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Task 2.04.08.01 Energy Conversion Technology**

Milestone Report

**METAL CORROSION IN A SUPERCRITICAL
CARBON DIOXIDE – LIQUID SODIUM POWER
CYCLE**

Robert Moore, Thomas Conboy
(Sandia National Laboratories)

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METAL CORROSION IN A SUPERCRITICAL CARBON DIOXIDE – LIQUID SODIUM POWER CYCLE

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Abstract

A liquid sodium cooled fast reactor coupled to a supercritical carbon dioxide Brayton power cycle is a promising combination for the next generation nuclear power production process. For optimum efficiency, a microchannel heat exchanger, constructed by diffusion bonding, can be used for heat transfer from the liquid sodium reactor coolant to the supercritical carbon dioxide. In this work, we have reviewed the literature on corrosion of metals in liquid sodium and carbon dioxide. The main conclusions are 1) pure, dry CO₂ is virtually inert but can be highly corrosive in the presence of even ppm concentrations of water, 2) carburization and decarburization are very significant mechanism for corrosion in liquid sodium especially at high temperature and the mechanism is not well understood, and 3) very little information could be located on corrosion of diffusion bonded metals. Significantly more research is needed in all of these areas.

Contents

EXECUTIVE SUMMARY	8
1.0 INTRODUCTION	12
2.0 MICROCHANNEL HEAT EXCHANGERS.....	16
3. CARBON DIOXIDE INDUCED CORROSION	19
3.1 Corrosion Mechanism and Passivation in CO ₂	19
3.2 Corrosion Studies in Supercritical CO ₂	20
3.3 CO ₂ Corrosion Experience from the Petroleum Industry	27
3.4 Corrosion in the CO ₂ Cooled Magnox Reactors.....	28
4.0 CORROSION IN LIQUID SODIUM.....	30
4.1 Corrosion of Steels.....	30
4.2 Reaction Products of CO ₂ and Liquid Sodium	30
4.3 Heat Exchanger Plugging and Damage	31
4.4 Carburization/Decarburization.....	31
5.0 SUMMARY AND ADDITIONAL RESEARCH NEEDS.....	34
5.1 Summary of Literature Data	34
5.2 Additional Research Needs.....	35
6.0 CONCLUSIONS.....	38
7.0 REFERENCES	40
APPENDIX A: COMPOSITION OF ALLOYS.....	46

Table of Figures

Figure 1 A comparison of thermal efficiency vs. temperature for various power cycles.....	13
Figure 2 Schematic of a system layout for a coupled sodium reactor and supercritical CO ₂ power conversion unit.	13
Figure 3 (L) A cross-sectional view of the microchannels in a Heatric PCHE	16
Figure 4 Heatric PCHEs are shown from the Sandia Split-Flow Recompression Brayton Demonstration System: (L) the Low Temperature Recuperator, and (R) the High Temperature Recuperator.....	17
Figure 5 Effect of water vapor concentration on corrosion of various alloys. (Lorier et al., 1968)	23
Figure 6 Effect of pressure on corrosion of various metals. (Loriers et al., 1968)	23
Figure 7 Weight gain vs. time at 500°C for pure iron, x rimming steel, o low alloy steel A, Δ low alloy steel B and √ low alloy steel C in a) dry CO ₂ at 1 atm and b) CO ₂ saturated with H ₂ O. (Antill et al., 1968)	24

Table of Tables

Table 1 Corrosion studies of metals in supercritical CO ₂	22
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EXECUTIVE SUMMARY

A supercritical CO₂ Brayton power cycle coupled to a liquid sodium reactor is an attractive option for the next generation of nuclear reactors. The system would be capable of reaching efficiencies as high as 45-50% operating at a temperature of 550 – 700°C. Furthermore, the high density of supercritical CO₂ and sizeable molecular weight results in a power conversion system with a small footprint, reducing capital costs. The moderate temperature range required for high efficiency operation suggests the use of common industrial materials, resulting in a system that is affordable and fabricable. Liquid sodium cooled reactor technology has been investigated for more than 50 years with many liquid sodium cooled reactors constructed and operated worldwide. The supercritical CO₂ Brayton cycle is relatively new and only in the demonstration phase on a small scale. In this work, the available literature is reviewed on corrosion issues in a supercritical CO₂ Brayton power cycle - liquid sodium reactor system.

Limited information is available for corrosion in a supercritical CO₂ environment. The information compiled in this work for CO₂ is from three major sources: (1) laboratory studies, (2) experience in transporting supercritical CO₂ in the petroleum industry for enhanced petroleum recovery operations, and (3) experience in operation of the British CO₂ cooled Magnox reactors. Laboratory experiments have mainly focused on corrosion in low temperature, low pressure humid environments. Far fewer studies focus on corrosion in supercritical CO₂. CO₂ is transported in the petroleum industry in the supercritical state as a cost saving measure. In this application, the supercritical CO₂ is pumped at approximately 100°C or less. The CO₂ cooled Magnox reactors were operated at high temperature, up to 650°C, but not at pressures above the critical point. The main conclusions that can be deduced from the literature data for corrosion in supercritical CO₂ are:

- Corrosion testing in supercritical CO₂ has mainly been performed through short-term coupon testing. Research has mainly focused on routinely used steels such as 316 s.s. and 304 s.s., with fewer studies reported on the more expensive high chrome and high nickel steels and nickel based alloys.
- From operational experience with the CO₂ cooled Magnox reactors, corrosion rates of steels in CO₂ are much higher for materials under stress.
- Pure, dry CO₂ is virtually inert at low temperatures <500°C. However, at high temperatures, >600°C, and in the presence of even small quantities of water (ppm levels) significant corrosion of steels and nickel alloys can occur.

- In general, austenitic alloys are more resistant to CO₂ induced corrosion than the ferritic-martensitic steel. High concentrations of chromium and nickel significantly increase the corrosion resistance of steel alloys in supercritical CO₂.

Data for corrosion of metals in liquid sodium was found from laboratory experiments and operational experience with liquid sodium cooled reactors. Reaction products of the CO₂ – liquid sodium interaction, and their impact on corrosion rates in sodium environments, were also considered. For a sodium cooled reactor coupled to a supercritical CO₂ Brayton cycle, carburization may be one such mechanism of corrosion. Heat transfer from the liquid sodium to the supercritical CO₂ takes places in the system's primary system heat exchanger. If a leak in the heat exchanger were to develop, CO₂ would enter into the liquid sodium loop resulting in the formation of carbon as one of the reaction products. Even small amounts of carbon (>1 ppm) in the liquid sodium can result in carburization of metal causing it to become brittle and significantly lose strength. In fact, liquid sodium is used by industry as a process fluid for applications in which it is desired to deliberately carburize steels. Therefore, improved characterization of this effect and procedures to mitigate damage deserve further attention.

The main conclusions based on the available literature data for corrosion in liquid sodium include:

- At low temperature, <500°C, pure liquid sodium is not corrosive to steels and nickel based alloys to any significant degree. However, higher temperatures and the presence of impurities such as O₂ can enhance corrosion. In general, corrosion rates for the austenitic steels increase exponentially with temperature and linearly with oxygen content and sodium velocity up to approximately 3 m/s.
- Diffusion bonding typically used in the construction of microchannel heat exchangers can produce a weld as strong as the base metal of construction, with good resistance to corrosion. However, if the weld is not correctly done, the welded area can have a significantly reduced strength. No information on the corrosive effects of CO₂, liquid sodium, carbon and other materials on diffusion bonded metals could be located in the literature.
- A leak in the primary heat exchanger will inevitably lead to supercritical CO₂ entering the liquid sodium loop. The products of the reaction of CO₂ and liquid sodium are mainly sodium carbonate and carbon. This information is based on a very limited amount of data, with large associated uncertainty.
- Carburization/decarburization is a potentially highly significant mechanism for corrosion in a supercritical CO₂ Brayton cycle – liquid sodium reactor system. The presence of carbon, even at very low

concentrations (<1ppm), in the liquid sodium can result in carburization of steels and nickel alloys. In general, nickel based alloys are more resistant to carburization than steels.

- Only a single study could be located that focused on channel plugging of a microchannel heat exchanger by the reaction products of CO₂ and liquid sodium. The results indicate channel plugging is strongly dependent on temperature, crack size and channel size.

Based on the information reviewed in the literature and the requirements for a supercritical CO₂ Brayton cycle-liquid sodium reactor system additional research is required in the area of corrosion. These include:

- Corrosion testing needs to be performed over long time intervals. No long-term corrosion testing is reported in the literature. The experience gained from operation of the Magnox reactors, that short-term coupon testing is inadequate for certain systems, reinforces the need for testing materials over long time intervals.
- Corrosion tests need to be performed under stress to simulate the operational conditions for the construction materials. Operational experience from the Magnox reactors indicated corrosion was not significant except for the components under stress.
- The effects of water, oxygen and other impurities need to be examined in more detail. The literature indicates water at ppm concentrations creates a very corrosive environment for many metals in the presence of CO₂.
- The mechanism of supercritical CO₂ corrosion at very high temperature in the absence of water needs to be better understood. The work of Glezakou et al., 2000 indicates that corrosion of metal surfaces can occur in the complete absence of water at temperatures in excess of 600°C.
- To minimize capital cost, studies need to be performed at low to moderate temperature with mild steel, low Cr steel and other relatively inexpensive materials that could be used for construction of the low temperature heat rejection and heat recuperator heat exchangers in the supercritical CO₂ Brayton cycle.
- Testing needs to be performed on a small scale microchannel heat exchanger constructed by diffusion bonding that is representative of the heat exchanger for use in a full scale supercritical CO₂ Brayton cycle. Tests should aim to find predictive failure thresholds based on candidate structural materials, degradation in materials due to

corrosion, various diffusion bonding fabrication conditions, and also microchannel flow channel patterns. This series of tests should aim to provide sufficient information for ASME code certification.

