CORROSION STUDY IN THE CHEMICAL
AIR SEPARATION (MOLTOX™) PROCESS

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1.0 SUMMARY

Results from pilot plant operation obtained from the previous MOLTOX™ agreement (No. DE-AC07-82CS40544) indicated that at high temperature locations, especially at the desorption unit, the corrosion rate was unacceptably high. The current work emphasizes understanding the important factors producing the high corrosion rates and subsequently reducing the corrosion in the high temperature regions. The main objective of this program was to find materials of construction that would provide acceptable corrosion rates under the conditions found in the MOLTOX™ process environment. In addition to the above DOE co-funded work, Air Products and Chemicals, Inc. pursued proprietary studies aimed at developing a less corrosive salt system without significantly reducing the kinetic performance of the salt system.

Intermetallic iron aluminides, under development at Oak Ridge National Laboratories, were sufficiently corrosion resistant under MOLTOX™ process conditions through the formation of a highly protective aluminum oxide layer. Laboratory tests indicate that the corrosion rates of the iron aluminides were an order of magnitude lower than conventional materials. The corrosion resistance appears to be greater in the aluminides with a higher aluminum content.

Promising laboratory and process economic results continue to show that the MOLTOX™ system is projected to be competitive with cryogenic air separation plants in those applications in which significant process heat integration can be achieved. This conclusion is dependent upon the continued development of two independent but related results from the research programs. The first is the encouraging performance of iron aluminide materials which ORNL has identified for development, and the second is the favorable new salt chemistry results from Air Products' program. The combination of these two results will allow the MOLTOX™ operating system to utilize 100% sodium salts, and operate at about 1250°F. The combination of the new material and new salt chemistry provides the potential for a 20% oxygen cost advantage.

Development of the iron aluminide materials has been shown to be the key need. The new salt system alone cannot provide enough oxygen cost advantage. The use of currently available, but more expensive, nickel alloys as construction materials does not provide low enough corrosion rates at the more severe operating conditions. Iron aluminide materials can provide low cost construction materials as well as the low corrosion rates required.

2.0 INTRODUCTION

This report presents the results of studies aimed at solving the corrosion problems encountered during operation of the MOLTOX™ pilot plant. These studies concentrated on the screening of commercial and developmental alloys under conditions simulating operating conditions in this high temperature molten salt process. Process economic studies were performed in parallel with the laboratory testing to ensure that an economically feasible solution would be achieved.

In addition to the above DOE co-funded studies, Air Products and Chemicals pursued proprietary studies aimed at developing a less corrosive salt mixture which would potentially allow the use of chemurgically available alloys such as stainless steels throughout the system. These studies will not be reported here; however, the results of corrosion tests in the new less corrosive salt mixtures are reported. Because our own studies on salt chemistry impacts heavily on the overall process and thereby has an influence on the experimental work conducted under this contract, some of the studies discussed here were impacted by our own proprietary data. Therefore, the reasons behind some of the experiments presented herein will not be explained because that information is proprietary to Air Products.

Two general classes of alloys gave promising performance in initial screening corrosion tests.

- a. Zirconium and hafnium in pure form showed excellent corrosion resistance to the salt mixture. Unfortunately none of the commercially available grades of the metals, nor their alloys, gave suitable performance. High purity, with resulting high costs, was shown to be necessary and produced an economically unattractive solution, though high purity zirconium or hafnium may prove to be a useful material for small items of equipment (such as valve trim) in corrosive service. Further long-term testing of these materials will, however, be necessary to ensure that the very corrosion resistant oxide that forms on these materials does not spill off during temperature and oxygen partial pressure cycling.

- b. Alumina forming alloys such as nickel and iron aluminides, currently under development by Oak Ridge National Laboratories (ORNL), have shown excellent promise in the corrosion tests. Of particular interest are the iron aluminides which meet our corrosion rate goal of less than 25 mpy while maintaining low cost. Combining the high corrosion resistance of iron aluminides, with the proprietary, less corrosive salt mixture developed in the Air Products laboratories, gives corrosion rates of about 1 mpy. The economics of this combination are good and an oxygen cost advantage of about 20% can be achieved over the traditional cryogenic technology currently used to produce tonnage quantities of oxygen.

Process economics were based on a revised summary of the salt loop containment vessels, using expected corrosion rates (extrapolated from the laboratory data) at actual pressure and temperature conditions throughout the salt loop. Sensitivity studies showed that increasing the baseline desorber temperature from 1200°F to 1250°F and changing the salt composition from 50-50 Na-K to 100% Na significantly reduced the size of the salt loop equipment and piping. Favorable economics with a 12 to 20% oxygen cost advantage were obtained even when the expected corrosion rates were doubled.

The promising economics of the combination of ORNL's iron aluminides and APCI's proprietary salt mixture has led to the recommendation that the DOE focus on further development and commercialization of the iron aluminides. APCI will continue development of its proprietary salt mixture until the new material is commercialized sufficiently for larger scale testing. If these tests are successful, then the existing pilot plant will be modified and performance testing will be done so that the design parameters necessary for a semi-works plant at an oxygen users site can be constructed and operated to fully demonstrate the technology.

3.0 MATERIALS CORROSION TESTING

Results from the MOLTOX™ pilot plant demonstrated that the process chemical performance essentially met all oxygen production expectations and produced high-purity nitrogen and argon from the absorber. Corrosion results indicated generally adequate protection everywhere except in high-temperature, two-phase locations, namely the desorption heat exchanger tubes. The program during FY1988 was directed toward building upon the promising corrosion reduction knowledge developed the previous year, with the goal of solving the corrosion problem in the desorber.

The objective of this program was to find commercially acceptable materials having corrosion rates below 25 mpy in the MOLTOX™ environment at the following operating conditions: 950°F/60 psia in the absorber and 1200°F/20 psia in the desorber. The target was to effect salt containment during the entire plant life. Figure 3.1 is logic diagram of how the materials corrosion experimental program would operate.

Pure zirconium and hafnium were thought to have acceptable corrosion resistance, assuming the protective scales would be stable during operation. As an alternative, various techniques for cladding zirconium and hafnium materials were also evaluated. We understood at the time that explosive cladding and electric-arc-welding techniques would be too expensive; however, melt spray or co-extrusion were possible candidates. Also there was a desire to identify materials that might be corrosion resistant through formation of self-healing, protective oxide scales in the MOLTOX™ process. Alumina, zirconia, hafnia, magnesia, or combinations of these might provide a solution to the materials problem in the MOLTOX™ process. However, zirconium and hafnium were suspected of being too expensive to make the process competitive.

High-temperature, intermetallic aluminum alloys such as nickel, iron, titanium, and zirconium-aluminides were investigated. These materials also have the potential of forming protective alumina scales and of being cost effective, as

Figure 3.1

SALT CHEMISTRY RESEARCH PLAN

well. We were to contact Oak Ridge National Laboratory, a leader in aluminide development that was working on commercializing a nickel-aluminide. Tough and inert ceramic material that would perform under MOLTOX™ conditions were also tested. Aluminas, magnesias, and zirconias are all very inert materials and may have low corrosion resistance. Aluminas have been used as vessel liners in our bench-scale salt bath reactors and been found to be chemically stable. These materials, however, are naturally brittle, rendering them difficult to fabricate and unreliable for structural applications. However, we kept apprised of any breakthroughs in technologies that would allow application of such materials to the MOLTOX™ process. The leading candidates were fiber-reinforced aluminas and phase-transformation-toughened zirconias.

3.1 BACKGROUND

3.1.1 Process Description

A range of process designs that incorporate one or both of two basic MOLTOX™ salt loop types, PSA (Pressure Swing Absorption) and TSA (Thermal Swing Absorption), are available to adapt MOLTOX™ oxygen plant processes for different market applications. The basic design choices are:

- Pure pressure swing for integration with gas turbines, for example.
- Pure thermal swing for integration with the heat recovery and steam generation section of industrial or utility steam boilers, for example.
- Intermediate cases combining pressure swing with thermal swing.

The MOLTOX™ oxygen system is a continuous, liquid phase absorption/desorption chemical air separation process that is based on a molten mixture of alkali (Na/K) nitrates and nitrites. The nitrate-nitrite salt mixture has proved to be stable once the equilibrium salt compositions are generated and the process conditions for oxygen transfer established. For either MOLTOX™ salt loop type, dry and CO₂-free air enters the absorber at 900-1200°F and 20-250 psia and is

contacted with the molten salt. The oxygen reacts chemically with the salt ($\text{NO}_2^- + 1/2\text{O}_2 \rightarrow \text{NO}_3^-$), is absorbed, and removed with the salt from the bottom of the absorber. The molten salt from the absorber flows to the desorber where the chemical reaction is reversed ($\text{NO}_3^- \rightarrow \text{NO}_2^- + 1/2\text{O}_2$), and gaseous oxygen is released from the salt and removed as product. The reversal of the chemical reaction in the desorber requires either pressure reduction (PSA) or temperature increase (TSA).

For the PSA salt loop, the pressure of the molten salt from the absorber is reduced across the pressure letdown valve before the salt enters the desorber. The pressure of the desorber is controlled by the gaseous oxygen pressure through a vacuum oxygen compressor. The salt is removed from the desorber by a salt pump and circulated back to the absorber at the necessary pressure for recontact with compressed air. The compressed air entering the absorber contains about 23 wt % oxygen and 77 wt % chemically inert (mainly nitrogen) gases. These vent gases, along with some unreacted oxygen, are removed from the top of the absorber at essentially the same pressure and temperature as they entered.

For the TSA salt loop (Figure 3.2), the temperature of the molten salt from the absorber is increased across salt heaters. The oxygen-rich salt from the absorber (Point B) is first heated against lean salt and then enters a desorber (Point D) where gaseous oxygen is released and removed from the salt. The salt is further heated by an external heat source, and then enters the final desorber (Point E). The 1200°F salt is withdrawn from the bottom of the desorber and is cooled to about 950°F in the salt cooler before entering the absorber (Point A) for recontact with the hot air. The salt from the absorber (Point B) is circulated around this TSA loop by a pump operating at the 950°F salt temperature. The expected corrosion rate of NiAl at various locations around this TSA loop in a 0.4 mole % Na_2O_2 catalyzed pure sodium nitrate-nitrite salt is demonstrated in Fig. 3.3. The corrosion rates are predicted from data obtained in our laboratory. The corrosion behavior of NiAl is expected to be similar to that of FeAl. The materials of construction and salt chemistry will be discussed in detail in Section 3.3.

Figure 3.2
MOLTOX™ TSA CYCLE

Figure 3.3

EXPECTED CORROSION RATE @ 0.4 MOLE % Na_2O_2 FOR 50:50 Na:K NITRATE SALT

The pure TSA MOLTOX™ system requires between 5 and 7 MM BTU of heat through the salt heater for each ton of oxygen product. Limited heat availability for certain TSA MOLTOX™ applications led to the development of process designs for combined PSA/TSA and TSA/PSA MOLTOX™ units. The thermal swing MOLTOX™ system utilizes the least net energy, but it also cogenerates steam to achieve this result. The thermal swing process is applicable at any site where fuel or high-quality heat is used to generate steam. The pressure swing process is applicable where fuel will be used in a gas turbine for mechanical or electrical power. Because the thermal swing MOLTOX™ system must be integrated with high-quality heat recovery and steam generation, it is not amenable to stand-alone oxygen applications. In contrast, the pressure swing process requires no imported heat, and, therefore, it can be used as a stand-alone oxygen plant.

3.1.2 Corrosion and Materials of Construction

The key results of the extensive corrosion monitoring in the MOLTOX™ pilot plant that was started up in December 1985 [Ref. 4] are summarized in Figure 3.4. Corrosion racks, containing metal coupons exposed to molten salt with flow velocities at about 0.2 feet per second (fps), showed corrosion rates similar to those found in the laboratory tests. The 316 stainless steel had a corrosion rate of about 10 mpy in the 950°F absorber bottoms, while Incoloy 800 had a corrosion rate of about 30 mpy in the 1200°F (07.83) salt separator bottoms. Pipe spool pieces, which were exposed to practical fluid velocities of about 1.5 fps, had corrosion rates of 34 mpy for 316 stainless steel in the 1050°F salt separator bottoms (07.80 in Figure 2.2), while Inconel 600 had corrosion rates of 2, 263, and 146 mpy, respectively, at the inlet (1050°F) and outlet (1220°F) of the desorber tubes and in the piping to the 07.83 salt separator (1200°F).

