

A eutectic salt high temperature phase change material: Thermal stability and corrosion of SS316 with respect to thermal cycling

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Abstract

Thermal energy storage (TES) is a critical component in a concentrated solar power (CSP) plant since it is able to provide dispatchability and increase the capacity factor of the plant. Recently the Brayton power cycle using supercritical carbon dioxide (s-CO₂) has attracted considerable attention as it allows a higher thermal to electric power conversion efficiency compared to the conventional Rankine cycle using subcritical steam. However, no commercial TES has yet been developed for integration with a s-CO₂ based plant. One reason is the lack of a suitable storage material. This work explores the use of a eutectic NaCl-Na₂CO₃ salt as a reliable high temperature phase change material (PCM). The PCM has been thermally cycled up to 1000 times. Its thermo-physical properties have been measured before and after it has been subjected to the thermal cycling and its corrosion behavior has been investigated. This eutectic salt shows good thermal stability without degradation after cycling 1000 times between 600 and 650 °C. The corrosion rate on stainless steel 316 (SS316) increases linearly up to 350 cycles, and thereafter it stabilizes at 70 mg/cm².

Key words: phase change material; thermal storage; thermal stability; dynamic gravimetric analysis; corrosion; containment material.

1. Introduction

Concentrated solar power (CSP) technology converts the sunlight to heat by using mirrors or lenses and a receiver, and the heat generated is used to produce electricity or process heat for industrial use. The integration of thermal energy storage (TES) solves the time mismatch between the solar energy supply and electricity/heat demand and also reduces the leveled cost of CSP-generated electricity. Sensible TES in a two-tank molten salt system has been deployed in commercial CSP plants. Latent TES using phase change material (PCM) is believed to be a cost effective alternative as it offers higher energy storage density and isothermal behavior during the phase transformation. It has been extensively investigated

40 over the last few years and is currently experiencing the transition from research to
41 industrial application via pilot-scale demonstration.

42

43 Due to the high temperature requirements for CSP systems, inorganic salts/salt eutectics
44 and metals/metal alloys with melting points over 300 °C are being considered as promising
45 PCM candidates and have been reviewed [1-4]. In order to build efficient and reliable PCM-
46 TES systems, the appropriate PCMs should possess suitable phase change temperature, high
47 latent heat of fusion, good thermal and chemical stability and acceptable corrosion on the
48 containment material at high temperatures and after repeated thermal cycles. It is also
49 critical to experimentally verify the thermo-physical properties of the PCM as calculated
50 values, sometimes used in the literature show significant discrepancy [5, 6]. In addition,
51 limited information exists on the stability and corrosion issues of high temperature PCMs
52 under thermal cycling.

53

54 Corrosion mechanisms in molten salt are complex and highly dependent upon impurities,
55 temperature, alloying elements and oxidant availability. Corrosion in molten salts generally
56 proceeds in five steps: (1) oxidant dissolving into melt, (2) oxidant transport in melt, (3)
57 corrosion reactions at salt/metal surface, (4) oxide scale dissolution into melt, and (5)
58 preferential dissolution of soluble products [7]. The majority of high temperature corrosion
59 tests have focused on steel in the presence of molten nitrate salt and the effect of
60 impurities under isothermal conditions [8-10].

61

62 Sodium nitrate (NaNO_3) has been found to be a suitable PCM for direct steam generation
63 and detailed analysis of fundamental material aspects has been carried out in [11-13]. No
64 degradation was detected after 172 thermal cycles [12]. A 1 MWh pilot-scale TES system
65 combining sensible and latent thermal storage with 14 tons of NaNO_3 was installed and will
66 be tested in Spain under real steam conditions [14]. Possible degradation of nitrate will lead
67 to increasing concentration of nitrite and it will decrease the storage material's melting
68 temperature and latent heat of fusion [15]. BaCO_3 -47.8 Na_2CO_3 (wt. %) has shown good
69 thermal stability after 36 cycles [16]. After evaluating six eutectic salts by thermal cycling up
70 to 100 cycles, Li_2CO_3 -35 K_2CO_3 -33 Na_2CO_3 (wt. %) and MgCl_2 -48 NaCl (wt. %) were identified
71 as promising high temperature PCMs [6]. Al-34%Mg-6%Zn (wt.%) alloy has a good thermal
72 reliability after 1000 thermal cycles and SS304L can be considered as a containment
73 material [17]. An X-750 alloy container was dissolved by molten aluminum under repeated
74 thermal cycles in a vacuum condition [18].

