AIR SEPARATION BY THE MOLTOX PROCESS

Energy Concepts Company

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ABSTRACT

The report describes results of a development program on a new and energy saving process for air separation. The Moltox process involves reversibly reacting oxygen in air with a recirculating salt solution, such that oxygen is extracted without depressurizing the remaining nitrogen. Energy savings of approximately 50% are indicated for this process compared to conventional cryogenic air separation.

The development program consisted of design, construction, and operation of a 6 liter/minute pilot plant; optimization of the process flowsheet through computer modelling; investigation of engineering aspects of the process including corrosion, safety, and NO_x generation; and an economic comparison to conventional cryogenic practice. All objectives were satisfactorily achieved except for continuous operation of the pilot plant, and the modifications necessary to achieve that have been identified. Economically the Moltox process shows a substantial advantage over large scale cryogenic plants which are powered by fuel vice electricity.

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I. INTRODUCTION

Under joint sponsorship of the U.S. Department of Energy and Energy Concepts Company, a program of research and development has been conducted on a new and energy efficient air separation process. This report details the progress towards commercialization that has been accomplished under that development program. The work has been partially supported by DOE Contract DE-AC01-79CS40287. The DOE Project Manager is Mr. Robert G. Massey.

The new air separation process, termed the "Molttox" process, involves a molten liquid which chemically reacts with the oxygen in compressed air via a reversible reaction. The oxidized liquid subsequently releases the oxygen as a pure gas by undergoing pressure reduction and/or temperature increase. The recycling liquid is predominantly a mixture of alkali nitrates and nitrites, at a temperature of approximately 1200°F. The key advantage of the process is that the exhaust nitrogen remains at pressure and high temperature after oxygen removal, and hence can be work expanded to recover all the energy needed for compression. This means that the only energy input necessary to the process in principle is a thermal input. In contrast, conventional cryogenic processes require a mechanical input which gives rise to substantial Carnot losses.

A previous feasibility study of this process, partially supported by the Energy Research and Development Administration, determined that energy savings on the order of 50% were obtainable. That study involved laboratory experiments to confirm process chemistry and also the generation of a baseline process flowsheet. That work was reported in reference I-1. Process improvements resulting from that feasibility study are described in reference I-2. The promising results obtained from that feasibility study led to the decision to continue to the current stage of development.

The current development program consisted of four major tasks: the construction and operation of a pilot plant of the process; a more detailed computerized modelling and operating parameter optimization of the process; an identification and analysis of key engineering concerns of the process; and an economic comparison to conventional O₂ generation processes. The development accomplished in each of these tasks is detailed in succeeding sections of this report.

II. PILOT PLANT

A. Design

The design basis of the laboratory scale pilot plant is an O₂ generation rate of 0.6 scfm, at a salt circulation rate of 0.6 gpm. The reaction vessels are 4 inch I. D. by 6 feet high SS 304 cylinders which are Alonized for corrosion protection. The absorber tower is sized to keep the gas velocity less than 50% of that which would cause flooding, per reference II-1 and to yield approximately two stages of countercurrent contact. All services to each reaction vessel enter through the top, in order to minimize corrosion opportunities. The nominal design pressures are 100 psig in the absorber and atmospheric in the desorber, with provision to also operate the desorber under vacuum. The design temperature is 1300°F.

A piston type pump with graphite asbestos packing is used to circulate the salt, and operates at a temperature of 850°F. Salt to salt heat exchange is used to raise the salt temperature to reaction vessel temperature. As a backup to the pump, two receiver vessels are provided which when necessary can be used to circulate the salt in a "blow case pump" mode of operation.

The entire salt loop is heat traced with tubular electric heaters in order to establish an initially molten state upon startup. Initially heat tracing was done with fiberglass or Samox insulated heat tapes, but it was found that leakage of salt onto the heat tape caused failure, hence, it was necessary to change to the metal encased tubular heaters. The salt inventory in the plant is approximately 40 pounds. A supply of commercial salt is being used which, at 40¢ per pound, is more than an order of magnitude less expensive than laboratory supply house salt. Batch experiments have shown that its behavior is not distinguishable from that of the high purity salt.

Process instrumentation includes the following. Temperature is monitored at twenty points with type K thermocouples. Pressure is measured at twelve points by Bourdon tube guages, and gas flow rate at seven points via rotameters. Oxygen concentration is measured at two points by polarographic sensors, and the salt level in the four containment vessels (absorber, desorber, and two receivers) is measured by four differential pressure guages. Sampling for NO_x is by Kitigawa length of stain indicator tubes, with 1 ppm sensitivity.

A simplified flowsheet of the laboratory pilot plant is included as Figure II-1. The supply air is normally provided by an oil free compressor, with bottled air as backup. Moisture and CO₂ removal is via molecular sieve, followed by an indicating Drierite dryer. Both air to air and salt to salt heat exchange is incorporated to minimize heat requirements. Each of the four vessels is individually heated with its own temperature controller. Thus, it is possible to operate the apparatus in either temperature swing or pressure swing mode, or any combination of the two. Forced cooling is available to one of the receiver vessels to remove reaction heat in the temperature swing mode, but it has been found that the normal heat leaks preclude need for additional cooling in this size apparatus.

Figures II-2 through II-5 present several views of the apparatus during the course of construction. Figure II-2 shows the reactor vessel closure heads. Each vessel requires six or seven services, and they are designed to all be supplied from the top through three openings. This allows the use of internal liners to contain the molten salt. Originally, fused alumina liners were used, but the corrosion tests showed them not to be necessary, and they have been removed. Figure II-4 shows the piping connection details to the two receiver vessels, including heat tape, prior to applying insulation. Figure II-3 shows the furnace and its control panel, the pump, and the temperature monitoring panel. Figure II-5 shows the approximate general arrangement of the equipment. The gas monitoring station, including flowmeters, control valves, oxygen monitors, etc., is shown to the right in that photo.

B. Pilot Plant Operating Results

The pilot plant operations which were conducted can be divided into three major phases: startup campaign, attempts to achieve continuous steady state operation, and batch operations. The startup campaign consisted of eight days of full plant operation/salt circulation, plus the accompanying pretreat operations, heatup or cooldown operations, and incidental repairs. The first operating day was a pump operability and liquid level indication check, conducted entirely at low temperature (300°C). The second day the temperature was raised to 350°C. The third day, heatup continued to 600°C, and different pump settings were checked. Also absorber pressure was increased to 50 psig. On the fourth day of operation the third day operations were repeated, but much steadier operating conditions regarding gas flow rates, pressures, and liquid levels were achieved due to increasing operator skill. On the fifth day of plant operation, heatup continued to 665°C. High air flow rates were achieved while holding 50 psig in the absorber and a vacuum in the desorber. Also a packing ring was added to the pump

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FIGURE II-2. Reactor Vessel Closure Heads

FIGURE II-3. Furnace with Control Panel, Pump and Temperature Monitoring Panel

FIGURE II-4. Piping Connections to Two Receiver Vessels, including Heat Tape.

FIGURE II-5. General Arrangement of Equipment. Gas Monitoring Station shown to the right of the photograph.

in the midst of the operation. The sixth day was the first time actual O_2 production was obtained, while at $675^{\circ}C$. The same temperature was maintained on the seventh and eighth days of operation, and O_2 was generated for 3 hours and 4 hours respectively on those two days. The initial O_2 production was a small trickle, less than the bleed rate of air into the deep leg of the level indicator. Hence the N_2 from that source caused the O_2 reading to be in the 30 to 50% range. By the eighth day however, O_2 generation rates were substantial (approximately 0.4 liters per minute), and the recorded O_2 readings went as high as 93%, implying corrected readings of better than 98%.

