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PROCESS FOR THERMAL FIXATION OF ATMOSPHERIC NITROGEN

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Summary

This paper discusses a new process for converting atmospheric nitrogen into nitric acid and nitric oxides based on technology and information developed by our aerospace programs. The basis of this process is the high temperature reaction of air to form appreciable percentages of nitric oxide. Nitric oxide is thermodynamically unstable at lower temperatures and the initial equilibrium must be frozen in a few milliseconds as the air temperature is decreased to a region of slow kinetics.

In this process, compressed air is heated in an electric arc to 3000 - 4000°K. Then it is immediately cooled very fast in a magnetohydrodynamic power conversion unit to about 2000°K and the generated electricity is recycled to the arc heaters. The nitric oxide (NO) formed in the arc is cooled further rapidly in a water spray to about 1400°K. This makes possible a recoverable concentration of 5.0 to 9.0% NO in air for this process. Finally, the nitric oxide reacts with more oxygen to form nitrogen dioxide which is converted to nitric acid by absorption in water.

Although some of the thermodynamics and kinetics for this process have been known for years, accurate quantitative determination of the equilibrium and reaction rate values was not done until the aerospace programs in reentry sciences and atomic physics were carried out in the last few years. Engineering and applied science data for this process are required for electric arc heaters, gas heat transfer, gas dynamics, and high temperature materials, and this has been obtained in various aerospace programs.

This process makes nitric acid and nitrogen oxides which are an important factor in the economy for fertilizer and industrial uses. At present, the world consumes 34 - 36 million tons per year of chemically fixed nitrogen, and it is increasing at a rate of 10 - 12% per year which is directly proportional to the food demand by the people of the world. This new process will decrease the cost of nitric acid (fixed nitrogen) by approximately 50% and the raw materials are: air, water, and electricity.

Introduction

This paper discusses a new high temperature process for converting atmospheric nitrogen into nitric acid and nitric oxides based on technology and information developed by our aerospace programs. These programs were in the reentry sciences, magnetohydrodynamics, atomic physics, and material sciences mainly. The basis of this process is the high temperature reaction of nitrogen and oxygen to form appreciable percentages of nitric oxide. The source of the nitrogen and oxygen is air. Nitric oxide is thermodynamically unstable at lower temperatures, so the initial equilibrium must be frozen in a few milliseconds as the air temperature is decreased to a temperature region of slow kinetics.

In this process, compressed air is heated in an electric arc to 3000 - 4000°K. Then it is immediately cooled very fast in a magnetohydrodynamic (MHD) power conversion unit to about 2100°K, and the generated electricity is recycled to the arc heater. The nitric oxide (NO) is still unstable and must be cooled further rapidly in water quench to about 1400°K. At this temperature the nitric oxide is fairly stable and minutes may then be used for further processing. The reaction gases are further cooled in a steam boiler which generates steam for more electricity. Finally, the nitric oxide reacts with more oxygen to form nitrogen dioxide. This may be converted to nitric acid by commonly used processes.[1]

Although some of the thermodynamics and kinetics for this process have been known for many years, accurate quantitative determination of the equilibrium and of the reaction rate values was not done until the aerospace programs in reentry sciences and atomic physics were carried out in the last few years. These data are used in the design of this process.
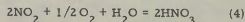
Overall Chemistry Of The Process

The overall chemistry of this process may be written in the three following chemical equations. The first one is the critically important one for this process. From air

$$N_2 + O_2 = 2NO \qquad (1)$$

For this, the equilibrium constant is:

$$K_p = \frac{P^2_{NO}}{P_{N_2} P_{O_2}} \qquad (2)$$

$$2NO + O_2 = 2NO_2 \qquad (3)$$

$$2NO_2 + 1/2\,O_2 + H_2O = 2HNO_3 \qquad (4)$$

Equation (1) actually represents the over-all sum of a group of reactions. These will be discussed later in this paper. Equations (3) and (4) represent the reactions which take place in the nitric acid absorption tower. [2] When nitric oxide (NO) is cooled in the presence of more oxygen, it forms nitrogen dioxide in a homogeneous gas reaction. Below 150°C the reaction is almost 100% to the formation of NO_2. This is completely discussed by Chilton. [3]

Reaction (4) has recently (1959) been completely understood after a half century of research by many workers. [4]

A quantitative understanding of reaction (1) has been necessary for developing a practical efficient process. Two kinds of data are required. The first is equilibrium data for the yield of nitric oxide as a function of temperature, pressure and reactant proportions. The second kind is kinetic data for the rate of formation and decomposition of nitric oxide as affected by temperature, pressure and reactant proportions. These data are described and discussed in following sections.

Equilibrium And Thermodynamic Data For The Formation Of Nitric Oxide

The basic question which must be answered is what is the best yield of nitric oxide that can be obtained at various temperatures, pressures, and proportions of reactants. This requires obtaining good thermodynamic data for equation (1) and the calculation of the equilibrium yield of nitric oxide according to equation (2).

The early data available from Nernst[5] was fairly reliable up to the region of 3000°K. The Norwegians (see Appendix) who actually built a plant did not determine the equilibrium yield of nitric oxide nor for that matter were able to accurately measure the temperature of the gas leaving the arc. However, Nernst in 1906 published the results of some experimental measurements for equation (1). This data covered 1811 to 2675°C. It is suprisingly good, being only about 25% low. Krase[6] in 1932 reports the Nernst data together with a calculated extrapolation to 3500°K, and also, for the case of equal proportions N to 0. This data also is about 25% low. However, it is clearly shown that it is advantageous to use equal molar amounts of reacting nitrogen and oxygen. This will give a 30 - 40% increase in the nitric oxide yield. Some German data[7] reported in 1935 is much too high showing a maximum yield of 13%. No information is given for the source of this. This yield is so high that it should have encouraged process development, but it did not.