75

76 A eutectic salt composed of NaCl - Na_2CO_3 was explored as a high temperature PCM by Jiang
77 *et al.* [19]. The PCM showed no decomposition under CO_2 atmosphere and little
78 decomposition (0.15% weight loss) under N_2 atmosphere up to 700 °C. Also, it showed good
79 thermal properties and stability after 100 thermal cycles. This preliminary test proved its
80 potential as a PCM. However, the corrosion issues of this PCM have not been investigated.
81 Previous research on corrosion of molten chloride salt showed that lower nobility transition
82 metals such as chromium and iron tend to be more susceptible to corrosion and dissolution

83 than higher nobility metals such as nickel [20]. Passive oxide scale on the surface of a metal
84 in a chloride salt has been found to slow ion dissolution from the metal, and its stability can
85 be improved by the introduction of carbonate ions [21]. However, the formation of passive
86 oxide films is difficult and depends upon specific conditions which may not be easily
87 maintained, causing the oxide to be removed by fluxing [22].

88

89 This paper presents work on the long-term thermal stability of eutectic NaCl-Na₂CO₃ by
90 measuring the thermo-physical properties of the PCM after repeated thermal cycles of
91 heating/cooling up to 1000 times. The corrosion behavior of a common containment
92 material (SS316) in the presence of eutectic NaCl-Na₂CO₃ salt with respect to thermal cycling
93 was also explored. The mass-loss corrosion rate of steel coupons with increasing number of
94 cycles was determined by the dynamic gravimetric analysis. The microstructure of the
95 corrosion product was evaluated by examining the cross sections of the metal coupons.

96 2. Experimental Methods

97 2.1 Sample preparation

98 The sodium chloride (NaCl) and sodium carbonate (Na₂CO₃) were supplied by ACE Chemicals
99 (Australia). They were technical grade with a purity of min. 99.4% and min. 99.2%,
100 respectively. The major impurities in NaCl are magnesium (mix. 0.05 %), calcium (mix. 0.1 %) and sulphate (max. 0.25 %). The major impurities in Na₂CO₃ are NaCl (max. 0.5 %), Fe₂O₃ (max. 0.005 %), CaO (max. 0.007 %) and MgO (max. 0.006 %). The salts were not further purified since the process is complicated and will increase the cost for industrial applications. The single salts were placed in a furnace at 120 °C for 24 hours to exclude moisture. The PCM was prepared by mixing NaCl and Na₂CO₃ in the weight proportion of 40.55 and 59.45 and the mixture was melted at 650 °C in a porcelain crucible and maintained for 2 hours at atmospheric pressure in air. Afterwards, the salt was pulverized to powder using a pestle and mortar and stored in sealed containers.

109

110 Ten SS316 coupons with dimensions of approx. 20mm×10mm×1.5mm were cut from a sheet
111 of stainless steel. The nominal composition of the SS316 is presented in Table 1. The
112 maximum service temperatures of SS316, which is the highest temperature at which it can
113 be used for an extended period without significant problems (e.g. oxidation and decrease of
114 mechanical properties), are 870 °C and 925 °C for intermittent and continuous service in air,
115 respectively [23]. The coupons were progressively polished using SiC abrasive papers of 400,
116 800 and 1200 grit, cleaned with acetone in an ultrasonic bath, further cleaned in deionized
117 water and weighed. All the coupons' weights and dimensions were recorded.

118

119 *Table 1. Nominal elemental composition of stainless steel 316.*

Element	C	Cr	Mo	Ni	Si (max.)	Mn (max.)	P (max.)	S (max.)	Fe
wt. %	0.07	17-18.5	2-2.5	10.5-13.5	1.0	2.0	0.045	0.030	Balance

120

121 **2.2 Thermal cycling test**

122 The PCM samples (each approx. 50 g) were placed into alumina crucibles as this material has
123 shown corrosion resistance to the investigated salt system. The SS coupons were inserted
124 into and fully submerged in PCM samples. Type K omega™ thermocouples with an accuracy
125 of ±0.75%, were used. They were covered with alumina sheaths to protect the
126 thermocouple from the corrosion. The sheathed thermocouples were inserted into one PCM
127 sample to record the sample temperature. Then, all the samples were covered by lids and
128 placed in a furnace. The temperature of the furnace was programed to cycle between
129 600 °C and 650 °C, including a heating process to 650 °C with a heating rate of 10 K/min, an
130 isothermal process at 650 °C for 2 hrs, a cooling process to 600 °C with natural cooling of
131 furnace and an isothermal process at 600 °C for 2 hrs. The temperatures inside the PCM
132 sample and the furnace were recorded every 10 seconds by using a data acquisition system.

133

134 One crucible with salt only as the sample was removed from the furnace after 200, 500, 650
135 and 1000 thermal cycles for thermo-physical property characterization, respectively. Two
136 crucibles with salt and SS coupons were removed from the furnace after 50, 100, 150, 350
137 and 500 cycles, respectively. One coupon was prepared for dynamic gravimetric analysis to
138 determine the corrosion rate and the other for microstructural analysis. The SS coupons
139 were preliminarily cleaned by washing off the salt using warm water and followed by
140 deionized water.

