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# PRODUCTION OF FERTILIZER IN A MULTIPURPOSE ATOMIC POWER REACTOR COMPLEX FOR DISTILLATION OF SEA WATER: A SURVEY

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#### **ABSTRACT**

A survey was made to determine the feasibility of producing large amounts of nitrogen, phosphate, and potassium fertilizers with the cheap power produced from a large atomic reactor. The optimum combination was a Multipurpose Plant to produce fresh water from sea water by distillation and fertilizer from the air, sea, and phosphate rock. No other raw materials are required and only the three principal fertilizers containing nitrogen, phosphorus and potassium are produced. Large amounts of by-products, requiring shipment and sale, are not produced.

The arc process is used for nitrogen fixation from air to produce nitric acid and fresh water is electrolyzed to produce hydrogen for nitrogen fixation from air as ammonia. Ammonium nitrate can be formed as the final product. Alternatively, nitric acid could be produced by oxidation of ammonia instead of the arc process, if cheaper. Dicalcium phosphate or triple superphosphates are produced by nitric acid leaching of phosphate rock or by treating phosphate rock in an electric furnace with coke and silica. In the furnace process, coke must be shipped in as a raw material but silica would be available at oceanside locations. Potassium is recovered from sea water by precipitation of potassium dipicrylamine. Acidification of the precipitate with nitric acid produces potassium nitrate and the dipicrylamine is freed for reuse. Potassium can also be precipitated as magnesium calcium potassium phosphate but additional caustic must be shipped in to neutralize the phosphoric acid.

World consumption of nitrogen (N), phosphate ( $P_2O_5$ ), and potassium ( $K_2O$ ) fertilizers is expected to rise from approximately  $27 \times 10^6$  metric tons per year in 1959-61 to  $181 \times 10^6$  m tons in the year 2000 if the world rate of fertilizer usage per population unit approaches that in the United States at present. The additional power required to produce this fertilizer in the year 2000 is estimated as  $207 \times 10^3$  megawatts (electric) or forty-two 5,000 megawatte reactors (each equivalent to ~30,000 megawatts of heat), if the high electrical efficiency electrolysis process is used to produce hydrogen for nitrogen fixation from air as ammonia or  $641 \times 10^3$  megawatts (electric) or a hundred and twenty nine 5000 Mwe reactors if the low efficiency arc process is used.



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The effect of reducing power costs per kwh from 8-10 mills for private industry or from 4 mill/kwh for TVA to 1 mill at a large multipurpose reactor station were estimated. The use of electrical power to replace natural gas as a process heat source was also assumed. Reductions in ammonia or dicalcium phosphate prices of less than 5% were predicted since these processes use large amounts of natural gas as process heat which has a cost equivalent to 1 mill/kwh. Conversely, however, the use of 1 mill/kwh electrical power would permit production of economical fertilizer at locations where natural gas is unavailable or must be conserved. The reduction of power cost from 4 to 1 mill/kwh decreased the cost of triple superphosphate produced in electric furnaces by 13%. This cost was estimated to be 16% cheaper than for superphosphate produced by the conventional sulfuric acid process at a Florida location.

The cost of producing ammonium nitrate, a very desirable solid form of fertilizer suitable for long distance shipment, was estimated. The cost, by the electrolysis of water (at 1 mill/kwh) to produce hydrogen, fixation of nitrogen and hydrogen as ammonia, and oxidation of ammonia to nitric acid route, was estimated to be about 50% higher than the present method which uses natural gas as a raw material to produce hydrogen. Since these steps are modern engineering techniques, little further reduction in cost is expected. Hence, the production of nitric acid by arc fixation of air is the key item which could potentially reduce costs significantly for the whole complex but one which could not be estimated with accuracy without a detailed cost estimate and design survey. At 1 mill/kwh, the power cost alone for arc fixation of nitrogen is \$0.029/lb N. Thus arc fixation nitrogen might be competitive with ammonium nitrate but not with ammonia which sell for \$0.104 and \$0.056/lb N, respectively. Since only 3% of the total energy of the arc process is used for nitrogen fixation, the wasted heat could be used to distill sea water and thus reduce the cost of nitrogen fixation. However, the reduction in cost of fixation nitrogen may be small since the energy has been degraded before return to the distillation system. For example, if 30% of the heat is recovered as high temperature steam (worth \$0.41 mill/kwh $_{\rm h}$  or 120 mill/10 $^6$  Btu) and 20% is useful as process heat (worth \$0.034 mill/kwhh or 10 mill/10<sup>6</sup> Btu) the reduction in total cost of power for nitrogen fixation (using 1 mill/kwhe) is 13%.