The group [8,9,10,11,12] that developed the Wisconsin process made the first accurate calculations for the equilibrium yield of equation (1).

In a paper published in 1948 they give results from 1800°K to 2500°K. These are essentially the ones that appear in Table I for a pressure of one atmosphere. These calculations were based on spectroscopic data obtained by Giaque in 1934 which was used in statistical mechanical partition calculations in order to obtain the value for the equilibrium constant K_p.

With the advent of the missile and space programs, it was early realized that effective design calculations for reentry into the earth's atmosphere would require accurate knowledge of the thermodynamics of high temperature air. In rapid succession, three different groups in the U.S. made extensive calculations for these cases. [13,14,15,16] They covered temperatures of 2000 to 24,000°K. This overlapped with the data calculated by the Wisconsin group and allows for accurate checking. All three groups used the same calculation methods: spectroscopic data was used to obtain information leading to partition functions. From these the thermodynamic functions and equilibrium yields were then calculated. For this temperature regions this is undoubtedly the most accurate method. All of the results from these sources is consistent with the Wisconsin data and each other, within 2%.

A summary of this data is presented in Table I.

The thermodynamic functions such as enthalpy and entropy were also calculated for the previously mentioned temperature ranges. This, of course, is highly important in calculating heat demands in various processing steps.

In the years since 1956, many experiments have yielded experimental data which confirms the values reported in Table I. Therefore the question asked at the beginning of this section may be considered to be reliably answered by the data in Table I.

The data considered so far is for equation (1) which is for the case of pure air. The question can be raised of the effect of other elements. For example, a high temperature can be reached in a flame in which carbon and air are burned. Experimental data reported in work on fossil fuel combustion magnetohydrodynamic power generators indicates a low yield of NO at 4500°F. This indicates that the presence of carbon in the reaction decreases the equilibrium yield of nitric oxide. [17]

Kinetic Data

Over the last 75 years there has been a slow but brilliant build-up of understanding of the kinetics of the reactions of the constituents of high temperature air. This is described in the Appendix of this paper. Since 1950 there has been a tremendous increase in the numbers of
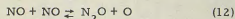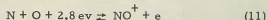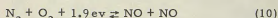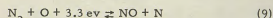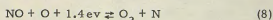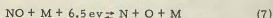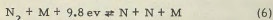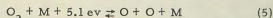
TABLE I

NITRIC OXIDE CONCENTRATION IN AIR
AT THERMODYNAMIC EQUILIBRIUM

Pressure (Atmospheres)	Temperature (°K)	Nitric Oxide (% of Volume)
0.1	1800 to 2500	Same as for 1.0 atmosphere for 1800 - 2500°K
	2800	3.65
	4000	5.5 max
1.0	1800	0.44
	2000	0.82
	2500	2.4
	2900	4.0
	3300	5.4
	3500	6.1
	4000	7.4 max
	4500	7.2
	5000	6.3
	6000	4.2
10.0	1800 to 2900	Same as for 1.0 atmosphere for 1800 - 2900°K
	3000	4.4
	3300	6.0
	3500	6.8
	4000	9.2
	4500	10.3
	5000	10.8 max
	6000	9.4
20.0	3000 to 4000	Same as for 10.0 atmosphere for 3000 - 4000°K
	4000	9.2
	4500	11.0
	5000	11.9 max
	6000	11.4

researchers and their efforts in understanding the chemistry of high temperature air. This has been motivated by the urgent need for understanding several important problems in man's conquest of space. The primary problem is the reentry phenomena associated with the return of a satellite such as Apollo or a missile reentering the earth's atmosphere at very high speed. At reentry speeds of 10 - 30,000 miles per hour, the air surrounding the objects is heated to many thousands of degrees. Hence it has been necessary to study the kinetics of high temperature air very intensively.

For ordinary purposes of kinetic study, air may be considered as a simple oxygen-nitrogen mixture. Wray[18] in 1961 made a comprehensive review of the pertinent literature on the kinetics of high temperature oxygen and nitrogen mixtures. In the temperature range considered (3000 - 8000°K), the atomic species such as O_3, NO_2 and other polyatomic oxides of nitrogen are not important. Also, reactions leading to the production of electronic excited species do not occur to any appreciable extent. With the above limitations Wray gives the following as the significant reactions occurring in high temperature air:

$$O_2 + M + 5.1\,ev \rightleftarrows O + O + M \qquad (5)$$

$$N_2 + M + 9.8\,ev \rightleftarrows N + N + M \qquad (6)$$

$$NO + M + 6.5\,ev \rightleftarrows N + O + M \qquad (7)$$

$$NO + O + 1.4\,ev \rightleftarrows O_2 + N \qquad (8)$$

$$N_2 + O + 3.3\,ev \rightleftarrows NO + N \qquad (9)$$

$$N_2 + O_2 + 1.9\,ev \rightleftarrows NO + NO \qquad (10)$$

$$N + O + 2.8\,ev \rightleftarrows NO^+ + e \qquad (11)$$

$$NO + NO \rightleftarrows N_2O + O \qquad (12)$$

M identifies a catalytic species. This species does not enter chemically into the reactions, but plays a catalytic role in energy transfer.