- As carburization appears to be significant concern following a leak in coupled CO₂-Sodium heat transfer systems, research is needed for the development of a technique for removing elemental C from liquid sodium flow to levels under 1 ppm to prevent widespread damage to the primary system.
- A claim by proponents of the coupled CO₂-Sodium reactor system is that cost may be reduced by eliminating the secondary sodium system required in sodium-steam power conversion plants. In this interest, fuel cladding materials should be investigated for susceptibility to carburization or other damage due to interaction with sodium-CO₂ reaction products.
 - An investigation of the inspection and repair procedures for microchannel heat exchangers following failure or materials degradation is needed.
- The reaction between CO₂ and liquid sodium needs further study with a complete analysis of the reaction products. In the few studies reported in the literature there are significant discrepancies and in one study a significant amount of the reaction products was reported as unknown.
- A significant effort needs to be performed detailing thermodynamic modeling of corrosion in supercritical CO₂.
- The information reviewed in this work did not include an economic analysis. As additional information on corrosion of construction materials is collected a complete engineering analysis including an economic analysis needs to be performed.

In summary, information exists in the literature that is relevant to the selection of materials for design, construction and operation of a supercritical CO₂ Brayton cycle – liquid sodium reactor system. However, the database of knowledge is far from complete and additional information is needed on corrosion, primarily in the areas of long-term corrosion testing, corrosion under conditions of supercritical CO₂ at high temperatures, carburization in liquid sodium, and corrosion of diffusion bonded materials. Finally, a number of research areas have been identified which, if pursued, will go a long way towards filling these knowledge gaps, enabling the pursuit of larger scale systems with significant reduction in technological risk.

1.0 INTRODUCTION

Because of its high thermal efficiency and small footprint, the supercritical CO₂ Brayton Power Cycle coupled with a sodium cooled reactor has received considerable interest as a next generation power system. Whereas sodium cooled reactors have been successfully demonstrated, the supercritical CO₂ Brayton cycle is still in the demonstration phase and coupling these technologies presents significant challenges including the selection of construction materials that are corrosion resistant to the widely varying chemical, pressure and thermal conditions of the system. In this report, the available literature data on the corrosion of metals in CO₂, liquid sodium and the reaction between CO₂ and liquid sodium are reviewed.

The supercritical CO₂ Brayton cycle is very appealing for several reasons. Compression of CO₂ near the critical point requires less compressor work due to the rapid increase of CO₂ density with a small increase in pressure (Dostal et al., 2006; Utamura, 2010). This allows for the cycle to be significantly more efficient than a conventional steam Rankine cycle, particularly in the configuration of a highly recuperated split-flow recompression Brayton system. These advantages result in a power conversion cycle that is capable of reaching efficiencies as high as 45-50% in a more moderate temperature range (550-700°C) than for a comparable helium Brayton cycle (Figure 1). This temperature range suggests the use of common industrial materials such as stainless steels and Inconells in construction of piping systems and heat exchangers in contact with CO₂ flow.

Due to its high density, the supercritical CO₂ power conversion system has a small compressor and very small piping in comparison to most Brayton systems. Moreover, the sizeable molecular weight of CO₂ leads to smaller turbines compared to helium or steam (Sardain, et al., 2007). These factors point to the prospect of a power conversion facility with an overall smaller footprint and decreased capital cost. Much of this advantage depends on the availability of affordable compact heat exchangers, as is discussed in the following chapter.

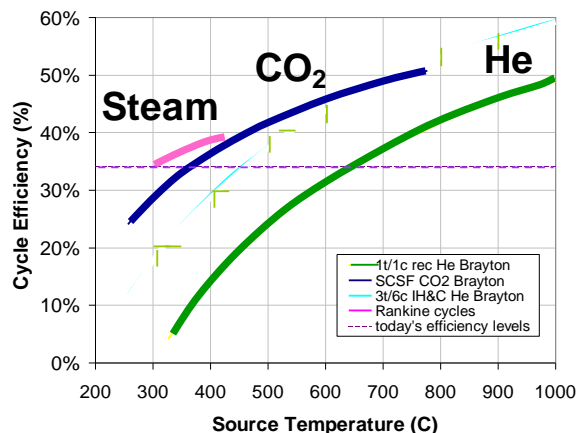


Figure 1 A comparison of thermal efficiency vs. temperature for various power cycles.

The use of liquid sodium as a reactor coolant was first investigated more than 50 years ago and several reactors have been constructed and operated. Sodium has a very low vapor pressure and can be operated at higher temperatures than water as a reactor coolant resulting in higher reactor efficiency. The main concern with sodium reactors is safety. Sodium, in the solid or liquid state, reacts violently with water. The reaction is highly exothermic with the reaction products being NaOH and H₂.

Heat from a liquid sodium cooled reactor is transferred to a supercritical CO₂ Brayton cycle through the system's primary heat exchanger. Figure 2 shows a rough depiction of a sodium reactor coupled with a split-flow recompression supercritical CO₂ cycle. In this example, sodium passes through the primary heat exchanger (in blue), elevating the CO₂ working fluid to 525°C. This is then passed through a turbine, and the high and low temperature recuperators (HT Recup and LT Recup), before the main flow is split off in two directions: one leg through the waste heat rejection unit and back to the main compressor, and the other leg to the recompressor. For optimum efficiency and to maintain compactness of the system layout, the primary heat exchanger coupling the supercritical CO₂ to the sodium reactor must be highly efficient with a large heat transfer area and low pressure drop. This can be accomplished using a microchannel heat exchanger such as the Printed Circuit Heat Exchangers (PCHEs) constructed by the Heatric Corp. Microchannel heat exchangers have demonstrated a very high efficiency of over 98% (Utamura, 2010). These units are typically constructed using diffusion bonding (Takeda et al., 1997, Li et al., 2011). Additional highly efficient heat exchangers are required in other sections of the supercritical Brayton cycle for heat recuperation and heat rejection.

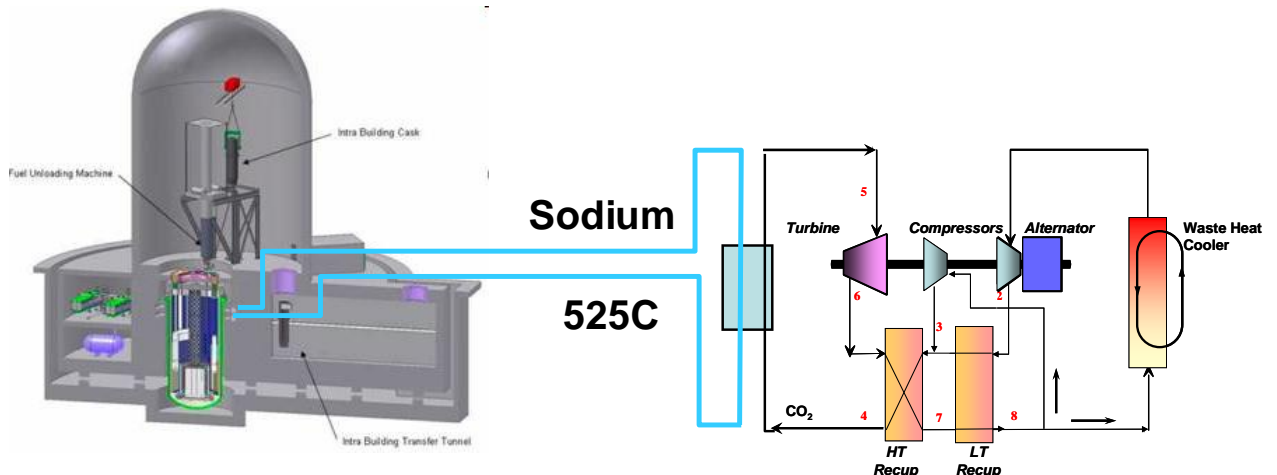


Figure 2 Schematic of a system layout for a coupled sodium reactor and supercritical CO₂ power conversion unit.

In a CO₂-liquid sodium power production system, corrosion may occur in the liquid sodium coolant loop, supercritical CO₂ power generation loop or from a leak in the primary heat exchanger resulting in a chemical reaction between CO₂ and liquid sodium. There is a significant, but by no means complete, body of knowledge on the corrosion of metals in liquid sodium and CO₂. Only a limited amount of information exists on the reaction and reaction products between CO₂ and liquid sodium with some discrepancies in the reported information. Additionally, much more data is available for steels than nickel based alloys that are more resistant to corrosion under harsh conditions but are much more expensive.

The database of knowledge for the corrosion of metals in supercritical CO₂ is relatively small and only a few studies have been performed at very high temperatures in the region where the supercritical CO₂ Brayton cycle operates most efficiently. Additionally, information is also lacking on the effect of contaminants and additives for supercritical CO₂ induced corrosion. Sources of CO₂ corrosion data include studies performed for the petroleum industry where CO₂ is transported in mild steel pipelines and used in enhanced oil recovery operations, studies of the CO₂ cooled Magnox nuclear reactors, and recent studies focused on advanced power cycle applications. No information could be located on supercritical CO₂ corrosion of diffusion bonded materials or components such as the microchannel heat exchangers being evaluated for use in supercritical CO₂ Brayton Cycles.

At low temperature, <500°C, pure liquid sodium is not corrosive to steels and nickel based alloys to any significant degree. However, higher temperatures and the presence of impurities such as O₂ can enhance corrosion. In general, corrosion rates for the austenitic steels increase exponentially with temperature and linearly with oxygen content and sodium velocity up to approximately 3 m/s (Chopera and Nateson, 2007).

Carburization may be a potentially significant mechanism for corrosion in a CO₂ – liquid sodium system. Carburization causes steel to lose strength and become brittle. Carbon and nitrogen are known to migrate in monometallic and bimetallic sodium loops due to differences in chemical activities of the elements in nonisothermal systems and different metals. (Chopera and Nateson, 2007). Carbon could be introduced into the liquid sodium loop through a leak in the primary heat exchanger. CO₂ would enter the liquid sodium loop and the subsequent reaction would form carbon as one of the reaction products.