At that point the basic lessons available from the startup campaign had been gained, and numerous possible improvements were evident. It was apparent that the salt chemistry had not yet reached equilibrium--a mass balance between oxygen entering the salt in the absorber and oxygen leaving the salt in the desorber had not yet been achieved. Also high NO_2 levels on the order of 1000 ppm were still being recorded (down from approximately 15,000 ppm on initial startup). One of the major modifications determined to be necessary at this point was removal of the internal fused alumina liner in the desorber. Desorber furnace temperatures of approximately $825^{\circ}C$ had been necessary to transfer the necessary heat through the vessel wall and liner and maintain $675^{\circ}C$ in the internal salt. Upon removal of the liner it was found that much salt had spilled over to outside the liner and hence was in a stagnant and very hot zone. This is believed to be the major cause of high NO_x readings. Accordingly several modifications were made including removal of the liner before resumption of further operations.

The next sequence of continuous pumped operation consisted of seven full days of plant operation. Overall the mechanical operation of the plant became quite dependable, although numerous small problems were discovered and lessons were learned. Considering the temperatures and pressures of this closed loop pumped liquid system, this is believed to be a new frontier of engineering accomplishment. However the plant was failing to achieve the intended chemical performance. Oxygen generation was never more than a trickle--every time the desorber reached conditions where oxygen desorption would be expected, the pump would unexpectedly stop pumping. Once flow stopped, the desorber would rapidly overheat and substantial oxygen would evolve transiently.

After several unsuccessful trials all involving this characteristic behavior, it was finally realized that the problem was due to loss of pump suction. This was due to the fact that in order to supply all desorber services from the top, the pump suction line comes out of the top of the desorber vessel. Thus once the salt reaches O_2 saturation, when the pump attempts to lift the salt above the desorber level, O_2

flashes out of the salt and gas binds the pump suction line. This problem can be solved by taking pump suction directly from the bottom of the desorber and keeping the suction line at all points below the desorber level.

In order to assure that this was in fact the problem, rather than some inherent chemical problem with the salt, a series of batch operations were then undertaken in the desorber vessel. These were of two types. In one type, the desorber containing loaded salt was heated to desorption temperature and then a constant vacuum was applied, and O₂ flow vs time was recorded. In the second type, a constant O₂ flow rate was established, typically 3 liters/min. and desorber vacuum was slowly decreased as necessary to maintain that flow. In either case the salt was recharged by lowering the temperature and bubbling air through it at atmospheric pressure overnight. In these tests, the amount of oxygen evolved from the salt each run increased until approximately the sixth time, and thereafter the behavior was repeatable. The desorber contained approximately 10 kg of salt. Approximately 100 liters of O₂ was desorbed from the salt each run. In a typical run, the initial pressure was 77 kPa absolute at 660°C, and the pressure was steadily decreased to a final value of 27 kPa thirty minutes later, while maintaining a steady 3 lpm O₂ generation rate. This substantial exchange of O₂ with the salt meets the expectations of the process chemistry. Also it was noted that oxygen absorption occurred at temperatures much lower than expected, even below 400°C. A total of 32 batch desorption runs were conducted.

III. PROCESS ANALYSIS

A. Analysis Procedure

The objective of this task is to determine both a process flowsheet and a set of operating conditions which are fully representative of the advantages of the Moltox process. The choice of flowsheet sets an upper bound on possible performance, and a computerized search of a model of the process flowsheet is used to determine the operating conditions which optimize the flowsheet performance, subject to the imposed constraints.

The flowsheet chosen for the major optimization effort is shown as Figure III-1. The rationale for this choice of flowsheet was presented in reference I-1. That reference also records a baseline set of operating conditions and performance value for the flowsheet, based on a very limited search of the operating parameters.

In this investigation, a much more detailed exploration has been conducted on the effect and interaction of each of the operating and design parameters involved in the reference process flowsheet. The parameters which were varied included the rotating machinery efficiencies, the heat exchanger ΔT (or equivalently efficiency), the absorber and desorber pressures, the preheat temperature of the absorber inlet air, the theoretical number of counter-current stages in the absorber, and the absorber gas/liquid ratio (or equivalently the salt flow rate). For each set of parameters a computerized process model was used to solve the mass and energy balance for the entire flowsheet, and tabulate the overall energy requirement, the absorber and desorber temperatures, and combustor conditions--temperature and excess oxygen available before and after combustion. The resulting data was reduced and graphically analyzed, yielding numerous graphs similar to Figures III-2 through III-4. Figure III-2 reflects the initial screening performed. It was found that for any set of operating parameters, a particular salt flow rate would yield the minimum energy requirement. Figure III-2 illustrates this behavior for three different sets of operating conditions--the process energy requirement, in BTU per pound of product O_2 , is plotted against the salt flow rate, in moles of salt per mole

FIGURE III-1. Flowsheet for 100 TPD Chemical Air Separation

FIGURE III-2. EFFECT OF SALT FLOW RATE ON PROCESS ENERGY REQUIREMENT

Constants: 5 States, P_{des} 0.5 ATA,
1160°F Inlet Temperature

of input air. The three curves reflect three different values of absorber pressure, whereas all other operating conditions are the same. For each absorber pressure, there is a definite salt flow rate which yields the minimum energy. Next, the collection of minimum energy points thus determined, numbering approximately one hundred, were further analyzed according to Figure III-3. Figure III-3 is a plot of contours of constant energy requirement as a function of desorber pressure and absorber pressure. It also includes contours of constant combustor outlet temperature (which is also the high pressure expander turbine inlet temperature). Graphs similar to Figure III-3 have been prepared for both 4 and 5 stage absorbers, and for absorber air inlet temperatures of both 1160° and 1180°F.

With the above information, it was possible to identify a new operating region which yielded the same high energy efficiency as recorded in reference I-1, but involved markedly less severe conditions in order to achieve it. Most notably the combustor outlet temperature has been reduced to the 1660°F range, primarily by decreasing absorber pressure.

Next, restricting attention to the new preferred operating region, the effects and interaction of compressor efficiency, expander efficiency, and heat exchanger efficiency were explored. Typical results are illustrated in Figure III-4. In that figure, the effect of compressor efficiency on the energy requirement is plotted for three different expander efficiencies, given a 50°F ΔT heat exchanger. Similar graphs were prepared for 25 and 100°F ΔT .

With these graphs, new baseline process equipment efficiencies have been identified which achieve the same overall process efficiency but reflect a more economic and conservative choice of equipment parameters. In particular, the compressor and expander efficiencies have been decreased to 77% and 82% respectively, whereas the heat exchanger ΔT has been decreased to 50°F (approximately 95% efficiency). Considering that in current cryogenic practice, a temperature difference of 4°F is achieved at better than 97% efficiency, this value is considered reasonable. The reduced rotating machinery efficiencies mean that much lower capacity and/or less complex machines can be used.

Other conclusions from this parametric analysis are as follows. The strong effect of desorber pressure on process efficiency is very apparent. Just how low this parameter can go is primarily a question of reaction kinetics, plus also the extent of vapor phase salt loss. The number of absorber stages has surprisingly little effect going from 4 to 5 stages--it yields only an approximate 10 BTU/lb O₂ improvement. Whereas the addition of a second countercurrent stage provides a marked improvement, for this process flow-sheet the improvement diminishes rapidly with further stages.

FIGURE III-3. EFFECT OF ABSORBER AND DESORBER PRESSURE ON PROCESS ENERGY REQUIREMENT AND MAXIMUM TEMPERATURE

Constants: 5 Stages, 1160°F Absorber Inlet Temp., Optimized
Salt Flow Rate $\eta_{\text{comp}} .8$, $\eta_{\text{exp}} .85$, HX ΔT 100

FIGURE III-4. EFFECT OF COMPRESSOR AND EXPANDER EFFICIENCY ON ENERGY REQUIREMENT

Constants: 5 Stages, P_{abs} 7.2 ATA, P_{des} 0.5 ATA,
 T_{abs} in 1180°F, HX ΔT 50°F, Salt Flow 14

This is probably due to the relatively large amount of residual O_2 left in the absorber exhaust. It has important implications--a process which performs nearly as well with 5 stages as with 20 is much more amenable to scale down to small sizes than, for example, current liquefaction processes.