Reactions (5) (6) and (7) lead to the formation of atoms by the direct dissociation of the molecules. At higher temperatures these reactions are coupled to the rate of relaxation of the vibrational state of the gas. At the lower range the above cited reactions are much slower than the vibrational relaxation time. The nitric oxide is formed by the exchange reactions (8) and (9) which are fast and tend toward local equilibrium early in the time history of this series of reactions. Reaction (10) also contributes to the production of nitric oxide. Reaction (11) is the dominant mechanism by which electrons are produced in the temperature range being considered.

The production of nitric oxide was studied again in 1966 by Camac, etal.[19] They found that the main production of nitric oxide was due to the dissociation reaction of molecular oxygen to atomic oxygen following by the atomic shuttle reactions (9) and minus (8). Their measurements indicated an overall rate of formation of nitric oxide under about 40% of that given by Wray.

Their work indicated the depletion of nitric oxide occurs by the above reactions and by an intermediate step involving the formation of nitrous oxide as shown in equation (12). This indicates that further work will have to be carried out to resolve the questions of the actual mechanism for the formation and decomposition of nitric oxide. However, the presently available information is adequate for designing and studying a process for the production of nitric oxide. The data show that both the formation and the decomposition of nitric oxide are very fast. Furthermore, they show that the rate of decomposition of nitric oxide is faster than the formation.

Since a practical rate of heating of air is inherently fairly slow, (we are now talking in

terms of fractions of milliseconds) the important part of the kinetics of this process is the prevention of decomposition. This obviously has to be done by very rapid cooling. This will freeze the equilibrium at a high temperature. Below 1500°K the rate of decomposition of NO is quite slow and measured in minutes. Therefore, the temperature of 1500°K may be taken as the goal for the rapid cooling in this process.

After study for this process it was concluded that a temperature range with a maximum of 4000°K offered practical possibilities for obtaining the required cooling rate in actual process equipment.

In examining the equilibrium yields theoretically possible at various temperatures and pressures it is also necessary to consider the enthalpy requirements for obtaining these temperatures. Calculations show that above 3000°K, the enthalpy requirements go up very rapidly due to the fragmentation of the molecular oxygen and nitrogen.

It must be recognized that any process for heating and cooling air on a practical basis must consider economics and hence requires efficient heat recovery for re-use. This, of course, is the description of a cyclic heat process. Therefore, in considering the equilibrium conditions to be achieved in the arc heater for this process attention must be given to the total enthalpy requirement which may be recovered in subsequent processing for reconversion to electricity. This process may be compared to the Carnot heat cycle as the theoretical best which may be obtained. Therefore, consideration must be given to the possible economics of the heat recovery as a trade-off to the possible yield of nitric oxide from the process. This indicated that an equilibrium yield at a maximum of 4000°K is a practical one to try to achieve.

The great contribution of the aerospace effort in studying the kinetics of high temperature air has been in quantifying with good accuracy the various reactions and in identifying all of the reactions which take place. [20, 21, 22, 23, 24]

Identification Of Practical Conditions

The data given for equilibrium and reaction rates must be examined and interpreted for the successful design of a practical process. The Wisconsin group[8] and Wise and Baker[25] considered the time requirements for decomposition and formation of NO. Wise and Baker in their work calculated curves for the decomposition of nitric oxide as a function of temperature and cooling rate given in degrees K per second. Although their reaction rate data were prior to 1950 and therefore not quite as accurate at the high temperatures as that given by Wray, their curves are still very useful. They show that for a maximum of 1% total decomposition the initial cooling rate required is 10^6 °K/sec. This

decreases down to rates of the order of 10^5 and 10^3 °K/sec. before 1500°K is reached. For a decomposition of 10%, the required cooling rates are approximately ten times lower than those above.

The ability to achieve the required cooling rates at the various temperature ranges are the dominant factor in the system design. It will do little good to heat air up to 5000°K and obtain an equilibrium yield of 12% NO if the required cooling rate is 10^9 °K/sec, and therefore, unobtainable by any known means.

Process Analysis And Design

The requirements for an efficient practical process[1] are:

A. The concentration of nitric oxide achieved is high enough to make recovery practical and economic.

B. The reaction temperature and pressure may be reliably obtained with current technology.

C. Operating conditions are suitable to materials technology.

D. The heating and cooling rates fulfill the requirements discussed in the previous section.

E. Provisions are made for economic and efficient heat recovery and re-cycle.

The flow sheet presented in Figure 1 shows the results of the process design study.[1] The important features are:

A. Heating to reaction temperature in an electric arc heater.

B. First cooling in an expansion isentropic nozzle.

C. Followed by magnetohydrodynamic cooling and electricity recovery.

D. Followed by water quench with just enough water to bring the temperature down to 1400°K.

An electric arc heater was selected as the means for obtaining the required reaction temperature. As is discussed in the section on Electric Arc Heaters this technology is now well developed as a result of a very large amount of work in the last 15 years of the Aerospace effort.

The first cooling takes place in an expansion nozzle. In such a nozzle, an isentropic expansion is obtained. Several previous workers, including Steinmetz,[26, 27] have suggested this as a means for obtaining very fast cooling in a nitric oxide process. Penner, et al[28] studied this in 1949 and showed that cooling rates of 10^7

degrees K per sec. may be obtained. By closely coupling a magnetohydrodynamic generator to the expansion nozzle which in turn is coupled to the heater a very compact arrangement is obtained. A Δt of hundreds of degrees Kelvin may be obtained in the expansion nozzle. The gas which is converted to supersonic speeds then traverses the MHD generator. The MHD generator converts the kinetic energy of the gas directly to electricity. The combination of the expansion nozzle and the MHD generator in essence are a means for obtaining an isentropic expansion with direct conversion of energy to electricity at a high efficiency of about 85%. In a practical MHD generator the residence time of the air will be less than one millisecond. Therefore, a cooling rate of 40 - 50,000°K/sec may be obtained in an MHD generator. For the operating conditions shown on the flow sheet at the reaction temperature of 3300°K, it is estimated that a cooling rate of 2.5×10^6 °K/sec is obtained in the nozzle and $40 - 45,000$°K in the MHD generator. Since the present technology of MHD generators would have an exit air temperature of approximately 2000°K it is necessary to cool the gas more with a water quench. Only enough water is added to bring the gas temperature down to 1500°K. The cooling requirement here is approximately 10^4 °K/second. All of the above is presently obtainable with presently developed technology mainly achieved through the aerospace effort.

