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Fast Track School #1

Molten Salt technologies and energy system applications

CASACCIA, ROME, 09.-10.05.2023

Compatibility of MS with metallic materials: Corrosion procedures

INTRODUCTION

REFERENCES

CORROSION TESTS

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Introduction

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General consideration taken from literature about corrosion of stainless steel in molten nitrates salts

Definition of corrosion rate

Oxidation/Reduction reactions for Austenitic stainless steel → oxide layers

Best practice for material to evaluate steel corrosion in molten salt environments

INTRODUCTION

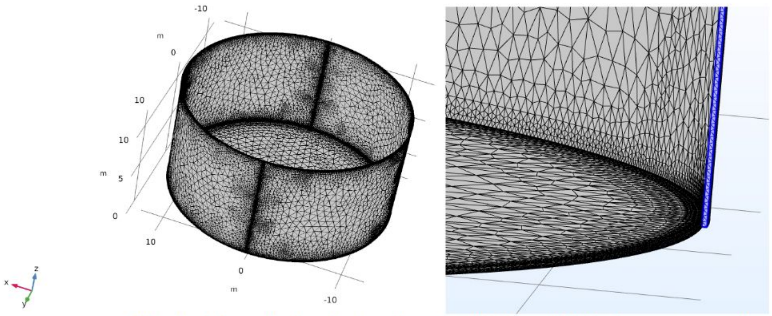
Example thermal storage 1300 MWh

	Solar salt	Hitec XL
Operating range	290-550	190-400
ΔT [°C]	260	210
Cp [J /kg °C] Binary 385°C, HXL 200°C	1509	1477
ρ [kg/m3] Binary 385°C, HXL 200°C	1845	2070
salts kg	11928429	15088500
salts MT	11928	15088
Volume salts m³	6465	7289
volume thermal capacity [MJ/ m³ °C]	2.8	3
Radius [m]	13	14
Diameter [m]	26	28

TYPE	Volume m3 Solar salt	Volume m3 HitecXL	ton bin	ton tern	M€ bin	M€ H. XL
321	56	66	449	528	1,6	1,9
347	50	59	392	466	1,5	1,8
304	64	77	507	610	1,6	2,0
430	37	45	287	349	0,36	0,44
316L	54	66	434	530	2,2	2,7

Stainless steel	PEELED Oct 2022 €/kg	PEELED May 2023 €/kg
430	2.06	1.25
304	4.14	3.25
316L	5.72	5.14
321	4.59	3.66
347	4.78	3.86

https://www.eureinox.it/extra-lega/
Steel price trend for italian market.



The tank have to be designed using ASME or API Code requirements

Volume steel, cylindrical shell and 2 disk for top/bottom

simple hypothesis

Mariotte-Barlow $t \geq \frac{P_i\, D}{\sigma_{allow}}$

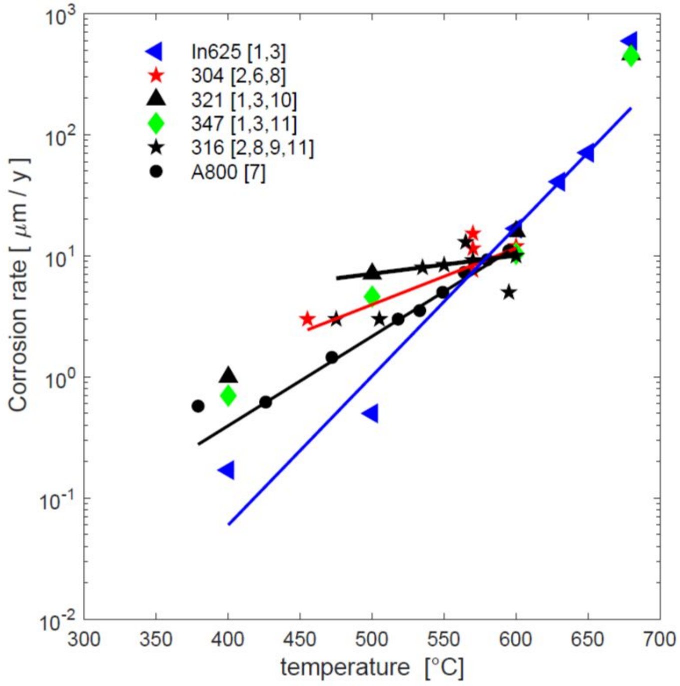
idrostatic pressure [kg/mm²]   Safety factor 1.5

