O₃ [30]) under cathode atmospheres [28]. Further discussion of possible thermodynamic phases of complex Fe/salt cation oxides readers should refer to [31].

Electrochemical data of nickel identified the major redox mechanisms that occur in carbonate salt. In a 64% H₂, 16% CO₂, and 20% H₂O cover gas the following oxidation reactions were identified [26]:



All reduction reactions were also identified, but not given here, as the ullage gas was representative of the MCFC anode. Additions of Cr to Ni were identified to slow the rate of weight gain significantly (see Figure 8)[32]. The formation of a LiCrO₂ (lithium chromite) was determined to be porous and non-protective [27].

Corrosion data 304 stainless steel indicated the formation of similar phases found in earlier studies (FeO, lithium ferrite and chromite, LiFe₅O₈, NiO and Li₂CrO₄) where no indication of a complex Ni/Fe/Cr oxide is formed at 650°C [28]. The probable explanation for increased oxidation resistance in Figure 8 is due to Cr₂O₃ formation, which was found to oxidize to soluble chromate under conditions of high oxygen activity [30]. It is unclear to what extent chromia will act as a protective layer and warrants further investigation. Alloying Mo with Ni decreased corrosion resistance [20].

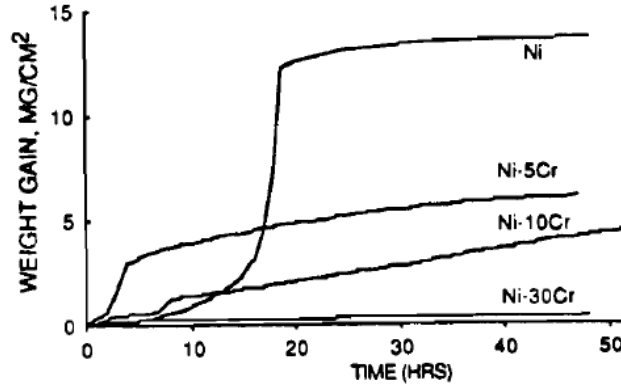


Figure 8: Weight gain for Ni or Ni-Cr alloys at 650°C in a $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ with 1% O_2 -bal CO_2 [32].

Aluminum passivation yielded formation of alumina (Al_2O_3) and lithium aluminate (LiAlO_2) [42]. Potentiostatic sweeps indicate that once the protective layer is formed the film remains intact over a wide range of potentials [42]. High Al content (4.5-5.8%) ferritic steels were found to perform better than 316 through the formation of protective aluminum oxides [43]. Titanium and Zirconium oxidation indicated formation of Li_2TiO_3 , Na_2TiO_3 or K_2TiO_3 , with formation of ZrO observed below 800°C and Li_2ZrO_3 formed at higher temperatures [42]. Stable Zr passivation layers form above electrode potentials of -0.5V. Ti oxide films did not exhibit pronounced active-to-passive transition at 700°C. No details relating to long term stability or to the protective nature could be ascertained from this study.

Manganese formed Li_2MnO_4 and K_2MnO_4 in the presence of carbonate salts [44]. No passivation region was observed; however current did decrease with temperature which may indicate a change in oxide phase or formation.

Rare earth (RE) elements such as Lanthanum (La), Dysprosium (Dy), or Cerium (Ce) have been suggested as additives to form protective pervoskite. Pervoskite is a mineral that can be represented by ABO_3 , where A is typically a RE and B is a transition metal, such as Co or Ni [29]. Additions of La to a NiAl found several interesting results [45].

First, cycle induced corrosion due to mismatches in thermal expansion was reduced. Pegging effects, where formation of a Ni-Al-La phase along the grain boundary, acts to improve adherence during air oxidation. It was found that corrosion resistance in the melt was worsened by additions of La. Figure 9 shows the growth of lanthanum oxide, which perturbs adjacent alumina oxide, thus decreasing corrosion performance.

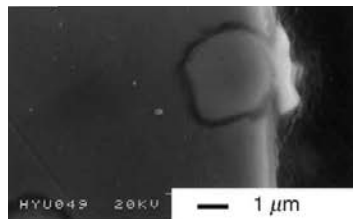


Figure 9: Growth of a La rich oxide disturbs alumina oxide, which decreases corrosion performance [45].

A review on the role of RE materials and corrosion performance on MCFC was done in 2006. It was suggested that alloys with low concentrations of RE materials may reduce dissolution of the metal cations into the melt [46]. Additionally, alloys of Dy and Ni found that weight gain was significantly decreased with additions of Dy over Ni alone. Ce and La were suggested as possible additives for stabilizing salt and for corrosion performance. La_2O_3 was later used as an additive in a carbonate salt and formed a bi-layer oxide, LaFeO_3 on the outer most with LiFeO_2 on the inner layer on 316L [29]. Corrosion protection with this structure was found to be quite good, however further studies involving long term stability need to be addressed.

The investigation of silicon additions in 2-¼ Cr steels in contact with nitrates yielded that high Si content (1-2%) resulted in better oxidation performance and an scales that were more robust in the presence of Cl [47]. Similarities in materials performance were observed between nitrate and carbonate salts and it is of interest to apply advances in nitrate salts for carbonate salt performance.

3.4. Effects of Impurities

It has long been known that chloride impurities in nitrate salts will accelerate corrosion. Limits as to allowable chloride content were determined and reported during the course of the Solar Two project, with acceptable levels at 0.6% by weight [48].

Carbonate corrosion was exacerbated in the presence of chloride anions. Chloride salt (10 wt%) was added to Li, Na, K carbonate. 304SS corroded ~25% faster in the chloride/carbonate solution [49]. Further investigations by developing rates of corrosion versus impurity concentration need to be established.