B. Baseline 100 TPD Process Flowsheet

Table III-1 in conjunction with Figure III-1 presents a new baseline set of operating conditions for a plant which produces 100 tons per day of gaseous oxygen product at one atmosphere pressure. Salient features are as follows. Both the absorber and desorber are adiabatic, i.e. there is no heat exchange with the salt. Hence, non-corroding refractory liners can be used for salt containment without efficiency penalty. The maximum absorber temperature is $1240^{\circ}F$, and $1206^{\circ}F$ for the desorber. The inlet air on a dry basis is 1776 pound moles per hour (MPH), of which the oxygen is 373 MPH. The product oxygen is 260.4 MPH. Hence, the absorber extracts 69.8% of the oxygen out of the air, and the exhaust supplied to the combustor contains 7.4% oxygen. Fuel is supplied to the combustor (preferably natural gas) at a rate of 680 BTU per pound of product oxygen, lower heating value basis. The stoichiometric combustion requirement for oxygen amounts to only approximately one third of the oxygen available in the exhaust gas, and the heat of combustion raises the gas temperature to $1668^{\circ}F$. Thus, the high pressure expander turbine inlet temperature is within the metallurgical capability of current nickel base blade alloys such as A286. The low pressure expander can be a conventional radial inflow design with aluminum blading. Each expander would preferably be directly mechanically coupled to one of the compressors, plus optionally also a generator to provide the remaining power requirements. The process is mechanically power balanced, i.e. the power generated by the two expanders is equal to the power required by the three compressors plus the pump, and hence, the only net energy requirement is the 680 BTU/lb thermal input, supplied in this case by natural gas.

The Figure III-1 flowsheet incorporates the preferred features for a large scale stand-alone power balanced plant producing only oxygen. As size increases above 100 TPD, the primary changes to the table 1 values would be increased efficiencies for the rotating machinery (pump, turbines and compressors), which lowers the energy requirement.

If the Moltex process is integrated into a high temperature process requiring oxygen, or if it is built to a smaller scale or for a locality having low electricity prices and high fuel prices, then alternative flowsheet features would become appropriate. The next section explores the possible alternatives.

TABLE III-1 Design and Operating Parameters for Baseline 100 TPD Flowsheet.

DESIGN PARAMETERS

ABSORBER PRESSURE	91 PSIG
ABSORBER ΔP	0.5 ATM
ABSORBER STAGES	5
ABSORBER AIR INLET TEMP	1180°F
DESORBER PRESSURE	0.5 ATM
DESORBER ΔP	0.15 ATM
SALT FLOW RATE	14 MOL/MOL AIR (2900 GPM)
PUMP EFFICIENCY	60%
ADIABATIC COMPRESSOR	77%
ISOTHERMAL COMPRESSOR	77%
ADIABATIC EXPANDER	82%
HEAT EXCHANGER ΔT	47%
AMBIENT HEAT LOSS	28 BTU/LB O ₂
C ₂ PURITY	98% EST.

ABSORBER PERFORMANCE

STAGE	TEMP (°F)	pO ₂ (ATM)	% NITRATE
ENTER	1206	1.51	--
1	1240	1.28	88.4
2	1231	1.01	87.8
3	1222	.76	87.2
4	1213	.61	86.7
5	1209	.54	86.4

MATERIAL AND ENERGY BALANCE

STREAM OR COMPONENT	DESCRIPTION	PRESSURE ATM	TEMP °F	ENERGY INPUT/OUTPUT	
				10 ⁶ BTU/HR	KW
A	SUPPLY AIR	1	140		
1	ISOTHERMAL COMPRESSOR			4.16	1193
B	1 DISCHARGE	4.5	140		
2	DRYER	4.5	140		
3	ADIABATIC COMPRESSOR			1.39	402
C	3 DISCHARGE	7.2	256		
4	HEAT EXCHANGER			12.10	
D	ABSORBER INLET AIR	7.1	1180		
5	ABSORBER			0	0
E	ABSORBER EXHAUST	6.8	1209		
6	COMBUSTOR			5.67	1644
F	COMBUSTOR EXHAUST	6.7	1668		
7	HP EXPANDER			5.40	1567
G	7 DISCHARGE	2.0	1230		
H	LP EXPANDER SUPPLY	2.0	302		
8	LP EXPANDER			1.17	338
I	8 DISCHARGE	1.0	207		
9	DESORBER			0	0
J	DESORBER DISCHARGE	0.37	1205		
10	PUMP			0.63	184
K	COOLER SUPPLY	0.36	300		
11	COOLER			0.33	
L	O ₂ COMPRESSOR INLET	0.35	140		
12	O ₂ COMPRESSOR			.42	122

C. Alternative Flowsheet Results

Two alternative flowsheets have been modelled and analyzed which reflect lower allowable expander inlet temperatures. In general, the higher the turboexpander inlet temperature, the more efficiently the process uses the fuel supplied to it. However, an inlet temperature of 1700°F reflects the approximate current limit for proven designs, beyond which complex blade cooling techniques or other costly and less reliable measures must be adopted. This temperature level also happens to be sufficient to yield an energy balance of the process, i.e. such that expansion of the hot exhaust gas supplies all of the mechanical energy required to the compressors and salt pump, and hence, no separate input of mechanical or electrical energy is required, other than for startup and instrumentation.

For lower expander inlet temperatures, part of the fuel input must be replaced by input mechanical power. In the limiting case, the combustor is eliminated, the hot exhaust gas is routed directly to the regenerative heat exchanger, and the cooled gas out of the heat exchanger is expanded. This case required all mechanical input and no fuel input. The power consumed in the process per pound of oxygen product is comparable to that in the high temperature expander case. Of course, it takes three times as much thermal energy to produce the required mechanical energy, and hence, the thermal efficiency of the process is greatly reduced. Nevertheless, there are circumstances wherein use of lower temperature expanders is of interest. In particular, in very small plants, where the cost of a high temperature expander becomes prohibitive, the capital savings of incorporating a lower temperature expander should offset higher energy costs. There are more suppliers and more off the shelf designs available for low temperature expanders than the high temperature ones, both of which drive down the cost.

Accordingly, two flowsheet modifications have been investigated, both targeted toward lower capacity plant sizes. For the smallest range, e.g. 5 to 50 tons per day O₂, a low temperature expander is incorporated, as described above. In the mid range, e.g. 20 to 200 TPD, a 1200°F expander is used. Exhaust from the absorber is routed to the combustor as before, then to partial heat exchange down to 1200°F, then to total expansion, and finally to tail end heat exchange. Typical operating conditions for both of these modifications are presented in Tables III-2 and III-3. In comparison with the 670 BTU/lb O₂ thermal input required in the high temperature expander case, the low temperature expander requires a 505 BTU/lb O₂ mechanical input, and the 1200°F expander requires 587 BTU/lb O₂ total input, of which 118 BTU/lb is mechanical and the remainder thermal (i.e. fuel at the combustor). Both the low and

TABLE III-2 BASELINE 50 TPD CHEMICAL OXYGEN PLANT WITH 1200°F TURBOEXPANDER

DESIGN PARAMETERS

ABSORBER PRESSURE	132.3 PSIG (10 atm)
ABSORBER ΔP	.25 ATA
ABSORBER STAGES	4
ABSORBER AIR INLET TEMP	1190°F
DESORBER PRESSURE	0.5 ATA
DESORBER ΔP	0.1 ATA
SALT FLOW RATE	14 MOL/MOL AIF
PUMP EFFICIENCY	60%
ADIABATIC COMPRESSOR	79%
ISOTHERMAL COMPRESSOR	—
ADIABATIC EXPANDER	83%
HEAT EXCHANGER ΔT	75°F
AMBIENT HEAT LOSS	28 BTU/LB O ₂
O ₂ RECOVERY	79.5%

ABSORBER PERFORMANCE

STAGE	TEMP (°F)	pO ₂ (ATM)	% NITRATE
ENTER	1234	2.1	--
1	1268	1.19	85.4
2	1248	.71	84.11
3	1238	.56	83.53
4	1235	.52	83.36
5	—	—	—