Hence, increasing the efficiency of the arc process (i.e., the yield of nitrogen/kwh<sub>e</sub>) through new research and modern technology is the best means for decreasing the cost of nitric acid produced by the arc method.

#### 1. INTRODUCTION

The purpose of this paper is to examine the effect of significant reductions in power costs and the availability of large additional sources of power on the synthetic fertilizer industry. The survey is not comprehensive, but includes enough information to determine the value of further economic-sociologic studies and experimental research and development. Other studies at ORNL have predicted that atomic reactors as large as 5,000 megawatts electrical (about 30,000 megawatts heat) would produce electricity for about 1 mill/kwh, a factor 4 to 10 cheaper than current costs. This cheap power or process heat could be used to distill sea water, produce fertilizer, or for other large scale industrial purposes which are not feasible at present power costs. About 70% of the people in the world exist on substandard levels of food intake because of lack of water and fertilizer. "What better use is there for atomic energy than to provide cheap massive supplies of both?"

The present survey was confined to fertilizer production and usage but it was apparent that other industries exert a controlling economic influence on industry as a whole and warrant separate special studies. Transportation is the most important in both the United States and world-wide since the relative location of production plants, raw materials, and markets and actual rate of consumption appears to depend primarily on transportation costs. Sulfuric acid production also warrants study since it is a primary base chemical for industry, in general, and is a major cost in production of phosphate fertilizers for processes requiring a minimum of power.

Appreciation is expressed to J. W. Ullmann of Oak Ridge National Laboratory and W. L. Albrecht of the Tennessee Valley Authority for reviewing this paper and making many helpful suggestions regarding calculations and context.

#### 2. SURVEY PARAMETERS

The following parameters were used to limit the scope of the survey.

- (1) Determine effect of reduced power cost and availability of large amounts of power on the three principal fertilizer types (a) nitrogen, (b) phosphate, and (c) potassium.
- (nitrogen), the oceans (potassium), and mineral deposits (phosphates) and limit the amount of by-products produced. In this way, the undeterminable, chain reactions occasioned by new demands on industry to supply tremendous quantities of raw materials or consume equally large amounts of by-products can be avoided. This is a common problem with previous estimates, such as for separation of isotopes, wherein the production of large amounts of by-products should help to pay for the separative cost if a suitable use for these products were apparent.
- (3) The primary criteria for site selection would be (a) ocean-side location where irrigation water is needed. Since nitrogen and potassium can be obtained from the air and ocean, respectively, an integrated multipurpose production complex is envisional for maximum use of high and low temperature heat. If the complex cannot be located near natural phosphate deposits, phosphate rock must be shipped in. Other possibilities include:
  - (b) Distillation of water and only nitrogen fixation located at ocean-side.
  - (c) Nitrogen fixation and phosphate production at natural phosphate deposit site.
- (4) Nitrogen fixation may be the keystone item since natural deposits and industrial by-product production of nitrogen compounds are limited. The phenomenal rise in nitrogen consumption in the last 40 years, relative to phosphate and potassium, illustrates the effect of a new large volume cheap supply. For example, the arc method of direct fixation of nitrogen and the use of Chilean mineral nitrate were supplanted in 2 decades by the much cheaper process for making ammonia from natural gas or petroleum products.

# 3. FERTILIZER CONSUMPTION STATISTICS

History. Virgin soils generally contain abundant total quantities of essential elements, but often only a small fraction is in a form that a plant can use. Loss of minerals by leaching and removal of crops is compensated for by natural weathering of minerals and by breakdown of organic residues by micro-organisms. Most of the world would soon be a desert without the natural fixation of nitrogen from the air by soil bacteria. The mineral ions such as potassium, phosphate, and magnesium are held in the soil by ion exchange with clay and humus colloids, but nitrogen, when converted to nitrate by micro-organisms, is not held and is lost by leaching. Hence, nitrogen is of primary importance as a synthetic fertilizer. But all essential minerals must be replaced, of course, as the intensity of farming and crop removal increases.