Materials selection for any system is based on the need to successfully operate in the particular environment balanced against materials and maintenance costs. A wide range of chemical and physical conditions exist within the supercritical CO₂ Brayton cycle and the liquid sodium reactor. The results from this investigation indicate that significantly more information on supercritical CO₂ corrosion is needed for designing supercritical CO₂ Brayton power cycles. The effect of temperature, pressure, presence of contaminants, and other process variables need to be further investigated in detail.

2.0 MICROCHANNEL HEAT EXCHANGERS

The primary heat exchanger for transferring high temperature heat from the sodium coolant to the supercritical CO₂ for power production must be capable of withstanding very high temperatures and pressures and the harsh conditions present in a sodium-supercritical CO₂ power production cycle. Also, as previously discussed, a microchannel heat exchanger is desirable for a large heat transfer area and small footprint. There are very few manufacturers of these types of heat exchanger. Heatric, a United Kingdom based company, is best known for microchannel Printed Circuit Heat Exchangers (PCHEs). Figure 3 shows a cross-sectional view of the perpendicular microchannels of a typical Heatric PCHE, and also a comparison of physical size and mass for a shell and tube unit vs. a microchannel PCHE for the same heat transfer rating. The large reduction in mass suggests the possibility of reduction in material cost of the units, though these cost savings have not yet been realized in practice.



Figure 3 (L) A cross-sectional view of the microchannels in a Heatric PCHE
(R) A schematic of the size and mass reduction for a Heatric PCHE.

The heat exchangers in the supercritical CO₂ Brayton system are subjected to a wide range of operating environments. The heat input temperature for the supercritical CO₂ Brayton cycle can range from 500 to >600 °C, depending on system design, whereas heat rejection occurs near the critical point (31°C). Carbon dioxide is supercritical at pressures exceeding 73 atm, though the hot leg CO₂ pressure typically exceeds 200 atm (3000 psi) within the primary heat exchanger. On the other side of the primary heat exchanger, the liquid sodium remains near ambient pressure. The large pressure differential between the sodium and CO₂ microchannels in these units at nominal operation is one reason for concern in design. Likewise, the heat rejection heat exchanger (gas chiller) will face a larger pressure differential between CO₂ near the critical point (1000psi) and water at ambient pressure.

As noted earlier, the supercritical CO₂ power conversion system is a highly recuperated cycle, requiring as much as 3-4 times more recuperation power than the reactor thermal power level to reach optimum efficiency. Therefore the heat transfer

area and mass of the high and low temperature recuperators will be a dominant concern in attempting to keep system layout relatively compact and affordable. These units will face high pressure CO₂ on both the hot and cold side microchannels, and consequently pressure differentials are greatly reduced.

Sandia National Labs, with subcontractor Barber Nichols Inc., is building a Split-Flow Recompression Brayton Cycle Demonstration System. This system has been designed for a 780MW thermal power input, a 2.3MW rated high temperature recuperator, a 1.6MW-rated low temperature recuperator, and a 0.5MW heat rejection unit. While the power input takes place in Watlow shell and tube heaters, the other heat exchangers are Heatric-brand PCHEs. One of the goals of this demonstration is to confirm the ability of these microchannel heat exchangers to perform as advertised in a compact package. Photographs below show the recuperator units as installed on the Sandia test loop (Figure 4).

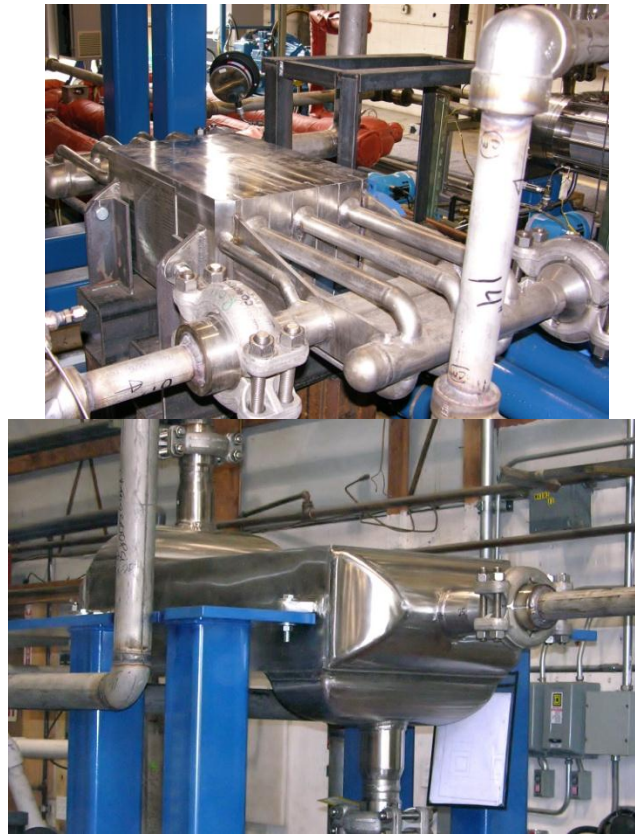


Figure 4 Heatric PCHEs are shown from the Sandia Split-Flow Recompression Brayton Demonstration System: (L) the Low Temperature Recuperator, and (R) the High Temperature Recuperator.

For optimal strength microchannel heat exchangers are typically constructed using diffusion bonding. Diffusion bonding is a solid state process where metal components are joined by placing them together under high pressure and high

temperature, but significantly lower than the melting temperature of the metal. In comparison to conventional welding, diffusion bonding typically does not produce a heat-affected zone (Takeshi et al., 1997).

Yeh and Chuang (1995) studied the low pressure diffusion bonding of SAE 316 stainless steel using a superplastic interlayer made of SuperDux 65 stainless steel. The resulting diffusion bonded material exhibited higher tensile strength and % elongation of the base metal. Additionally, failure did not occur in the bond plane but in the base metal.

Takeda et al., (1997) performed a feasibility study on the applicability of a diffusion-welded compact intermediate heat exchanger for the next generation high temperature gas-cooled reactor. The heat exchanger was constructed of Hastelloy XR plates joined by solid state diffusion welding. In their work, a small scale diffusion-welded concavo-convex plate compact heat exchanger was constructed and installed in a test loop. No leaks were observed for tests at ambient temperature and 63 MPa. The heat exchanger was not tested under pressure at higher temperatures.

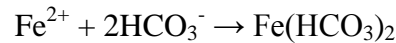
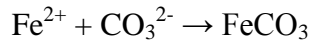
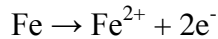
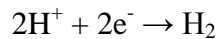
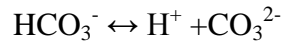
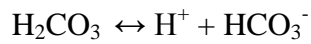
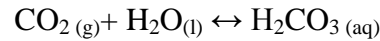
Li et al., (2011) investigated the corrosion of diffusion bonded 316L stainless steel using an electrochemical potentiokinetic reactivation method. Samples of the metal were diffusion bonded at 1100°C for 2, 8, 30, 50 and 100 h. After bonding the samples were examined and chromium carbides were observed in the base metal but not in the diffusion bonded joint. The authors conclude that diffusion bonding will not increase intergranular corrosion susceptibility of 316L stainless steel.

Although no information on supercritical CO₂ induced corrosion of diffusion bonded joints could be located, the literature data indicates diffusion bonding of certain metals is as strong as the based metal and suggests corrosion of the joints would not be a problem. However, the information on this subject is very limited. A small scale diffusion bonded heat exchanger needs to be tested under the operating conditions of a full scale supercritical CO₂ Brayton cycle.

3. CARBON DIOXIDE INDUCED CORROSION

3.1 Corrosion Mechanism and Passivation in CO₂

Dry CO₂ is considered practically inert at low temperatures. However, in the presence of even small amounts of water carbonic acid forms that is quite corrosive to many metals. The mechanism of CO₂ corrosion of iron and mild steel in an aqueous environment is given by:

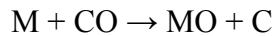
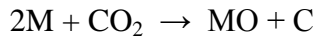
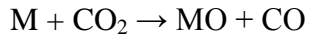


Below temperatures of 360°C magnetite, FeCO₃ acts as a protective layer on the steel. Above this temperature and with high CO₂ pressures, breakaway oxidation can occur through the formation of a duplex layer and carburization (Madina, 2008). Carburization is a potentially significant mechanism of metal degradation and is discussed in detail in proceeding sections of this report.

Although it is well established that CO₂ is corrosive in the presence of water, recent data indicates dry CO₂ may be corrosive under certain conditions. Based on computer simulations, Glezakou et al., 2000 indicated that corrosion of metal surfaces can happen in the presence of very small amounts of water or complete absence of water when very high temperatures exist. The authors state in the absence of water, CO₂ can dissociate and react with other CO₂ molecules to form CO₃²⁻.

Oxidation of Fe-Cr steels is dependent upon the Cr content. Steels containing less than 9-12% Cr form a duplex scale comprising an outer layer of iron rich oxide and an inner layer of Cr-Fe spinel. Ferritic steels containing greater than 20% Cr will form a single Cr₂O₃ oxide. Ferritic steels with a Cr content between 12 and 20% will form either a single layer of Cr₂O₃ or a duplex spinel oxide (Gibbs, 2008).

For *austenitic* steels, defined as having a maximum C content of 0.15% and minimum Cr content of 16% with a face centered cubic structure, several reactions commonly occur in a CO₂ and O₂ environment given by:



where M is a metal in the steel. The formation of C can lead to carbide formation. However, once a protective oxide layer has been established these reactions cease. The high Cr content in austenitic steels enables the formation of a Cr₂O₃ layer that is highly protective (Gibbs, 2008).

Nickel based alloys, such as Inconel and Hastelloy, form a continuous protective oxide layer. Gibbs (2008) states the protective layer is composed of 50% NiO and 50% Cr₂O₃. Both of these oxides are highly stable.