MATERIAL AND ENERGY BALANCE

STREAM OR COMPONENT	DESCRIPTION	PRESSURE ATM	TEMP °F	ENERGY INPUT/OUTPUT	
				10 ⁶ BTU/HR	KW
A	SUPPLY AIR	1	71		
1	LP COMPRESSOR			9.5	275
B	1 DISCHARGE	3.16	202		
2	DRYER		140	4.4	—
3	ADIABATIC COMPRESSOR			10.9	315
C	3 DISCHARGE	10.1	295		
4	HEAT EXCHANGERS			62	—
D	ABSORBER INLET AIR	10.0	1190		
5	ABSORBER			0	0
E	ABSORBER EXHAUST	9.75	1235		
6	COMBUSTOR			19.3	588(th)
F	COMBUSTOR EXHAUST	9.75	1200		
7	HP EXPANDER			21.6	626
G	7 DISCHARGE	1.2	905		
H	LP EXPANDER SUPPLY				
8	LP EXPANDER				
I	8 DISCHARGE				
9	DESORBER			0	0
J	DESORBER DISCHARGE	.4	1234		
10	PUMP			3.0	87
K	COOLER SUPPLY	.39	305		
11	COOLER			2.7	
L	O ₂ COMPRESSOR INLET	.38	100		
12	O ₂ COMPRESSOR			1.4	39.6

TABLE III-3 BASELINE 1C TPD CHEMICAL OXYGEN PLANT WITH 550°F TURBOEXPANDER

DESIGN PARAMETERS

ABSORBER PRESSURE	102.9 PSIG (8 atm.)
ABSORBER ΔP	.5 ATA
ABSORBER STAGES	5
ABSORBER AIR INLET TEMP	1180°F
DESORBER PRESSURE	0.5 ATA
DESORBER ΔP	0.15 ATA
SALT FLOW RATE	14 MOL/MOL AIR
PUMP EFFICIENCY	60%
ADIABATIC COMPRESSOR	70%
ISOTHERMAL COMPRESSOR	70%
ADIABATIC EXPANDER	80%
HEAT EXCHANGER ΔT	100°F
AMBIENT HEAT LOSS	28 BTU/LB O ₂
O ₂ RECOVERY	79.5%

ABSORBER PERFORMANCE

STAGE	TEMP (°F)	pO ₂ (ATM)	% NITRATE
ENTER	1180	1.68	--
1	1245	1.33	88.2
2	1234	.98	87.4
3	1222	.72	86.7
4	1215	.58	86.3
5	1211	.53	86.0

MATERIAL AND ENERGY BALANCE

STREAM OR COMPONENT	DESCRIPTION	PRESSURE ATM	TEMP °F	ENERGY INPUT/OUTPUT 10 ³ BTU/HR KW	
A	SUPPLY AIR	1	140		
1	LP COMPRESSOR			3.015	87.43
B	1 DISCHARGE	2.828	140		
2	DRYER				
3	ADIABATIC COMPRESSOR			3.511	101.82
C	3 DISCHARGE	8	436.7		
4	HEAT EXCHANGER			8.796	
D	ABSORBER INLET AIR	8	1180		
5	ABSORBER			0	0
E	ABSORBER EXHAUST	7.5	1211.3		
6	COMBUSTOR				
F	COMBUSTOR EXHAUST	7.5	1211.3		
7	HP EXPANDER				
G	7 DISCHARGE	7.5	1211.3		
H	LP EXPANDER SUPPLY	7.5	536.7		
8	LP EXPANDER			3.46	100.37
I	8 DISCHARGE	1	255.3		
9	DESORBER			0	0
J	DESORBER DISCHARGE	.35	1209.3		
10	PUMP			.68	19.7
K	COOLER SUPPLY	1	140		
11	COOLER			.469	
L	O ₂ COMPRESSOR INLET	1	140		
12	O ₂ COMPRESSOR			.700	20.3

mid temperature cases yield attractive small capacity options having much greater energy efficiency than currently available plants in those size ranges. These plants would supply oxygen needs such as nonferrous metallurgy, sewage treatment plants, pulp mills, hospitals, airports, or some industrial chemical synthesis requirements. Several of these applications are currently served only by hauled-in liquid oxygen, at great economic and energy cost.

IV. ENGINEERING ANALYSIS

A. General

The purpose of this task is to analyze unique or unusual aspects of the process which may require unusual items of process equipment, and to identify available and suitable equipment for the service conditions where possible. In some areas it was determined that fairly conventional off the shelf equipment would suffice. These include the salt control valve, the salt pump, and the gas to gas heat exchanger, which are discussed in the next paragraph. In other areas, more extensive analysis and even some experimentation was necessary. Those areas, which include salt corrosiveness, combustor and expander, and NO_x considerations, are each treated individually in succeeding sections.

The alkali nitrate salt attacks conventional valve packing materials. However, packless valves incorporating a welded bellows seal of the stem are available at the required temperature and pressure rating. The salt similarly will attack conventional pump packing materials. However, standard vertical submerged pumps are available with a cantilever shaft such that neither pump bearings nor the shaft seal is exposed to the salt, and with the pressure, temperature, head, and capacity ratings necessary for the intended commercial use. Finally, although a variety of heat exchanger designs are available to withstand the temperature and pressure requirements of the gas to gas heat exchange, one type appears particularly suited to also providing the high efficiency that is desired while keeping the cost reasonable. That type is the stainless steel brazed plate fin type. (Interestingly, the aluminum brazed plate fin heat exchanger is widely used in cryogenic processes for much the same reason.) At least several manufacturers are available for each of the above types of equipment.

B. Combustor and Expander

The process analysis studies confirmed the expected behavior that the higher the temperature the exhaust is expanded at, the more mechanical power is recovered, and the lower the overall fuel requirement. For the process conditions analyzed, a mechanical energy balance was achieved

at approximately 1670°F expander inlet temperature. A higher temperature would result in excess power available for export, whereas a lower temperature would require importation of some mechanical power (but use of less fuel since not as much heating is required). Thus, clearly the process performance is dependent upon the allowable expander inlet temperature, and also contingent upon availability of a combustor which can achieve that temperature.

Standard industrial gas turbines are rated for inlet temperatures on the order of 1670°F. Thus, in principle power recovery expanders can be provided for this service. In practice, however, they are not available, probably because of no previous demand. The two existing extensive markets for high temperature expanders are fluidized catalytic cracker units and nitric acid plants. References IV-1 through IV-4 describe typical use conditions and ratings for available expanders in those fields. The temperature ratings vary from 1260°F to 1400°F, depending on the manufacturer. Several of those designs, and also a very interesting gas bearing design expander could be upgraded to the 1670°F region provided the design costs and/or an assured market were provided the manufacturer.

A second area where in principle equipment could be made available but in practice none currently is having the desired performance is the combustor. Every percent O₂ that is fully combusted in an O₂-N₂ mixture such as air causes approximately a 200°F adiabatic temperature rise. In a conventional gas turbine combustor only on the order of 40% of the air is reacted with fuel, causing flame temperatures well over 3000°F, such that no catalyst is necessary. The remaining air then dilutes and cools the combustion gas to the desired turbine inlet temperature.

In the Moltox process the residual oxygen in the nitrogen exhaust will typically be in the 2 to 7% range. Only approximately 2½% is required to support the combustion necessary to raise the exhaust to 1670°F. Although residual O₂ levels higher than 2½% do not necessarily decrease the energy efficiency of the process, it is highly desirable to minimize the residual O₂ content from the viewpoint of maximizing the utilization of the capital equipment. Under those conditions, all of the exhaust must be mixed with the fuel, i.e. no localized higher temperatures are possible due to excess availability of oxygen. Combustion will not proceed reliably at 1670°F for the gas concentrations of interest. Hence, a catalytic combustor is mandatory.

Commercially available catalytic combustors for nitric acid tail gas expansion are available for the pressures and gas compositions of interest here, but are limited to temperatures below 1500°F (reference IV-5). Precise construction

details are proprietary, but they generally involve a precious metal catalyst on a honeycomb support. Catalyst attrition is too severe above the design temperature, imposing an economic penalty. However, a great deal of research and development is currently being performed on catalytic combustion with the object of reducing NO_x emissions. Reference IV-6 reports on developmental precious metal catalysts having operating temperatures in the 2000°F to 2500°F range. More recently a zirconia supported nickel catalyst has been shown to effectively catalyze O_2 and NO combustion in CO (reference IV-7). These results and others referenced therein give cause for optimism that suitable low cost combustion catalysts can be made available for 1670°F operation whenever expander turbines become available.