Description Of Process

In Figure 1 is shown the complete flow sheet for this process. For the sake of clarity, specific reaction conditions are shown for a typical set of reaction conditions. Clean air is compressed in a centrifugal compressor, pre-heated and sent to the electric arc heater. The temperature is immediately brought up to 3300°K. From there it expands through a close-coupled nozzle and goes through the magnetohydrodynamic generator. In these two units the gas is cooled down to 2100°K. About 50% of the total electricity requirement of the arc is recovered in the MHD generator and re-cycled to the arc. The air is then sent to a water quench and enough water is added to bring the total gas down to 1400°K. A nitric oxide loss of 0.5% is assumed at this point giving a yield of nitric oxide of 5.5% in the remaining air. The gas then goes through a trap which separates out the cesium or potassium seed originally added to make the MHD generator operate efficiently. Cooling is then obtained in a high pressure steam boiler with the feed water being furnished by the cooling water from the MHD generator. Final cooling is obtained in a process steam generator. At this point the air containing 5.5% nitric oxide is cool and may be sent to a conventional nitric acid absorption tower system. This system is shown in Figure 1. This technology has been well developed over the last 50 years and is very efficient. The gas is again compressed, cooled and sent into an absorption tower where it bubbles through a descending stream of dilute nitric acid. Substantially all of the nitric oxide is oxidized

to nitrogen dioxide and then absorbed in the water with subsequent conversion to nitric acid product. The remaining unreacted air containing appreciable amount of oxygen rises out of the absorption tower. Since this air is still at a pressure of about 110 psia fuel is injected here, burnt, and the hot gases are sent to a gas turbine. The gas turbine under these conditions will recover enough energy to power both of the compressors. The steam from the high pressure boiler may be used to generate electricity. When this is added to that recovered by the MHD generator about 80% of the total energy used in the electric arc furnace is recovered. This means that only 20% of new electricity must be brought in from the outside to power the entire process. The raw materials for this process are air, cooling water, boiler feed water, electricity, and a moderate amount of fuel. The product is commercial grade nitric acid.

Electric Arc Heater

The only practical known way to obtain the high temperature required for this process is by electric arc or plasma heaters. A large amount of experience and literature has been accumulated on the science and design of arc heaters.

The initial efforts go back to 1900 and the work done by Birkeland and Edye[6] on heaters for their nitric oxide process. Their work is described in the appendix. In the 1940's and 50's more work was carried out at Huls, Germany by Finkelnburg and Maecher.[29] However, no real concerted research effort was carried out in this field until 1950 when the missile and space programs started in the United States. With the advent of the missile and space age, the need became apparent for producing reentry conditions in the laboratory for investigation of the many phenomena that missiles and spacecraft encounter as they travel back to earth. The effort to produce these conditions has lead to the development of large arc heaters and plasma jets which can be controlled precisely to give the exact parameters desired.[30] Small, compact and low powered, thrusters have also been developed leading to small cutting and welding torches and high intensity light sources. NASA has sponsored a large technological survey of arc and plasma jets.[31] Recently arc heaters have been designed and built up to 100,000 kw in size. Many heaters have been used for high temperature, high speed wind tunnels. It is highly desireable to use a high air velocity in the heater and thus obtain a high material throughput to heater volume ratio. This is advantageous because it makes the heater smaller in size and therefore cheaper. Also, the high material throughput rate reduces the heat losses per unit weight.

For this nitric oxide process the heaters will have to operate for long periods of time without stopping as the economics of the process demand this. Based on all of the previous work of the last 70 years it appears now possible to
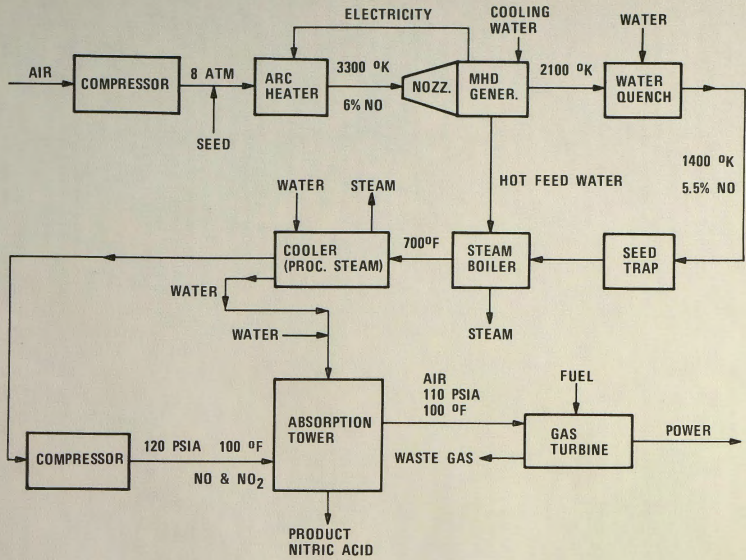
Figure 1. High Temperature Arc Nitrogen Fixation Process

design and build practical electric arc heaters of large capacities (100,000 kw) to be used for the oxidation of air in this process.