141

142 **2.3 PCM characterization (differential scanning calorimetry)**

143 A high temperature differential scanning calorimeter (DSC 404 F1 Pegasus®, Netzsch) was
144 used to measure the phase change temperature and phase change enthalpy of the fresh
145 and cycled PCM samples. The samples were pulverized to powder after removal from the
146 furnace and dried in a furnace at 120 °C for 2 hours before the measurement. Six specimens
147 (15±1 mg each) were taken from each sample and the average values were obtained. The
148 eutectic NaCl-Na₂CO₃ was shown to decompose at temperatures beyond 638 °C under air
149 atmosphere [24]. Therefore, the specimen was obtained from at least 10 mm below the top
150 surface. In the real storage tank, a CO₂ atmosphere should be applied, under which the salt
151 remains stable to 700 °C [19]. The specimen was loaded into the 85 µl Pt/Rh crucible with an
152 alumina liner and it was subject to two heating and cooling cycles with a heating/cooling
153 rate of 10 K/min in nitrogen atmosphere.

154

155 The software Proteus® from Netzsch was used to evaluate the heat flux signals. The baseline
156 onset temperature during heating and cooling was regarded as the melting and
157 solidification temperature, respectively. The phase change enthalpy was estimated by the
158 integration of the heat flux under phase transformation.

159

160

161 2.4 Containment material characterization

162 2.4.1 Dynamic Gravimetric Analysis (DGA)

163 The effect of corrosion was determined by measuring the amount of corrosion products
164 formed on the surface of the SS316 sample, by using the dynamic gravimetric analysis (DGA)
165 [8]. The traditional methods proposed by the ASTM Standard G1-03 [25] requires intensive
166 sample manipulation, while the DGA technique reduces human handling when determining
167 the corrosion rate, and improves the accuracy of results.

168

169 Initially, the residual salts adhered to the SS surface were removed by submerging the SS
170 coupons into 10 % v/v sulphuric acid solution for 15 mins. Sulphuric acid at low
171 concentrations also makes the oxide layer become less compact and thus facilitates the
172 oxide descaling process without removing the corrosion layer itself. Following this
173 procedure [8], the coupon was then hung from an analytical balance (Ohaus Explorer) with
174 an accuracy of ± 0.1 mg and submerged in the cleaning solution, allowing the dissolution of
175 the formed scales. The balance was connected to a computer (*software RealTerm: Serial
176 Capture Programme 2.0.0.43*) which recorded the weight of the coupon every second,
177 providing a real-time weight loss of the descaling process.

178

179 The cleaning solution used in this work was defined in the ASTM Standard G1-03 and it
180 consists of 100ml 69% v/v HNO₃, 20 ml 48% v/v HF and distilled water up to 1L [25]. Each
181 studied SS coupon was immersed in the solution for 50 minutes following the DGA
182 procedure. This duration was experimentally determined to ensure that the oxide layer was
183 completely removed. Finally, the samples were cleaned with distilled water, dried with
184 absorbent paper, and weighed.

185 From the data captured by the software, a curve of weight loss versus time can be depicted.
186 This curve depends on the amount of oxide formed on the surface of the SS coupon, and
187 therefore, it can be related to the corrosion resistance. From the curve, the thickness x_M of
188 corroded steel can be calculated by Eq. (1)

$$189 \quad x_M = \frac{w_i^{air} - [w_f^{air} + (w_{ox}^{CS} - w_f^{CS}) \times B]}{S \rho_M} \quad (1)$$

190 where w_i^{air} and w_f^{air} are the initial and final weights of the SS coupon in air before and
191 after the DGA test, w_{ox}^{CS} is the weight of the SS coupon inside the cleaning solution when all
192 the oxide layer has been removed (the point on the graph in which the slope changes [8]),
193 w_f^{CS} is the final weight of the SS coupon inside the cleaning solution, S is the surface area,
194 and ρ_M is the density of the steel (7.85 g/cm³). B is the experimental buoyancy of cleaning
195 solution, which can be determined by the ratio of weight loss in air (Δw^{air}) and weight loss
196 inside the cleaning solution (Δw^{CS}) as shown in Eq. (2).

$$197 \quad B = \frac{\Delta w^{air}}{\Delta w^{CS}} = \frac{w_f^{air} - w_i^{air}}{w_f^{CS} - w_i^{CS}} \quad (2)$$

198 where w_i^{CS} is the initial weight of the SS coupon inside the cleaning solution before the DGA
199 test.

200 Although the plates were cut as precisely as possible, they were not identical in weight and
201 surface area. Thus for comparative purposes, the weight loss per unit area, w_{loss} (mg/cm²),
202 is calculated by multiplying the thickness of corroded steel (x_M) by its density (ρ_M).

203 On the other hand, the thickness of the oxide layer (x_{oxide}) can also be calculated from the
204 thickness of corroded steel, taking into account the stoichiometry of the iron oxide (for
205 example, Fe_xO_y), its molecular weight (M_{oxide}), and its density (ρ_{oxide}), by Eq. (3).

$$206 \quad x_{oxide} = \frac{x_M \rho_M M_{oxide}}{n_{Fe} \rho_{oxide} A_{Fe}} \quad (3)$$

207 n_{Fe} being the number of iron atoms per mole of oxide, and A_{Fe} the atomic weight of iron.