Carburization is a corrosion process in which carbon diffuses into a metal resulting in hardening and a decrease in ductility of the material. If sufficient carbon diffuses into the metal it transforms from an austenite to a martensite material and the metal becomes brittle, loses its strength and can no longer be welded. A common method for carburization of metals is to expose it to a carbon source in a liquid sodium bath. Therefore, in the event of a leak in the primary heat exchanger of a supercritical carbon dioxide/liquid sodium power system, CO₂ and liquid sodium will mix with carbon being a product of the reaction. Therefore, carburization is a potential problem in this system.

3.2 Corrosion Studies in Supercritical CO₂

Table 1 lists the available corrosion studies of metals in supercritical CO₂ reported in the literature along with the results of the studies. The composition of all of the steel alloys listed in Table 1 is given in Appendix A. The studies have been separated into low and high temperature studies.

The influence of cosolvents on metal corrosion in supercritical CO₂ is reported by Russick et al., 1995. The cosolvents selected are used to enhance the solubility of polar and ionic compounds in supercritical CO₂ for cleaning applications. The cosolvents included water, methanol, tetrahydrofurfuryl alcohol. Sample coupons of the metals 304L and 316 stainless steels, aluminum grades 2024, 6061 and 7075, 1018 carbon steel and CDA 101 copper were statically exposed to pure supercritical CO₂ and mixtures of the cosolvents and supercritical CO₂ at 323K and 3500 psig for 24 hours. The samples were examined by gravimetric analysis,

visual inspection, electron microprobe analysis, X-ray photoelectron spectroscopy and Auger electron spectroscopy. The results indicated no evidence of corrosive attack on any of the metals by pure supercritical CO₂.

Water saturated supercritical CO₂ significantly attacked 1018 carbon steel. 2024 aluminum and CDA101 copper were attacked in a 10% methanol supercritical CO₂ environment. Both stainless steels showed no change with the exception of a white residue on the surface in the 4% tetrahydrofurfuryl alcohol supercritical CO₂ tests. An elemental analysis indicated the residue is primarily organic and is believed to be caused by inhibitors added to the tetrahydrofurfuryl alcohol to prevent degradation of the alcohol to form ethers.

The corrosion rate of carbon steel in supercritical CO₂ with varying amounts of water is reported by Thodla et al., 2009. Tests were performed at 31°C and 1150 psi under static conditions with water amounts varying from 0 to 1000 ppm and with 0 to 1000 ppm of Mono ethanol Amine, a corrosion inhibitor. The results indicated even small amounts of water can cause high corrosion rates in carbon steel, 1-2 mm/yr, and the presence of MEA can significantly decrease the corrosion rate.

Choi et al., 2000 reports on corrosion studies of carbon steel in supercritical CO₂ saturated with water and containing O₂ and SO₂ as impurities. Experiments were performed at 50°C and 80 bar for 120 hours in a static apparatus. O₂ was found to significantly enhance corrosion rates.

Corrosion testing in supercritical CO₂ was performed for 10 metals by Loriers et al., 1968. All of the alloys had Cr, Mo and Ni concentrations less than 2.5%, 1.0% and 0.6%, respectively. Testing was performed at 550°C, and 60 bar for 6000 hours. All metals exhibited significant corrosion. The alloy containing the highest Cr and Mo concentrations of 2.5% and 1.0% showed acceptable corrosion resistance up to temperatures of 525°C. The effect of water on corrosion is shown in Figure 5. In general, the alloys with high Ni content and high Cr exhibited the best corrosion resistance. The effect of pressure on corrosion rate is given in Figure 6. Over the range of pressures tested, 25 to 50 bar, there is little effect of pressure on corrosion.

The use of organic corrosion inhibitors is limited to low temperatures where the organic will not thermally degrade. The use of amines to inhibit CO₂ corrosion of metals is described by Fan et al., 2003. Corrosion inhibiting formulations are given comprising amino thiol or amino disulfide compounds with acidic amino acid polymers. Another study by Lopez et al. (2003), indicates benzimidazole is also an effective inhibitor against CO₂ corrosion.

Table 1 Corrosion studies of metals in supercritical CO₂

Study Description	Testing Temperature, Pressure and Duration	Materials and Testing Method	Results	Reference
Low Temperature Studies				
Corrosive effects of cosolvents on corrosion in supercritical carbon dioxide	50°C, 350 psig, 24 hours	304L.s.s., 316s.s., aluminum grades 2024, 6061 and 7075, carbon steel 1018, copper CDA 10. Static tests. Cosolvents were water, methanol and tetrahydrofurfuryl alcohol.	No evidence of corrosive attack on any of the metals by pure supercritical CO ₂ . Water saturated supercritical CO ₂ significantly attacked 1018 carbon steel. 2024 aluminum and CDA101 copper were attacked in a 10% methanol supercritical CO ₂ environment.	Russick et al., 1995
Materials performance in supercritical CO ₂ environments in the presence of small amounts of water	31°C, 1150 psi, 24 hours	Carbon steel. Water at concentrations of 100 ppm and 1000 ppm.	Small amounts of water (100 ppm) can cause high corrosion rates in carbon steel. Amine inhibitors were used to significantly reduce corrosion rates.	Thodla et al., 2009
Effect of impurities on corrosion of steel pipe in supercritical CO ₂ saturated with water	50°C, 80 bar, 120 hours	Carbon steel (API 5 L X65). Static testing.	Very high corrosion rate. Corrosion enhanced significantly with O ₂ present.	Choi et al., 2010
High Temperature Studies				
Corrosion of 10 metals in supercritical CO ₂	550°C, 60 bar, 6000 hours	All low Cr steel. Alloys compositions are presented in Appendix A	2.5% Cr, 1% Mo steel had acceptable corrosion resistance up to 525°C. All other steels showed significant corrosion.	Loriers et al., 1968
Oxidation of mild and low alloy steels in CO ₂ .	500°C, atm. 20 atm., 4000 - 10000 hours	Pure Fe, rimming steel, 3 low alloy steels. Static testing. Small amounts of H ₂ O and CO.	Water was shown to significantly enhance the corrosion rate of several alloys.	Antill et al., 1968
Electrochemical Impedance Spectroscopy used to study the surface film of carbon steel .	90°C, 8.274 MPa, 24, 96 and 144 hours	Carbon steel. Testing in supercritical CO ₂ with simulated produce water. Static testing	Tests performed at The protective film that forms on the steel surface is enhanced with increasing exposure time and that films formed at higher temperatures were more protective than ones formed at low temperature because the film was more compact and continuous	Wu et al., 2004
Supercritical CO ₂ Brayton Cycle development at INL	1000°C, 10 Mpa, 500 hours for MA754. 1000°C, 7 MPa, 175 hours for I-617	Alloys MA 754, I-617.	Significant intergranular corrosion of I-617 was observed. Uniform corrosion of MA 754. High corrosion rate at first then corrosion rates quickly decreased.	Totemeier, T.C. and T.M. Lillo 2005; Totemeier et al., 2005; Oh, et al., 2004, 2006
Corrosion testing of various alloys in supercritical CO ₂	650°C, 11.5-22.5 MPa, 1000 to 3000 hours.	316L, MA956, MA957, PM2000, HT9, TP1, Russian EP823	Materials that formed alumina/chromia scale (MA956 and PM2000) are most resistant to general corrosion. 316L performed the worst but was acceptable.	Lim et al., 2008
Corrosion testing in supercritical CO ₂	550°C, 250 bar, 310 hours	T91, 316L, 800H and S30815. Static tests.	High Cr austenitic steels more corrosion resistant than martensitic steels.	Rouillard et al., 2010
Corrosion of FBR structural materials in supercritical CO ₂	400 - 600°C, 20 Mpa, 2000 hours	12Cr steel, 316 s.s. CO ₂ circulated over samples.	High Cr 316FR steel performed significantly better than 12Cr martensitic steel. Carburization was observed for both steels.	Furukawa et al., 2010
Corrosion testing of various alloys in supercritical CO ₂	650°C, 20 Mpa, up to 3000 hours	F91, HCM12A, 316s.s., 310s.s., AL-6XN, 800H, Haynes 230, Alloy 625, PE-16, PM200.	Alloys with high Cr and Ni content performed best followed by stainless steel with intermediate Cr content.	Gibbs, 2010
Corrosion testing of pure iron and Cr, Al and Si containing allows to high temperature CO ₂	800C, low pressure.	Pure Iron and model alloys containing 2.25, 9, and 20 wt% Cr, 2, 4 and 6 wt% Al, 1, 2 and 3 wt% Si, and dilute Fe-Si-Al ternaries exposed to dry and wet CO ₂ .	Exposure of pure iron to CO ₂ with increasing H ₂ O concentration indicated that neither of these oxidants has a strong influence on the growth mechanism of FeO surface films. Cr ₂ O ₃ growth was affected, with low Cr alloys failing to form protective scales in both wet and dry CO ₂ . Alloys containing 6% Al or with both Al and Si showed excellent oxidation resistance in dry CO ₂ . Water vapour accelerated the oxidation rate of all binary alloys except alloy Fe-3Si.	Thomas et al., 2010
Experience from Magnox CO ₂ cooled reactors	up to 600°C, 4 Mpa (subcritical)	Mild steel. Results from operation of Magnox reactors. Temperatures up to 600°C. 4 MPa CO ₂ (subcritical)	Significant oxidation of structural mild steels at temperatures above 350°C. Corrosion was more significant than anticipated based on initial corrosion testing.	Shropshire, 2004