C. Corrosion

One of the major concerns which must be addressed and satisfactorily resolved in regard to commercial viability of the Moltox process is the identification of acceptably long lived materials for salt containment. The alkali nitrates and nitrites are relatively inert to most metals at temperatures below 480°C , and several industrial processes have experienced long term satisfactory behavior using mild steel for salt containment in those conditions (references IV-8 and IV-9). Similarly, SS304 has been used up to 550°C with satisfactory results. However, above that temperature most alloys undergo accelerating degrees of attack, and conventional stainless steels experience excessive rates of attack at the approximate 650°C temperature of the Moltox process. The basic problem is that conventional stainless steels achieve corrosion protection via an adherent Cr_2O_3 surface layer, whereas the molten alkali nitrate readily attacks and dissolves Cr_2O_3 (provided the temperature is high enough to form alkali oxide). Thus, the usual alloy selection criterion that higher chromium content provides greater corrosion protection is not applicable with high temperature molten alkali nitrates.

Dense aluminum oxide has been shown to be impervious to some of the most aggressive alkali salts (references IV-10 and IV-11). Apparently a thin impervious layer of NaAlO_2 forms on the surface, inhibiting further attack (reference IV-12). Hence, any metal which relies on a layer of Al_2O_3 vice Cr_2O_3 is a good candidate material for molten alkali nitrate salt containment. Aluminum per se cannot be used because of the low melting point. However, most metals can be treated by a pack aluminizing process in which aluminum is diffused several mils into the surface of the metal. In subsequent service metal so treated forms an Al_2O_3 protective layer. The layer is very adherent, and also is self renewing to a certain extent due to the depth of diffusion. The main detriment of this treatment is the extreme brittleness of the resultant surface layer.

In order to form a preliminary assessment of the corrosion problem and also to help select appropriate materials for pilot plant construction, a simple and inexpensive corrosion screening test was devised and performed. The test procedure was based on earlier reported observations (reference I-1) that corrosion by alkali nitrate is accompanied by nitrogen evolution, i.e. that the nitrogen partial pressure of a closed reaction vessel steadily increases as corrosion proceeds. If the corrosion reaction were merely oxidation, the pressure change would be minimal, since the large inventory of nitrate and nitrite in an equilibrated salt mixture strongly buffers the pO_2 to a near constant value. Hence, obviously the corrosion mechanism was tying up alkali as well as oxygen, thus accounting for net N_2 evolution. This behavior is corroborated by considering the thermodynamics of the alkali metalates for the various metals present in alloys of interest. The alkali chromates, manganates, molybdates, and aluminates all have substantial stability relative to alkali oxide plus metal oxide, showing that equilibrium would strongly favor alkali metalate formation over simple metal oxide formation. Thermodynamic data on the ferrates and nickelates has not yet been found, but similar behavior is expected to prevail there.

A second key thermodynamic question involves the melting point of the alkali metalate, as that determines how much accumulates in liquid solution before solid phase will accumulate in the melt. The relatively low melting point of Na_2CrO_4 (1057K) indicates it would accumulate in a 900K melt on the order of several percent before activity equivalent to solid formation is reached, and observed experimental behavior bears this out (references IV-9, IV-13, and IV-14). Conversely, the lack of proportional amounts of dissolved nickelates and ferrates in the salt suggests that they have much higher melting points. One more observation pertinent to the preceding discussion is the color caused by contaminated salt after dissolving in water. During earlier experiments, when KNO_3 was reacted in an SS316 reactor vessel at 1500°F, the dissolved salt caused a deep purple color, suggestive of $KMnO_4$. All subsequent observations involving SS304 corrosion have yielded a yellow solution, suggestive of chromates. Although the Mn concentration in SS316 is substantially less than the Cr content, it may be that its transport capability is much better.

Sandia National Laboratories has embarked on an extensive research program of alkali nitrate corrosion at temperatures up to 600°C in support of a central solar station heat collection and storage concept (reference IV-9). The time dependent morphology of the corrosion films has been well characterized in that program. For the stainless steels and Incoloy 800, the corrosion layer is very predominantly Fe_3O_4 . There is a virtual absence of Ni in the corrosion layer. Cr has an anomalously high concentration at the inner layer of corrosion, next to Cr depleted substrate, and the concentration rapidly drops to zero through the film. The oxygen concentration increases through the film, with Cr

disappearing as CrO_3 becomes available for Na_2CrO_4 formation and the film terminating as Fe_2O_3 becomes favored. The reported data does not distinguish between metal oxide and alkali ferrate in the film, nor does it indicate the alkali availability in the film.

In view of the above discussion of the theoretical and observed behavior of alkali nitrate corrosion, it is believed that N_2 gas generation is one of the more reliable and sensitive measures of that corrosion, certainly as reliable as either weight change or film thickness. The main question to be resolved is whether the N_2 generation reflects the total corrosion (i.e. alkali ferrates are formed) or simply the nonferrous corrosion (ferrous and ferric oxides are formed). This can be simply resolved by adding ferric oxide to equilibrated salt and measuring the resulting N_2 evolution. In the data reported below, the measured N_2 was converted to corrosion rate data ($\text{mg}/\text{m}^2 - \text{hr}$) by assuming all corrosion resulted in N_2 generation, i.e. each corroded metal atom became Na_2MO_4 (M = metal) and hence released one N_2 molecule.

The simplified corrosion test was used to test three ceramic materials (tower packing candidates) and four metals: 304SS, Inconel 600, Alonized 304 SS and Alonized carbon steel. The salt (equal weights of NaNO_3 and KNO_3 initially) was contained in a fused alumina liner placed in a closed SS316 reactor vessel. After equilibrating the salt, each specimen was placed in the salt and held at constant temperature in the range of 660°C to 775°C for between 3 and 15 days, while recording pressure buildup. Characteristically a rapid pressure increase was observed for up to 24 hours tapering to a steady linear increase thereafter, and the recorded data reflects the steady or linear rate. Several blank runs without specimen were also conducted, and these evidenced slow pressure buildups. Originally this was believed to be due to corrosion of the alumina liner. However, after several months of testing with no observed weight or appearance changes of the liner, it was concluded that the blank run corrosion was from vapor phase transport out of the liner and reaction with the interior reactor vessel walls. The below results are contaminated by this effect, and hence should be considered qualitative in nature. Future tests should make use of Alonized reactor vessels to preclude this source of error.

Table IV-1 records the test results obtained using this procedure. For those specimens showing multiple entries, the tests were conducted sequentially in the order shown. For one of the tests, the final one on the Alonized SS304 specimen, 6 w/o (20 gm) of $\text{Ba}(\text{NO}_3)_2$ was added to the melt. The following observations are based on these tests and the recorded data:

TABLE IV-1. Corrosion Test Results in $\text{NaK}(\text{NO}_3)_2$ (Equilibrated)

Specimen	Temperature	Duration	$\Delta P/\text{day}$	mg
				$\text{m}^2\text{-hr}$
1. Alonized SS 304	775°C	6 days	6 psi	432
2. SS 304	660	3	1.5	120
	770	3	20	1543
	720	9	9	694
	*720	15	18	1390
3. Inconel 600	725	15	2.8	210
4. Alonized CS	600	2	2	154
	710	6	12	924

*.6 w/o $\text{Ba}(\text{NO}_3)_2$ added to melt

1. Untreated SS 304 corrodes at a rate of 700 mg/m²-hr in the alkali salt mixture at 720°C.
2. Untreated SS 304 corrodes at approximately double the above rate in the Ba²⁺ containing salt.
3. Alonized SS 304 corrodes at one fourth or less of the rate of the untreated SS 304.
4. Untreated Inconel 600 corrodes at one third the rate of untreated SS 304.
5. The fused alumina liner which contained the salt during tests spanning a seven month period showed no visible attack. The 560 g liner gained 0.4 g over that period.
6. Alonized carbon steel showed good protection where the Alonizing was intact but showed near catastrophic attack where unprotected.