Corrosion results from the pilot plant operation generally confirmed the earlier laboratory reactor data [Ref. 5] with two exceptions:

MOLTOX™ PILOT PLANT FLOW DIAGRAM

i) When 316 stainless steel was used in high-fluid-velocity regions, catastrophic corrosion occurred, even at low temperature. The dramatic increase in corrosion rate with fluid velocity is shown in Figure 3.5. Because Incoloy 800 and Inconel 600 do not suffer from this velocity effect at low temperature, these alloys were successfully used instead of 316 stainless steel in regions of high velocity;

ii) The 1200°F, two-phase flow region in the oxygen desorber and the piping into oxygen/salt separator vessel 07.03 experienced very severe corrosion; the corrosion rate of Inconel 600 was about 250 mpy. This high-temperature, two-phase corrosion rate must be reduced to enable commercial development of the MOLTOX™ system.

Thus, results from pilot plant operation generally confirmed that adequate materials of construction have been identified, except at the high-temperature locations, especially the oxygen desorption heat exchanger. The current work emphasizes understanding the important factors producing the high corrosion rates and subsequently reducing the corrosion in the high-temperature, two-phase flow region of the desorber. The plan comprises three programs:

- i) find and test better materials,
- ii) identify and test less aggressive salt mixtures, and
- iii) investigate engineering solutions to the problem.

Based on the results of these three programs the pilot plant will be modified and will be operated at design conditions to demonstrate materials of construction compatibility.

3.1.3 Development of New Materials/Salt System

Monitoring of the MOLTOX™ pilot plant has shown very high corrosion rates in the desorber area. Inconel 600, the best material identified at that time, experienced a greater than 200 mpy corrosion rate. Therefore, efforts were made to reduce corrosion rates by testing less aggressive salt mixtures and identifying materials with better corrosion resistance.

Figure 3.5
**EFFECT OF FLOW VELOCITY
 ON CORROSION**

Alloys with high aluminum content have been shown to have good resistance to corrosion in molten salts because the protective aluminum oxide scales (Al_2O_3 or NaAlO_2) are virtually insoluble in this environment. However, there are few commercially available high-temperature alloys which utilize aluminum as a major alloying component. We had earlier evaluated aluminum diffusion coatings on 316 SS, Incoloy 800 and Inconel 600 and found they were unacceptable [Ref. 4 and 6]. Intermetallic iron and nickel aluminides, under development at Oak Ridge National Laboratories (ORNL), are potential low-cost, corrosion-resistant materials of construction suitable for the MOLTOX™ process. The nickel aluminide and iron aluminide materials show favorable high-temperature and low-corrosion characteristics in molten nitrate/nitrite salts. The aluminides show increasing corrosion resistance as the aluminum content is increased (up to 50 mol %). The corrosion rate of NiAl at simulated desorber conditions was less than 1 mpy. Unfortunately, because of their high aluminum content, these materials currently have low ductility, which may present fabrication problems. ORNL is working toward the further development and fabricability of aluminide materials by the addition of other alloying elements.

Therefore, the new intermetallic materials being developed and commercialized at ORNL are crucial to future MOLTOX™ development. Iron aluminide development is especially important, since its potential to be a low-cost construction material is a key to the MOLTOX™ system cost advantage.

3.1.4 Hydrodynamic Effects

The rate of corrosion of metals can be affected by flowing fluids. Thus, consideration of a material of construction for handling a flowing fluid should include an evaluation of the effect of fluid flow rate on corrosion. It has been shown [Ref. 1] that modeling of the velocity-affected corrosion mechanism in one geometry by using another geometry is feasible. The rotating cylinder

electrode is a practical geometry that is useful for investigating corrosion processes under dynamic conditions. Equations in the literature allow rotation rates to be calculated, so that mass transfer coefficients for the rotating cylinder will be similar to those for the modeled pipe geometry.

3.2 EXPERIMENTAL APPARATUS AND PROCEDURE

3.2.1 Static Reactors

Reactors #1 and #2 were used to obtain corrosion data in a static environment. The advantage of the static reactors was that many coupons (up to 18) could be tested simultaneously. The use of static reactors was particularly timesaving during the preliminary screening of corrosion-resistant materials. Reactors #1 and #2 were similar in design and each operated in a semibatch mode. The molten salt was held in a 3-liter high-density fused alumina container [Ref. 5]. The liner was supported by a 316-L, stainless-steel reactor vessel. Feed gases were sparged through the molten salt, which was maintained at constant temperature and pressure. Figure 3.6 gives the reactor dimensions. Corrosion test coupons were installed on racks constructed of coiled hafnium or zirconium wires.

The corrosion system for reactors #1 and #2 is shown schematically in Figure 3.7 and was used to test the corrosion resistance of candidate alloys for varying periods. These reactors were designed to maintain a constant salt temperature, which was achieved by furnace temperature control and by sparging zero-grade air through the salts at a flow rate of about 0.25 lpm. The air purge kept the molten salt well mixed. The salt temperature was measured at three locations to verify uniform salt temperature. Vessel pressure was regulated and controlled by using a back-pressure regulator, and inlet and outlet gas flow rates were measured using rotameters. The reagents employed in the experiments were of known purity and composition: sodium and potassium nitrates were assayed as 99% pure, and sodium and potassium nitrites were not less than 97% pure; catalysts for the nitrate-nitrite reaction, were 98% pure; and zero-grade feed gases with a purity of 99.998% were used in both reactor

Figure 3.6
**SPARGED BATCH REACTOR
CROSS SECTION**

Figure 3.7

CORROSION REACTOR SCHEMATIC

systems. Calibration standards for the oxygen and NO_x analyzers were certified to within 1% of the minor component.

The following procedures were followed to prevent reagent exposure to atmospheric water: Reagents received from the vendor were stored unopened in a cool, dry place until used. Sodium and potassium oxides were stored continually under nitrogen because of their affinity for water. Once a salt mixture was weighed, the containers were sealed and left in the glove box. The oxides were isolated in a separate container to prevent them from absorbing moisture that might be present in the nitrates and nitrites. Before the reactor was charged with salt, it was dried and cleaned for oxygen service by degreasing with trichloroethane. The reactor was then baked out for 2 hours at 600°F to ensure that the system was free of moisture. To prevent atmospheric water exposure as the nitrate/nitrite salts were being charged into the vessel, a regulated stream of zero-grade air was sparged through the salts at about 0.5 lpm. The reactor top was covered, and the salts were heated to just above their melting point. The vessel was then charged with about 3500 g of salt, which was activated by alkali oxide addition [Ref. 5] before the coupons were inserted into the salt. Alkali oxides are known to catalyze the oxygen separation reactions. The coupons, usually 3/4 in. x 1/2 in. x 1/16 in., were degreased, dried, and weighed before being installed on the rack. The catalyst was added at a concentration normally less than 1 mol %.

The test procedure was as follows:

- 1) charge the vessel with the NaNO_3 and KNO_3 salt
- 2) dry the salt
- 3) heat the salt to the melting point and add the catalyst
- 4) heat the salt to the test temperature and insert the coupon rack
- 5) conduct the test for the prescribed time (usually 2 to 3 days) with a continuous purge of zero-grade air or oxygen
- 6) cool the salt, open the vessel, and remove the coupons.

Salt samples were taken for most tests prior to and at the end of the test and analyzed for the pH to keep the catalyst concentration constant. After exposure, the coupons were cleaned and descaled using the mechanical and chemical procedures. To allow metallographic examination of the oxide scales, some coupons were not chemically descaled. The coupons were weighed after cleaning, and the corrosion rates calculated. The coupon corrosion rates [in mils per year (mpy)] were determined by measuring the mass lost during exposure. No serious pitting or other type of localized attack of the bare metal coupon was observed. Zirconia and Havana coupons were handled differently and will be discussed later.

3.2.2 Dynamic Reactor

Reactor #3 was a dynamic system in which the material under investigation was exposed to hydrodynamic effects by using rotating cylindrical specimens. Reactor #3 was therefore designed for the practical evaluation of the effect of fluid velocity on corrosion. Figure 3.8 shows the reactor configurations. The apparatus consisted of two concentric cylindrical coupons blanketed with cover plates at both ends which were made of the same materials as the coupons to be tested. The cylindrical test coupons and cover plates were fastened to the stirring rod with hafnium bolts. The reactor was equipped with a Magnedrive-II system designed for the operating requirements by Autoclave Engineers, Inc. The Magnedrive housing was made of 316 stainless steel and the internal bearings were composed of Rulon® and were water-cooled. The whole assembly was tested for mechanical stability before the experiment to minimize vibrational effects.

A set of control coupons, under static conditions, was also inserted into the reactor for comparison of their corrosion rates with those of the dynamic coupons. As shown in Figure 3.8, the static coupons consisted of rectangular specimens of the same material as the cylindrical coupons. The static coupons were hung on a rack that was isolated from the flowing fluid by an open-ended alumina cylinder.

Figure 3.8

DYNAMIC CORROSION REACTOR CROSS SECTION

The molten salt in Reactor #3 was contained in a high density fused alumina liner, since alumina is chemically inert to the molten salt system. The liner was supported by a stainless steel reactor vessel. The stirring rod and coupon fasteners were made of hafnium, and all other wetted parts were made of high-purity alumina. The vessel was usually charged with 1600 g of salt, which was catalyzed by alkali oxide catalyst addition before the coupons were inserted into the salt. The materials handling and general operating procedures were similar to those for the static reactors.

3.3 RESULTS

3.3.1 Effect of NA-K Ratio on Corrosion Rate and Oxygen Carrying Capacity

The objective of the program at the beginning of FY1988 was to find a salt system in which the corrosion rates of the materials of construction would be significantly reduced. Experiments in our lab had shown that the corrosion rate of SS-316 was very high, even at 950°F. A series of runs was made in 50/50 Na/K nitrate/nitrite salt on SS-316 at 950°F and at a partial pressure of oxygen of 15 psia with amounts of sodium peroxide varying from 0.2 to 1 mol % (Figure 3.9). The minimum corrosion rate for 0.2 mole % sodium peroxide was only slightly less than 100 mpy, which is unacceptably high. To approach this problem from the standpoint of changing the salt chemistry required that not only must the corrosion rates be adequately reduced, but the kinetic performance of the salt mixture must also be adequate to drive the process. A variation that was considered over a year ago was the performance of the potassium salt system versus the sodium salt system.

3.3.1.1 Comparison of Pure Sodium and Pure Potassium Nitrate-Nitrite Systems

In the MOLTOX™ process, where the oxygen-carrying capacity of the salt is set for economic reasons, thermodynamics dictates the operating temperature and the oxygen partial pressure necessary to attain this oxygen-carrying capacity. To

Figure 3.9

EFFECT OF ALKALI OXIDE ON SS-316 CORROSION

illustrate this, the following analysis was done to determine the temperatures for the corrosion studies of the pure sodium and pure potassium salt systems that in the MOLTOX™ process would give the same kinetic rate as the 50/50 Na/K nitrate/nitrite salt system. The purpose was to evaluate whether a significant advantage would exist for either of these pure systems as compared to the 50/50 Na/K nitrate/nitrite salt system. Derivation of the temperatures of the pure potassium and sodium salt systems having equivalent X_{NO_3} and P_{O_2} to those of the 50/50 Na/Nitrate/nitrite salt at 1200°F is illustrated as follows:

Equilibrium nitrite to nitrate conversion for the reversible reactions of the MOLTOX™ salt system may be expressed as:

$$\frac{(X_{NO_3})^2}{(X_{NO_2})^2 P_{O_2}} = \text{EXP} \left(- \frac{\Delta H_M}{RT_M} - \frac{\Delta S_M}{R} \right) \quad (3.2)$$

where M is either Na, K, or Na + K. Then, the temperature of the salt system has the following relationship:

$$T_M = \frac{- \Delta H_M/R}{\ln[(X_{NO_3}/X_{NO_2})^2 / P_{O_2}] + \Delta S_M/R} \quad (3.3)$$

Equation (3.3) shows that the temperature does not have any degree of freedom when X_{NO_3} , P_{O_2} , and M are defined. Therefore, for a given X_{NO_3} and P_{O_2} :

$$T_M = \frac{- \Delta H_M/R}{C + \Delta S_M/R} \quad (3.4)$$

$$\text{where } C = \ln\left[\left(\frac{x_{\text{NO}_3}^2}{x_{\text{NO}_2}}\right) / P_{\text{O}_2}\right]$$

The equilibrium constant of the binary salt mixtures, assuming an ideal solution, has a relationship of:

$$\ln K_M = x_{\text{Na}} \ln K_{\text{Na}} + x_K \ln K_K \quad (3.5)$$

where x_{Na} and x_K are mol fractions of the Na and K salts, respectively,

$$\text{and } K = \exp\left(\frac{-\Delta H}{RT} - \frac{\Delta S}{R}\right) \quad (3.6)$$

Then, ΔH_M and ΔS_M for mixtures of the salts are:

$$\Delta H_M = x_{\text{Na}} \Delta H_{\text{Na}} + x_K \Delta H_K \quad (3.7)$$

$$\Delta S_M = x_{\text{Na}} \Delta S_{\text{Na}} + x_K \Delta S_K \quad (3.8)$$

The values of ΔH and ΔS for the pure K and Na systems currently in use [Ref. 5] are:

$$\Delta H_K = -92,450 \text{ BTU/lb mole O}_2 = -51.361 \text{ kcal/g.mole O}_2$$

$$\Delta S_K = 44.69 \text{ BTU/lb mole O}_2 \text{ } ^\circ\text{R} = 44.69 \text{ cal/g.mole O}_2 \text{ } ^\circ\text{K}$$

$$\Delta H_{\text{Na}} = -73,150 \text{ BTU/lb mole O}_2 = -40.639 \text{ kcal/g.mole O}_2$$

$$\Delta S_{\text{Na}} = 37.89 \text{ BTU/lb mole O}_2 \text{ } ^\circ\text{R} = 37.89 \text{ cal/g.mole O}_2 \text{ } ^\circ\text{K}$$

Values of $\Delta H_M/R$ and $\Delta S_M/R$ for the various salt mixtures calculated from equation (3.7) and (3.8) are shown in Table 3.1.