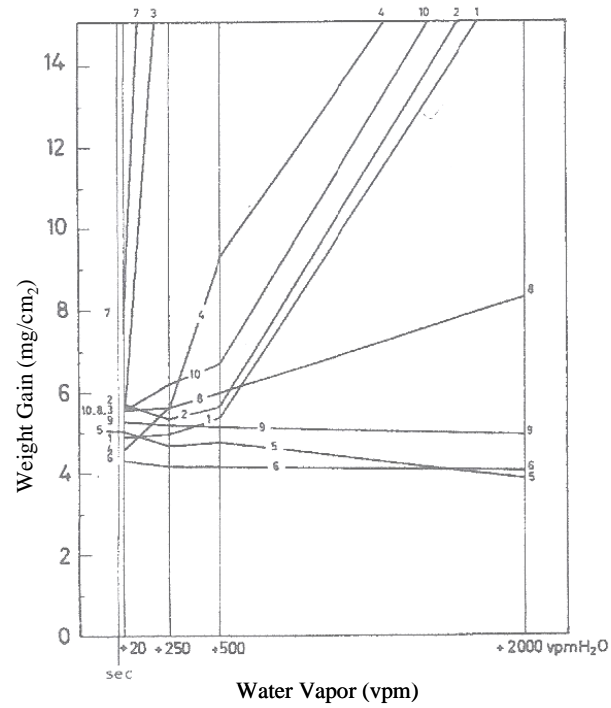


Figure 5 Effect of water vapor concentration on corrosion of various alloys. (Lorier et al., 1968)

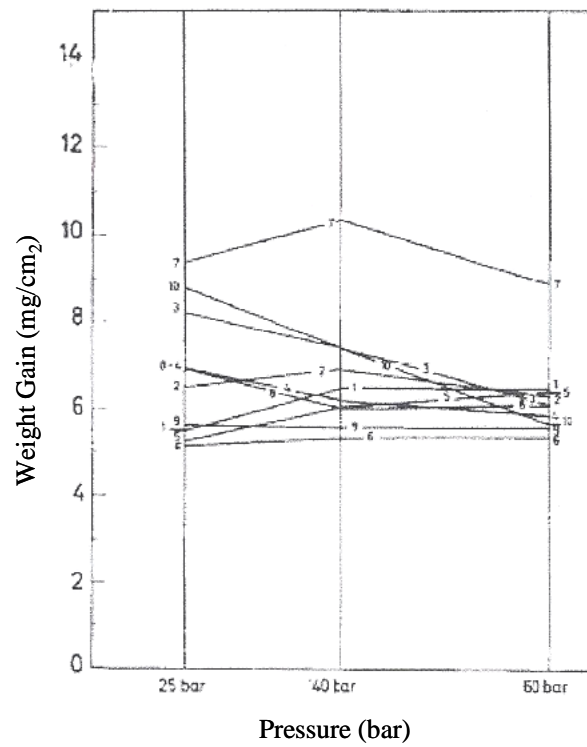


Figure 6 Effect of pressure on corrosion of various metals. (Loriers et al., 1968)

The corrosion of pure iron, rimming steel and three low alloy steels is reported by Antill et al., 1968. Testing was performed at 500°C and 1 or 20 atm for 4000 to 10000 hours. The results for tests performed with and without water present are given in Figure 7. The presence of water was shown to significantly increase the corrosion rate of low alloy steel A but did not significantly affect the corrosion rate of the other metals tested. The corrosion rate of pure iron decreased in the presence of water. The authors state typically, for mild steels, a protective layer of magnetite forms at temperatures less than 350°C. Non-protective oxides are often formed at temperatures of 400°C and above. It has been established that the formation of a non-protective oxide layer requires the presence of water and high pressures of CO₂.

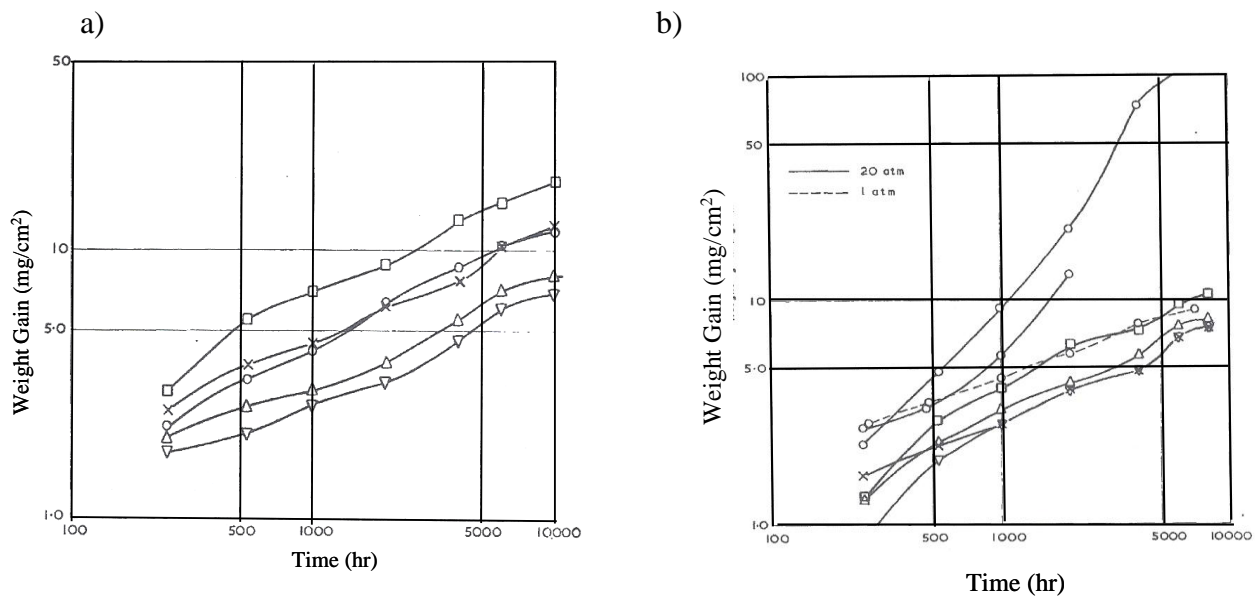


Figure 7 Weight gain vs. time at 500°C for pure iron, x rimming steel, o low alloy steel A, Δ low alloy steel B and √ low alloy steel C in a) dry CO₂ at 1 atm and b) CO₂ saturated with H₂O. (Antill et al., 1968)

Electrochemical impedance spectroscopy was used by Wu et al., 2004 to investigate the characteristics of the surface film formed on carbon steel in simulated produced water saturated with supercritical CO₂. The simulated produced water consisted of a solution of 15 g/L CaCl₂ and 1.1g NaHCO₃ with a pH of 5 ± 0.5. The mechanism of corrosion is the same previously presented by Glezakou et al., 2009. Tests were performed in a high-pressure static autoclave at 90°C and 8.274 MPa CO₂ for 4 to 8 hours. The results indicated the protective film that forms on the steel surface is enhanced with increasing exposure time and that films formed at higher temperatures were more protective than ones formed at low temperature because the film was more compact and continuous.

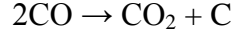
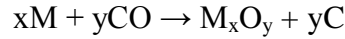
Research on creep behavior and corrosion of alloy MA 754 in supercritical CO₂ is reported by Oh et al., 2004, 2006. Material testing was performed at 1000°C and 1500 psi in time ranges from 47 to 335 hours. The authors concluded that MA 754 possessed high creep resistance at 1000°C better than other high temperature metal alloys and exhibited acceptable corrosion resistance to supercritical CO₂. An examination of the metal surface showed a thin deposit that was green in color indicating the presence of nickel or chrome oxide. At short exposure times the corrosion rate was high, but decreased significantly over time indicating the layer may provide protection. Initial corrosion rates, for exposure times less than 100 hours, ranged from approximately 2 to 4.5 mm/year. After 300 hours exposure time the corrosion rate decreased to approximately 1.0 mm/year.

Lim et al., 2008 reports on corrosion testing of the alloys 316L, MA956, MA957, PM2000, HY9, T91 and Russian alloy EP823 in supercritical CO₂ at 650°C and CO₂ pressures from 11.5 - 22.5 MPa for 1000 to 3000 hours. Testing was performed in a “bleed and feed” autoclave with a CO₂ flowrate of approximately 1L/hr. The results indicated that alumina/chromia film forming metals have superior general corrosion resistance. However, these same materials may be susceptible to localized corrosion. 316L s.s. exhibited the poorest performance, but corrosion resistance was categorized as acceptable.

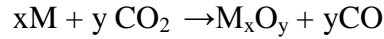
Rouillard et al., 2010 performed corrosion studies of different metallic materials in supercritical CO₂ at 550°C and 250 bars. Impurities in the CO₂ media were 6 volumes per million water and 2 volumes per million O₂. The materials were tested in a static environment and included 9wt% Cr ferric-martensitic steel (T91) and the austenitic alloys 316L, 800H and S30815. The corrosion products were examined using Glow Discharge Optical Emission Spectroscopy, Scanning Electron Microscopy, Wavelength-Dispersive Spectroscopy and X-Ray Diffraction. The results indicated the austenitic alloys 316L, S30815 and alloy 800 were much more corrosion resistant than the ferritic-martensitic T91 steel. After 310 hours, a thin protective chromium rich oxide layer forms on the austenitic steels whereas a thicker iron rich duplex scale grows on the T91 steel. No spalling was observed for any of the metals tested. The detrimental effect of the thick iron rich layer on the T91 steel would be a reduction in heat transfer if the material was used for heat exchanger construction. The authors indicate longer term corrosion testing is underway. An analysis of the corrosion layer in the Rouillard et al. study indicated it was composed of two layers; an outer layer of Fe₃O₄ and an inner layer of Fe(Fe_{1.61}Cr_{0.69})O₄. Carbonization was also detected. The authors propose the formation of the metal oxides and carburization could be through the direct reaction of CO with the metal and/or through the Boudouard reaction.