After completion of the above tests, Sandia National Laboratories kindly volunteered to treat the exposed specimens to the same micrographic and x-ray analysis as is being performed in their research program. Figures IV-1 and IV-2 are the results furnished by SNL. Figure IV-1 shows the Alonized SS 304 specimen both before and after exposure and Figure IV-2 shows the SS 304 and Inconel 600 specimens after exposure. The Ni plating was applied by SNL as part of the mounting and polishing procedure.

D. NO_x Generation

The tendency of alkali nitrate melts to generate NO_x gases (primarily NO₂ and NO) at high temperature has been well documented. Reference I-1 outlined the thermodynamics governing this behavior. In summary, for a pure alkali nitrate and/or nitrite melt the N₂ and NO_x tension is infinite. NO_x generation is apparently the low energy path to relieve this tension, and as temperature approaches the necessary activation energy for this reaction path, thermal decomposition results in up to several percent NO_x in addition to O₂ in the evolved gas. That gas mixture however is highly non-equilibrium. As NO_x generation causes buildup of alkali oxide in the melt, that in turn catalyzes the decomposition of NO_x to more stable N₂ and O₂. Thus shortly into the decomposition transient the N₂ concentration exceeds the NO_x concentration. NO_x concentration decreases towards equilibrium concurrently with alkali oxide increasing toward equilibrium, and when both are attained the NO_x is decreased to the 10 ppm order of magnitude. Such a salt is termed the equilibrated salt.

During both the laboratory experiments and the pilot plant operations, it was rare that NO_x levels that low were obtained. Values below 10 ppm were only recorded after several days of operation at temperature. After every shutdown, values in the order of 1000 ppm were measured, and were still in the 100 to 200 ppm range after several hours of operation. Thus apparently the alkali oxide is partially consumed while shutdown, either by reacting with N_2 and O_2 back to nitrate or by reacting with metal oxide to cause corrosion.

If in fact long term continuous operation of the plant results in NO_x readings consistently below 10 ppm, the NO_x should be no problem whatsoever. The respective threshold limit values in air are 5 ppm for NO_2 and 25 ppm for NO . Even if the steady state NO_x reading were 100 to 200 ppm, the N_2 exhaust would pose no problem, since by the time it were diluted with sufficient air to provide a breathable mixture, the NO_x reading would be well within allowable limits. The product oxygen would not be breathable without further purification, using techniques such as these described in reference IV-4. However most contemplated uses for the oxygen involve high temperature combustion, e.g. partial oxidation of coal or steel or lime production. The high temperatures in those processes would decompose or otherwise obliterate the significance of the small amount of NO_x involved here.

It also should be noted that until recently untreated tail gas from nitric acid plants typically contained 1000-2000 ppm NO_x , but that under NSPS the tail gas is purified to below 100 ppm. (reference IV-3)

E. Safety Aspects

There are three primary areas of concern in regard to safety of the Moltox process. First is the existence of fluids at high temperature and elevated pressure; second is the question of whether the salt melt is susceptible to a runaway chemical reaction or potential explosion; and third is the potential for NO_x generation to levels exceeding allowable breathing standards. The third concern was treated in the preceding section on NO_x generation.

The gas and salt at high temperature and pressure can be sprayed or projected from system leaks, forming an extreme hazard to personnel and also potentially damaging nearby equipment. The highly oxidative nature of the salt adds a further dimension to this hazard, as it would readily support combustion of any combustible material it contacts without the need for air. Although this safety concern warrants careful design attention, it is not significantly different from similar conditions widely encountered in the chemical processing industry. It is dealt with by incorporating barriers or enclosures to isolate leaks, by choice of materials and configurations to minimize the possibility of leaks, and by removing all combustible material from potential leak areas.

The chemical reactivity or explosion potential of the alkali nitrate melt is a natural question since alkali nitrate is one constituent of gunpowder. However the explosivity of gunpowder requires two circumstances, neither of which is present in the Moltox melt. First, there must be both sufficient fuel (carbon) and the oxidizing agent (alkali nitrate) present. Secondly, the two must be thoroughly dispersed and intimately mixed to an extent which is only possible in a low temperature or solid state. With the Moltox melt, there is no normal mechanism by which fuel can be introduced into the melt. Any chemical reactions which are capable of occurring in the melt per se, e.g. decomposition, are highly endothermic and hence self extinguishing. Even if fuel is intentionally introduced into the melt, simple combustion occurs rather than an explosion. Note that this is one advantage of Moltox over cryogenic processes--any traces of acetylene introduced with the air will immediately combust, and not have the potential to accumulate to explosive levels as in cryogenic plants.

Reference IV-16 reports numerous experiments conducted by DuPont in order to determine the combustion or explosion hazard of alkali nitrate-nitrite melts. A variety of combustibles were injected into the melt, including gasoline, crude oil, paraffin, ground coke, and aluminum and iron filings. Some of these vaporized and burned with the gas over the salt, and others were oxidized directly by the salt. Only the metal filings gave rise to violent combustion.

Alkali nitrate salt is used for heat treating aluminum parts, and there are recorded instances wherein excessive temperatures caused molten aluminum to be in the salt. Some of these incidents have resulted in explosions, as reported in reference IV-15. However the investigation reported in that reference reveal that the explosion was not due to direct chemical reaction between alkali nitrate and aluminum. Rather it was due to the alkali nitrate corroding through the iron crucible, allowing molten aluminum to spill on hot fire brick under the crucible which resulted in a thermite reaction.

Ni Plating

Aluminum Rich
Layers

Parent Alloy

200X

Ni Plate for Mounting

GAD
Corrosion Product (NiO)

Parent Alloy

200X

Ni Plating for
Mounting and
Polishing Pur-
poses

Alonized Layers

Ni Plating for Mounting
and Polishing

Blisters

Oxide Corrosion Product
(Barium Iron Oxide)

Parent Alloy

FIGURE IV-1 Alonized SS 304
Before (Top) and After (Bottom) Exposure

FIGURE IV-2 Inconel 600 After Exposure (Top)
and SS 304 After Exposure to $\text{Ba}(\text{NO}_3)_2$ Melt
(Bottom)

V. ECONOMIC COMPARISON

A. General

In order for the Moltox process to attract commercial interest it must show an economic advantage in addition to the energy efficiency advantage already determined. Hence, this research project has included a rough scoping type of cost analysis of both the Moltox and conventional oxygen plants, in order to ensure there is at least a reasonable prospect that such a savings can be realized.

The size chosen to be analyzed is 1000 tons/day (TPD) oxygen product. This is currently the workhorse of the industry, although occasional larger plants are built. It is large enough that such plants have nearly achieved their full energy efficiency potential, i.e. any improvement that larger plants may achieve in terms of reduced heat leakage or increased rotating machinery efficiency is quite small. In this size range economy of scale is due strictly to lower capital costs as size increases, not to higher efficiency. Also the results can be scaled with reasonable confidence from 1000 TPD to either 500 or 2000 TPD, covering the full range of large plants of interest.

One ground rule that has been imposed in the economic analysis is that the equipment chosen be off the shelf vice state of the art. This stipulation allows firmer price estimates and provides greater confidence the equipment will perform as claimed, although it leaves room for further process improvement with future choice of less proven equipment.

The main determinants of the cost of the oxygen product are the cost of the fuel supplied to the process, the capital cost of the plant, and the capital recovery factor applied (sum of depreciation, interest, and return on investment). Each of these is discussed below, to explain or justify the conventions adopted for this analysis.

The Moltox process generates its own mechanical power through use of an expander turbine, thus requiring only heat or gas turbine fuel as the energy input. The conventional cryogenic plant on the other hand imports mechanical power in the form of electricity, relying on the turbine and generator (and steam plant) provided by an electric utility company.