208

209 **2.4.2 Microstructural characterization**

210 Microstructural characterization was undertaken using a Zeiss Sigma Field Emission
211 Scanning Electron Microscope (SEM) and an Oxford XMax 50 Silicon Drift (SDD) EDS detector
212 provided Energy Dispersive X-ray Spectroscopy (EDS) mapping. Samples were cross
213 sectioned, mounted in resin and polished via the following procedure:

- 214 1. SiC Foil 320 grit, with water lubricant for 1 minute at 30N per sample.
- 215 2. MD Largo, with DiaPro Allegro/Largo lubricant/suspension for 3 minutes at 20N per
216 sample.
- 217 3. MD Mol, with DiaPro Mol B3 lubricant/suspension for 3 minutes at 20N per sample.
- 218 4. MD Nap, with DiaPro Nap B1 lubricant/suspension for 2 minutes at 20N per sample.
- 219 5. MD Chem with OP-U colloidal silica lubricant/suspension for 1 minute at 10N per
220 sample.

221 Both surface and cross-section areas were examined.

222

223 **3. Results and discussion**

224 **3.1 Thermal stability of PCM**

225 The onset melting and solidification temperatures and phase change enthalpy was
226 evaluated for six specimens for each fresh and cycled PCM sample. The results obtained
227 from the second freezing process were not included as a result of the salt creeping after two
228 melting processes. The experimental difficulty with molten salt creeping has been reported
229 previously [6, 13, 26]. A thin film of molten salt forms on the surface, which will wet the
230 crucible material and creep up the crucible wall and even out of the crucible. The maximum
231 and minimum values for each specimen were excluded from the calculation and the average
232 value and its standard deviation was calculated based on the remaining four values. The
233 average phase change temperature, sub-cooling and enthalpy during melting and
234 solidification, together with their standard deviations, at various numbers of thermal cycles
235 are listed in Table 2. The low standard deviation confirms that the four value points are
236 close to the average value and the error (σ , standard deviation divided by average value) for
237 all the measurement is below 3.64 %, which is within the measurement error of the DSC.

Cycle no.	1 st Melting Process		1 st Solidification Process		2 nd Melting Process		Sub-cooling (K)	Storage efficiency (%)
	T _{onset} (°C)	ΔH _m (J/g)	T _{onset} (°C)	ΔH _m (J/g)	T _{onset} (°C)	ΔH _m (J/g)		
Fresh	642.6±0.7	322.8±3.9	633.6±0.2	308.8±1.1	635.0±0.7	311.6±1.0	1.4	99.1
200	642.1±3.7	323.4±4.1	631.9±0.6	305.4±1.1	634.9±1.4	313.6±4.6	3.0	97.4
500	636.2±1.1	324.4±3.9	632.0±0.1	310.7±4.8	632.6±0.3	313.3±3.4	0.6	99.2
650	638.1±3.2	320.3±11.7	631.9±0.7	305.7±2.4	633.9±1.4	311.1±2.1	2.0	98.3
1000	639.5±3.5	319.4±8.8	632.2±0.5	304.6±6.5	634.1±1.1	310.2±3.7	1.9	98.2
σ	0.58 %	3.64 %	0.10 %	1.53 %	0.22 %	1.48 %		

239 T_{onset}: onset temperature; ΔH_m: phase change enthalpy.

240 Generally, the melting temperature, phase change enthalpy and their variations amongst
 241 specimens in the first melting process were higher than those in the succeeding
 242 solidification and the melting processes. The difference is between 3.7 °C and 7.7 °C for
 243 melting temperature and between 9.2 J/g and 11.2 J/g for the phase change enthalpy,
 244 respectively. A similar trend was observed by Shukla *et al.* [27] and Liu and Chung [28]. This
 245 discrepancy is likely due to the high thermal contact resistance between the salt and the
 246 crucible pan in the initial melt. The contact is improved in the second melt as space is
 247 eliminated between the salt and pan due to the initial melt. The phase change temperature
 248 during the second melting process was regarded as the melting temperature of the sample
 249 as discussed below.

250 The melting temperature and the phase change enthalpy measured in this work along with
 251 their theoretical values calculated using FactSage 6.4 and the data reported in previous
 252 literature are listed in Table 3. It shows that the differences of melting temperature
 253 between the theoretical and measured values are small, the maximum difference being 5 K
 254 (0.8 %). The phase change enthalpy measured in this work and another study [19] is 16.73
 255 J/g (5.7 %) higher and 11.6 J/g (3.9 %) lower than the calculated value in FactSage 6.4,
 256 respectively, which is acceptable as the discrepancy. However, values obtained in [29] are
 257 around two thirds less than the other three values. This could be due to the impurities in the
 258 salt, salt creeping, salt decomposition or improper calibration of the DSC as insufficient
 259 information is given in [29].