Other than the formation of FeCO₃ as the corrosion layer, Rouillard et al., (2010) reports carburization can occur when steels are exposed to supercritical CO₂ at high temperatures, 550°C, and high pressures, 250 bars. The authors propose that carburization can be attributed to the direct reaction of carbon monoxide with metal,

either iron or chromium, or through the Boudouard reaction given by the following equations:



where M is the metal, MO the metal oxide and C is elemental carbon. CO would be from the reaction of the metal with carbon dioxide given by:



Furukawa et al., (2010) studied the corrosion behavior of FBR structural materials at 400 - 600°C in supercritical CO₂. The materials tested were high chromium martensitic steel (12Cr) and FBR grade type 316 s.s. (316FR). Tests were performed for 2000 hours. The 12Cr steel demonstrated parabolic weight gain with exposure time. The corrosion layer was identified as two successive oxide layers, Fe-Cr-O as the inside layer and Fe-O as the outside layer. No effect of pressure was observed on oxidation. For the 316FR, the weight gain was significantly lower than for the 12Cr steel. No dependency of either temperature or exposure time on oxidation was observed. Nodule shaped oxides consisting of Fe-Cr-O and Fe-O were observed on the 316FR specimens. Carburization was observed for both steels.

The oxidation of dilute iron-silicon alloys in carbon dioxide is reported by Moseley et al., (1982). Samples of polycrystalline iron doped with varying amounts of Si, 0-1%, were exposed to a gas composition of 99% CO₂/1% CO at ambient pressure and 500°C. Corrosion rates significantly decreased with the increase in Si.

Gibbs (2010) reports corrosion testing of ten alloys were tested in supercritical CO₂ for up to 3000 hours at 650C and 20 MPa. The alloys studied were F91, HCM12A, 316SS, 310SS, AL-6XN, 800H, Haynes 230, Alloy 625, PE-16 and PM2000. Multiple coupons of each material were tested in an autoclave with fresh CO₂ continuously flowing through the apparatus. Samples were removed every 500 hours for analysis. The results of the testing indicate overall the alloys with high chromium and nickel content were the most resistant to corrosion followed by the stainless steels with intermediate chromium content. The author recommends longer exposure times should be investigated and additional tests should be performed with the materials under stress.

Thomas et al., 2010 studies Iron and model alloys containing 2.25, 9, and 20 wt% Cr, 2, 4 and 6 wt% Al, 1, 2 and 3 wt% Si, and dilute Fe-Si-Al ternaries exposed to dry and wet Ar-CO₂ gases at 800°C at low pressure. Exposure of pure iron to CO₂ with increasing H₂O concentration indicated that neither of these oxidants has a strong influence on the growth mechanism of FeO surface films. Cr₂O₃ growth was affected, with low Cr alloys failing to form protective scales in both wet and dry

CO₂. Alloys containing 6% Al or with both Al and Si showed excellent oxidation resistance in dry CO₂. Water vapor accelerated the oxidation rate of all binary alloys except alloy Fe-3Si.

Young et al., 2010 reports reacting iron and alloys containing 2.25, 9, and 20 wt% Cr, 2, 4 and 6 wt% Al, 1, 2 and 3wt% Si, and dilute Fe-Si-Al ternaries with dry and wet Ar-CO₂ gases at 800°C and low pressures. Pure iron exposed to CO₂ with increasing H₂O concentration showed that neither of these oxidants had a strong influence on the growth mechanism of FeO surface film. Cr₂O₃ growth was affected, with low Cr alloys failing to form protective scales in both wet and dry CO₂. Alloys with 6% Al or containing both Al and Si showed excellent oxidation resistance in dry CO₂. Water vapor accelerated the oxidation rate of all binary alloys except alloy Fe-3Si.

The corrosion of steel samples, cast iron and titanium were corrosion tested in a carbon monoxide and carbon dioxide medium by Kolomogorov and Ershova (1968). Depending on the material being tested, corrosion tests were performed in a synthesizing column or a circulating compressor apparatus. Tests were performed media with CO levels from 60 to 94% at temperatures from 40 to 250°C and pressures from 270 to 300 atm. Test durations were from 600 to 2400 hours and weight loss was used to determine corrosion rates. For corrosion experiments performed in synthesizing columns, the materials with the greatest resistance to corrosion were 30KHMA steel, OkhM steel and 35U steel. Slight pitting was observed for these materials. For materials tested in the circulating compressor apparatus the materials with the greatest corrosion resistance were cast irons SCh 18-36 and SCh 21-40 and steel 40.

3.3 CO₂ Corrosion Experience from the Petroleum Industry

The United States has over 30 years experience with transportation of CO₂ through an extensive pipeline network. CO₂ is used in enhanced oil and gas recovery operations. The CO₂ is mainly from natural sources and relatively free of impurities. It is transported in the dense supercritical state for economical reasons (Seevam et al., 2008).

Dry CO₂ gas is not corrosive at the temperatures encountered within the oil and gas production industry. However, the presence of any water creates a very corrosive environment. Corrosion failures, the majority of which are related to CO₂ corrosion, have been reported to account for 25% of all safety incidents in the oil and gas industry. The majority of CO₂ induced corrosion failures are with mild steels due to the poor corrosion resistance of these materials. Although CO₂ corrosion of low carbon and low-alloy steel has been studied for over 4 decades in the oil and gas production industry it remains a complex phenomenon and its mechanism, realistic prediction and control remain key challenges to facility design, operation and integrity assurance (Kermani and Morshed, 2003; Ropital, 2009).

Supercritical CO₂ transported to wellheads for enhanced oil recovery operations is of high purity, >95% by volume contains only trace amounts of water. However, enhanced oil recovery operations require injection of both CO₂ and water into the well creating a corrosive environment. For this reason, where corrosion may be severe, stainless steels are used instead of mild and alloy-alloy steels. For wellhead construction, Meyer reports 316 s.s. is very resistant to corrosion, but 410 s.s. can suffer from severe pitting.

3.4 Corrosion in the CO₂ Cooled Magnox Reactors

A significant amount of information can be gained by reviewing the operational experience of the British Magnox nuclear reactors. The Magnox reactors were cooled with high pressure subcritical CO₂. Shropshire (2004) presents a summary of lessons learned from operation of the Magnox reactors. The Magnox reactors operated with natural uranium metal fuel and a graphite moderator. The reactor inlet temperature was typically at 330 - 380°C. Operating pressures were typically at 4MPa with temperatures as high as 650°C. The author reports when steels were exposed to CO₂ at temperatures in the range of 350 to 450°C, a thin protective coating of magnesite forms on the steel surface. The coating thickens and ultimately cracks resulting in the formation of pimples and excrescences permitting more rapid oxidation.

Information on CO₂ induced corrosion in the design stage of the Magnox reactors indicated oxidation rates were moderate and mild steel was used for most applications. Stainless steel was used for essential applications. If mild steels had not been extensively used then construction cost would have been cost prohibitive.

Corrosion tests were performed on materials during the design phase of the early Magnox reactors. Materials identified with excellent resistant to CO₂ corrosion were 18/8/1/ stainless steel, Commercial Al and sintered Al powder. These materials showed no attack after 5 months. Materials rated as good against CO₂ corrosion with oxidation rates of approximately 0.1 mg/cm² were pure Mg, Magnox C, Mg alloy AM503 and Al alloy RR58. Mild steel has a corrosion rate of 0.15 to 1.11 mg.cm² and cast iron was 2.72 mg/cm². However, oxidation of certain components was significantly greater than determined in corrosion experiments.

The main conclusions from the Shropshire study were:

- Corrosion testing at 400°C indicated moisture almost doubles corrosion rates.
- Oxidation rates were predominantly influenced by operating temperature and rates doubled for every 25°C increase in temperature.
- High silicon steels were more resistant to oxidation than steel with low silicon content.

- Alloys with high Cr and/or high Cr and Ni were very resistant to CO₂ induced corrosion.
- Oxidation was most severe on trapped surfaces between nuts and bolts and the surfaces held together by them.

Carbon deposition on the fuel cladding proved to be a problem with the Magnox reactors. Carburization occurred according to the Boudouard reaction in which CO is formed from radiolysis of the CO₂ coolant. CO has the beneficial effect of preventing radiolytic corrosion of core graphite. Therefore, CO levels in the coolant needed to be optimized to balance the negative effect of carbon deposition against the positive effect of core graphite protection.

4.0 CORROSION IN LIQUID SODIUM

4.1 Corrosion of Steels

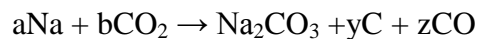
An excellent review of sodium corrosion of certain austenitic and ferric steels is given by Chopera and Nateson (2007). The report discusses corrosion rates and mechanisms for type 304 and 316 s.s. and Fe-2 ½ Cr-1Mo and Fe9-Cr-Mo ferric steels. Additionally, other degradation mechanisms including interstitial element transfer, thermal creep, fatigue and creep, fatigue and creep-failure, thermal aging, neutron radiation damage and carburization- decarburization are discussed. Nickel based alloys were not covered in the study.

Chopera and Nateson (2007) draw the following conclusions from their study: 1) The corrosion behavior of austenitic s.s. in liquid sodium between 455 to 755°C, oxygen concentrations from 1 – 30 ppm and sodium velocities from 0.1 to 12 m/s is well documented; 2) The austenitic steels are more corrosion resistant to liquid sodium than the ferric steels however more work is required for alloy Fe9-Cr-Mo. Corrosion rates for the austenitic steels increase exponentially with temperature and linearly with oxygen content and sodium velocity up to approximately 3 m/s; and 3) Carbon and nitrogen are known to migrate in monometallic and bimetallic sodium loops due to differences in chemical activities of the elements in nonisothermal systems and different metals. The migration of carbon is of particular significance because it can result in metal carburization-decarburization a potentially serious corrosion mechanism.

4.2 Reaction Products of CO₂ and Liquid Sodium

A leak in the primary heat exchanger would result in high pressure carbon dioxide entering and mixing with the liquid sodium. This would result in pressurization of the low pressure liquid sodium loop and a chemical reaction between the carbon dioxide and liquid sodium. (Corradini et al., 2010) The reaction products and their chemical behavior in the system need to be known for materials selection and system design.