Table 3.1

Thermodynamic Data for the Mixtures of Na and K Salts

Na	Mol % K	$\frac{\Delta H}{R}$ -----(°R)	$\frac{\Delta S}{R}$
0	100	-46,523	22.4890
25	75	-44,095	21.6336
50	50	-41,667	20.7781
75	25	-39,239	19.9226
100	0	-36,811	19.0671

For the equimolar Na-K salts and 1200°F:

$$C = \ln\left(\frac{x_{\text{NO}_3}}{x_{\text{NO}_3}}\right) / P_{\text{O}_2} = - \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

$$= 4.3224$$

and,

$$T_M = \frac{-\Delta H_M/R}{4.3224 + \Delta S_M/R}$$

Therefore, the temperatures of pure sodium and potassium salts corresponding to 1200°F of the equimolar salt mixture having equivalent X_{NO_3} and P_{O_2} are:

$$T_{\text{Na}} = \frac{-\Delta H_{\text{Na}}/R}{4.3224 + \Delta S_{\text{Na}}/R} = 1113.8^\circ\text{F}$$

$$T_{\text{K}} = \frac{-\Delta H_{\text{K}}/R}{4.3224 + \Delta S_{\text{K}}/R} = 1275.2^\circ\text{F}$$

Similarly, the temperatures of the reactive absorbers in which the pure sodium and potassium salt systems have nitrate concentrations equal to the nitrate concentrations in equimolar Na/K salt at the same P_{O_2} were calculated. For each of these cycles the nitrate concentrations in mole % in the absorber and desorber, the nitrate swing between these vessels, and the equivalent oxygen-carrying capacity in both mole and weight % is given in Table 3.2.

Table 3.2

Salt Composition vs. Corresponding Temperature*
 $P_{\text{O}_2} = 20 \text{ psia}$

<u>Salt System</u>	<u>Mol %</u>		<u>Absorber</u>		<u>Desorber</u>		<u>Nitrate Swing</u>	<u>Oxygen Yld</u>		
	<u>Na</u>	<u>K</u>	<u>°F</u>	<u>Nitrate</u>	<u>°F</u>	<u>Nitrate</u>				
				<u>mole%</u>		<u>mole%</u>	<u>mole%</u>		<u>mole%</u>	<u>wt%</u>
Baseline	50	50	950	98.9	1200	91.0	6.7	3.4	1.2	
Pure Potassium	0	100	1028	98.9	1275	91.0	6.7	3.4	1.1	
Pure Sodium	100	0	862	98.9	1114	91.0	6.7	3.4	1.3	

* Conditions: X_{NO_3} and P_{O_2} are equivalent.

A number of corrosion tests on the pure salt system were made at these temperatures on C-214, I-600, I-800H and SS-316 at four different oxygen partial pressures, as shown in Table 3.3. These results indicate that the sodium oxide-catalyzed sodium nitrate-nitrite system and the potassium oxide-catalyzed potassium nitrate-nitrite system, are unlikely to provide a sufficiently low corrosive salt system in which conventional metal alloys such as SS-316, I-800H, I-600 and Cabot-214 can be used for the materials of construction for the desorber. The pure sodium salt system was generally more corrosive than the pure potassium salt system under conditions of oxygen-carrying capacity equal to the equimolar Na/K system. The corrosiveness of each salt system depends strongly upon the oxygen partial pressure. For example, the corrosion rates of Cabot-214 in the 1114°F pure sodium salt system were 160 and 270 mpy at P_{O_2} of 15 and 0.8 psia, respectively. These results indicate that different corrosion mechanisms may predominate at different oxygen partial pressures.

The effect of temperature on the corrosiveness of the salt systems depended upon the nature of the cations present, the test materials, and the oxygen partial pressure. For example, the apparent activation energies derived from the corrosion rate data of I-600 with the sodium salt system were 98 BTU/lb mol-°R and 53 BTU/lb mol-°R at P_{O_2} of 15 and 0.8 psia, respectively, whereas with the potassium salt system they were 132 BTU/lb mol-°R and 172 BTU/lb mol-°R at P_{O_2} of 15 and 0.8 psia, respectively.

3.3.1.2 Effect of Oxygen Partial Pressure on Corrosion

The nitrate-nitrite system in the absence of alkali oxides has been shown to be essentially noncorrosive. The dramatic influence of oxygen partial pressure on the corrosion rates of alloys was the first clue that alkali oxides were involved in the corrosion process. This also indicated that different oxide species had different degrees of corrosiveness, since the oxygen partial pressure affects the distribution of the oxides.

Table 3.3
Comparison of Corrosion Rates (mpy)
In Different Salt Mixtures

P_{O_2} , psia	<u>60</u>	<u>60</u>	<u>60</u>	<u>15</u>	<u>17.4</u>	<u>15.7</u>
T, °F	1114	1200	1275	1114	1200	1275
Salt	<u>Na</u>	<u>50Na/50K</u>	<u>K</u>	<u>Na</u>	<u>50Na/50K</u>	<u>K</u>
C-214	66	25	14	161	63	20
I-600	65	32	14	127	71	25
I-800	144	63	237	330	452	766
SS-316	819	821	981	2034	2827	2086
P_{O_2} , psia	<u>3.1</u>	<u>3.5</u>	<u>3.2</u>	<u>0.3-0.75</u>	<u>0.13</u>	<u>0.8</u>
T, °F	1114	1200	1275	1114	1200	1275
Salt	<u>Na</u>	<u>50Na/50K</u>	<u>K</u>	<u>Na</u>	<u>50Na/50K</u>	<u>K</u>
C-214	229	137	146	274	231	150
I-600	224	168	185	266	2397	842
I-800H	410	549	1182	647	2102	833
SS-316	1337	2829	2170	2159	1518	2457

In Figure 3.10, corrosion rates of I-600 are shown at various oxygen partial pressures. As the oxygen partial pressure decreased from 4 atm to 0.03 atm, the corrosion rates of I-600 increased from about 90 to 300 mpy at 1114°F in the pure sodium nitrate-nitrite system containing 1 mol % Na_2O_2 , and from about 10 to 1000 mpy at 1275°F in the pure potassium nitrate-nitrite system containing 1 mol % K_2O_2 . The effect of oxygen partial pressure on the corrosion rates of I-600, I-800, SS-316, C-214, and NiAl in 50/50 Na/K nitrate/nitrite at 1200°F are shown in Figures 3.11 to 3.15. In all cases, corrosion rates decreased with increasing oxygen partial pressure.

Figure 3.10

EFFECT OF OXYGEN PARTIAL PRESSURE AND CATION ON CORROSION

Figure 3.11
EFFECT OF pO_2 ON CORROSION OF I-600

50Na-50K/NO₃-NO₂, 1 MOLE % Na₂O₂, 1200°F

Figure 3.12

EFFECT OF pO_2 ON CORROSION OF I-800

50Na-50K/NO₃-NO₂, 1 MOLE % Na₂O₂, 1200°F

Figure 3.13

EFFECT OF pO_2 ON CORROSION OF SS-316

50Na-50K/NO₃-NO₂, 1 MOLE % Na₂O₂, 1200°F

Figure 3.14
EFFECT OF pO_2 ON CORROSION OF C-214

Figure 3.15
EFFECT OF pO_2 ON CORROSION
OF NICKEL ALUMINIDE (NiAl)

3.3.2 Materials Testing

Corrosion tests were initially carried out on various materials that are commercially available to identify those having adequate corrosion resistance at process conditions. Conventional alloys containing various amounts of cobalt, chromium, and nickel were tested in the laboratory. The refractory metals zirconium and hafnium, which are characterized by very high melting points compared with iron and steel, were also considered. The high temperature intermetallic aluminide materials, under development at Oak Ridge National Laboratory (ORNL), are being tested at Air Products.

Both mechanical strength and corrosion resistance must be considered for high-temperature service in the MOLTOX™ environments. Tensile strength, yield strength, and ductility are some of the mechanical properties important in structural applications. Creep, or the continuous plastic elongation of a metal under an applied stress, becomes increasingly important at high temperatures.

3.3.2.1 Zirconium/Hafnium

Zirconium has found increased use primarily because of its excellent resistance to corrosion at high temperature [Ref. 8 and 9]. This resistance is due to a protective oxide film. Corrosion tests were therefore carried out on ultra-pure grade zirconium to evaluate its resistance under MOLTOX™ process conditions. The purity of the material is crucial to its performance, as will be shown by data presented below. In the initial studies, we found that the corrosion rate of the zirconium and hafnium was two orders of magnitudes less than for I-600 and Cabot-214. I-600 was the material used in the pilot plant for the areas requiring the most corrosion protection. Measurements on zirconium were made on 50/50 Na/K salt containing 1 mol % sodium peroxide at 1250°F (see Table 3.4). The corrosion rate was 6 mpy in the 50/50 Na/K mixture containing 1 mol % sodium peroxide.

Table 3.4

CORROSION RATE BY WEIGHT, MPY

(50 Na / 50 K)/ NO₂₊₃

Na₂O₂ = 1 mol %

P_{O₂} = 3.2 psia

T = 1250°F

Inconel-600	607
Cabot-214	356
Zr	6

Inspection of the specimen cross section from the corrosion studies with a Scanning Electron Microscope (SEM) showed the formation of a tenacious, nonporous oxide layer that was impervious to cations but pervious to oxygen atoms, which were free to move through this layer (see Figure 3.16). Presumably the oxide layer will continue to grow inwardly until it reaches equilibrium because zirconium is well known to be good oxygen-conducting material. Under an optical microscope the same type of pattern was observed, indicating the presence of an oxide layer (see Figure 3.17). The crystalline and physical properties of zirconium are shown in Figure 3.18 and in Table 3.5. Zirconium has a hexagonal structure, and the oxide has a monoclinic structure. The lattice parameters of the two are so similar that the volumes of their unit cells are almost identical. The α (hexagonal) to β (body-centered cubic) phase transition, which changes its mechanical and physical properties due to changes in crystallographic structure, occurs at 862°C and is higher than our MOLTOX™ operating temperature, which circumvents the complications of such a transition.