Magnetohydrodynamic Electricity Generator

As was described previously, the magnetohydrodynamic power generator has a dual role in this process. It is both a very fast cooler and a direct convertor of heat to electricity for recycle to the electric arc heaters. An MHD unit is not ordinarily considered a cooler. However, the working gas in the generator undergoes an insentropic expansion which, of course, gives extremely rapid cooling. Also, the units are usually designed so that the gas plasma velocity is sonic or super sonic, giving a residence time of the gas in the MHD unit of less than a millisecond.

At the temperatures of this process air itself is not sufficiently conductive. Therefore a seed material, usually a compound of potassium or cesium, must be added at the entrance of the MHD unit and removed after. This technique is well developed and described in various documents.[32,33] The amount of seed material which is used is very small.

A great deal of the work for generating power has been based on using fossil fuels.[34] The products of combustion of these fuels cause a considerable problem in the form of corrosion and erosion. However for this process, since only clean air will be used in the MHD unit practically all of the corrosion and erosion problems will be greatly diminished.

The use of an MHD unit in this process gives a good thermodynamic efficiency (Carnot) since it is a means for direct conversion of heat to electricity at the highest possible temperature.

Most of the magnetodynamic work which has been carried out in this country has been as part of the various aerospace programs.[50] The literature has numerous references. Further work in the development of MHD will be required before it may be used as a practical piece of equipment in this process. To date, the considerable effort on MHD has proved the principles and shown the way to the design of practical working units. However, an effort will be required to design and build a continuous operating reliable piece of equipment for this process.

High Temperature Materials For The Process

As has been discussed before in this paper, the only parts of this process which are new center around the high temperature section. The material problems for the other parts are fairly well solved in commercial practice today. However, in the preheaters, the electric arc heater, and the MHD unit the question of what high temperature materials to use is a serious one.[32,34]

Fortunately, the large program carried out by NASA and the Department of Defense has given considerable experience in selecting and fabricating materials for these high temperature purposes. The NASA plasma survey has a long discussion on the materials for electric arc and plasma heaters. Metals such as copper and tungsten are favored for electrodes. If air contamination is not worried about carbon and various ceramics may also be used as electrodes. High pressure water cooling has proven to be very effective when combined with metal electrodes and can lead to long term operation with very little erosion. It appears that suitable reliable long time operating electric arc heaters for the range of 3000 - 4000°K can be designed and built based on the present knowledge.

Considerable work has also been carried out on the development of magnetohydrodynamic power generators. A large amount of work was done on the material aspects of MHD. Good ceramic to metal fabrication techniques have been developed. Also, segment electrodes and pressure water cooled copper electrodes have been designed and tested satisfactorily. The test results indicate that MHD power generators operating on the clean air of this process in this temperature region can be built for long time reliable operation.

Considerable work has been done on developing high temperature ceramics for furnace lining and preheater use. Ceramics based on very pure magnesium oxide and zirconium oxide have been used in these temperature regions.[9,11] Although the Wisconsin group had trouble using magnesium oxide ceramic balls in their process, their problems will not likely be encountered in this process. Their main problems were caused by the need for fast temperature cycling in their pebble bed furnaces at 2400°K. This leads to bad thermal expansion and spalling problems. Also, they encountered slow vapor diffusional corrosion from high temperature to low temperature regions. Since in this process the temperature regions will remain constant for long periods of time thermocycling and diffusional problems should be at a minimum.

Economics Of Process

The economics of this process have been studied in order to compare with those of the conventional methods for making nitric acid and nitric oxide. Based on the flow sheet given in Figure I, a cost estimate for a plant to make 500 tons of nitric acid (100% basis) was carried out. This estimate is shown in Table 2 as $11 million dollars. The plant size was chosen as typical of a medium size modern plant in the United States.

Next the manufacturing cost for nitric acid was estimated. The electricity requirements was based on heat balance calculations for the

TABLE 2

MANUFACTURING COST - ARC PROCESS
500 TONS NITRIC ACID/DAY (100% BASIS)

		$/Day
Raw Materials - Zero		
Utilities		
Fuel Gas at $.25/MM Btu		
400 MM Btu		$ 100.00
Electricity at $.002/KW Hr.		
20,000 KW		1,000.00
Treated Water $.13/M/gal 120,000 gal		16.00
Cooling Water .05/Mgal		50.00
	TOTAL	$ 1,166.00
Process Steam Generated (credit)		120.00
		$ 1,046.00
Labor & Supervision		
Operating Labor		500.00
Maintenance 2% Cap. $268,000/Yr.		790.00
Services & Administration 40% labor		390.00
	TOTAL	$ 1,680.00
Fixed Charges (Plant Cost $11,000,000)		
Depreciation, 10%/Yr. plus		
Taxes, Insurance, 2 1/2%		3,600.00
	Total Manufacturing Cost	$ 6,326.00
	Manufacturing Cost Per Ton	$12.7

whole process. The breakdown of the manufacturing cost is shown on Table 2.

Since this process requires cheap electricity, three different prices have been shown in the manufacturing cost table. These are for two, three, and four mills per kilowatt hour. These are the base prices available from currently building large nuclear power plants. The revolution in the economics of electricity being inaugurated by the new generation of nuclear power plants is sweeping the world. Since the cost of transportation of nuclear fuel is a minor consideration on the cost of electricity, one of the major effects of the nuclear power plants is an independence of location as far as cost is concerned. This means that the cost of nuclear electricity is substantially the same in any part of the country or the world. This is an unusual factor. Heretofore, cheap electricity has been dependent on generation close to low cost coal mines, gas fields, or convenient water resources. For this particular process, the critical fact is the availability of cheap nuclear power near the farm customers.