Little change has occurred in the type of synthetic fertilizers used since their introduction about 120 years ago. Potassium is still obtained as potassium chloride from salt deposits and phosphate from phosphate rock. Fortunately, the single major change that did occur, affected nitrogen production, the most critical area. Both potassium and phosphate minerals occur in the United States and Europe but in the 19th Century sodium nitrate from Chile was almost the sole source of the world's supply of nitrogen.<sup>2</sup> The advent of the electric arc process for fixation of nitrogen from air in about 1900 and more importantly the cheap Haber process for production of ammonia from air, water, and coke or natural gas in about 1915 released the world from dependence on Chilean nitrate. The wide distribution of phosphate rock is illustrated by the production statistics for the year 1961.<sup>4</sup> The United States produced about 43% of the total with the USSR the next largest, producing about 17% (Table 1). France and Germany produced about 70% of the world's supply of potassium in 1960-61 but production in the United States is rising rapidly.<sup>2</sup>

<u>World Consumption.</u> About 4% of the world's nitrate was obtained from Chilean nitrate and 81% from ammonia in 1960<sup>3</sup> (Table 2). The price of nitrogen, now set by ammonia, dropped from \$0.14 to \$0.05 per lb N over the period of 1910 to 1963. The sharp upsurge in nitrogen (N) usage compared to phosphate (P<sub>2</sub>O<sub>5</sub>) and potassium (K<sub>2</sub>O) reflects the combined influence of reduced production costs for ammonia, ease of direct

Table 1. Production of Phosphate Rock in 1961 (From Minerals Yearbook 1961) <sup>17</sup>

		Percent of
	(10 <sup>6</sup> long tons)	Total
United States	18.6	43
Brazil	0.27	
Peru	0.16	
USSR	7.6	1 <i>7</i>
China	0.6	
Christmas Island	0.69	
India	0.02	
Indonesia	0.009	•
Israel	0.22	
Jordan	0.36	
Viet-Nam, North	0.61	
Algeria	0.42	
Morocco: Southern zone	7.83	
Senegal	0.2	
Togo	0,28	
Tunisia	1.9	4.3
Union of South Africa	0.29	
United Arab Republic (Egypt)	0.56	
Australia	0.002	
Makatea Island	0.36	
Nauru Island	1.28	2.9
Others	1.5	
World Total	43.8	

Table 2. World Nitrogen Production in 1960 (From Strelzoff)<sup>3</sup>

Synthetic Ammonia	81%
By-Product Ammonia	7.5%
Calcium Cyanamide	7.5%
Chilean Nitrate	4.0%

ammonia application, and ease of shipping as liquid ammonia. World consumption of nitrogen fertilizer increased by 100% compared to 43 and 52% for  $P_2O_5$  and  $K_2O$ , respectively, over the years 1951–52 to 1958–59 (Fig. 1).

Strelzoff has stated the case for nitrogen as follows.<sup>3</sup>

"Under the pressure of a possible rise in world population from 3 to 6 billion people during the 20th century, synthetic nitrogen output could increase from the present 12-million-ton/yr level to 80 million tons. Such a prediction assumes an increase in rate of fertilizer consumption from a 1961 world figure of 4,000 tons per year per million inhabitants to 14,000 tons (which is the 1961 U.S. rate). Between 1950 and 1960, world production capacity of synthetic nitrogen increased from about 5 million to over 11 million tons/yr, at an average annual rate of 7.6%. By the end of 1961, it was about 12 million tons, and will probably continue to grow at an average rate of at least 7%/yr (Table 3).

"There is a remarkable upsurge in demand for nitrogen fertilizers in both advanced and underdeveloped countries. In Western Europe, demand is approaching 18,000 tons of nitrogen per million inhabitants. But India with its 450-million population only produces 550 tons per million inhabitants. To reach the world average, India needs eight times its present 250,000 ton capacity, or about 2 million tons/yr. If Indian agriculture should reach the same level of consumption as the western world, the demand for nitrogen alone will have to be about 8 million tons/yr. The same situation prevails in heavily populated Pakistan and Indonesia. To some degree, a similar upsurge is observed in Mexico, but very little as yet in the rest of Latin America."