Mechanical properties, test temperature 371°C	Yield strength 0.2% offset [MPa]	Tensile strenght [MPa]	Thickness [mm] binary	Thickness [mm] ternary
316	159	500	26	29
347	174	462	24	26
304	134	427	31	34
321	157	414	27	29
430	228	396	18	20

Mark Mehos, Craig Turchi, Clifford Ho, William Kolb, Alan Kruizenga, "**Concentrating Solar Power Gen3 Demonstration Roadmap**", Technical Report NREL/TP-5500-67464, January 2017

CR corrosion rate summary from literature

$$CR = \frac{86700 \cdot \Delta m}{\rho_s\, t} \quad Corrosion\ rate\ [\mu m/y]$$



$$\Delta m = \frac{m_i - m_f}{S} \text{ descaled mass loss } [mg/cm^2]$$

$$\Delta moxide = \frac{m_t - m_f}{S} \text{ mass of descaled oxide } [mg/cm^2]$$

S_0 initial metallic surface of the steel sample $[cm^2]$

$$t_{oxide} = \frac{\Delta m_{oxide}}{\rho_{oxide}} \text{ [μm] average thickness of oxide layer } \rho_{oxide}(Fe, Cr)$$

- t testing time [h]
- ρ_s alloy density $[g/cm^3]$
- m_i initial mass of the specimen before the test [mg]
- m_t mass of the specimen before chemical descaling [mg]
- m_f mass of the specimen after chemical descaling [mg]

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References

Literature data

[7] All 800	Conv. loop 4991 h solar salt 600°C	
	temperature	Descaled weight loss [mg/cm^2]
	379	0.456
	426	0.49
	472	1.157
	518	2.45
	533	2.8
	549	4.03
	564	5.78
	580	7.36
	595	8.7

[1,3] In625	
temperature	CR [μm/year]
400	0.2
500	0.5
600	16.8
630	40.92
650	71.02
680	594

[1,3,10]-321	
temperature	CR [μm/year]
400	1
500	7.1
600	15.9
680	460

[1,3,11]-347	
temperature	CR [μm/year]
400	0.7
500	4.6
600	10.4
680	447

[11]-304	7008 h solar salt 570°C	
	temperature	CR [μm/year]
	570	7.6
	7008 h solar salt+1wt%NaCl 570°C	
	temperature	CR [μm/year]
	570	11.5
	7008 h solar salt+1.3 wt%NaCl 570°C	
	temperature	CR [μm/year]
	570	15.3
[2]-304	Conv. loop 4500 h solar salt 375- 600°C	
	temperature	CR [μm /year]
	455	3
[6]-304	temperature	CR [μm /year]
	600	12

[2]-316	Conv. loop 4500 h solar salt 375-600°C	
	temperature	CR [μm/year]
	475	3
	485	10
	505	3
	535	8
	565	13
	595	5
	600	10
[11]-316	7008 h solar salt 570°C	
	temperature	CR [μm/year]
	570	9.2
[9]-316	3000h solar salt static 550°C	
	temperature	CR [μm/year]
	550	8.4

REFERENCES

Oxidation/Reduction reactions for Austenitic stainless steel

Multiphase surface oxides are composed primarily of iron-chromium spinel, iron oxides, and sodium ferrite.

Metal loss in nitrate salt results from metal oxidation and chromium dissolution.

The corrosion process for austenitic stainless steel can be described by the following reactions

$$NO_3^- + 2e^- \leftrightarrows NO_2^- + O^{2-}$$ reduction

$$Fe + O^{2-} \leftrightarrows FeO + 2e^-$$ oxidation

$$3FeO + O^{2-} \leftrightarrows Fe_3O_4 + 2e^-$$

$$2Fe_3O_4 + O^{2-} \leftrightarrows 3Fe_2O_3 + 2e^-$$

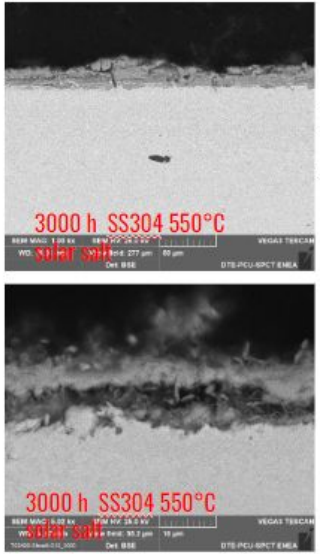
Hematite can also react with chromium and manganese leading to spinels $FeCr_2O_4$ and $FeMn_2O_4$, the former iron chromite acts as protective layer for the austenic steels