Since this process is not dependent on a specifically located raw material it has a great advantage over the conventional nitrogen-ammonia plants. The conventional ammonia plants must be located at the site of cheap raw material, which in most cases is natural gas.[35] It has been pointed out that the location of the cheap raw material seldom coincides with the sites of the farm consumers. Therefore large amounts of money are required for transportation of the nitrogen to the consumer. All of this can be avoided in this present process since the raw materials, air and water, are freely available any place in the world.

The modern conventional ammonia and nitric acid plants are obtaining their low cost principally by going to very large size plants.[36] This gives an inflexibility of operation and leads to many hidden costs such as large investments for storage over many months of the year and costly transportation. On the other hand, this arc process can be built in small and medium size capacities with almost the same economics as for a large plant. Therefore, small or medium size plants could be built in the farm regions. This will give increased flexibility of operation and improved economics ending up with low costs to the consumer.

In Table 3, the manufacturing costs per ton for the arc process is compared with the

TABLE 3

NITRIC ACID MANUFACTURING COSTS

Arc Process

Electricity, ¢/kwhr	0.2	0.3	0.4
Manuf Cost, $/ton	12.7	13.7	14.7

Conventional Process

Manuf Cost, $/ton	24. to 35.
Additional Transport Cost, $/ton	4. to 15.

conventional process for making nitric acid.[37] The estimates show that the arc process will make nitric acid for about 50% of the cost of the conventional process. This is indeed encouraging. It is true that the arc process is not completely developed so that some aspects of it are still in doubt. However, the present studies have been carried out in sufficient detail to show that there is a very substantial advantage possible in developing and using the arc method for the manufacture of nitric acid versus the present conventional process.

The cost given for the nitric acid manufactured in a conventional plant is for a 500 ton per day unit, but the ammonia raw material used in this plant is based on the production in very large units making 1000 tons per day of ammonia.[36] This combination which is being used in the newest plants gives the best economics for conventional process. However, it also gives increased inflexibility of operations. On the other hand, since the arc process converts the nitrogen of air to nitric acid and does not go through the ammonia step, this process does not require the massive inflexible investment of very large plants. This point is emphasized since it actually has an important bearing on the overall economics of nitrogen fixation and shows the good features of operating economics which may be obtained with the arc process.

Economics And Markets

Besides being an extremely interesting topic of study for scientific reasons, the fixation of nitrogen by either the formation of nitrix oxide, or as is commonly done now, the formation of ammonia, is of vital importance to the welfare of the world's population. Nitrogen, converted into suitable compounds, is the prime plant food (fertilizer) used in growing food throughout the world. It accounts for more than 1/3 of all the plant food used for the growth of crops. This, of course, is the prime reason for interest in the development of better, more efficient, and cheaper methods for fixing nitrogen.

Nitrogen in air is inert and chemically not available to growing plants. However, nitrogen atoms constitute a vital portion of all plant or animal tissues, principally in proteins. Therefore, in order to use the nitrogen in the air, it is necessary to convert it into compounds which can be assimilated by plants.

The commonly used materials are anhydrous ammonia, aqueous ammonia, ammonium nitrate, ammonium sulfate, urea, and ammoniated phosphate rock. All of the materials are characterized by containing nitrogen atoms in a water soluble form. In 1968, 82% of the total nitrogen produced in the world was used as a plant food, industrial uses accounted for the remaining 18%. [37.1] Although nitrogen is used in many forms it is easiest to report it and consider its economics as contained atomic nitrogen (N).

The plant food requirements of the world are directly proportional to the number of people in the world, and their food demand increases with their standard of living. In 1958, the estimated world population was 2.8 billion and in 1970 the estimate is 3.5 billion. The effect of this population increase together with the well known drive of all peoples to improve their standard of living is illustrated in Table 4 showing the production rate of fixed nitrogen in thousands of short tons. The usage of fixed nitrogen in the last ten years has tripled.[37.1] This is indeed an amazing trend.

There have been many predictions of world food shortages by the year 2000 as the world population steadily increases toward 6 billion. It has been pointed out that as of now the most efficient and surest way of increasing food production on the present available farm area is with the use of chemical plant food, such as fixed nitrogen.

The industrial uses of nitrogen are also growing very rapidly. The principle areas of use are in plastic resins, synthetic fibers (nylon and orlon) and industrial explosives. Thus fixed nitrogen is also being used to clothe man and make shelter for him.

Effects Of Raw Material Location

The present method for fixing atmospheric nitrogen by reaction with hydrogen to form ammonia is necessarily based on cheap sources of hydrogen. These sources are the fossil fuels: natural gas, oil, and coal. Many studies have shown the direct dependence of the manufacturing cost of ammonia on the raw material costs of the hydrogen. At present the cheapest material available throughout the world for this purpose is natural gas (methane - CH_4). Sweeney[35] has discussed this effect in location of new large-size ammonia plants in the United States. He points out that all of the new plants are being located at the source of the cheapest natural gas in the U.S. As of now, approximately 1/2 of the ammonia production of the U.S. is along the Gulf Coast. In other parts of the world the same trend is evident; the expansion of ammonia plants is at the location of natural gas and oil fields. Countries not blessed with these natural resources are

TABLE 4

PRODUCTION OF FIXED NITROGEN (N)
IN THOUSANDS OF SHORT TONS

Year	United States [42]	World [*]
1935	257 [38]	2,200 [39]
1945	600 [41]	2,750 [39]
1955	2,740 [41]	9,880 [40]
1960	4,300 [41]	14,700 [40]
1965	6,170 [40]	27,400 [40]
1968	10,300 [40]	36,400 [37.1]
1970	12,900 [E]	45,500 [E]
1975	[E]	73,000 [E]

* This excludes mainland China
E Estimated at 12% per year increase

forced to import large quantities of oil in the cheapest manner as their raw material. India, with its huge rapidly growing population, has become a classic example of this problem. It has very little natural gas, oil and coal. Therefore it is dependent on outside sources for its hydrogen for manufacturing ammonia.