Table 3. World Nitrogen Production and Consumption\*

(From Strelzoff)<sup>3</sup>

(Thousand metric tops)

		Consumpti	on by
Prod	uction	Agriculture	Industry
1950	4,718	3,715	702
1955	7,896	6,296	1,239
1960	12,294	10,326	1,767
1961	13,592	10,933	1,900

Includes synthetic ammonia, by-product ammonia and natural nitrates.

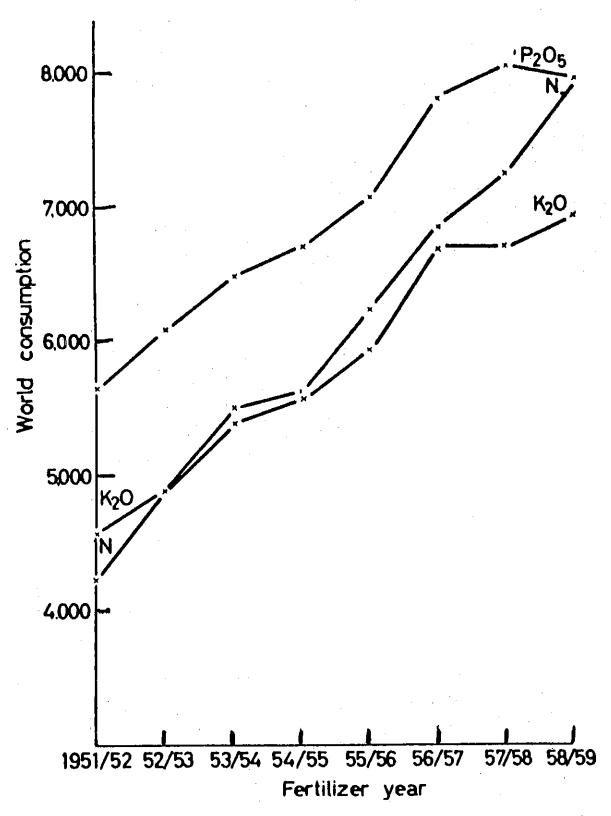


Fig. 1. World Consumption of Fertilizers (in 1000 metric tons of plant nutrients). (From  $\mathsf{Smith}^2$ )

Application of the same factor of  $80/12~(\approx 6.7)$  predicted above for increase in nitrogen usage over the years 1960-2,000 to  $K_2O$  and  $P_2O_5~(7\times 10^6$  mtons and  $8\times 10^6$  mtons in 1958/1959) shows 47 and 54 million metric tons, respectively, and a total N +  $P_2O_5$  +  $K_2O$  consumption of  $181\times 10^6$  metric tons (Table 4).

Table 4. Predicted World Consumption of Fertilizer by Year 2000 (Million metric tons)

Nitrogen (N)	80
Phosphate (P <sub>2</sub> O <sub>5</sub> )	54
Potassium (K <sub>2</sub> O)	47
Total	181

A survey by Smith showed the following consumption statistics.<sup>2</sup>

"Highly industrialized countries are the chief producers and users of fertilizers, and of the 23 million tons of fertilizer nutrients used in 1958/59, about four-fifths was used in Europe and the U.S.A., although these countries together possess only about 30 per cent of the agricultural land of the world. (Figures exclude USSR, Chinese People's Republic, and North Korea.). Table 5 shows the consumption of fertilizer nutrients by continents per 1000 hectares of agricultural land. Some of the heaviest user countries are shown in Table 6 with the United Kingdom for comparison."