A review of the literature data for the reaction of steels in liquid sodium and carbon dioxide is presented by Latge et al., 2005. The authors indicate the main reaction products to be Na₂CO₃, Na₂O, Na₂O₂, C and CO. The results from another recent study where carbon dioxide was injected into liquid sodium is reported by Miyahara et al., 2011. In that work, Na₂CO₃, CO and C were identified as the major reaction products of with the overall reaction represented as:



An analysis of the reaction products indicated it was composed mainly of Na_2CO_3 . Carbon was present only in very small amounts, 0.4 – 0.7 weight percent. The authors report the formation of only trace amounts of Na_2O_2 . Additionally, the authors indicate, because of the analytical method they used, that impurities in the experiment may have given a false positive result for the presence of Na_2O_2 . However, the authors report 8.8 – 18.1 % of the reaction products were not identified in their work and are reported as unknown material.

Based on the results of the two studies, the products of reaction between liquid sodium and carbon dioxide can potentially lead to serious problems. The sodium carbonate formed could plug sections of the heat exchanger, plate out on cooling system piping or in the reactor and affect heat transfer. Carbon in the liquid sodium can cause carburization corrosion and significantly decrease the service life of materials. Carburization in the main heat exchanger could force the replacement of this expensive component involving a lengthy shut down of the system.

4.3 Heat Exchanger Plugging and Damage

The formation of sodium carbonate in the main heat exchanger can result in plugging of a flow channel or sodium carbonate coating surfaces that decrease heat transfer. Eoh et al., (2010) investigated a wastage phenomenon in regard to structural damage adjacent to the leak position and potential channel plugging by the reaction products of CO_2 and liquid sodium. The results of their study indicate no further damage occurs near the CO_2 leak, but self-plugging of the channel can take place under certain conditions; sodium temperatures over 500°C and the equivalent diameter of the crack opening is less than 1.5 mm with a leak rate of less than 1 g/s of CO_2 . The testing was performed with a heat exchanger with 2.0 mm dia. Sodium channels and 1.5 mm dia. CO_2 channels.

4.4 Carburization/Decarburization

Because carbon is a product of the reaction between CO_2 and liquid sodium and it can potentially be formed in large quantities in the event of a leak in the primary heat exchanger, carburization is of particular interest for a coupled sodium reactor-supercritical CO_2 Brayton cycle. Carbon is only sparingly soluble in liquid sodium. Ainsley et al., 1974 measured the solubility of carbon in liquid sodium between 490 and 832°C . At 600°C , the solubility of carbon in liquid salt is 5 ppm. However, even low concentrations of carbon in sodium can cause severe embrittlement of austenitic stainless steels (Anderson and Sneesby, 1960; Andrews et al., 1965; Kolodney, 1968). Carburization of austenitic steel in sodium exposed to 0.4 ppm carbon at 550°C has been shown to significantly reduce rupture life and increase the minimum creep rate of the metal (Chopra and Natesan, 2007). On the

other hand, low-alloy ferric steels may lose carbon, decarburization, to sodium and become weaker as a result (Kolodney, 1968).

Carburization resistance in alloys is conferred almost entirely by the protective oxide scale along with the nickel content of the metal. The presence of chromium and silica also enhances carburization resistance. High nickel alloys resistant to carburization are RA330, RA333, RA600, RA353 MA, RA601 and RA602 CA. 800H lacks silicon and does not perform as well.

The extent of carburization is strongly dependent on the concentration of carbon, exposure time and temperature. Processes for carburization of metals is typically performed at a very high temperature process, $>800^{\circ}\text{C}$. However, carburization can occur at significantly lower temperatures. Snyder et al., 1973 reports carburization of austenitic s.s. in liquid sodium at temperatures ranging from 400 to 800°C .

Snyder et al., 1974 presents a mathematical analysis and model for the carburization-decarburization kinetics of austenitic s.s. in high-temperature flowing sodium. The analysis was used to evaluate carburization-decarburization of 316 s.s. and 304 s.s. for fuel cladding and primary and secondary heat exchangers in nuclear reactors for periods up to 30 years. The results indicate carbon migration in steels is inevitable at temperatures between 400 and 800°C . The amount of carburization or decarburization is strongly dependent upon the temperature and carbon concentration in the sodium. The initial carbon concentration and the thermal mechanical treatment of the metal have a smaller influence on carbon-diffusion profiles.

The corrosion behavior and tensile properties of ANSI 316LN s.s. exposed to flowing sodium at 823K are given by Pillai et al., 2000. ANSI 316 NL is an austenitic steel that contains 16.8% Cr and 10.4% Ni and 0.53% Si, all known to enhance corrosion. Tests were performed at 550°C for 6,000 hrs. The results indicate generation of a carbide precipitate at the grain boundaries and leaching of Cr and Ni. The surface hardness of the metal was increased because of carburization and nitridation.

Because the solubility of carbon in nickel is low, nickel alloys are more resistant to carburization than steels and the use of nickel alloys in carburizing environments is widespread. (Cramer and Covino, 2003). However, it is known that a mixture of sodium and graphite is a strong carburization environment for nickel alloys (Hoffman et al., 1958a; Hoffman et al., 1958b). Carburization tests performed for nickel alloys exposed to graphite and liquid sodium is reported by Manly et al., 1968. For Inconel and INOR-8 no carburization was observed at a temperature of 649°C . However, both alloys showed carburization to a depth of 0.09-0.10 in. at a temperature of 815°C .

Carburization of Hastelloy Alloy X is reported by Muraoka et al., (1975) in a study performed between 700 and 1100°C in vacuo and a helium environment. It was determined that carburization in vacuo was dominated by grain boundary diffusion. Both carburization and decarburization were observed in experiments in a helium environment with prefilmed hastelloy specimens, i.e. an oxide layer on the Hastelloy surface. The oxygen had an inhibitive and accelerative effect on carburization. Oxide formed at the alloy surface delays carburization. This was observed at the surface oxide layer and internal oxidation layers. However, oxygen promoted the penetration of carbon in the metal substrate. This was observed inside the internal oxidation layer only. Carburization was strongly dependent upon temperature in both systems.

Low temperature gas phase carburization of nickel based alloy IN718 is reported by Sharghi-Moshtaghin et al., 2010. Experiments were performed in an atmosphere containing varying amounts of CO. The results indicate at temperatures above 510°C loss of Cr can occur with a significant decrease on corrosion performance. A carbide free case, a hardened surface layer, with up to 12% carbon in solid solution forms. Below 510°C carburization was not observed.

Three projects examining liquid sodium are underway at Argonne National Laboratory. These are studies on the corrosion of advanced materials in liquid sodium (Meimei et al., 2011), self plugging of channels, leaks, in a liquid sodium/supercritical carbon dioxide microchannel heat exchanger (Reed et al., 2011) and gas formation from the interaction of liquid sodium with metals (Gerardi et al., 2011). The project address the three most significant issues for construction of a liquid sodium/supercritical carbon dioxide heat exchanger for use in a power production cycle coupled to a liquid sodium cooled fast reactor. Corrosion experiments at ANL are focused on corrosion of the alloys HR Ht-UPS, H1 NF616, H2 NF616 and G91 in liquid sodium at 550°C to 650°C for up to 5064 hours. After exposure to liquid sodium a tensile test was performed on the alloys. Exposure to liquid sodium at 550°C had no significant impact on tensile properties whereas exposure at 650°C reduced tensile strength by nearly half. The authors recommend further microstructural analysis and evaluation of decarburization/carburization behavior to understand the decrease in tensile strength at 650°C. The two other programs at ANL are still in the construction and testing phase of the experimental apparatus.

5.0 SUMMARY AND ADDITIONAL RESEARCH NEEDS

5.1 Summary of Literature Data

In the supercritical CO₂ Brayton cycle – liquid sodium reactor system there are several mechanisms for corrosion of construction materials to occur; corrosion due to CO₂, liquid sodium and from the reaction products of CO₂ and sodium. Additionally, there are multiple high efficiency heat exchangers (heat input, heat recuperation and heat rejection) in the Brayton cycle that are subjected to widely varying chemical and physical conditions. Fortunately, there is a considerable, but by no means complete, body of knowledge for corrosion in CO₂ and liquid sodium. Far less information is available on the reaction between supercritical CO₂ and liquid sodium. The following statements can be concluded from the available literature data:

- Whereas liquid sodium cooled reactor technology has been around for more than 50 years, the supercritical CO₂ Brayton cycle is only in the demonstration phase with significantly more work required to bring it to maturity.
- Corrosion testing in supercritical CO₂ has mainly been performed through short-term coupon testing.
- Research has mainly focused on routinely used steels such as 316 s.s., 304 s.s., with fewer studies reported on the more expensive high chrome and high nickel steels and nickel based alloys.
- From operational experience with the CO₂ cooled Magnox reactors corrosion rates of steels in CO₂ is much higher for materials under stress.
- Pure, dry CO₂ is virtually inert at low temperatures. However, at high temperatures, >600°C and in the presence of even small quantities of water, ppm levels, significant corrosion of steels and nickel alloys can occur.
- In general, austenitic alloys are more resistant to CO₂ induced corrosion than the ferritic-martensitic steel.
- High concentrations of chromium and nickel significantly increase the corrosion resistance of steel alloys in supercritical CO₂.
- There are very few studies that have focused on the effect of additives for CO₂ induced corrosion. Organic additives and some inorganic

additives will not withstand the conditions in the high temperature section of the Brayton cycle.