Thus, the cost comparison between the two plants primarily reduces to a comparison of the cost of producing mechanical power via expander turbine plus fuel vs. producing it via electricity. One way to avoid the difficulties of such a comparison is to require the conventional plant to also generate its mechanical power from fuel. In many cases this is required anyway, due to remoteness of location, limits on available power, etc. Thus, in this analysis both the electric drive conventional plant and turbine drive conventional plant were considered.

B. Fuel Cost

The cost of electricity to industrial customers is set at a representative late 1980 value of 3.2¢/kWhr. This amounts to \$9.38 per million BTU(e). The cost of fuel is set at \$3.13/MMBTU. This is a representative cost for any of several clean fluid fuels: distillate, new natural gas, or medium BTU gas from coal. It is also exactly one third of the electricity cost. Approximately three units of fuel are required to generate one unit of electricity, and, hence, if the electrical generation plant uses the same fuel as the O₂ process, the electricity cost would only cover the cost of the fuel necessary to generate it. Of course, most electricity is generated from coal with a cost currently on the order of \$1.50/MMBTU, and, hence, somewhat less than half of the 3.2¢/kWhr reflects fuel cost.

The essential difference between the baseline Moltox process and the electric drive version of the conventional cryogenic process is that the Moltox process incorporates its own mechanical drive power, and feeds on fuel, whereas the conventional process imports mechanical power in the form of electricity. The Moltox plant only requires half as much fuel as that required by the electrical supplier, but the electrical supplier only pays half as much for fuel, so the net fuel cost is roughly equal. The Moltox turbine drive costs approximately \$400/kW, whereas the electrical supplier currently pays \$600/kW for a coal fired electric plant. However, most of the electrical supplier's plant was built years ago, at much lower cost, interest, and depreciation rates. Thus, the capital recovery factor required by the electrical supplier is much lower than that required by a new Moltox plant, and the current price of electricity correspondingly suggests it to be the bargain approach to obtaining mechanical power. However, one consideration should be kept in mind. Even if there is no further increase in fuel prices, the price of electricity will continue to rise.

This is because the electrical supplier must continually replace old fully depreciated equipment with new high cost equipment, paid for with high cost financing, thus driving the required capital recovery factor up. In contrast, the required Moltox capital recovery factor never increases once the plant is built and financed. In other words, both the fuel cost and the electricity cost will continually increase over the life of the plant, but the electricity cost may increase somewhat faster than the price of raw fuel, since it reflects higher cost new generating facilities, as well as higher cost fuel. This analysis assumes a cost escalation rate of 10% per year over the next five years for both fuel and electricity.

C. Capital Cost

The flowsheet which was used as the basis for estimating capital cost was modified slightly from that recorded in Table III-1. One modification involved limiting the maximum combustor and turbine inlet temperature to 1400°F. This was necessary in order to obtain a reliable cost estimate for those equipments reflecting off the shelf equipment which is already in similar industrial service. Higher temperature equipment is available within the state of the art, but cost and performance estimates are much less reliable. This change reduced the power recovery capability of the expander turbine, making it necessary to import electrical power to drive the pump. The revised total power required is 47.2 MMBTU/hr thermal (566 BTU/lb O₂) and 1490 kW electrical (61 BTU(e)/lb O₂). The pump efficiency is increased to 75% due to its very large size; its flow rate is reduced to 20,000 gpm due to the contribution of the peroxide-superoxide reaction, as described previously. The thermal power input at the catalytic combustor results in approximately a 400°F temperature rise of the exhaust gas. Hence, it was necessary to heat exchange it against the incoming air down to 1000°F, then catalytically combust it to 1400°F, then fully expand to 1.2 ATA, and then continue the regenerative heat exchange against incoming air. 1000°F is well above the natural gas ignition temperature of the catalytic combustor (approximately 875°F).

The compressor is an axial multistage design, which may have a final radial stage, depending on the manufacturer. It consists of two sections, and the cooling and molecular sieve drying is accomplished between the two sections. Thus, the compression heat from the second section is conserved in the process. The axial expander has 4 to 7 stages depending on the manufacturer, and uses Nimonic or similar blading to withstand the high temperature. Similar compressor-expander combinations are presently found in nitric acid plant service. A motor-generator rated at 1/3 shaft horsepower is also provided on the drive train to facilitate startup and control. The catalytic combustor is also borrowed

directly from current nitric acid plant service. It is a precious metal (palladium) supported on a honeycomb structure, providing minimal pressure drop (< 1 psi). Its maximum service temperature is 1490°F , so adequate margin exists to allow for temporary upsets.

Two process modifications were incorporated to increase the O_2 recovery from the 69.8% shown in Table III-1, to 86%. One change was to increase the number of equilibrium contact stages from five to ten, requiring taller towers (50'). The increased recovery is beneficial in several respects. Proportionately less air must be compressed for a given output, and hence power rating and cost of the compressor and expander decrease. Absorber tower diameter decreases slightly. And, the O_2 content of the final exhaust is only .1 or .2%, making it suitable for many inerting applications or other N_2 uses.

The absorption tower is 30 feet in diameter and 50' tall and the desorber is slightly smaller. The pressure shell is 650°F carbon steel with external insulation. Additional internal insulation (high alumina) is used to separate the shell from a metallic liner which contains the molten salt and tower internals. The liner is a thin shell of SS 304 with a roll bonded inner layer of Inconel 600, and is Alonized. The tower packing is dense alumina shapes and the packing support structure is Alonized Inconel 600.

A guard reactor of BaO is incorporated after the final stage of compression, to ensure that final traces of moisture or CO_2 do not reach the salt. The regenerative heat exchanger is a brazed plate fin type similar to those found in cryogenic plants, except it is made from stainless steel vice aluminum. These heat exchangers are presently used as rogenerators for gas turbine sets, and achieve 88% or higher efficiency at conditions more severe than required in this application.

The salt pump is a vertical cantilever shaft design with a submerged suction. The sump in which it is located also serves as a draindown tank for the molten salt, and is fitted with heaters to establish an initially molten condition.

Table V-1 tabulates both the purchase cost of the above equipments and their installed costs, where installation includes necessary foundations, piping, valves, insulation, control, instrumentation, auxiliary services, and labor, to the extent not included in the purchased equipment.

TABLE V-1

INVESTMENT COST (\$MM)
1000 TPD MOLTOX PLANT

<u>Equipment</u>	<u>Purchase Cost</u>	<u>Direct Installed Cost</u>
SINGLE TRAIN COMPRESSOR AND EXPANDER (16,000 kW)	4.2	10.5
PUMP (1100kW)	.4	1.0
TOWERS (2)	1.9	6.0
VACUUM COMPRESSOR (900 kW)	.3	.8
HEAT EXCHANGERS	.9	2.7
CATALYTIC COMBUSTOR	.2	.5
DRIER AND GUARD	.5	1.2
DIRECT INSTALLED COST		23.8
INDIRECT COST (30%)		7.1
TOTAL CAPITAL INVESTMENT		<u>\$ 30.9 MM</u>

The conventional cryogenic plant cost was estimated similar to the above procedure, with the added benefit of several published estimates appearing in references V-1 through V-7. The costs tabulated are battery limits for low pressure oxygen. Additional costs for offsites or for an oxygen compressor would be approximately equal for each process, and would not change the relative comparison. Two versions of the conventional plant are presented--conventional electric drive, and steam or gas turbine drive. The investment cost of the turbine drive is taken to be \$400/kW, i.e. a purchase cost of approximately \$125/kW. This is necessary and appropriate for the larger size plants because in those air separation applications which are remotely sited the large required electrical capacity is generally not available. Even in some established service areas it may not be in the best interest of the utility or utility customers to supply that much electricity. For example, cost studies of air separation plants for coal conversion complexes frequently assume turbine drive (references V-7 and V-8). Accordingly, this study includes a turbine drive version of the conventional plant.