Table 5. Average Consumption of Fertilizer Nutrients per 1000 Hectares of Agricultural Land, 1957/58, in metric tons

 $P_2O_5$ K20 Ν Europe (exc. USSR) 14.24 16.51 17.54 North and Central America 3.77 3.81 3.05 South America 0.33 0.40 0.25 Asia (exc. mainland China) 2.11 0.84 0.72 Africa 0.31 0.31 0.10 Oceania 0.15 1.71 0.20 World 2.41 2.56 2.18

(From Smith)<sup>2</sup>

Table 6. Total Consumption of Fertilizer Nutrients per 1000 Hectares of Agricultural Land, 1957/58, in metric tons 2

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	N + P2O5 + K2O	
Belgium	204	
Netherlands	204	
Japan	194	
Norway	130	
Denmark	116	
United Kingdom	53	

United States Consumption.<sup>5</sup> The United States produces and uses more N, P2O<sub>5</sub>, and K<sub>2</sub>O than any other country. Total domestic usage was 8,788,000 short tons in 1961–62. Exports of  $P_2O_5$  and  $K_2O$  (not including phosphate rock) exceed imports while imports of N exceed exports (Table 7). U.S. consumption is twice that of 1949-1950 and 12% more than 1960-61.

Table 7. U. S. Exports and Imports of Fertilizer in 1961-62<sup>5</sup> (1,000 short tons)

	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
Domestic Sources	3,236	3,134	2,733
Imports	286	76	298
Exports	253	272	450
Net Domestic Use	3,269	2,938	2,581
Net Domestic Use (1941) <sup>4</sup>	450	985	460
			<del> </del>

U. S. production and export of ammonia continues to increase rapidly. Anhydrous ammonia has increasing popularity both in the U.S. and abroad. The U.S. capacity of  $1.7 \times 10^6$  short tons of ammonia from 20 plants in 1951 increased to an estimated  $5.9 \times 10^6$  short tons with 62 plants in 1962–63 and to  $6.8 \times 10^6$  short tons by the end of 1963. Most U. S. exports in 1961-62 were as solids, i.e. 40% as ammonium sulfate, 21% as ammonium nitrate, 13% complex fertilizers, 9% calcium nitrate etc. Potash

(K<sub>2</sub>O) imports from Europe are confined to the East Coast because their competitive position vanishes with transportation costs to the interior vs the U. S. western salt deposit supply sites.

# 4. PRODUCTION METHODS AND COSTS

# 4.1 Nitrogen

# 4.1.1 Arc Fixation Process<sup>6</sup>

In the arc fixation method, air is passed through specially designed arc furnaces to produce nitric oxide (NO). The hot gases (1000-1200°C) containing 1.25 to 1.8% NO are passed through brick-lined iron pipes to steel boilers, aluminum coolers and thence to acid and alkaline absorption towers. The NO is oxidized to NO<sub>2</sub> as the gas cools and about 70% is oxidized by the time the gases enter the absorption system. About 4% of the NO is lost up the stack. A waste heat boiler reduced the temperature from about 700°C to 200°C and a water cooler to 20°C. In a series of towers, the gas is then oxidized, the NO<sub>2</sub> absorbed in water to make nitric acid, and the acid neutralized with lime to form the final product calcium nitrate. The process efficiency is 3%, i.e. 3% of the energy is used to fix nitrogen, the remainder appears as heat.

Arc fixation was developed between 1900 and 1915 but became obsolete by about 1930. The largest units were located at Rjukan, Norway, with a total of 210,000 kw (≈ 28,000 ton of nitrogen per year) and a 16,000 kw unit at Pierrefitte in southern France. About 1930 the Norwegian plants were diverted to electrolysis of water to produce hydrogen for making ammonia.

Two specially designed arc furnaces were most widely used, the Birkeland-Eyde and the Schonherr units. In the former, a magnetic field causes the arc to spread in a semi-circle first in one direction then the opposite, according to the direction of the current through the arc. In the latter, a continuous arc is maintained through a 6-8" diam tube up to 20 feet long. Furnace gases are heated to about 1200°C but are around 800°C at the furnace exit since heat is transferred to incoming gases. Both furnaces have about the same overall efficiency. The Schonherr furnace is simpler, more durable, has lower capital cost, and has a slightly higher concentration of NO

in the product gas (1.8 vs 1.25 v/o), whereas the Birkeland-Eyde units are much larger. Other operating statistics are shown in Table 8.