Figure 3.16

SEM CROSS-SECTIONAL VIEW OF ZIRCONIUM COUPON

α -Zr

α -Zr + O_{abs}

M-ZrO₂

TEST CONDITIONS

1200-1250°F, ATM AIR, 89.5 Hrs
50Na-50K/NO₃-NO₂, 1 MOLE % Na₂O₂

Figure 3.17

CROSS-SECTIONAL VIEW

Figure 3.18

SUPERIMPOSITION OF HEXAGONAL Zr AND MONOCLINIC ZrO_2

α - Zr = HEXAGONAL, $a = 3.232\text{\AA}$, $c = 5.147\text{\AA}$
 $V_h = 139.68\text{\AA}^3$

ZrO_2 = MONOCLINIC $a = 5.1477\text{\AA}$, $b = 5.2030\text{\AA}$,
 $c = 5.3156\text{\AA}$, $\beta = 99^\circ 23'$, $\alpha = \delta = 90^\circ$
 $V_m = 140.46\text{\AA}^3$

Table 3.5

Properties of Zirconium

Zr⁴⁰_{91.22}

- MELTING POINT = 1,852°C
- SPECIFIC GRAVITY = 6.51
- VALENCE = +2, +3, +4
- HEXAGONAL (α) TRANSITION TO BODY CENTERED CUBIC

Because of the excellent results obtained in our laboratory with zirconium, corrosion rates were obtained on both zirconium and hafnium in a 100% sodium nitrate/nitrite salt system containing 1 mol % sodium peroxide at 1114°F and 3 psia oxygen pressure (Table 3.6). The initial rate data indicate that the oxide scales grow at rates approximately proportional to the cube root of the exposure time (see Figure 3.19). The correlation predicts that the oxide scale would grow to 6 mils in thickness for zirconium and 1 mil for hafnium in 25 years. However, the corrosion rate would increase significantly if the oxide scale spalled off prematurely before its full extent of growth. Therefore, the morphological stability of the oxide scale seems to be the key parameter, determining the fate of the long-term corrosion rates.

Figure 3.19
RATE OF OXIDE SCALE GROWTH

Table 3.6

CORROSION RATES OF Zr AND Hf

Basis:

Salt System = Na (NO₃/NO₂) + 1 mol % Na₂O₂

Temperature = 1114°F

P_{O₂} = 3 psia

	<u>Corrosion Rate</u>	<u>Exposure Time</u>
Zr	less than 1 mpy	up to 1 month
Hf	less than 1 mpy	up to 2.5 months

These results pointed out the exceptionally slow corrosion rate of zirconium versus I-600, the formation of the tenacious monoclinic zirconium oxide layer, and the barrier of that layer to sodium and potassium ions. The conductivity of oxygen atoms and the fact that both zirconium and its oxide are poor thermal conductors (Table 3.7) are potential problems for use of the materials in heat exchanger applications in the MOLTOX™ process.

Ignition behavior of zirconium and effects of variables (e.g., surface preparation, metallurgical history, sample size, additives, oxygen content, and moisture in the oxidizing gas) have been studied [Ref. 7]. Oxide films formed on zirconium are under compressive stress, which may enhance the protective nature of the film by opposing the formation of cracks. Pyrophoric products on zirconium have been analyzed and found to be a mixture of zirconium oxides, hydrides, acid salts and finely divided metal.

Table 3.7

COMPARISON OF THERMAL CONDUCTIVITIES

(in BTU/hr/ft²/in/°F)

T = <u>25°C</u>	
Zr	16
Ni	62
Fe	59
T = <u>1000 - 2000°F</u>	
ZrO ₂	8
Al ₂ O ₃	19
SiC	150

3.3.2.2 Zirconium/Hafnium Alloys

Zirconium and hafnium are very similar chemically and form solid solutions over their entire range of compositions. By combining these two metals, the thickness of oxide on the alloy surface may lie between the very large value for zirconium and the very small value for hafnium. Several alloys of these two metals were exposed for 6 days to a 100% sodium salt system containing 1 mol % sodium peroxide at 1114°F.

The thickness of the oxide formed on the various alloys was found to be approximately proportional to the weight percent of zirconium in the alloy (Figure 3.20). Zirconium and hafnium absorb oxygen atoms by up to 29 and 20 atomic %, respectively. They also lose ductility as they absorb oxygen atoms [Ref. 9]. We do not yet know the impact of oxygen embrittlement on the long-term structural stability and potential maintenance difficulties of aged zirconium/hafnium alloy materials.

Figure 3.20

OXIDATION OF Zr-Hf ALLOYS

Even though ultra-pure zirconium and hafnium appeared to be adequately corrosion resistant in the MOLTOX™ environment, an economic evaluation indicated that they are not cost-effective materials nor available in sufficient quantities for piping and vessels. However, both materials may be useful for small items such as pumps and valves in severe service.

3.3.2.3 Commercial Zirconium Alloys

Because of the excellent corrosion resistance of the pure grades of zirconium and hafnium, several commercially available zirconium materials were tested for their corrosion resistance:

Zr-2	Unalloyed reactor grade
Zr-4	Sn = 1.00 to 2.00 %, reactor grade
Zr-702	Unalloyed
Zr-704	Sn = 1.00 to 2.00 %
Zr-705	Nb = 2.0 to 3.0 %

In the corrosion tests, all of these impure zirconium containing materials performed poorly under MOLTOX™ conditions. Impurities in zirconium, especially iron, chromium, and carbon, were detrimental to corrosion resistance. Alloying elements like tin and niobium were also detrimental to corrosion resistance. SEMs on each of these materials are provided in Figure 3.21, which clearly shows segregation of the oxide layer caused by the impurities.

3.3.2.4 Cobalt-Based Alloys

Since cobalt forms a protective oxide film with low solubility in molten sulfates, it may form a similar film in molten nitrates. Corrosion tests were performed on cobalt-based alloys in 50/50 Na-K nitrate/nitrite salt catalyzed by 1 mol % Na_2O_2 at 1200°F and 3 psia P_{O_2} ; the results are shown in Table 3.8 and Figure 3.22. The corrosion rates of all the alloys containing

Figure 3.21
OPTICAL MICROGRAPH
OF COUPON CROSS SECTION

ZIRCADYNE - 702
9817-24-2 250X

ZIRCADYNE - 702
9817-24-2 62.5X

Table 3.8

CORROSION RATE OF COBALT BASE ALLOYS

Basis: Salt mixture = (50Na/50K)/(NO₃/NO₂)
Na₂O₂ = 1 mol %
T = 1200°F
P = Atm. Air

Materials	I-600	H-230	I-617	MultiMet	H-130	H-150	H-25	H-6B	Co
Corrosion Rate in mpy	168	50	29	284	94	2563	1774	7791	1258
Composition, Wt. %									
Co	1.0*	3.0*	12.5	18.93	38.17	46.42	49.74	57.24	99.9975
Ni	73.2	55.58	54.0	20.71	22.42	3.0*	10.38	2.69	
Cr	15.0	22.0	22.0	20.79	22.48	28.0	20.01	29.93	0.0003
Fe	8.0	3.0*		30.75	1.73	20.0	2.62	2.54	0.0001
W		14.0		2.63	13.99		14.56	3.82	
Mn	1.0			1.28	0.69	0.65	1.67	1.33	
Mo		2.0	9.0	3.07		1.5*	0.78	0.85	
Ta				1.05					
Ti	0.3*								
La		0.02			0.058				
Al	0.4*	0.3	1.0						0.0002
C	0.08*	0.10	0.07	0.09	0.08		0.12	1.05	
P				0.017	0.011		0.011		
S				0.006	0.006		< .002		
Si	0.50*			0.55	0.36	0.35	0.11	0.55	0.0002
N				0.13					
B					0.004				
Cu	0.5*								

*Maximum

Figure 3.22
CORROSION OF COBALT-CONTAINING ALLOYS

cobalt (from less than 1% to pure cobalt) were unacceptably high. The most corrosion-resistant material appeared to be I-617, which contained 12.5 wt % of cobalt and had a corrosion rate of 29 mpy. Thus, cobalt does not appear to be an effective alloying element for the reduction of corrosion in the MOLTOK™ system.

3.3.2.5 Chromium-Based Alloys

The corrosion rates of alloys containing various amounts of chromium are shown in Figure 3.23. An increase in the amount of chromium in the alloy tends to increase the corrosion rate. For the alloy containing 30% Cr (Haynes-6B in Table 3.8), the corrosion rate was greater than 7000 mpy. Our data show that alloys with substantial amounts of chromium in conventional alloys [Ref. 5 and 6] are not suitable for use in the MOLTOK™ system.

3.3.2.6 Nickel Alloys

An important group of alloys for corrosion applications is based on nickel. The corrosion rate of nickel and its alloys seems to be dependent on the amount of impurities present in the metal. The investigation on low-sulfur nickels was conducted to determine if they are sufficiently corrosion-resistant for the MOLTOK™ system. The interest in sulfur-free nickel is based on the possibility that trace amounts of sulfur retained in the nickel materials, such as Nickel-200, may cause grain boundary corrosion attack, leading to catastrophic failure. The effect of carbon and sulfur impurities on the corrosion behavior of nickel is summarized in Table 3.9 and Figure 3.24. The corrosion rates of Ni-200, Ni-201, Ni-270 and a pure nickel material were 233, 197, 219 and 132 mpy, respectively. The vendor-specified maximum sulfur and carbon impurities in these materials were 100 ppm sulfur and 0.15 wt % carbon for Ni-200, 100 ppm sulfur and 0.02 wt % carbon for Ni-201, 10 ppm sulfur and 0.02 wt % carbon for Ni-270, and essentially no sulfur and carbon for the pure-nickel specimen. The results based on the equimolar sodium and potassium salt mixture containing 1

Figure 3.23
CORROSION OF CHROMIUM-CONTAINING ALLOYS

Figure 3.24
EFFECT OF CARBON AND SULFUR
ON CORROSION OF NICKEL

mol % Na_2O_2 at 1200°F and 15 psia P_{O_2} showed that the sulfur impurity was not the major cause of corrosion.

Table 3.9

CORROSION RATE OF NICKELS

Basis: Salt Mixture = (50Na/50K)/ NO_3/NO_2)

Na_2O_2 = 1 mol %

T = 1200°F

P = Atm. with air

<u>Materials</u>	<u>Ni-200</u>	<u>Ni-201</u>	<u>Ni-270</u>	<u>Ni</u>
Composition				
<u>Wt %</u>				
Ni	99.0*	99.0*	99.97*	99.9975*
C	0.075	0.025	0.020	0.0073
S	0.0007	0.0013	0.0013	0.0019
Corrosion				
<u>Rate, MPY</u>	233	197	219	132

*Minimum

Previous testing [Ref. 5] has shown that nickel alloys such as Inconel 600 and Ni/15.5 Cr/8 Fe have good corrosion resistance in the MOLTOX™ salt system. The corrosion rates of alloys containing various amounts of Ni are presented in Figure 3.25. It can be seen that, in general, increasing the nickel content serves to reduce the corrosion rate. Alloys containing more than 50% Ni had corrosion rates of less than 25 mpy in an equimolar Na-K/NO₃ - NO₂ with 1 mol % Na₂O₂ at 1200°F. The results differ sharply from results presented in Figure 6 in Reference 5, in some cases by two orders of magnitude. The cause of this discrepancy has not been analyzed but the results from the pilot plant are more consistent with the data in Figure 3.25.

3.3.2.7 Nickel Aluminides

The nickel aluminide, Ni₃Al, is an intermetallic compound which has attractive properties for structural use at elevated temperatures [Ref. 10]. The aluminide containing 25 at.% Al is resistant to air oxidation because of its ability to form adherent oxide films that protect the base metal from excessive attack. Unlike conventional metallic alloys, the yield stress of Ni₃Al increases substantially with increasing temperature. The aluminide is the most important strengthening constituent of commercial nickel-base superalloys and is responsible for their high-temperature strength and creep resistance. In spite of these attractive properties, the use of polycrystalline nickel aluminide as an engineering material suffers from the severe problem of poor ductility and brittle intergranular fracture.

Intermetallic nickel aluminides, under development at Oak Ridge National Laboratories (ORNL), have the potential to be sufficiently corrosion resistant in the MOLTOX™ process through the formation of the highly protective aluminum oxide layer. The corrosion rates of NiAl and Ni₃Al in equimolar Na-K/nitrate-nitrite with 1 mol % Na₂O₂ at 1114 and 1250°F are shown in Table 3.10, which also lists the corrosion rate of I-600 under the same conditions. The corrosion rates of nickel aluminides developed by ORNL appear to be an order of magnitude lower than those of I-600. The corrosion rates of

Figure 3.25
CORROSION OF NICKEL-CONTAINING ALLOYS

various nickel aluminides with lower aluminum content is presented in Table 3.11. The nickel aluminides listed in Table 3.10 contained more than 30% Al, while those in Table 3.11 contained less than 12% Al. A comparison of the data in these tables shows that corrosion resistance appears to be much greater in the aluminides with high (>30%) Al content.