260

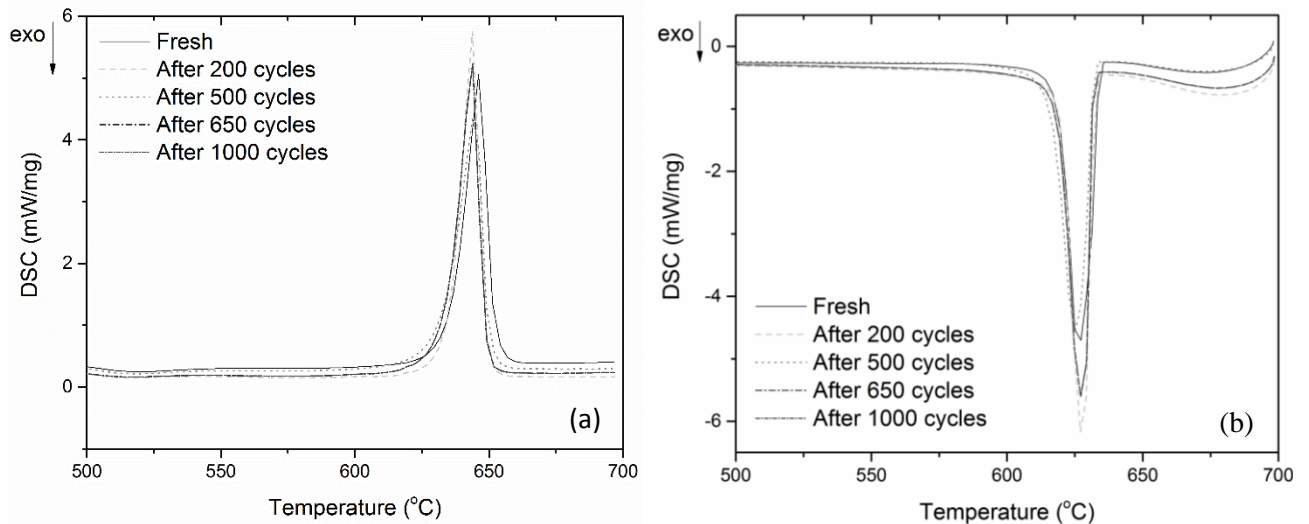
261 Table 3. A comparison between the melting temperature and phase change enthalpy of eutectic NaCl-Na₂CO₃ from the
 262 present work and other sources.

Source	Melting temperature (°C)	Phase change enthalpy (J/g)
FactSage 6.4 [19]	632.0	294.9
Jiang <i>et al.</i> [19]	637.0	283.3
Ye <i>et al.</i> [29]	635.85	101.12
this work	635.0	311.6

263

264 Figure 1 provides the typical DSC curves of the fresh PCM sample and the samples after 200,
 265 500, 650 and 1000 thermal cycles. This PCM has a sharp endothermic peak (during melting)

266 and exothermic peak (during solidification), which indicates this PCM has good energy
267 storage and release characteristics. The melting temperature is between 632.6 °C and
268 635.0 °C and phase change enthalpy is between 310.2 J/g and 313.6 J/g. As seen in Table 2
269 and Figure 1, the change in phase change temperature and enthalpy with increasing number
270 of cycles is not significant, indicating its good thermal stability over 1000 thermal cycles.



271

272 *Figure 1. DSC curves of eutectic NaCl-Na₂CO₃ after various numbers of thermal cycles: (a) melting process and (b) freezing*
273 *process.*

274

275 The solidification temperatures of the PCM were determined as 631.9– 633.6 °C over
276 cycling, which is 0.6 – 3.0 °C lower than its melting temperature as a result of subcooling.
277 Due to the subcooling phenomenon, the phase change enthalpy obtained from the
278 solidification process is lower than obtained from the melting process. The energy storage
279 efficiency is calculated by dividing the phase change enthalpy during the solidification
280 process by the phase change enthalpy during the melting process. The minimum storage
281 efficiency is 97.4% and it means that 97.4% of the stored energy can be recovered during
282 the solidification, indicating a good energy recovery of the PCM.

283

284 **3.2 Mass-loss corrosion rate**

285 Corrosion rate measurements as a function of the number of cycles, for the studied salt
286 mixture are shown in Figure 2. The assessment of the corrosion data is based on purely
287 uniform corrosion. As can be observed from Figure 2, initially, the mass loss increases with
288 the number of cycles, and the increase is nearly linear. Then it reaches around 70 mg/cm²
289 until 350 cycles. Further cycles up to 500 do not influence the corrosion rate, thus indicating
290 that a passivation layer could be formed that prevents further corrosion.