One of the great virtues of the process being discussed in this paper is that the raw materials are available free, evenly distributed throughout the world. Therefore, all of the complications of location of natural resources is avoided. Every country has equal access to air and water; and with nuclear power, access to cheap electricity.

Effect Of Transportation Costs

Whereas fixed nitrogen ammonia plants are located at the source of cheap natural gas, oil or coal as dictated by the manufacturing economics, consuming farm and industrial areas are quite commonly a long distance away. A typically example in the United States is manufacture of anhydrous ammonia at Houston, Texas with the farm consumption area based around Chicago, Ill. Sweeney [35] has discussed this aspect of ammonia manufacture. He points out that the bulk cost of transporting liquid anhydrous ammonia by barge from Houston, Texas to Chicago, Ill. is $7.00 per ton and shipment by railroad is about $23.00 per ton with terminal storage costs of $7.00 per ton. These costs must be compared to the manufacturing cost in Houston of $20 - 35 per ton. This case is typical of the raw material and consumer locations in other parts of the world. In the previously mentioned case of India, oil has to be transported from such areas as Iran and Arabia over a thousand miles away.

Therefore, this present process for high temperature production of nitric oxide directly from air in avoiding this transportation cost requires that the real comparison of cost of this process with that for ammonia be at a location such as Chicago. When this is done, the case for the high temperature nitric oxide process looks even better.

Replacement Of Sulfuric Acid

Sulfuric acid is now commonly used for treatment of phosphate rock, another required plant food nutrient, in order to produce various super phosphates. It can be easily shown that when the price of nitric acid is in the range of $35 - 45 per ton it becomes economically competitive with sulfuric acid for the treatment of phosphate rock. Furthermore, the price of sulphur which is the raw material for sulfuric acid is rising in the world.

This process which can make nitric acid for a selling range of $30 - 45 per ton, therefore could be used as an economic replacement for sulfuric acid. When this happens, the acid requirements in the world for treating phosphate rock will require an additional tens of millions of tons of nitric acid.

The net result will be the increased availability of nitrogen and phosphorous plant foods at significantly lower cost throughout the world.

Conclusions

This paper describes a process for the conversion of atmospheric nitrogen to nitric acid and nitric oxides by a high temperature process. As a result of research and development work undertaken for the vast aerospace programs of the last 15 years, considerable good quantitative data and information have been acquired which can be directly used for the technology of this process. This process can manufacture nitric acid for approximately 50% of the cost of the present most efficient plants. Furthermore since it is based on freely available raw materials whereas the present plants are based on cheap natural gas and oil as a raw material, this process has a great economic flexibility for any place in the world. The world demand for nitrogen fertilizers and nitric acid for industrial uses is increasing at a very high rate; therefore there is a tremendous market justification for further development of this process.

The development of a high temperature nitrogen fixation process is one of the potentially greatest spin-off benefits which may be achieved from the United States Aerospace Effort.

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Appendix

History of High Temperature Nitrogen Fixation

During the period around 1900 several factors gave impetus to the beginning work on high temperature fixation of atmospheric nitrogen. Large amounts of electricity became available for the first time. This was a time of great developments involving high temperature electric furnaces. Concurrent with this, people such as Nernst and Arrhenius were doing fundamental work on the basic laws of thermodynamics[5] and kinetics of gas reactions. Since the reactions of nitrogen and oxygen were considered of a very simple nature, this reaction was studied at length. Nernst, Thompson and Berthelot gathered good data on the heat of reaction[6] and the equilibrium of the reaction of nitrogen and oxygen to form nitric oxide. Arrhenius developed his famous reaction rate equation in which the rate is dependent on an activation energy and the absolute temperature. Finally, and probably of most importance from

a practical point of view, the use of nitrogen for making explosives and for fertilizer in increasing crop yield was just becoming generally recognized.[6] When this is considered in conjunction with the nationalism sweeping Europe at this time, it can be seen that the politics and economics were right for work in this field.

It was established that nitric oxide could be made by heating air in an electric arc. Furthermore, the nitric oxide when cooled was converted to nitric acid by bubbling through water. The first patent on this process was in 1901 by two Americans, Bradley and Lovejoy. They built a fairly large plant at Niagra Falls in 1902 and ran tests on it until it was closed in 1904. The nitric acid produced by this process was too expensive to compete with the conventional methods and the effort was dropped.

About the same time, Birkeland and Eyde were experimenting and magnetically distorted electric arcs. This lead to the design of an alternating current arc in which a semi-circle disk of flame is formed alternately at right angles to a constant magnetic field. The Norwegians recognized that this was a practical way of heating air and designed a full sized furnace. These furnaces were rated at 3500 to 4000 kw each. Air was passed at right angles through the flattened disk of plasma. The gases left the heater at about $1000^{\circ}C$. They were then sent to a boiler house where some of the heat was recovered by generating steam. From there the gases were sent to the acid recovery towers where they were bubbled up through water. In the series of absorption towers, commercial strength nitric acid (30%) was made. This was sometimes converted to calcium nitrate by reaction with limestone. Krase[6] has an excellent discussion of this process, having made a personal visit to the plant in Norway.