Table 3.10

CORROSION RATE OF NICKEL ALUMINIDES (>12% Al)

Basis: Salt = Equimolar Na-K/Nitrate-Nitrite
Oxygen Partial Pressure = 3 psia
Catalyst = 1 mole % Sodium Peroxide

Corrosion Rate in MPY

<u>Materials</u>	<u>1250°F</u>	<u>1114°F</u>
NiAl	25	7
Ni ₃ Al	145	18
I-600	2500	154

Even though the nickel aluminides appear to show sufficient corrosion resistance for use in the MOLTOX™ system, an economic evaluation indicated that the cost of nickel aluminides was too high for commercial applications. Therefore, interest was shifted from nickel aluminides to iron aluminides, which have the potential to be a low-cost, corrosion-resistant material for the MOLTOX™ system.

Table 3.11

CORROSION RATE OF NICKEL ALUMINIDES (<12% Al)

Basis: Salt Mixture = (50Na/50K)/NO₃/NO₂)

Na₂O₂ = 1 mol %

T = 1200°F

P = Atm. with air

<u>Materials</u>	<u>IC-50</u>	<u>IC-218</u>	<u>IC-221</u>	<u>IC-50PAH</u>	<u>IC-218PAH</u>
Composition					
<u>Wt %</u>					
Ni	88.08	82.88	81.98	88.08	82.88
Al	11.3	8.5	8.5	11.3	8.5
Cr	--	7.8	7.8	--	7.8
Zr	0.6	0.8	1.7	0.6	0.8
B	0.02	0.02	0.02	0.02	0.02
Corrosion					
<u>Rate, MPY</u>	147	163	125	84	69

3.3.2.8 Iron Aluminides

Figure 3.26 shows the effect of aluminum content on the corrosion rate of the iron aluminides in a 50/50 Na/K nitrate-nitrite salt mixture at 1250°F and 20 psia pO_2 with three different catalysts, two of which (A and B) are proprietary. The much higher corrosion rates of all the samples in the presence of Na_2O_2 indicate that particular salt-catalyst combination to be much more corrosive than the other two. Generally, the aluminides show increasing corrosion resistance as the aluminum content is increased, although there is some scatter in the data.

Additional iron aluminide corrosion data were obtained in 50/50 Na/K nitrate-nitrite at the same conditions of temperature (1250°F) and pressure (20 psia pO_2) in the presence of a third proprietary salt-catalyst combination C, as shown in Figure 3.27 and 3.28. The effect of decreasing corrosion rates with increasing aluminum content of the iron aluminides is even more clearly demonstrated when the temperature of Salt C is increased from 1250 to 1300°F (Figure 3.27). All of the iron aluminides (from 26-50% Al content) had less than 10 mpy corrosion rates at 1250°F, but at 1300°F, the corrosion rates of the iron aluminides with low aluminum content (<30%) increased dramatically. Corrosion rates of iron aluminides containing 30-40 atomic % aluminum and 0-10 atomic % chromium exposed to Salt C at 1250°F and 1300°F at 20 psia are presented in Figure 3.28. The effect of increasing chromium content on the corrosion rate was not obvious from these results. However, increasing the aluminum content (from 30 to 40 atomic %) definitely resulted in a reduction in the corrosion rate of the aluminides.

These new intermetallic iron aluminides are currently being developed and commercialized at ORNL and are crucial to the future of MOLTOX™ development. The potential of iron aluminides to be low-cost construction materials is a key to the MOLTOX™ system cost advantage. The cost of the base elements of the iron aluminides is compared to that of stainless steel 316 in Table 3.12. Based on world market prices as of March 1988, the cost of the base materials of the iron aluminides was approximately two to three times less than that of SS-316. Therefore, an iron aluminide alloy containing 38% aluminum would have a potential 30% cost advantage over SS-316 if the fabrication costs are the same.

Figure 3.26

EFFECT OF ALUMINUM CONTENT ON CORROSION RATE OF IRON ALUMINIDES

Figure 3.27
EFFECT OF TEMPERATURE ON
CORROSION RATE OF IRON ALUMINIDES

Figure 3.28
EFFECT OF CHROMIUM CONTENT ON
CORROSION RATE OF IRON ALUMINIDES

Table 3.12

COST OF IRON ALUMINIDES VS TYPE SS-316

	<u>Composition (wt%)</u>					
	Fe	Cr	Ni	Mo	Al	Others
Type SS-316	65-69	16-18	10-14	2-3	0	1Si-2Mn-.08C
Fe-Al alloys	58-72	2-10	0	0.1-2	26-30	proprietary
Cost/pound	\$0.11	\$3.50	\$3.80	\$3.25	\$1.04	

Approximate cost of Type SS-316 per pound = \$1.08 - 1.33

Approximate cost of Fe-Al alloys per pound = \$0.42 - 0.79

Type SS-316 to Fe-Al alloys Cost Factors per weight basis: 1.7 - 2.6
per volume basis: 2.1 - 3.2

Ductility, tensile strength, and creep are three parameters which control fabricability and toughness of materials. Improving ductility has been one of the fundamental goals of intermetallic aluminide development because aluminides are inherently poor in ductility, especially at room temperature. ORNL is currently working towards the further development and fabricability of aluminide materials by the addition of other elements. The effect of aluminum content on the ductility of a base iron-aluminide system at various temperatures is shown in Figures 3.29 and 3.30. In general, increasing aluminum content and decreasing temperature in the iron-aluminide system decreased its ductility, marginally up to about 40 atomic % and then drastically beyond this point [Ref. 11]. For example, the room temperature ductility increased from 2 to 8% as the aluminum content was increased from 25 to 28% and decreased to 3 and 1% as the aluminum content was increased to 38 and 40%. Beyond 40% the ductility decreased dramatically, making fabrication extremely difficult. A minimum of 5% elongation (at room temperature) is necessary for good fabricability, although the ASTM guideline recommends a minimum of 1% (room temperature ductility of SS-316 is 30-35%). This goal can be achieved with up to 38% aluminum in the alloy by controlling purity, grain size, and composition of the alloy [Ref. 11]. From the MOLTOK™ standpoint, the optimum aluminum content would be between 35 and 40 atomic %. This is based upon consideration of both ductility and corrosion performance.

The effect of aluminum content, time, and temperature on tensile strength is presented in Figures 3.31 and 3.32. Tensile strength increases with increasing aluminum content at temperatures of interest (i.e., at about 700°C). The tensile strength of iron-aluminides is generally superior to conventional austenitic alloys such as alloy-800 (I-600 and SS-316) at all temperatures (Figure 3.33). Hot fabricability of iron-aluminides is reportedly much easier than that of nickel aluminides, therefore making adoption of conventional methods, such as hot piercing for pipe fabricating relatively easy.

ASTM specifications and code approval requires extensive tensile and creep data, including 10,000- hour creep testing with a minimum of three samples from

Figure 3.29
**EFFECT OF Al ON DUCTILITY
OF FeAl**

Figure 3.30 EFFECT OF TEMPERATURE ON DUCTILITY

Figure 3.31
EFFECT OF Al CONTENT ON TENSILE STRENGTH
OF FeAl

Figure 3.32
EFFECT OF TIME AND TEMPERATURE ON
TENSILE YIELD STRENGTH

Figure 3.33

NICKEL ALUMINIDES—NEW SUPERALLOYS FOR THE FUTURE

YIELD STRENGTH OF ADVANCED ALUMINIDES
COMPARED WITH OTHER ALLOYS.

*ASTM ALLOWABLE TENSILE STRENGTH

commercial heats. Therefore, a major component of ORNL's future thermomechanical processing program will involve acquisition of these data, especially creep data and the correlations predictive of creep behavior for the ASTM specifications and code approval. The correlations developed for nickel aluminides will serve as an initial framework until a full-scale data base for the iron-aluminides is developed.

The milestones presented by ORNL for development of these alloys are as follows:

1989:

Determine final composition of the target iron-aluminide by early FY1989. Thermomechanical processing study involving three steps of scale-up from 500 g to 150 kg to 250-500 kg heats by September 1989. The first commercial trial heat will be scheduled at the end of the fiscal year.

1990:

Obtain ASTM specifications and code approval for the MOLTOX™ application by March 1990. Accomplish commercial-scale heats at or above 2500 kg. Expand the technology to other types of industrial applications which require high-temperature corrosion resistance under oxidation and sulfidation corrosion environments.

1991:

Obtain full-scale ASTM specifications and codes for generalized commercial applications. Broaden commercial potential sufficiently to convince industry involvement. Work with steel companies for the steel initiative programs. Initiate technology transfer to industry.

3.4 EFFECTS OF HYDRODYNAMICS ON CORROSION

The results of the extensive corrosion monitoring in the MOLTOX™ pilot plant are summarized in Figure 3.4. Corrosion racks, containing metal coupons exposed to molten salt with flow velocities at about 0.2 feet per second, showed corrosion rates similar to those found in the laboratory tests. The 316 stainless steel had a corrosion rate of about 10 mpy in the 950°F absorber bottoms, while Inconel 600 had a corrosion rate of about 30 mpy in the 1200°F salt separator bottoms. Pipe spool pieces, which were exposed to practical fluid velocities of about 1.5 fps, had corrosion rates of 34 mpy for 316 stainless steel in the 1050°F salt separator bottoms, while Inconel 600 had corrosion rates of 2, 263, and 146 mpy, respectively, at the inlet (1050°F) and outlet (1220°F) of the desorber tubes and in the piping to the salt separator (1200°F).

The effects of velocity on corrosion rate are complex and depend on the characteristics of the metal and environment. Velocity often strongly influences the mechanisms of the corrosion reactions. Corrosion can occur on metals and alloys that are completely resistant to a particular environment at low velocities. Increased velocity may increase or reduce attack, depending on its effect on the corrosion mechanism involved. The effect may be nil until a critical velocity is reached, and then the attack may increase at a rapid rate. Some materials show little effect when the velocity is increased from 1 to 5 ft/sec but destructive attack occurs around 20 ft/sec. An example of this phenomena was found in the MOLTOX™ pilot plant where SS-316 showed dramatically increased corrosion rates above a critical velocity of 16 ft/sec. When SS-316 was used in the high fluid velocity regions, catastrophic corrosion occurred, even at relatively low temperatures of 920°F. The dramatic increase in corrosion rate with fluid velocity for SS-316 is shown in Figure 3.5. Obviously, the protective film on SS-316 was no longer resistant to the corrosive media above the critical velocity of 16 ft/sec. Velocity may increase attack by increasing the supply of corrosive species in contact with the metal surface by increasing diffusion by reducing the thickness of the diffusion layer at the surface.

Figure 3.4

Figure 3.5
**EFFECT OF FLOW VELOCITY
 ON CORROSION**

The effect of increasing velocity on the corrosion rate of I-800 at 855°F is also shown in Figure 3.5. In contrast to the SS-316, velocity did not seem to have any significant effect on the corrosion rate of I-800, suggesting that different mechanisms were controlling the corrosion rates of the two metals in the same molten salt.

The effect of fluid velocity on corrosion was also investigated in the laboratory using a rotating cylinder in Reactor #3. Dynamic corrosion tests were conducted on alloy 316 at 950°F and 3 psia P_{O_2} using an equimolar sodium and potassium salt mixture with 0.2 mol % Na_2O_2 . The corrosion rate at a shear rate of 8.7 ft/sec and Reynolds number of 1.785×10^5 was 600 mpy, whereas the rate under sparged conditions where the coupons were stationary was 250 mpy. The coupons under shear did not form any oxide scales in contrast to the oxide scale formation observed with the stagnant coupons.

Dynamic corrosion tests were also conducted on alloy 600 using the spinning cylinder apparatus with an equimolar sodium and potassium salt system containing Catalyst A. Preliminary laboratory test results showed that the corrosion rate of alloy 600 increased from 2 mpy under sparged stationary conditions to about 7 mpy at 7.5 ft/sec ($Re = 5.8 \times 10^5$) at 1250°F and 20 psia P_{O_2} . In comparison, the corrosion rate of a spool piece of alloy 600 in the PDU exit stream was about 260 mpy at desorber exit conditions of 1220°F and 20 psia P_{O_2} at 0.4 ft/sec ($Re = 1.6 \times 10^4$), with an equimolar sodium and potassium salt system containing 0.4 mol % Na_2O_2 .