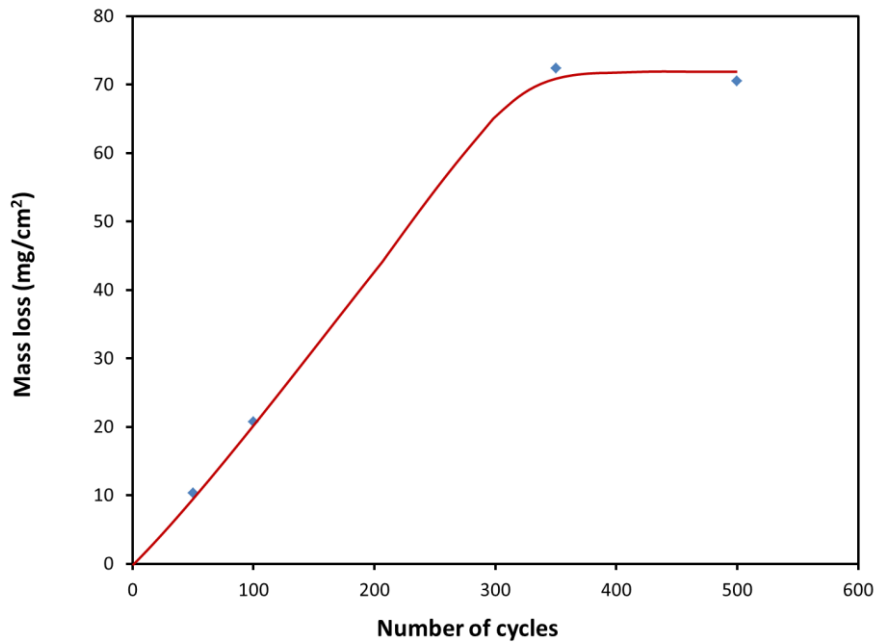


Figure 2. Mass loss as a function of the number of cycles, obtained from the DGA methodology.

291

292

293

294 Using Eq. (3) the total thicknesses of oxide layer can be determined with this technique. If
 295 we consider the oxide formed as pure and compact iron oxide (Fe_2O_3 , with a theoretical
 296 density of 5.26 g/cm^3), the calculated thicknesses of the oxide layer become: 28, 56, 197,
 297 and $192 \mu\text{m}$, for 50, 100, 350, and 500 cycles, respectively. Unfortunately, as will be later
 298 explained, EDS analysis of the corroded surfaces indicate that the composition of scales are
 299 far from being pure and compact iron oxide and thus these values should be considered as
 300 an order of magnitude .

301

302 3.3 Microstructure of containment material

303 A typical SEM image with EDS analysis on the surface of the submerged coupon that
 304 underwent 100 cycles is presented in Figure 3. There are four distinct corrosion products as
 305 shown in Figure 3: sodium iron oxide (dark region in lower left), iron oxide in lower right,
 306 iron nickel chromium oxide on the top and base metal (bright central section).