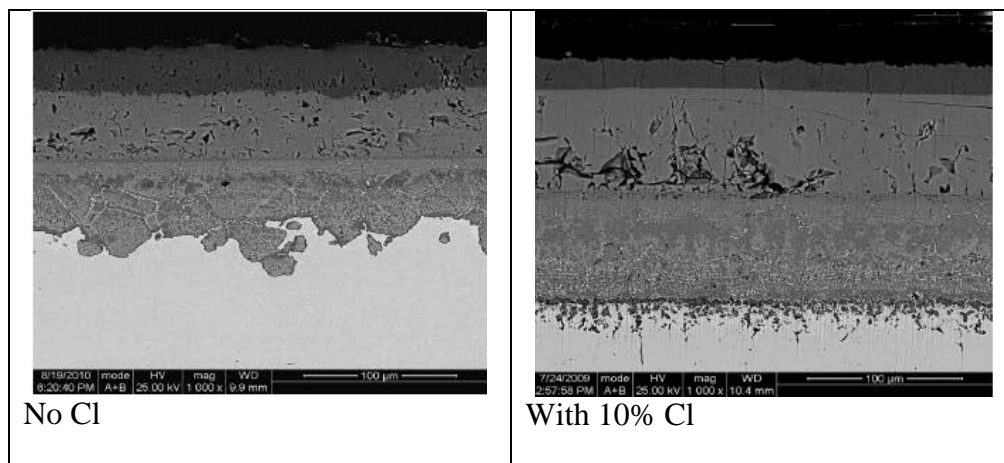


Figure 10: Corrosion structure of alloy 304 with and without chloride salts [49]

3.5. Alloys to consider for carbonate salts:

HA 556

Cr	Mo	Ni	Mn	Si	C	N	Fe	Co	W	Al	Ta	La	Zr
22	3	20	1	0.4	0.1	0.2	31	18	2.5	0.2	0.6	0.02	0.02

Reasoning: Additions of minor alloying elements such as Al, La, and Zr, coupled with large additions of Ni, may provide stable oxidation layers [42].

In 600

Cr	Ni	Mn	S	Si	C	Fe	Cu
15.5	72	1	0.015	0.5	0.15	8	0.5

Reasoning: High nickel content coupled with moderate Cr content.

In625

Cr	Mo	Ni	Mn	P	S	Si	C	Ti	Fe	Co	Al	Cb
20-23	8-10	58	0.5	0.015	0.015	0.5	0.1	0.4	5	1	0.4	3.15-4.15

Reasoning:

Haynes 230

Cr	Mo	Ni	Mn	Si	C	Fe	Co	W	Al	B	La
22	2	57	0.5	0.4	0.1	3	5	14	0.3	0.015	0.02

Reasoning: Minor alloying element La coupled with large additions of Ni, may provide stable oxidation layers [42]. Shown to have superior cycle fatigue performance is also favorable for solar applications.

HA 214

Cr	Ni	Mn	Si	C	Fe	Al	B	Zr	Y
16	75	0.5	0.2	0.05	3	4.5	0.001	0.1	0.01

Reasoning: High nickel content, with high Al and small amounts of Zr [22] and Y [46]

HR 224

Cr	Ni	Fe	Al
20	48.7	27.5	3.8

Reasoning: High Aluminum content [22]

253MA

Cr	Ni	Mn	P	Si	C	N	Fe	Ce
20-22	10-12	0.8	0.04	1.4-2	0.05-.1	0.14-0.2	63-68	0.03-0.08

Reasoning: High Si [47] and trace amounts of Ce [46]

HR-120

Cr	Mo	Ni	Mn	Si	C	N	Fe	Co	W	Al	B	Cb
25	2.5	37	0.7	0.6	0.05	0.2	33	3	2.5	0.1	0.004	0.7

Reasoning: (5.0 % Mo+W, 3% Co) may indicate better performance [22], despite the high concentration of Fe.

4. CONCLUSIONS

Chloride and carbonate based salts have been reviewed for materials compatibility considerations. Both salts exhibit preferential dissolution of active alloying elements, such as chromium.

Chloride salts have not been observed to form stable, passivated oxide layers. Attempts to form stable oxides in salt through additions of nitrate oxidizers and imposing over-potentials were found to be unsuccessful. Short lived protective layers were periodically disrupted so that no protection occurred.

Chlorides suffer from impurities in the form of oxygen and moisture. Ullage gas must be oxygen and moisture free, as oxygen content as low as 10% of the overall cover gas caused excessive corrosion. Furthermore, many purification techniques have been explored in the past, but development of a well characterized process for the handling of salts must be established and thoroughly vetted. Initial purity of salt was found to be a major source of uncertainty in many studies and is thought to be responsible for seemingly conflicting results.

Alloying elements, specifically refractories, are thought to improve corrosion resistance in chlorides by stable spinel layer formation that tend to slow diffusion of Cr from the base alloy to the melt.

Carbonates have been studied extensively under MCFC conditions, where ullage gases are high in CO₂ content. Protective oxide layers required minimum oxygen content to promote surface oxide formation, as ullage gas was dissolved in the carbonate. Investigation of carbonates under atmospheric conditions has been limited and need to be investigated more thoroughly for conditions applicable for CSP.

Impurities in the form of oxygen and moisture are much less of an issue in carbonates; however, the addition of chlorides will cause accelerated materials degradation. Chloride impurities on the order of 10% by weight have been studied. Typical industrial levels would be lower than this, but it will be necessary to determine the maximum allowable level, as was done during initial investigations with nitrate based salts.

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