Preliminary test results indicated that Catalyst A would be significantly less corrosive than Na_2O_2 catalyzed salts under dynamic conditions with a velocity of 8.7 ft/sec ($1.8 \times 10^5 N_{Re}$) in the equimolar Na and K salt mixture at 950°F and 3 psia P_{O_2} . The corrosion rate of alloy 316 was about 40 mpy with Catalyst A compared to 600 mpy with 0.2 mol % Na_2O_2 in the equimolar sodium and potassium salt mixture.

These results suggest that the effects of velocity on corrosion rate could be complex and depend on the characteristics of the metal and the environment to which it is exposed. The nature of the protective film that forms on a given

metal depends upon the specific environment to which it is exposed, and this determines its resistance to corrosion to that fluid. Velocity also often strongly influences the mechanisms of the corrosion reactions. Because of these reasons, hydrodynamic corrosion testing was suspended at that time until a final salt composition and material was selected.

The rotating cylinder generated well-defined hydrodynamic conditions simulating those encountered in the pilot plant. It has been shown that the rotating cylinder can simulate corrosion from pipe flow more closely than any other geometry. D. C. Silverman (Ref.1) found that velocity-sensitive corrosion rates obtained from the rotating cylinder agreed well with those obtained from pipe and annulus flow, irrespective of the type of corroding media. Velocities based on equality of mass transfer coefficients were used as the basis of comparison. To duplicate the corrosion mechanism of pipe geometry with a fluid velocity of U_2 , the equivalent rotating cylinder velocity (U_1) should be:

$$U_1 = (0.11845(\text{density}/\text{viscosity})^{1/4}(d_1^{3/7}/d_2^{5/28})Sc^{-0.0857})U_2^{5/4}$$

where Sc = Schmidt number
 density = kg/m^3
 viscosity = kg/ms
 d = diameter (m)

This equation will be used to establish approximate test conditions for the rotating cylinder in our laboratory. Since the effect of hydrodynamics may be significant, it is important that a range of varying conditions with different velocities be tested in the laboratory to simulate the changing conditions around a plant.

3.5 CONCLUSIONS

3.5.1 Salt Chemistry

A salt system was identified for use in the MOLTOX™ process in which the corrosion rates of the materials of construction are significantly lower than observed in the pilot plant. In addition, the kinetics of this system were found to be sufficiently high to maintain design parameters.

The main results are as follows:

- The strong dependency of the corrosion rates of alloys on oxygen partial pressure in the MOLTOX™ system suggests that the oxidation state of the oxygen anions, generated from the alkali oxides, has a dramatic impact on corrosion. The corrosiveness of the oxygen anions appears to increase with the decreasing oxidation state of the anions.

Pure sodium and pure potassium systems were evaluated to determine whether the pure salt systems would provide a significant advantage over the equimolar sodium/potassium system in terms of the oxygen-carrying capacity. The results indicated that the pure salt systems were unlikely to provide a sufficiently low corrosive salt system for conventional alloys like SS-316 and I-600. However, the new iron aluminides may provide adequate corrosion resistance in the pure salt systems.

3.5.2 Materials of Construction

Intermetallic aluminides were found to provide acceptable corrosion rates under the MOLTOX™ desorber conditions. The main results are as follows:

- Intermetallic nickel aluminides, under development at Oak Ridge National Laboratories, were sufficiently corrosion resistant under MOLTOX™ process conditions through the formation of a highly protective aluminum oxide layer. Laboratory tests indicate that the corrosion rates of nickel aluminides were an order of magnitude lower than conventional materials

like I-600. Corrosion resistance appear to be greater in the aluminides with higher aluminum content. The cost of nickel aluminides, however, was too high for commercial MOLTOX™ applications.

- Intermetallic iron aluminides, also under development at ORNL, were also sufficiently corrosion resistant under MOLTOX™ process conditions. Like the nickel aluminides, corrosion resistance was greater in the aluminides with higher aluminum content. The cost of the iron aluminides is projected to be no greater than that of SS-316. The ductility and fabricability of iron aluminides, however, need to be improved before commercialization of these materials is possible.

Zirconium and hafnium appeared to be adequately corrosion resistant in the MOLTOX™ environment due to their protective oxide films. An economic

evaluation, however, indicated that they were not cost-effective materials for piping and vessels. Both materials may be useful for small items such as pumps and valves in severe service environments.

- Cobalt, chromium and nickel based alloys were tested for their corrosion resistance in the laboratory. Experimental results suggest that the corrosion rates of these materials were generally high in the MOLTOX™ salt system at desorber operating conditions.

4.0 PROCESS ECONOMICS

4.1 BASELINE OXYGEN PLANTS

When Task 1 of the development work under Contract No. AC07-82CE40544 was being performed, the cryogenic air separation industry standard for the production of large quantities of oxygen was the low pressure process with mechanically refrigerated, front end clean-up and oxygen product compression as shown in Figure 4.1 and as described more fully in References 12 and 13. In that process, ambient air was compressed to 86 psia and passed through molecular sieve purifiers for the removal of CO₂ and water after being cooled to approximately 40°F against a refrigerant stream. The purified air then was cooled by heat exchange with the process effluents. A small portion of the compressed air was expanded in a cryogenic turbo expander, to provide the heat leak and heat exchanger delta T losses. The separation was accomplished in a high pressure and low pressure distillation column, with oxygen product being produced at essentially atmospheric pressure from the low pressure column. This was compressed in the oxygen product compressor to the final pressure of 615 psia. The pressure energy in the air was completely expended in providing reflux for the distillation columns, and all the effluent gases were vented at atmospheric pressure and temperature.

Since about two-thirds of the value of atmospheric gases is energy related, there has been an ongoing effort to develop cryogenic air separation with reduced energy requirements. This has led to the use of a modified low pressure cycle as shown in Figure 4.2 and as described in References 13 and 14. Efficiency improvements have been made in the separation and purification process areas. In the separation section, the oxygen product is removed from the low pressure distillation column as a liquid rather than as a gas. The liquid then is vaporized at an elevated pressure against condensing air. With this cycle, the oxygen can be produced at a pressure of 7 psi higher than that produced by the standard low pressure cycle without increasing the maximum air

Figure 4.1
CRYOGENIC LOW PRESSURE CYCLE

Figure 4.2

CRYOGENIC MODIFIED LOW PRESSURE CYCLE

compressor discharge pressure. Likewise, higher oxygen pressures can be obtained by increasing the air pressure as shown in Figure 4.2. In the purification section, the mechanical refrigeration system has been replaced by a direct contact aftercooler and a waste nitrogen evaporative cooling tower which chills water. The chilled water is produced by both latent and sensible heat transfer to the cold nitrogen gas, and, thereafter, the water is pumped to the aftercooler to finish the cooling of the air stream. In addition, to further save energy, the air compressor heat of compression is used to reduce the reactivation energy requirement. Over half of the energy required to reactivate the adsorbers can be obtained from this heat source. Finally, machinery advances have made the air and oxygen compressors even more power efficient in recent years. Larger intercoolers, which reduce interstage pressure drops and temperature approaches, and aerodynamic enhancements, such as improved scroll, diffuser, and impeller designs, have become available.

A comparison of the capital investments and energy requirements for both the cryogenic low pressure and modified low pressure cycles are summarized in Table 4.1 for a 1,000 short ton/day (ST/D) plant. This size is large enough to achieve good energy efficiency of the various components and is representative of the size required to fit the majority of the market needs in new market applications. The investments show both the differences in process design scope and the escalation in time from 1982 to 1988 while the energy consumptions, which are based upon "summertime" ambient conditions of 14.7 psia, 85°F, and 60% relative humidity, represent the differences in process design and improved machinery efficiencies.

Table 4.1

CRYOGENIC PLANT INVESTMENT AND UTILITIES SUMMARY

1,000 ST/D of 99.5% Purity Oxygen at 615 psia

Cycle	<u>Low Pressure</u>	<u>Modified Low Pressure</u>
<u>Investment (MM\$)</u>		
Cost Base Year	1982	1988
GNP Deflator	1.00	1.21
Air Compression	5.0	4.8
Purification	2.4	2.0
Heat Exchange and Separation	7.6	11.1
Oxygen Compression	<u>3.6</u>	<u>4.1</u>
Total - Base Year	18.6	22.0
Total - 1988	22.5	22.0
<u>Utilities</u>		
Electric Power (KWH/Hr)		
Main Air Compressor	9,920	10,260
Refrig./Pumps/React. Heater	360	220
Cryo Turbine	(120)	(120)
Product O2 Compressor	4,520	3,770
Off-sites	<u>420</u>	<u>370</u>
Total	15,100	14,500
Total (KWH/ST)	362	348

4.2 MOLTOX™ PLANTS

As reported in the final report under Contract No. AC07-82CE40544, the MOLTOX™ system was projected to be competitive with cryogenic air separation plants in those applications in which significant process heat integration can be achieved. Specifically, the salt heater integration can be used in the radiant and convective heat transfer sections of fired or unfired steam boilers. The example cited in that final report is shown in Figure 4.3 and its material and energy balance in Table 4.2. The "summertime" ambient air feed was compressed to about 25 psia in the turbo blower and first passed through the air purifiers for water and CO₂ removal to the 1 ppm level. The air then was preheated in the heat exchange section against returning oxygen and nitrogen gases. After preheating, the air was passed through the absorber column where molten salt chemically absorbed oxygen from the air at about 950°F and 20 psia. The waste nitrogen exited the absorber and was cooled to about 400°F in the heat exchanger and was used as regeneration gas in the air purifiers before being vented to the atmosphere.

The oxygen-rich molten salt left the absorber column and was pumped to a pressure of about 35 psia and preheated to about 1100°F against the oxygen-lean molten salt exiting the desorber/salt heater. The final stage of heating to 1200°F was supplied by the flue gases in the heat recovery steam generator. The final cooling of the oxygen-lean molten salt was achieved in the salt cooler, which was a second steam generator. The molten salt then was returned to the absorber to continue the cycle. The product oxygen at 28 psia was cooled against the incoming air and compressed to final use pressure in the product oxygen compressor.

Figure 4.3

INITIAL LOW PRESSURE INTEGRATED THERMAL SWING MOLTOX™ SYSTEM

Table 4.2

INITIAL LOW-PRESSURE INTEGRATED THERMAL SWING
MOLTOX™ SYSTEM HEAT AND MATERIAL BALANCE

1,000 ST/D of 99.9% Purity Oxygen at 615 psia

Point	Flow		psia	Pressure	Temperature		Enthalpy
	Mlbs/hr	Mkg/hr		1E+6 Bar	°F	°C	BTU/Hr
1	398.9	180.9	22.0	1.52	325.2	162.9	102.64
2	398.9	180.9	21.0	1.45	900.0	482.2	160.23
3	9,325.8	4,230.2	21.0	1.45	949.5	509.7	-791.04
4	9,289.1	4,213.5	32.0	2.21	1132.9	611.6	-176.96
5	9,289.1	4,213.5	30.0	2.07	1200.0	648.9	133.45
6	83.4	37.8	30.0	2.07	1170.8	632.7	36.80
7	83.4	37.8	28.0	1.93	90.0	32.2	15.16
8	83.4	37.8	615.0	42.41	90.0	32.2	14.32
9	9,242.4	4,192.4	20.0	1.38	878.3	470.2	-820.32
10	315.5	143.1	20.0	1.38	918.9	492.7	130.95
11	315.5	143.1	18.0	1.24	400.0	204.4	88.95
12	315.5	143.1	14.7	1.01	318.6	159.2	82.59

Feed and Product Stream Composition, Vol. %

	1	8	12
Nitrogen	78.12	0.08	96.33
Oxygen	20.95	99.92	2.52
Argon	0.93	0.00	1.15
	100.00	100.00	100.00

Utility Summary

<u>Electric Power</u>	<u>KWH/Ton</u>	<u>KWH/Nm³</u>
Air Compressor	96	0.151
Oxygen Compressor	93	0.146
Other	5	0.008
	194	0.305
<u>Heat</u>	<u>1E+6 BTU/Ton</u>	<u>1E+6 BTU/Nm³</u>
Salt Heater	7.46	0.0117
Salt Cooler	-7.28	-0.0115
Purification	0.40	0.0006
		Makes 62 bar, 482°C steam
		Uses 10.3 bar, sat. steam
<u>Cooling Water</u>	<u>Gal/Ton</u>	<u>m³/Nm³</u>
	3198	0.019
		11°C rise, ex. compression

This initial design had several areas of weakness. Both the purification section and heat integration method were not well defined. Also, as the pilot plant operation demonstrated, the materials of construction were not adequate in the separation section for the high fluid velocity regions and for the high temperature, two phase, flow region of the desorber/salt heater.