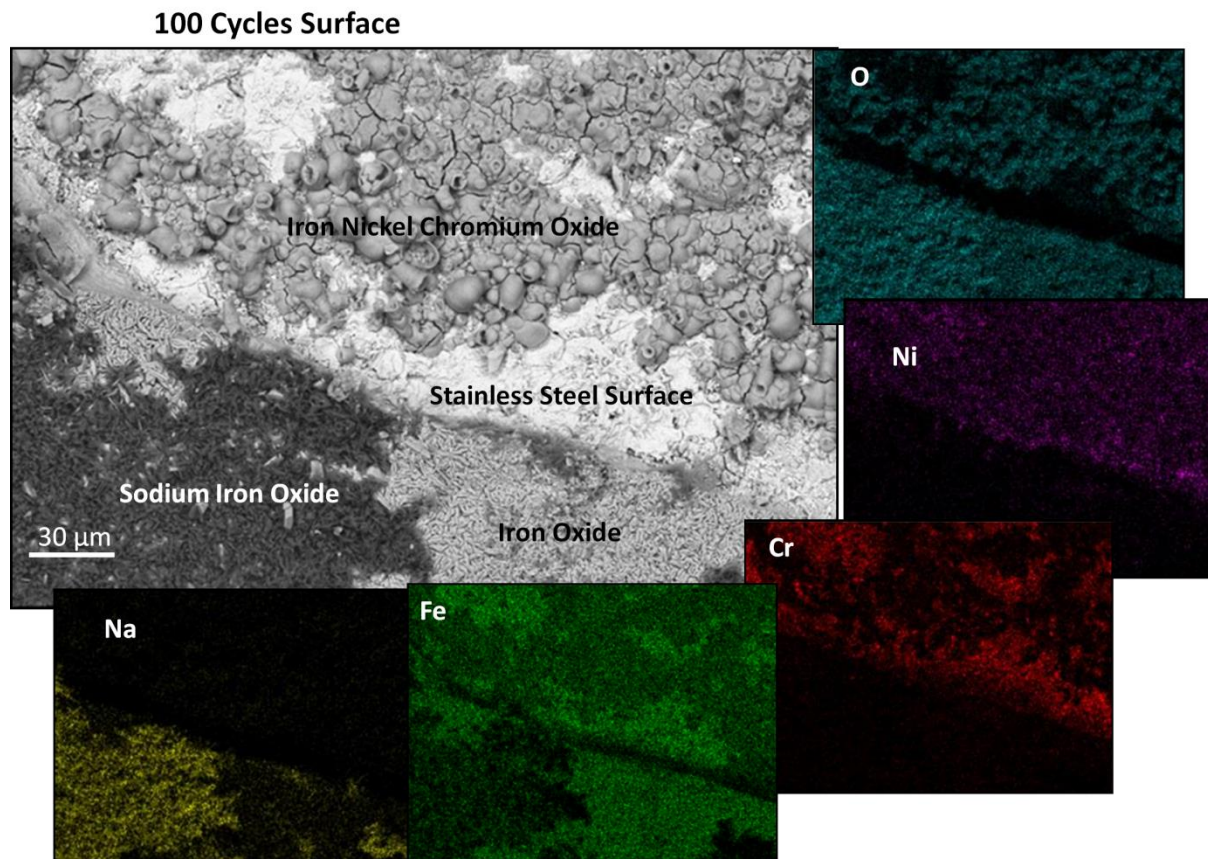
307

308 Backscatter SEM images with EDS insets of cross-sectioned samples are shown in **Error!**
 309 **Reference source not found.**a-d. These were undertaken for the SS coupons that have been
 310 subject to 50, 100, 350 and 500 thermal cycles submerged in the salt. The corrosion
 311 products were studied and the thickness of the products was measured and summarized in

312 Table 4.

313

314 The 50-cycle sample shows a two layered corrosion film, a thicker outer layer of primarily
 315 iron oxide and a thinner inner layer which includes chromium and nickel. Three to four
 316 layers exist in the 100-cycle sample, an inner iron chromium nickel oxide of approximately
 317 10 μm thickness, an intermediate iron oxide layer also 10 μm thick and a very thin
 318 (approximately 5 μm) sodium iron oxide layer. There is also an outer iron chromium nickel
 319 oxide layer present in some sections.
 320
 321



322
 323 *Figure 3. Electron Backscatter image with EDX plots and compositions for 4 different products.*

324
 325 *Table 4. Cross-section corrosion layer thickness with number of thermal cycles.*

<i>Sample</i>	<i>Total oxide layer thickness (μm)</i>	<i>Thickness of iron nickel chromium oxide, outer (μm)</i>	<i>Thickness of sodium iron oxide (μm)</i>	<i>Thickness of iron oxide (μm)</i>	<i>Thickness of iron nickel chromium oxide, inner (μm)</i>
<i>50 cycles</i>	25 – 30	-	-	15-20	10-15
<i>100 cycles</i>	35 – 45	~10	~5	~10	10-15
<i>350 cycle</i>	90 – 110	-	~20	25-30	50-60
<i>500 cycles</i>	80 - 85	-	~20	5-10	50-60

326
 327 Three distinct layers are evident in the well-developed corrosion layers of the samples
 328 subject to 350 and 500 cycles. A sodium iron oxide layer with a thickness of approximately
 329 20 μm is present at the salt/corrosion interface. An intermediate layer of primarily iron
 330 oxide 25-30 μm thick in the 350 cycles sample is reduced to 5-10 μm in the 500-cycle

331 sample. The inner layer in both samples is a 50-60 μm thick iron chromium nickel oxide in
332 contact with the bulk metal.