Table 8. Production Data on Arc Fixation of Nitrogen (From Curtis)<sup>6</sup>

70 g HNO3/kwh
7.3 kwy/metric ton N
1.2 - 1.8 volume % NO in exit gas
2.2 m<sup>3</sup> air/kwh
50% of heat as hot water
17% of heat is lost by radiation
30% of heat to make steam
3% of heat to produce NO

The distribution of capital and operating costs are shown in Table 9. They do not include power plant investment or power costs nor acid concentration or conversion costs. The capital cost per ton of fixed nitrogen per year was estimated as \$450 in 1932.<sup>5</sup>

Table 9. Distributions of Capital Costs in an Arc Plant (From Curtis)<sup>6</sup>

Section of Plant	Capital Cost	Total Operating Expense
Furnace	23	35
Boilers	8	. 7
Coolers	2	6.5
Oxidation	1.5	2
Acid absorption	35	15
Alkaline absorption	8	15
Blowers, etc.	4.5	7
Miscellaneous	19	12

(Does not include power investment, power costs, acid concentration or conversion costs.)

A complete cost compilation for fixation of nitrogen by the arc process could not be found in the literature. Direct power costs alone, however, for arc process nitrogen, at current power costs of 4-10 mills/kwh, are \$0.116 to \$0.290 per pound of nitrogen (Table 10) compared to the present selling price of ammonia, ammonium nitrate, and ammonium sulfate of \$0.056, \$0.104, and \$0.071 per pound of nitrogen, respectively. The latter numbers include, of course, profit, production, and marketing costs. Hence, it is readily seen that, even with 1 mill/kwh power equivalent to \$0.029 per pound of nitrogen, arc fixation would not be cheaper than anhydrous ammonia produced from natural gas and air but may be competitive with ammonium sulfate, ammonium nitrate or urea. These solids constitute 57% of the nitrogen exported from the United States whereas liquid ammonia was 32%. It appears that arc fixation nitrogen must have been competitive with Chilean nitrate in 1910 at \$0.142 per pound of nitrogen. It also appears that arc production of NO at \$0.029 per pound nitrogen as a raw material for nitric acid production could be competitive with commercial 58-68% nitric acid now sold for \$0.177 per pound of nitrogen (Table 11). Ammonia is used to neutralize the acid to produce solid ammonium nitrate selling at \$0.104 per pound of nitrogen. Hence, the most economical manner to use fixation nitrogen may be in a plant complex where the nitric acid product of the arc process can be used advantageously to produce a desirable solid fertilizer.

Table 10. Direct Power Cost for Arc Fixation of Nitrogen
7.3 kwyr/m ton N<sup>b</sup>

Mills/kwh	100% Charge \$/lb N	50% Charge <sup>a</sup> \$/Ib N
1	0.029	0.025
4	0.116	0.10
10	0.290	0.25

The remainder charged to water distillation.

<sup>30%</sup> of energy recovered as steam and 20% as 200°F water.

bFrom Curtis.6

Table 11. Commercial Fertilizer Prices
(From Oil, Paint, and Drug Reporter, February 1963)

-		Nitrogen	
	% N	\$/2,000 lb (bulk)*	\$/lb N
Anhydrous ammonia	82	92	0.056
Ammonium nitrate	33	70	0.104
Ammonium sulfate	21.2	30 37 (100 lb bags 1963) 44 (100 lb bags 1929) 60 (100 lb bags 1910)	0.071 0.086 0.104 0.142
Urea	45	90	0.100
Chilean sodium nitrate	16	44 48 (100 lb bags 1963) 43 (100 lb bags 1929) 45 (100 lb bags 1910)	
Nitric acid	(58-68% HNO <sub>3</sub> ) (94-95% HNO <sub>3</sub> )	 Di sankata	0.177 0.222
		Phosphate	<del>1</del> 70 5 6
	% P <sub>2</sub> O <sub>5</sub>	\$/2,000 lb (bulk)	\$/lb P <sub>2</sub> O <sub>5</sub>
Super phosphate	22	20.4	0.047
Triple superphosphate	48	48.9	0.051
Calcium metaphosphate	65		(~0.051)**
Phosphorus (white)	100	eri sak	0.91
		Potassium	
	% K <sub>2</sub> O	\$/2,000 lb (bulk)	\$/lb K2O
Potassium muriate	60	25.80	0.021

<sup>\*</sup>Cost at factory or port.

Pilot plant amounts at TVA; assumed to be competitive with triple superphosphate.