The first detailed design for the purification section consisted of a circulating salt system for water removal and a molecular sieve purifier for trace water and CO₂ removal. A one psi pressure drop was allowed in all heat exchanger gas circuits in both the purification and heat exchange sections. This set the turbo blower discharge pressure at 30 psia. Reactivation of the circulating salt required low level heat (i.e. 150 psi steam) while the molecular sieve purifiers were reactivated by the returning waste nitrogen gas.

The effect of pressure drop on both the heat exchanger surface area and air compressor power was evaluated as well as an alternative purification system. The second detailed purification design consisted of a "conventional" molecular sieve purifier operating at 40°F. The cooling was achieved by gas-to-gas heat exchange and by mechanical refrigeration. A 0.5 psi pressure drop was used in all the heat exchanger gas circuits. This design reduced the turbo-blower discharge pressure to 23.5 psia and eliminated the low level heat requirement for reactivation. Finally, vendor quotes were obtained for the turbo blower and included in the final cost basis. A comparison of the capital investments and utility requirements are summarized in Table 4.3 for a 1,000 short ton/day (ST/D) plant.

Table 4.3

MOLTOX™ PLANT INVESTMENT AND UTILITIES SUMMARY
FOR PURIFICATION OPTIMIZATION

1,000 ST/D of 99.9% Purity Oxygen at 615 psia

Purification Type	<u>Salt + Mole Sieve</u>	<u>Refrigerated Mole Sieve</u>	<u>Final Refrigerated Mole Sieve</u>
<u>Investment (MM\$)(1)</u>			
Air Compression	2.4	2.1	1.3
Purification	3.7	3.7	3.7
Heat Exchange	<u>2.9</u>	<u>3.3</u>	<u>3.3</u>
Total	9.0	9.1	8.3
<u>Utilities</u>			
Electric Power (KWH/Hr)			
Main Air Compressor	4,200	2,790	2,830
Refrig./Pumps/React. Heater	<u>50</u>	<u>490</u>	<u>490</u>
Total	4,250	3,280	3,320
Heat (MMBTU/Hr)			
Reactivation	9.0	0	0

(1) Dollars are 1988 dollars.

To define the heat integration method, it was desired to establish the technical feasibility of an integrated MOLTOX™ heat exchange arrangement and the incremental cost between a baseline boiler and the integrated boiler. For a baseline boiler, it was desired to know the steam capacity and conditions, the flue gas conditions, the general coil arrangement, and the cost. For the integrated boiler design, it again was desired to know this information as well as basic details about the MOLTOX™ heater and the MOLTOX™ cooler. These details included tube diameter, length, wall thickness, tube count, fin details if used, tubes/row, number of rows, and overall bundle dimensions. Several vendors were contacted, and one agreed to perform a study using existing in-house designs.

The vendor provided a preliminary design for a salt heater/integrated boiler based on retrofitting a 250 MW boiler, which required the salt cooler to be used as a steam superheater. This resulted in an inefficient and costly design. As a result, the vendor's baseline information was modified to develop designs for integrated and conventional boilers, producing 400M to 1,400M lbs/hr. The 400M lbs/hr steam quantity is the amount that is produced by the salt cooler in a 1,000 ST/D oxygen plant and, thus, set the boiler size lower limit. For the 400M lbs/hr case, the boiler feedwater preheat and steam superheat occur in the integrated boiler convection section, and the salt is heated in the radiant section of the boiler. All of the steam is produced in the salt cooler. For the other steam production cases, all of the boiler feedwater preheat and steam superheat occurs in the convection section of the integrated boiler. 400M lbs/hr of the steam is produced in the salt cooler, and the remaining steam is produced in the boiler's radiant section. The salt heating is moved from the radiant section to the convection section of the boiler.

The cost premium for the difference in the heat exchange area between designs for each size was estimated. High alloy, seamless tubing with and without a corrosion allowance was used for the salt heater while conventional materials were used for the boiler feedwater, steam, and steam superheater coils. The most expensive case was that for the minimum steam production where the salt was heated in the radiant section of the boiler.

The higher incremental cost for this case was caused by the larger salt heater pipe diameter (i.e. 6 inch vs. 3 inch for the other integrated designs) and larger pipe spacing which were required to limit the heat flux to the salt. This caused the boiler height of the radiant section to be much greater than that for the baseline boiler. In the other integrated designs, the salt heater pipe diameters and spacing were similar to those used in the baseline boilers, and the heights of the integrated boilers were less than those for the baseline boilers. Thus, it was determined that the quantity of steam produced in the integrated boiler has to equal or exceed that produced by the MOLTOX™ salt cooler.

The focus of the design update for the MOLTOX™ separation section was to minimize the amount of heat integration (i.e. heat input in the salt heater). This resulted in a design in which the absorber and desorber operated at essentially the same pressure and in which the salt was pumped in both directions. For a 50/50 sodium/potassium salt limited to a 1200°F maximum operating temperature (Case A), the salt flowrate was reduced by 1/3 and the heat input by approximately 10%. A summary of all the process design changes to the MOLTOX™ process is shown in Figure 4.4, and the material and energy balance for Case A is given in Table 4.4.

The effect of changing the operating temperature and/or salt composition upon equipment sizes and power requirements is shown in Table 4.5. Increasing the operating temperature (Case B) and changing the salt composition to 100% sodium (Case C) are both beneficial to the integrated thermal swing MOLTOX™ system.

Figure 4.4

TYPICAL LOW PRESSURE INTEGRATED THERMAL SWING MOLTOX™ SYSTEM

Table 4.4

TYPICAL LOW-PRESSURE INTEGRATED THERMAL SWING
MOLTOX™ SYSTEM HEAT AND MATERIAL BALANCE

1,000 ST/D of 99.9% Purity Oxygen at 615 psia

Point	Flow		Pressure		Temperature		Enthalpy 1E+6 BTU/Hr
	Mlbs/hr	Mkg/hr	psia	Bar	°F	°C	
1	378.0	171.4	20.0	1.38	146.0	63.3	80.86
2	378.0	171.4	19.0	1.31	850.0	454.4	146.93
3	6,473.8	2,936.0	19.0	1.31	949.2	509.6	-549.76
4	6,440.1	2,920.7	17.5	1.21	1,121.2	605.1	-127.86
5	6,440.1	2,920.7	16.5	1.14	1,200.0	648.9	155.27
6	83.4	37.8	16.5	1.14	1,168.9	631.6	36.67
7	83.4	37.8	15.0	1.03	90.0	32.2	15.16
8	83.4	37.8	615.0	42.41	90.0	32.2	14.82
9	6,390.5	2,898.2	18.0	1.24	848.5	453.6	-575.41
10	294.6	133.6	18.0	1.24	905.2	485.1	121.24
11	294.6	133.6	17.0	1.17	273.5	134.2	73.97
12	294.6	133.6	14.7	1.01	253.4	123.0	72.51

Feed and Product Stream Composition, Vol. %

	<u>1</u>	<u>8</u>	<u>12</u>
Nitrogen	78.12	0.04	97.60
Oxygen	20.95	99.96	1.24
Argon	<u>0.93</u>	<u>0.00</u>	<u>1.16</u>
	100.00	100.00	100.00

Utility Summary

<u>Electric Power</u>	<u>KWH/Ton</u>	<u>KWH/Nm³</u>	
Air Compressor	68	.107	
Oxygen Compressor	106	.167	
Other	<u>18</u>	<u>.028</u>	
	192	.302	
<u>Heat</u>	<u>1E+6 BTU/Ton</u>	<u>1E+6 BTU/Nm³</u>	
Salt Heater	6.80	.0107	
Salt Cooler	-6.54	-.0103	Makes 62 bar, 565°C steam
<u>Cooling Water</u>	<u>Gal/Ton</u>	<u>m³/Nm³</u>	
	2,015	0.012	11°C rise, ex. compression

Table 4.5

TYPICAL LOW PRESSURE INTEGRATED THERMAL SWING
MOLTOX™ SYSTEM SEPARATION SENSITIVITY

1,000 ST/D of 99.9% Purity Oxygen

Case	A	B	C
Desorber Temp. (deg F)	1200	1250	1250
Mol Fraction Sodium	0.5	0.5	1.0
Salt Line Sizes, inches	36	30	24
Adsorber			
Diameter, Ft	16	15	14
Bed Height, Ft	1-20	1-20	1-20
Oxygen/Salt Separators			
Diameter, Ft	12.5	10.0	8.0
Height, Ft	16.25	12.25	10.5
Salt Pump-A			
GPM	7,185	4,689	2,959
BHP	123	80	51
Salt Pump-B			
GPM	7,449	4,949	3,199
BHP	80	53	34
Salt/Salt Exchanger			
Area, Ft ²	57,059	39,471	24,158
Salt Heater			
Duty, MMBTU/Hr	283.13	263.39	223.90
Integrated Boiler			
Incremental Heat, MMBTU/Hr	10.65	11.85	10.60

Finally, the economics based on the materials of construction in the separation salt loop went through several iterations. In the initial iteration for Case A (1200°F, 50/50 salt), the materials specified were based on the pilot plant performance and subsequent laboratory testing. This required the use of Inconel in areas of high velocity and in the salt-to-salt exchanger, zirconium clad 304SS for the O₂ separators and salt heater, and 316SS for the remainder of the loop. The zirconium clad vessels were estimated based on vendor information which gave a range of costs from 50% to 200% of that for Inconel vessels. Thus, both the vessels and associated piping were assumed to be fabricated of Inconel. A sensitivity assuming that 316SS could be used throughout the entire salt loop also was made. The economics showed that the materials of construction beyond 316SS incrementally added 15% to the oxygen cost when compared to that for the updated cryogenic cost. This effectively eliminated the MOLTOX™ system cost advantage.

There were other "shortcomings." The corrosion results from the parallel laboratory programs on commercial grades of zirconium material were poor due to small impurities in commercial grades and the resultant scale formation rate. The higher cost of hafnium clad 304SS, which appeared to be acceptable from a corrosion standpoint, was even more economically prohibitive. Also, while the specified materials of construction were included in the analysis, the corrosion rates and conditions had not been specified, and, therefore, corrosion allowances and material fabrication (e.g. seamless vs. welded) were not specifically included.

During this same time frame, other laboratory work indicated that a combination of new improved salts and the ORNL developmental iron aluminide alloys had the potential to solve the MOLTOX™ corrosion rate problem and material cost problem. Corrosion rates are a strong function of the operating temperature, the oxygen partial pressure, salt velocity, and of the salt composition. Figure 3.2 in Section 3 of this report shows the variation in temperature and oxygen partial pressure as the salt is pumped around the salt loop. A prediction of the corrosion rates for the base case salt system (Case A), which

Figure 3.2
MOLTOX™ TSA CYCLE

is the 50/50 salt at a maximum operating temperature of 1200°F again was selected as the initial basis for the economics. Figure 3.3 in Section 3 shows the corrosion rate criteria for this base rate system.

The surface area exposed to the salt loop was calculated at all of the points around the loop, from Point A at the top of the absorber through Point B at the bottom of the absorber to Point C entering the salt to salt heat exchanger, to Point D at the exit of the salt to salt heat exchanger, through Point E the final temperature at the salt discharge from the salt heater, and then returning back through the salt to salt exchanger and the salt cooler to return to Point A again.

Two additional cases also were chosen for study. Case B was selected to show the effect of higher operating temperature at point E in Figure 3.2 of 1250°F. Case C was selected to show the impact of utilizing a 100% sodium based salt, also at the 1250°F maximum operating temperature. To establish the corrosion targets for the research program, the corrosion rates in Figure 3.3 were increased by 10% for Case B, and by 70% for Case C. Table 4.6 summarizes the surface area and the annual corrosion loss of the construction material that is exposed to the salt at the various points around the salt loop for Case C.

Revised baseline economics for Case A (1200°F, 50/50 salt) then were prepared. The salt loop containment materials were based on iron aluminides, whose cost, fabricability, and strength were assumed, based on guidance from ORNL, to be equal to 316SS. The baseline capital investment was revised to incorporate the corrosion allowances and fabrication requirements in the salt loop equipment as well as the other process refinements mentioned earlier. Process Cases B (1250°F, 50/50 salt) and C (1250°F, 100% Na salt) also were prepared as a sensitivity study. The summary of the plant investments and utilities are shown in Table 4.7. A further sensitivity with twice the expected corrosion rates for all three alternates showed that the capital investments would increase by \$0.8MM, \$0.6MM, and \$0.5MM respectively.