Schonherr starting around 1905 developed a somewhat different type of arc furnace in Germany. His arc was centered in a tube some twenty feet long. The pre-heated air was passed longitudinally along this tube. Tangential flow gave a circular arc motion centering the arc in the tube. The electrodes of course were at either end. The power input was 800-1000 kw per arc. The air was heated to approximately $1,200^{\circ}C$ and was cooled by heat exchange with incoming feed air. In the Birkeland-Eyde process the best concentration of nitric oxide in the product gases was about 1% while in the Schonherr arc process the best concentration was about 1.8%. Both of these furnaces were used in full scale plants in Norway. The first plant was rated at about 120,000 kw and the second plant was rated at about 140,000 kw. Krase gives a heat balance about a Schonherr furnace which shows it was highly inefficient. At this time there was no means for adequately measuring the temperature of the gases in the arc so that the real temperature of the air in the arc was unknown. Also, it is interesting to note that at this time the designers and operators of these

plants were unaware of the need for rapid cooling of the hot air leaving the arcs. However, they did show that by taking rather slow cooling means it is possible to get about 1% nitric oxide in the exit gases.

This type of process for nitrogen fixation never did prove to be very popular except in Norway. There the famous company Norsk-Hydro, A.G. has a source of very low price hydro-electric power which is famous to this day. It is interesting to look at the world production of nitrogen in 1919. According to World Trade Notes[38] the world total was 840,000 short tons of nitrogen. Of this more than half was mined in Chile as natural sodium nitrate. Norway produced 22,000 tons apparently all by high temperature arc fixation.

Simultaneously with this development of the arc process, other scientists were working on other means of making nitrogen reactive. Haber starting about 1911 established in his laboratory that nitrogen and hydrogen will react quickly over a special iron catalyst to form ammonia. In a succession of brilliant papers he established the thermodynamics and equilibrium constant for this reaction at various temperatures and pressures. By 1913 this data was being very rapidly implemented into a full size factory by the largest German chemical company. The first World War started about this time and this process, Haber process, was used as the basis for the famous German independence of Chilian nitrates for the manufacture of military explosives. At the end of World War I in 1919, all the other countries of the world, including the United States, recognized the great value of the Haber process and instituted large efforts to gain this knowledge (previously only residing in Germany) for building plants of their own. Meanwhile, the Norwegian arc plants continued producing. However, the newly built Haber ammonia plants proved much superior in economics so that by 1930 it was reported that the Norwegian high temperature arc furnace factories were shut down.[43]

In the 1920's Dr. N. W. Krase while a member of the Fixed Nitrogen Laboratory, U.S.A. investigated the arc method of nitrogen fixation. His chapter in the book "Fixed Nitrogen" is an excellent summary of this work up to that time.[6]

Although the arc heater plants were shut down, chemists and physicists were still studying the reactions of nitrogen and oxygen as a means for pursuing the science of gas kinetics.

Several of them recognized the need for rapid cooling of the gases leaving the arc. In fact Steinmetz suggested the use of an expansion through a nozzle as a means for converting the equilibrium enthalpy to kinetic energy and thus dropping the temperature extremely rapidly.

Dr. Farrington Daniels while at the Fixed Nitrogen Laboratory in 1920 became interested in the nitrogen oxygen reactions.[12] Later, in 1939, Cottrell,[44] a former co-worker, suggested the use of pebble bed furnaces as a means for obtaining high efficiency in heat transfer. This would enable rapid cooling of the gas. This lead to several patents covering the Wisconsin process[45,46] for thermal fixation of nitrogen. In this process air is preheated in a pebble bed and then heated further in the flame of natural gas-air combustion. It is then immediately passed through a cool pebble bed furnace. This gives a cooling rate of 20,000 to 30,000°C/sec. The concentration of nitric oxide in the air leaving this furnace was about 1.5 to 2.1% NO. Of just as great importance, Daniels over a period of many years, at the University of Wisconsin developed quantitative information for the equilibrium of the formation of NO up to about 3000° K. and good quantitative information on the kinetics up to that temperature. Thus for the first time workers in this field had good quantitative data toward which to work.

This work was so successful that in 1952-1954 the U.S. government financed a demonstration plant at Lawrence, Kansas.[9] This plant operated intermittently at the rate of 40 tons nitric acid per day. A total of 2400 tons was produced during this time period. They had many troubles mainly do to the inability of materials to withstand tremendous operating temperatures and changes in temperature. The concentration of nitric oxide in the gases leaving the furnace was about 1.8%. This process has not been developed further because it is still more expensive than the ammonia process. However, it is not much more expensive.

In 1958, Glick, etal at the Cornell Aeronautical Laboratory patented the production of nitric oxide from air in shock tubes.[47,48,49] This work is of importance because for the first time experimental results showed the formation of 7% nitric oxide by heating air to a high temperature and cooling rapidly. In a shock tube filled with air, a shock wave is created at one end which traverses the tube at high speed. As it travels down the tube, it creates a wave front of adiabatic compressed air. The temperature reaches thousands degrees °K. This compression wave front is very thin. Immediately following the wave front, there is an expansion wave which in turn adiabatically cools the heated air very rapidly. The result of this process is given by Glick is 7% NO in air. It costs too much to form the shock wave so that production by this method proves to be uneconomic.

Starting immediately after World War II and gaining very great impetus by 1955, the chemistry and physics of air at high temperatures has been studied and quantified at many locations as part of the gigantic missile and space effort.