- At low temperature, $<500^{\circ}\text{C}$, pure liquid sodium is not corrosive to steels and nickel based alloys to any significant degree. However, higher temperatures and the presence of impurities such as O_2 can enhance corrosion. In general, corrosion rates for the austenitic steels increase exponentially with temperature and linearly with oxygen content and sodium velocity up to approximately 3 m/s.
- Diffusion bonding typically used in the construction of microchannel heat exchangers can produce a weld as strong as the base metal of construction, with high resistance to corrosion. However, if the weld is not correctly done, the welded area can have a significantly reduced strength. No information on the corrosive effects of CO_2 , liquid sodium, carbon and other materials on diffusion bonded metals could be located in the literature.
- A leak in the primary heat exchanger will lead to supercritical CO_2 entering the liquid sodium loop. The products of the reaction of CO_2 and liquid sodium are mainly sodium carbonate and carbon. However, this information is based on a very limited amount of data.
- Carburization/decarburization is a potentially highly significant mechanism for corrosion in a supercritical CO_2 Brayton cycle – liquid sodium reactor system. The presence of carbon, even at very low concentrations ($<1\text{ppm}$), in the liquid sodium can result in carburization of steels and nickel alloys. In general, nickel based alloys are more resistant to carburization than steels.
- Only a single study could be located that focused on channel plugging of a microchannel heat exchanger by the reaction products of CO_2 and liquid sodium. The results indicate channel plugging is strongly dependent on temperature, crack size and channel size.
- The corrosion studies reviewed in this work did not include an economic analysis. For construction of the Magnox reactors, the use of expensive alloys had to be restricted to areas where corrosion was the most severe in order to construct a cost effective system.

5.2 Additional Research Needs

Based on the information reviewed in the literature and the requirements for a supercritical CO_2 Brayton cycle-liquid sodium reactor system additional research is required in the area of corrosion. These include:

- Corrosion testing needs to be performed over long time intervals. No long-term corrosion testing is reported in the literature. The experience gained from operation of the Magnox reactors, that short-term coupon testing is inadequate for certain systems, reinforces the need for testing materials over long time intervals
- Corrosion tests need to be performed under stress to simulate the operational conditions for the construction materials. Operational experience from the Magnox reactors indicated corrosion was not significant except for the components under stress.
- The effects of water, oxygen and other impurities need to be examined in more detail. The literature indicates water at ppm concentrations creates a very corrosive environment for many metals in the presence of CO₂.
- The mechanism of supercritical CO₂ corrosion at very high temperature in the absence of water needs to be better understood. The work of Glezakou et al., 2000 indicate that corrosion of metal surfaces can occur in the complete absence of water at temperatures in excess of 600°C.
- To minimize capital cost, studies need to be performed at low to moderate temperature with mild steel, low Cr steel and other relatively inexpensive materials that could be used for construction of the low temperature heat rejection and heat recuperator heat exchangers in the supercritical CO₂ Brayton cycle.
- Testing needs to be performed of a small scale microchannel heat \ exchanger constructed by diffusion bonding that is representative of the heat exchanger for use in a full scale supercritical CO₂ Brayton cycle. Tests should aim to find predictive failure thresholds based on candidate structural materials, degradation in materials due to corrosion, various diffusion bonding fabrication conditions, and also microchannel flow channel patterns. This series of tests should aim to provide sufficient information for ASME code certification.
- The reaction between CO₂ and liquid sodium needs further study with a complete analysis of the reaction products, and the dependence on temperature and pressure. In the few studies reported in the literature there are significant discrepancies and in one study a significant amount of the reaction products was reported as unknown.

- As carburization appears to be significant concern following a leak in coupled CO₂-Sodium heat transfer systems, research is needed for a development of a technique for removing elemental C from liquid sodium flow to levels under 1 ppm to prevent widespread damage to the primary system.
- A claim by proponents of the coupled CO₂-Sodium reactor system is that cost may be reduced by eliminating the secondary sodium system required in Sodium-steam power conversion plants. In this interest, fuel cladding materials should be investigated for susceptibility to carburization or other damage due to interaction with sodium-CO₂ reaction products.
- Investigation of inspection and repair procedures for microchannel heat exchangers following failure or materials degradation.
- A significant effort needs to be performed detailing thermodynamic modeling of corrosion in supercritical CO₂.

6.0 CONCLUSIONS

The high efficiency and small footprint of a supercritical CO₂ Brayton cycle coupled to a liquid sodium reactor make this system a promising candidate for a next generation power system. However, significantly more research is required before entering into the design phase. Although liquid sodium cooled reactor technology has been around for more than 50 years, the supercritical CO₂ Brayton system is in its infancy and many issues with corrosion are likely to be discovered as the technology is brought to maturity.

Corrosion in a supercritical CO₂ Brayton cycle coupled to a liquid sodium reactor system can occur in the liquid sodium reactor coolant loop, supercritical CO₂ power cycle loop or as a result of a failure in the primary heat exchanger where CO₂ would enter the liquid sodium loop and react to form sodium carbonate and carbon.

In general, for supercritical CO₂ and liquid sodium, corrosion is a strong function of system impurities, H₂O, O₂, etc. in the system. For both media, corrosion is much more significant at higher temperatures such as temperatures encountered in the primary heat exchanger. The use of high chromium and/or high nickel alloys or nickel based alloys are the most corrosion resistant materials under all conditions reported in the literature studies. However, these materials are much more expensive than more routinely use stainless steels and a complete engineering and economic analysis needs to be performed prior to entering the design phase of system.

The program at Argonne National Laboratory is examining the three most significant areas for construction of a microchannel heat exchanger for liquid sodium and supercritical carbon dioxide: materials corrosion, self-plugging and gas formation from corrosion. These programs will provide valuable information for design, construction and operation of any future full-scale heat exchanger for a sodium cooled fast reactor utilizing a supercritical carbon dioxide cycle for power production.

Additional work on corrosion is required and much of the work can be performed at the Argonne National Laboratory facilities. In particular, long-term coupon corrosion tests need to be performed with and without the presence of potential contaminants in the system that may accelerate corrosion rates. Corrosion testing needs to be performed under conditions relevant to the supercritical CO₂ Brayton cycle coupled to a liquid sodium reactor system with components being placed under stress. The primary heat exchanger is a critical unit in the system. For optimum efficiency, a microchannel heat exchanger constructed by diffusion bonding is a promising technology for the unit. Corrosion testing of diffusion bonded materials need to be performed with the materials in an environment simulating real operating conditions. A potential mechanism for corrosion in the supercritical CO₂ – liquid sodium system is carburization. It is known that

decarburization/carburization occurs in a liquid sodium loop and the potential for a significant amount of carbon to be introduced into the system through a leak in the primary heat exchanger must be addressed.

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APPENDIX A: COMPOSITION OF ALLOYS

Material	Fe %	C %	Cr %	Ni %	Si %	Mo %	Mn %	Mg %	P %	S %	Al %	V %	W %	Yt %	Cu %
carbon steel	balance	0.05 - 0.15					0.25-1.7		0.04	0.08-0.24					
316 s.s.	balance	0.08	16-18	10-14	1	2-3	2		0.045	0.03					
316L s.s.	balance	0.03	16-18	10-14	1	2-3	2		0.045	0.03					
T91	balance	0.08-0.12	8-9.5			1	0.05-1.05					0.18-0.25			
800H	39.5	0.06-0.1		30-35	1		0 - 1.5				0.15-0.6				0 - 0.75
304 s.s.	balance	0.08	18-20	8-10.5	1		2		0.045	0.03					
310 s.s.	balance	0.15	24-26	19-22											
S30815	balance	0.08	21	11	1.7		0.8		0.04	0.03					
HCM12A	balance	0.11	10.8	0.39	0.27	0.3	0.45		0.016	0.002		0.19	1.89		1.02
commercial Al	39.5 min	0.05 - 1.0 max	19-23	30-35							0.15-0.6				
Al-6XN	balance	0.02	20.5	24	0.40	6.20		0.40	0.02	0.001					0.2
Al alloy RR58	0.96			1.14	0.19			1.47			balance				2.47
Haynes 230	3	0.1	22	57	0.4	2	0.5				0.3		14		
Alloy 625	5 max		20 - 23	58.0 max							0.4 max				
PE-16	balance	0.04-0.08	15.5-17.5	42-45	0.5	2.8-3.8	0.2	0.2		0.015	1.1-1.3			0.5	0.5
PM2000	balance	0.006	19.4								5.38				
Al 2024	0.5 max		0.1 max			0.5 max	0.3-0.9	1.2-1.8			90.7-94.7				3.8-4.9
Al 6061	0.70 max		0.04-0.35		0.4-0.8		0.15 max	0.8-1.2							0.15-0.4
Al 7075	0 - 0.5		0.18-0.28				0-0.3	2.1-2.9			balance				1.2-2.0
1018 carbon steel		0.15-0.20					0.6-0.9								
MA 754	1.0	0.05	20	78					0.04	0.05	0.03			0.6	

Material	Cr (%)	Mo (%)	Mn (%)	Si (%)	C ppm	S ppm
Pure iron					15	100
Rimming Steel	0.03	0.01	0.35	0.01	370	590
Low-Alloy Steel A	1.1	0.57	0.47	0.07	960	520
Low Alloy Steel B	1.1	1	0.45	0.46	110	140
Low AlloySteel C	0.9	0.6	0.5	0.5	400	210

Metal Designation	Designation Number	C (%)	Si (%)	Mn (%)	Cr (%)	Ni (%)	Mo (%)	Al (%)	V (%)	S (%)	P (%)
A42	1	0.17	0.28	0.69						0.25	0.22
A48	2	0.18	0.15	0.85						0.2	0.009
Mo-Cr	3	0.18	0.28	0.6	0.22		0.26			0.17	0.011
Mo-Cr-Mo	4	0.17	0.23	1.39	0.08		0.27			0.14	0.029
Mn-Mo-Ni-V	5	0.1	0.23	1.02	0.07	0.29	0.42		0.06	0.008	0.009
Mn-Ni-Mo	6	0.17	0.33	1.37	0.18	0.53	0.32			0.009	0.006
1/2% Cr- 1/2% Mo	7	0.14	0.09	0.71	0.37		0.46			0.018	0.008
1% Cr-1/2% Mo	8	0.15	0.26	0.56	0.8		0.44			0.01	0.006
2 1/4% Cr-1%Mo	9	0.1	0.32	0.46	2.15		0.95			0.008	0.025
2 1/2% Cr-Mo-Al-V	10	0.09	0.22	0.45	2.11		0.28	0.46	0.07	0.01	0.012

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