Figure 3.3

EXPECTED CORROSION RATE **@ 0.4 MOLE % Na_2O_2** **FOR 50:50 Na:K NITRATE SALT**

Table 4.6

TYPICAL LOW PRESSURE INTEGRATED THERMAL SWING
MOLTOX™ SYSTEM SALT LOOP SUMMARY FOR CASE C

1,000 ST/D of 99.9% Purity Oxygen

Salt Loop Location	Surface Exposed to Salt (Sq. Ft.)	Corrosion Metal Lost ⁽¹⁾ (Lb./Yr)
Absorber	6,730	903
Pipe/Pump	1,190	63
Salt/Salt Exchanger (Tubeside)	18,160	1,182
Pipe/Separator	820	81
Salt Heater	18,680	2,507
Pipe/Separator	880	123
Salt/Salt Exchanger (Shellside)	25,140	2,454
Pipe	550	36
Salt Cooler	3,310	175
Pipe/Pump	1,030	34
Total Salt Loop	76,490	7,558

¹⁾ Estimate based on aluminide materials with 0.4% Na₂O₂ catalyst, from limited lab test data.

Table 4.7

MOLTOX™ PLANT INVESTMENT AND UTILITIES SUMMARY

1,000 ST/D of 99.9% Purity Oxygen at 615 psia

Case	A	B	C
Desorber Temp. (°F)	1200	1250	1250
Mole Fraction Sodium	0.5	0.5	1.0
<u>Investment (MM\$) (1)</u>			
Air Compression	1.3	1.3	1.3
Purification	3.7	3.7	3.7
Heat Exchange	3.3	3.3	3.3
Separation	14.4	12.1	10.3
Oxygen Compression	<u>4.5</u>	<u>4.5</u>	<u>4.5</u>
Total	27.2	24.9	23.1
<u>Utilities</u>			
Electric Power (KWH/Hr)			
Main Air Compressor	2,830	2,830	2,830
Refrig./Pumps/React. Heater	490	490	490
Salt Pumps	160	110	70
Product O2 Compressor	4,410	4,410	4,410
Off-sites	<u>130</u>	<u>130</u>	<u>130</u>
Total	8,020	7,970	7,930
Total (KWH/ST)	192	191	190
Fuel (MMBTU/Hr HHV) (2)	11.74	13.06	11.68

(1) Dollars are 1988 dollars.

(2) Incremental firing duty for the integrated boiler.

4.3 OXYGEN COST COMPARISON

The economic analysis criteria utilized in this cost comparison are summarized in Table 4.8. The same criteria were used both for the baseline cryogenic oxygen plant and for the various MOLTOX™ system versions. All of the costs used are in 1988 dollar values. This dollar value base was chosen so that the results would be recognizable in today's terms.

For the energy values, the current APCI energy cost forecast was used to determine the underlying inflation rates for the time frame in which a commercial plant would operate. The MOLTOX™ system presently is envisioned to be commercialized by the mid-1990s. The capital portion becomes fixed once a plant is on-stream, which was assumed to be 1994. However, energy costs continue to escalate with inflation over the plant operating life. Because first year operating costs understate the true costs viewed on a present value basis for a 15 year contract, the seventh year, i.e., 2000, was selected as being representative. Therefore, cost inflation was included in the cost increments between the first year (1994) and the seventh year (2000). This inflation is forecasted to be approximately 5% per year for electric power and approximately 9% per year for natural gas. Compounding the 1988 energy values of 4.95/KWH and \$1.87/MM BTU (HHV) for electric power and natural gas (delivered Gulf Coast), respectively, produced the values used in the cost comparison.

The unit oxygen costs (\$/ST) also assume that the oxygen using process requires 340 operation days per year, at the full capacity oxygen use rate. The labor, maintenance and overhead charges were estimated in detail, but it was found that 7% per year of the capital investment was representative of these costs for cryogenic oxygen plants with electric drives. This included local taxes, insurance, and all necessary home office overhead and administrative costs normally associated with operating facilities under long term contracts. An additional 2% per year was used for the extra maintenance materials and labor that are required for hot process equipment such as the MOLTOX™ salt loop

Table 4.8

ECONOMIC ANALYSIS BASIS

Capacity:

For New Markets	1000 ST/D O ₂ , 99.5% purity, 615 psia
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Investment Basis:	1988 Dollars
-------------------	--------------

On-Stream:	1994
------------	------

Operation Analysis Year:	2000
--------------------------	------

Operation Days Per Year:	340
--------------------------	-----

Energy Values:

Electric Power	6.7¢/KWH
----------------	----------

Natural Gas	\$3.10/MMBTU (HHV)
-------------	--------------------

Labor, Maintenance, Overhead, etc.:

For Cryogenic Equipment	7% ⁽¹⁾
-------------------------	-------------------

For Hot Equipment	9% ⁽¹⁾
-------------------	-------------------

Capital Related Charges	17% ⁽¹⁾
-------------------------	--------------------

Plant Life:	15 Years
-------------	----------

⁽¹⁾Percentage of Capital Investment to determine annual costs.

(separation). The capital related charges include depreciation at 15 years, state and federal taxes and return on investment. The return on investment assumed normal debt to equity investment ratios for current industry practice.

These criteria are typical of the current industry practices involved in selling oxygen over the fence through pipelines from independent electric drive oxygen plants. However, many of the emerging market opportunities may involve different practices. Several major emerging markets, such as the electric utility industry and the iron and steel industry, may use a longer economic life than the 15 years that is employed in the base case. On the other hand, the enhanced oil recovery market may utilize a much shorter economic life. Financing in the utility industry also differs from these industrial practices, with typically lower overall capital charges.

The results of the cost comparison showed a potential oxygen cost improvement of about \$8/ST or about 20% for the integrated MOLTIX™ system over a modern cryogenic plant. Table 4.9 summarizes these results.

4.4 CONCLUSIONS

The goal of this task was to update the process economics for two purposes. The first was to provide guidance to the research program, to establish goals for the work on salt chemistry and corrosion resistant materials. The second purpose was to establish if there was sufficient cost advantage, based on the process design and heat integration method and on the research results to date on salt chemistry and corrosion resistant materials, to justify the next step in the development of the process.

The final results of the process sensitivity study are shown in Figure 4.5. The surface area of construction material exposed to the salt is shown in Figure A, the resultant total corrosion based on the goals established for the research program is shown in Figure B, and the resultant oxygen cost advantage based on the use of iron aluminide materials is shown in Figure C.

Table 4.9

OXYGEN COST COMPARISON

1000 ST/D of Oxygen at 615 psia (1), (2)

Plant Type	Cryogenic	MOLTOX™ Integrated Thermal Swing System			
		A	B	C	
Case	Modified Low Pressure	1200°F, 50/50	1250°F, 50/50	1250°F, 100% Na	
Investment (\$MM)	22.0	27.2	24.9	23.1	
Utilities					
Electric Power (KWH/Hr)	14,500	8,020	7,970	7,930	
Fuel (MMBTU/Hr HHV)	-	11.74	13.06	11.68	
Energy ⁽³⁾	Annual Cost (\$M)	Annual Cost (\$M)	Annual Cost (\$M)	Annual Cost (\$M)	
	\$/ST	\$/ST	\$/ST	\$/ST	
Electric at 6.7/KWH	8,050	4,450	4,425	4,400	12.94
Fuel at \$3.10/MMBTU (HHV)	-	300	335	300	.89
Other					
Labor, Maintenance, Overhead	1,540	2,260	2,060	1,890	5.56
Chems, Lubes, Water, Etc.	305	365	365	365	1.07
Capital Related	3,740	4,625	4,240	3,925	11.54
Total Cost	13,635	12,000	11,425	10,880	32.00
Difference (\$/ST)	Base	(4.80)	(6.50)	(8.10)	
(%)	Base	(12.0)	(16.2)	(20.2)	

(1) Cryogenic plant at 99.5% purity oxygen and MOLTOX™ systems at 99.9% purity.

(2) Utilization is 340 days/year.

(3) Operation is 345 days/year.

Figure 4.5

PROCESS CONDITIONS (1000 T/D O₂)

A. SALT LOOP EXPOSED SURFACE

	°F	% NA
CASE A =	1200	50
CASE B =	1250	50
CASE C =	1250	100

B. TOTAL CORROSION

CORROSION RATE (MIL/YEAR)

CASE A. 0.5 TO 4.0

CASE B. PLUS 10%

CASE C. PLUS 70%

C. WITH IRON ALUMINIDE ALLOY, THEN:

ASSUMED

INSTALLED COST = STAINLESS STEEL

5.0 ALTERNATE DESORBER DESIGNS

Several alternate designs were investigated as shown in the attached figures.

The staged desorption option (Figure 5.1) allowed for pumping the molten salt before heating in order to suppress oxygen release in the exchanger. By deleting the vapor-liquid interface, the rate of corrosion could be reduced. The limit of a 1250°F wall temperature necessitated a three-stage desorber. The three stages increased total desorber surface, increased the power requirement and increased the operating risk by increasing the pumps to three instead of one. The combination of the above made this option unattractive for a large commercial unit.

Direct contact of hot oxygen with the salt (Figure 5.2) would reduce the surface in contact with salt and also lower the velocity of the salt. Both are important factors in considering corrosion. The oxygen circulation rate, however, would have been three times the flow of flue gas in our base desorber design and forty-five times the product oxygen rate. This would definitely not be economical.

The bayonet tube (Figure 5.3) is a ceramic exchanger design, again, to reduce the metal surface contact with the salt. The design is to keep the salt velocity low. The heat transfer was fairly poor and resulted in a large surface requirement. In addition, an exchanger of this type would itself require some development program. The idea was dropped from future consideration.

The heat tube design (Figure 5.4) was suggested to simulate pool boiling of the molten salt with an intermediate fluid for heat transfer. A suitable intermediate fluid, one that would condense and vaporize in the limitations of the desorber conditions, could not be found. This idea was dropped from further consideration.

STAGED DESORPTION

FIGURE 5.1

DIRECT CONTACT HOT O₂

FIGURE 5.2

CERAMIC HEAT EXCHANGER (DON ERIKSON)

HIGH-DENSITY FUSED ALUMINA BAYONET TUBES
TUBESHEET SEAL IS GAS, ALLOWS PACKING
LEAKAGE OXYGEN TO FLUE
FREE-DRAINING

FIGURE 5.3

HEAT TUBE DESIGN OPTION

FIGURE 5.4

6.0 RESEARCH PLAN AND RECOMMENDATION

The iron aluminide materials show low corrosion rates and low cost. These materials are developmental, and their fabricability needs to be demonstrated. A commercial supplier has not been identified. Therefore, the first recommendation is that ORNL be funded to proceed with the development of these materials, including the data needed to achieve ASME coding, and the data needed to provide the incentive for a commercial supplier.

The new salt chemistry work has shown very promising results. However, for the aluminide materials there is very limited corrosion rate data at the higher process conditions, and there is also no data to show the life of this material. The issues on the salt chemistry itself, are that it has not been demonstrated to have long term stability at the higher process conditions, and also the kinetics of the process need to be established. A remaining issue is that the fouling products based on the aluminide material and the new salt have not been analyzed nor explored. The second recommendation is therefore that a continued laboratory testing program be established at both Air Products' facilities, and at ORNL's facilities to do the longer term corrosion testing and performance testing of the new salts.

The objective of this cooperative agreement is to develop the process to the point, based on pilot plant operation which can justify proceeding to the next larger scale. The agreement is in two phases, the first phase being a laboratory program, the results of which have been reported above. At the end of the laboratory program, a decision on Phase II to modify and operate the 0.25 T/D pilot plant is to be made. The results from the Phase I laboratory program have been very favorable, and significant achievements have been made. However, a continuation of the laboratory development work is needed, as is shown in the previous two recommendations. Therefore, the final recommendation is that the decision on proceeding with Phase II of this agreement be placed on hold, for an additional period until the milestone recommendations from the

laboratory programs are achieved. Therefore the decision to proceed to Phase II should be retained on hold until the ORNL iron aluminide development program, and the Air Products salt program have reached the point where the materials required for pilot plant modification are available from ORNL, and the engineering design basis for the revised salt chemistry and process operating conditions are available from the Air Products' program.

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