D. Capital Recovery Factor

The capital recovery factor is the percentage of the invested capital which must be recovered annually through sale of product to adequately compensate the investors. It includes both depreciation and the interest or return on the investment. Many factors have a bearing on its value. The life of the plant determines the depreciation value appropriate for each year. The prevailing interest rates determine the payoff available to investors from alternative investments. However, there is a very important distinction between investing in a fixed income security and in an income producing asset. The former must earn a competitive rate of interest initially, since the real value of the earnings will decline with inflation. On the other hand the earnings of the latter will continue to climb with inflation as the product price is increased, and hence the initial return can be much lower than prevailing market rates. One approach to quantifying this frequently overlooked effect is presented in reference V-9.

Other factors which have a bearing on the capital recovery factor are as follows. A guaranteed long term purchase contract for the product reduces risk and hence lowers CRF. Utility vs. investor financing lowers the CRF. Any governmental inducements to conserve energy via increased capital expenditure, e.g. investment credit or accelerated depreciation schedule, tend to lower the CRF.

On balance, capital recovery factors in the range of 15 to 35% are normally encountered. Reference V-1 cites a 35 million dollar air separation plant which will recover 68 million dollars plus fuel costs over seven years of operation. This works out to a maximum of 27.5% CRF, and is probably closer to 20% when operating cost deductions are considered. This study has adopted a baseline 20% CRF, and has indicated the other values of CRF.

E. Operating Cost Comparison

The operating costs for an air separation plant consist of the cost of fuel, the cost of capital recovery, plus an operating overhead cost, where the latter includes labor, administration, insurance, maintenance, and other utilities. The operating overhead can be approximated as 7% of the capital investment per year. The cost of capital recovery is set at the 20% CRF for the baseline analysis. Both of these costs are fixed over the life of the plant. The fuel or electricity costs however will escalate with inflation over the life of the plant. Hence, the total operating cost is time dependent. Clearly the first year operating costs will understate the true overall significance of fuel or electricity cost on oxygen cost. Accordingly, the convention is applied here of stating fuel or electricity costs as of the fifth year of plant operation. For a ten to fifteen year plant, fifth year costs reflect a representative compromise between initially very low and terminally very high energy costs.

At 10% energy cost inflation per year, the fifth year energy costs are $(1.1)^5$ or 1.61 times the current cost. Table V-2 tabulates the various operating costs of all three types of plants, including both first year and fifth year energy costs. As shown, whereas the cost via Moltox is some 13% higher than the electric drive cryogenic plant in the first year of operation, the Moltox plant cost is already comparable by the fifth year, and the Moltox advantage steadily increases thereafter. Possibly more significant is that the Moltox plant shows substantial superiority to the turbine drive cryogenic plant over the entire operating life.

A full assessment of the comparative economics of these processes must consider several additional factors: the effect of by-product credits and the effect of increasing plant size and/or changing capital recovery factor.

Regarding by-product credits, the conventional plant can co-produce high purity gaseous nitrogen and argon, and also some liquid oxygen and nitrogen. Most industrial complexes require some of these products: argon for welding, nitrogen for inerting, and liquid oxygen for an emergency reserve. To the extent these by-products can be consumed

TABLE V-2
OXYGEN PRODUCTION COST COMPARISON

CAPACITY: 1000 TPD O₂, Purity 97+%, 3 psig

YEAR: 1981

UTILIZATION: 330 Days/Year

CAPITAL INVESTMENT: Moltox \$30.9 MM
Electric Drive Cryogenic \$21.5 MM
Turbine Drive Cryogenic \$29.5 MM

COST ITEM	MOLTOX		CRYOGENIC (Electric)		CRYOGENIC (Turbine)	
	Annual Cost	\$M \$/Ton	Annual Cost	\$M \$/Ton	Annual Cost	\$M \$/Ton
FUEL (First Year)						
elec @ 3.2¢/kWh	410	1.24	2,956	8.96	--	--
Fuel @ \$3.13/MMBTU	1,170	3.55	--	--	2,956	8.96
1. FUEL (Fifth Year)	2,545	7.71	4,762	14.43	4,762	14.43
2. OPERATING OVERHEAD (7% Inv.)	2,160	6.55	1,510	4.58	2,070	6.27
3. CAPITAL RECOVERY (CRF 20%)	6,130	18.74	4,300	13.03	5,900	17.88
TOTAL O ₂ Cost (Fifth Year)	10,835	33.00	10,751	32.04	12,911	38.58
(First Year)		(30.08)		(26.57)		(33.11)

locally, they reflect substantial value. On the other hand, any availability beyond the local requirements is largely wasted due to high handling and transportation costs.

Although the Moltox process does not produce high purity nitrogen or argon, its clean warm exhaust product has potential by-product value at some industrial complexes. In contrast to ordinary flue gas, it has neither soot nor a sulfuric acid dewpoint. Many fixed bed coal gasification units (such as Lurgi) cannot operate on caking coals unless they have been pretreated to prevent agglomeration by lightly oxidizing the surface of each coal particle. This is one potential use for the Moltox exhaust gas. Furthermore, the possibility of a flowsheet variation whereby Moltox yields pure nitrogen should not be excluded.

As plant size increases, per unit capital cost tends to decrease, particularly as long as single train units are feasible. This relation is expressed as an exponent which is applied to the factor increase in size which will yield the factor increase in capital cost. For example, if plant capacity doubles, and the cost growth exponent is .6, then the larger plant will cost $(2)^{.6}$ or 1.52 times as much as the smaller. For conventional oxygen plants over the size range of 1000 TPD to 2000 TPD, reference V-7 indicates a cost growth exponent of .55. Figure V-1 shows the effect of increasing plant size on the oxygen selling price from the three analyzed plants, using cost growth exponent of .55 and CRF of 20%.

Figure V-2 similarly shows the selling price for a cost growth exponent of .6 and a CRF of 25%. Both figures are based on fifth year energy prices. As shown on those figures, the O₂ price via the Moltox plant steadily improves relative to either type of cryogenic plant as the plant size increases. The Moltox price vs. the electric drive cryogenic price is basically a tradeoff situation--the two are so close that other factors would most likely determine the choice. However, for the turbine drive version of the cryogenic plant the Moltox advantage is very substantial at all combinations of analyzed conditions. Thus, whenever local conditions preclude long term availability of large amounts of low cost electricity, the Moltox process is indicated to be the more economical route to oxygen production.

Figure V-1. Effect of Plant Size on O₂ Selling Price

Figure V-2. Plant Size vs Fifth Year O_2 Price (25% CRF)

VI. CONCLUSIONS

All research completed to date confirms the promise of the Moltox process of being an energy saving and economical new approach to oxygen generation. All major tasks and objectives of this stage of development were satisfactorily completed save one, the continuous operation of the pilot plant. The source of that difficulty and the modifications required to overcome it have been identified.

Successful mechanical operation of the pilot plant was achieved at high temperature and high differential pressure. The expected chemical behavior in the continuous mode was not achieved due to the desorber vessel design--the salt pump relied on a suction lift out of the desorber vessel, and therefore whenever the salt reached O₂ saturation, desorption occurred in the pump suction line causing it to lose suction. This will be solved by rerouting the pump suction directly out of the bottom of the desorber. Batch operations of the pilot plant, wherein pumping was not involved, resulted in expected chemical behavior of the salt.

In the process analysis task a detailed search of possible operating conditions was conducted, and their interaction was determined. A new set of baseline operating conditions was selected which still results in approximately 50% energy savings compared to cryogenic plants, but which reflects more conservative and easily attainable conditions. Also two other flowsheets were analyzed for possible interest in special situations.

The engineering analysis task considered various potential problem areas for the process: corrosion, expander, NO_x generation, and safety. The state of the art in each area was assessed, and solutions to or possible avenues for dealing with each problem were identified. The analysis suggests that none of these problems will be a "fatal flaw" which would prevent commercial viability; further development will be required to confirm this.

The economic comparison shows the Moltox process to be at least competitive with many large scale cryogenic oxygen plants, and substantially superior to some. In particular, the Moltox process shows greatest advantage over very large scale cryogenic plants which are powered by fuel vice electricity. That is the type plant normally associated with a coal conversion complex, and hence that industry would appear to be one of the greatest beneficiaries of this new technology.

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