At higher temperature the nitrite reduction produces N_2 nitrogen and NO_x, sodium oxide reacts with hematite resulting sodium ferrite

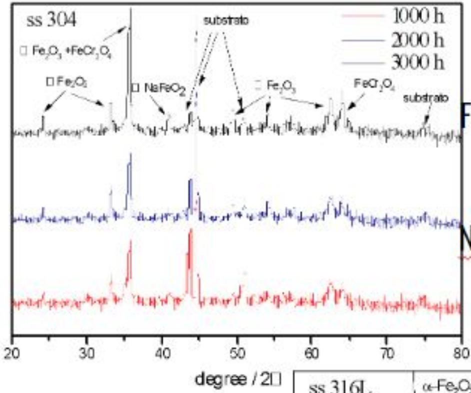
$$Na_2O + Fe_2O_3 \leftrightarrows +2NaFeO_2$$

- **chromium** dissolves in the molten salt as **chromate** (sodium chromate Na_2CrO_3 and sodium bichromate $Na_2Cr_2O_7$)
- **iron** dissolves as hematite.

Oxidation layer for Austenitic stainless steel XRD patterns



304 SS, 430 SS
3000 h in solar salt
550°C, v=0.7 m/sec

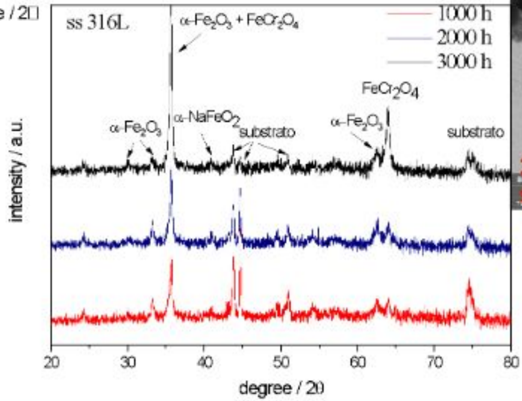


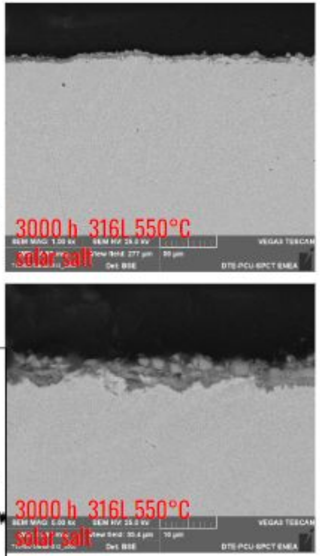
Corrosion products

$FeCr_2O_4$ Iron chromite

Fe_2O_3 hematite

$NaFeO_2$ SODIUM FERRITE





316L SS, 430 SS
3000 h in solar salt 550°C,
v=0.7 m/sec

Corrosion literature, 10MW Solar Two pilot plant

- Several metal alloys are reported to be suitable for CSP applications up to 600 °C. In particular, the AISI 300 stainless steels series exhibited good corrosion properties; type **AISI 316** was proposed for the **receiver in the Solar Two system** [14] and type **AISI 304 for the hot salt storage tank and piping**[14] , **the cold tank on Solar Two was built of carbon steel ASTM A516-70**, and they basically maintain their features in dynamic HTF flow conditions, during thermal cycling and in presence of anionic impurities (chloride, for instance).

- However, from the experience gained by the Solar Two plant [15], it was noticed that these compatibility properties are maintained only when molten nitrates are in contact with the steel; during certain typical plant **maintenance procedures** an **aqueous environment** can be present on interior surfaces of receiver tubes and hot-salt piping, and **in this case conditions for an intergranular corrosion (IGC) attack can be attained**, leading to leakage problems when molten salts are recirculated again into the pipelines.