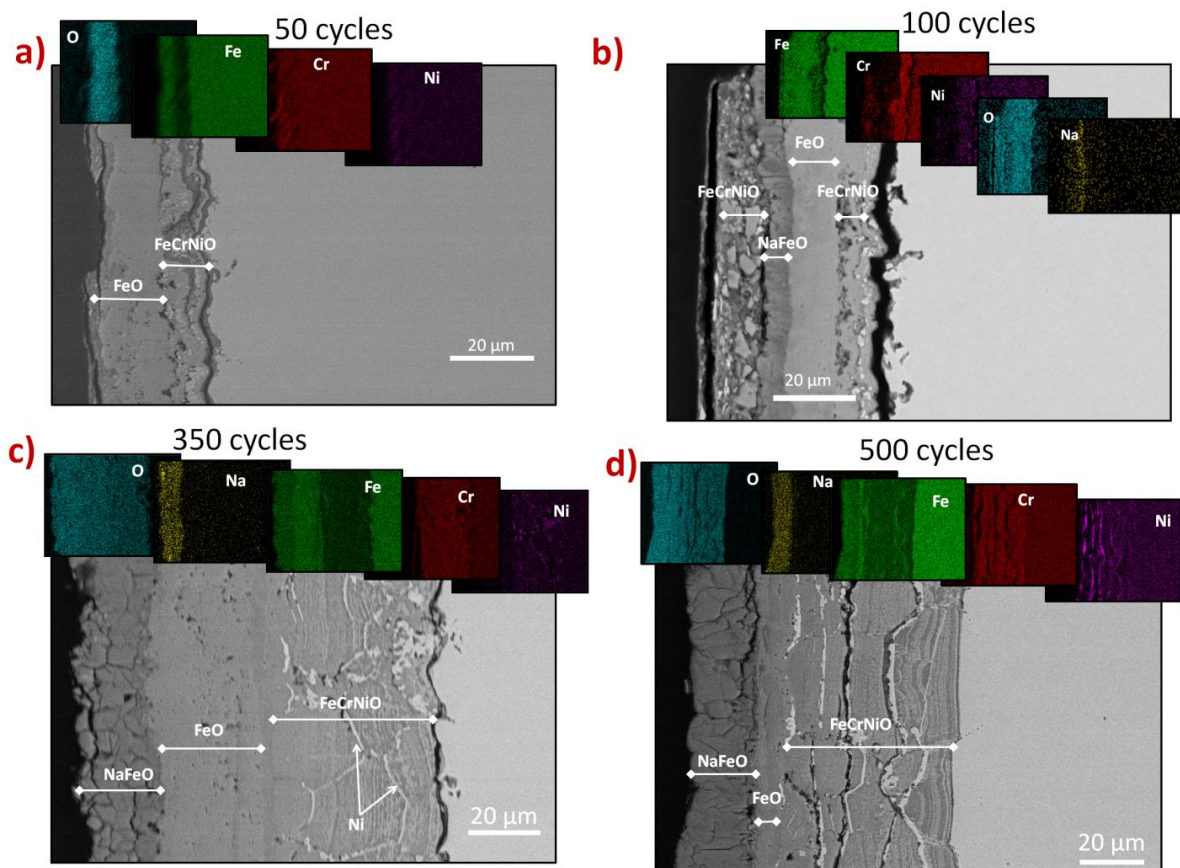
333

334 The corrosion layer in the 50-cycles sample has not yet formed the sodium iron oxide outer
335 layer which appears to be developing in the 100 cycles sample and it is significant in the
336 longer term test samples. It is likely that the iron oxide layer is formed when the chromium
337 oxide present on the surface is dissolved by the salt. Optical Emission Spectroscopy (OES)
338 tests performed on the salts after testing reveals the presence of both iron and chromium.
339 The higher chromium and nickel concentration in the oxide at the metal surface is likely due
340 to the growth of the oxide layer into the bulk metal and the outer iron oxide layer inhibiting
341 chromium migration into the salt. When the iron oxide layer gains enough thickness, it
342 prevents chromium migration into the salt. This is evident in the 350- and 500-cycle samples
343 with thick iron chromium nickel layers. The nickel in this layer forms a metal lattice as nickel
344 is less reactive to oxidization than iron and chromium. Both the presence of an alkali metal
345 anion/iron oxide outer layer, and chromium depletion from bulk metal and oxide layers
346 have been identified previously in the literature [7, 30, 31].

347

348 Finally, it is noted that the 500-cycle sample has a reduced total oxide layer thickness
349 compared with the 350-cycle sample. This reduction appears to be related to the
350 intermediate iron oxide layer which has shrunk considerably. The sodium iron oxide layer
351 has been previously identified as non-protective under similar conditions [32]. This layer is
352 likely to be removed during cycling, but retains its thickness as it progressively transforms
353 the iron oxide layer.

354



355

356 *Figure 4. Electron Backscatter and EDX images of the composition of a) 50 cycles, b) 100 cycles, c) 350 cycles and d) 500*
357 *cycles corrosion layers – sodium iron oxide, iron oxide and iron, chromium, nickel oxide (labels represent the presence of*
358 *indicated elements).*

359 **4. Conclusion**

360 A long-term stability test has been conducted on a eutectic NaCl-Na₂CO₃ PCM. The
361 measured thermo-physical properties of this PCM did not vary significantly over 1000
362 thermal cycles. This verifies the potential of this material as a candidate PCM due to its
363 ability to maintain its thermal energy storage capacity.

364 The oxide film remaining on the surface of the test coupons grew to a thickness of 90 –
365 110 µm and developed from a primarily iron oxide layer into three distinct layers, an inner
366 iron chromium nickel oxide layer at the metal surface, an intermediate iron oxide layer and
367 a sodium iron oxide layer at the salt interface. This oxide film appears to have prevented
368 significant chromium depletion and damage to the samples submerged under that salt.

369 During the experiments, some of the formed scales are dissolved or fall into the melted
370 salts. Therefore, the thickness of the outer scale layer determined by SEM could not include
371 them. From DGA, the corrosion rate can be calculated more precisely as it takes into
372 account those scales lost during experiments and handling. For this reason, results obtained
373 for thicknesses are greater than those observed by SEM. The mass loss increases linearly
374 with the number of cycles, reaching around 70 mg/cm² at 350 cycles. From SEM results it
375 can be observed that the first oxide layer on the steel (mainly formed by chromium, iron
376 and nickel oxides), has approximately the same thickness at 350 and 500 cycles, which could
377 indicate the stable passivation layer formation.

378 To identify the full potential use of SS316 as the containment material for the developed
379 PCM, longer term thermal cycling testing has to be performed to: (1) verify the no/slow
380 growth of this passivation layer after 350 cycles and (2) examine the stability of this
381 passivation layer after 500 cycles.

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