- **(IGC)** is due to **chromium depletion** at grain boundaries caused by **chromium carbide (**Cr_3C_2) formation between 530 and 590 °C; eventually, during the described operations, water together with chlorides (present as impurities in the solar salt mixture) can come in contact with the steel surface, and corrosion can occur [16]. As a consequence, 321H and 347 H are used instead, therefore, other elements (Titanium, Niobium) are added, which preferably precipitate as carbide.

AISI (321) stabilised with Titanium

AISI (347) stabilised with Niobium

SALT PURITY Chemical composition specifications of molten salt

Best practice for material to evaluate steel corrosion in molten salt environments

Name	Mix potassium nitrate + sodium nitrate	
Composition	Sodium nitrate NaNO3	60 %
	Potassium nitrate KNO_3	40 %
	Minimum nitrate %	99 %
MAX PERCENTAGE OF IMPURITIES		
Nitrite		0.20 %
Chloride		0.03 %
Carbonates		0.05 %
Sulfates		0.15 %
Alcalinity hidroxile		0.04 %
Perclorates		0.04 %
Magnesium		0.04 %
Calcium		0.04 %
Insoluble		0.06 %

IMPURITIES

It is not accepted the use of anticaking agents [24]

Parameter	Unit	Specification	Test method
Sodium nitrate	g/100 g	min. 99.5	Titrimetry
Water (loss on drying)	g/100 g	max. 0.2	Gravimetry
Sodium nitrite	mg/kg	max. 50	Titrimetry
Sodium carbonate	mg/kg	max. 400	Titrimetry
Sodium chloride	mg/kg	max. 250	Titrimetry
Sodium sulfate	mg/kg	max. 50	IC
Insolubles	mg/kg	max. 50	Gravimetry

PRODUCT SPECIFICATIONS

ANALYSIS	UNITS	TYPICAL	SPECIFICATION
Assay (as KNO_3)	%	99.7	99.4 min
pH (10% sol.)		7.0	6.0-8.5
Sodium (Na)	ppm	150	300 max
Calcium (Ca)	ppm	13	25 max
Magnesium (Mg)	ppm	5	10 max
Iron (Fe)	ppm	3	10 max
Chloride (Cl)	ppm	160	300 max
Water Insolubles	ppm	180	350 max

- In the salt the impurity level may affect the CR and the thermal properties (Tmelting, fusion point) of the salt mixtures.
- There is no protocol that specifies the admissible level of impurities in the salt [13,21,23]

TEST CONDITIONS → **SAMPLE PREPARATION** → **GRAVIMETRIC analysis** → **DESCALING PROCESS** → **METALLOGRAPHIC examination**

- TEST CONDITIONS: Temperature, velocity, salts
- SAMPLE PREPARATION: Measure sample dimensions, surface pre-treatment
- GRAVIMETRIC analysis: Measure the mass of the steel sample before, after the test and after descaling

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Corrosion tests

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Methodology for corrosion tests [13, 19]

- **Test conditions** Temperature, velocity, salts
- **Sample preparation** measure sample dimensions, surface pre-treatment to maintain an identical surface finish for the samples prior to exposure
- **Gravimetric analysis** measure the mass before and after the test
- **Descaling process**
- **Metallographic examination**

corrosion test

- Static isothermal, (vessel)
- Dynamic (stirred vessel, circuit loop) isothermal and thermal cycle

Characterization methods	Corrosion testing method	Metallographic analysis
Steel ❑ gravimetric analysis ❑ SEM/EDS morphological and structural analysis of corrosion ❑ products X-ray diffraction analysis	**ISO 17245:2015** Corrosion of metals and alloys — Test method for high temperature corrosion testing of metallic materials by immersing in molten salt or other liquids under static conditions	**ASTM E3 – 11 (2017)** - Standard Guide for Preparation of Metallographic Specimens.
Salt ❑ elemental analysis (ICP) for metals, Fe, Cr, Ni, Mo ❑ Ion chromatography for nitrites ❑ Acid/base Titration for oxides compounds	**ISO 8407** Corrosion of metals and alloys — Removal of corrosion products from corrosion test specimens The chemical descaling is necessary to remove the corrosion product and measure the metal loss DESCALING PROCESS [22] ⬇ Removal of corrosion oxides avoiding the attack of the metal surface	**ASTM E407 - 07(2015)** - Standard Practice for Microetching Metals and Alloys.

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