The foregoing discussion has assessed the total cost of the power used in the arc process to the cost of fixation nitrogen. Probably, the most important concept of this paper is the possibility that a major fraction of the cost of arc fixation of nitrogen could be charged to the distillation of sea water in a multipurpose plant. Since only 3% of the total energy of the arc process is used for nitrogen fixation, the wasted heat could be used to distill sea water. Table 8 shows that 30% of the heat is recovered as steam and 50% as hot water and Spiewak has estimated that high temperature steam has a value of 0.41 mill/kwh or 120 mill/10<sup>6</sup> Btu and hot water (200°F) a value of 0.034 mill/kwh or 10 mill/10<sup>6</sup> Btu in an atomic reactor sea water distillation plant. Hence assuming an energy recovery of 30% as steam and only 20% as 200°F water, the energy cost for arc fixation using 1 mill power is reduced by 13% (Table 10).

$$\frac{(0.13) (100)}{1.0} = 13\%$$

Actually a detailed cost estimate using modern engineering techniques for gas absorption and arc technology is required to determine the cost of recovering nitrogen values from the dilute gases from the arc process both as a separate unit and as a combined arc process-distillation plant. It is apparent, however, that increasing the efficiency of the arc process (i.e. the yield of nitrogen/kwh) through new research and modern technology is the best means for decreasing the cost of nitrogen fixation by the arc method since hot water has so little value in sea water distillation.

# 4.1.2 <u>Ammonia Synthesis</u>

From Natural Gas. Production of synthetic ammonia is now the primary method for fixation of nitrogen and about 80% of the estimated world fixed nitrogen production in 1961 used this method.<sup>3</sup> Nearly 85% of the total nitrogen is consumed by agriculture as fertilizer either as liquid or aqueous ammonia or as ammonium salts. Solids such as ammonium sulfate, ammonium nitrate, and urea are favored for shipment and

account for 57% of nitrogen exported from the United States in 1961-62. Also most of the nitric acid and urea is now made from ammonia. Commonly, natural gas is used as the source of hydrogen and energy for ammonia production but petroleum fractions are also used. Anhydrous ammonia contains 82% nitrogen and sells for \$0.056 per pound of nitrogen, about half that of ammonium salts (Table 11). Other advantages of ammonia are minimum shipping weight because of high nitrogen concentration and the feasibility of direct injection into the earth. Retension by soil colloids is rapid and with an application of 100 lb per acre to a depth of 4", little ammonia diffuses beyond two inches.

A modern ammonia synthesis plant using gas generation by pressure reforming of natural gas has been described and the production costs estimated by Eichmeyer and Marshall<sup>7</sup> in 1955 (Table 12). Production steps are:

- (1) Catalytic desulfurizing of natural gas
- (2) Catalytic pressure reforming with steam to form CO and H<sub>2</sub>
- (3) Catalytic second pressure reforming with air (introduces N)
- (4) Catalytic CO conversion with steam to form CO<sub>2</sub> and H<sub>2</sub>
- (5) Heat recovery (exchange)
- (6) CO2 removal by K2CO3 liquor scrubbing
- (7) Compression
- (8) CO removal by copper liquor scrubbing
- (9) Catalytic NH3 synthesis at 5,000 lb pressure and ~200°C

The estimated cost of production in 1955 exclusive of profit was \$37.32 per ton NH<sub>3</sub> vs a selling price\* of about \$85.00 per ton in 1955. The direct electric power cost is \$1.78 or 4.8% of the production cost or 2.1% of the selling price. Little reduction in cost is expected, therefore, by using 1 instead of 8 mill electricity or by substituting 1 mill electric power for fuel gas used for heat (Utilities, Table 12), since fuel gas at 30¢/10<sup>6</sup> Btu is equivalent to approximately 1 mill/kwh. The use of 1 mill electric power for these items could permit production of ammonia economically in areas where natural gas or petroleum products are not readily available or economical as energy sources. They could probably be shipped in for use as a raw material. If

<sup>\*</sup>Selling price FOB works varied between \$72-92 per ton for 1950-1960.

Table 12. Ammonia Syntheses - Gas Generation by Pressure Reforming of Natural Gas

(From Eickmeyer and Marshall)<sup>7</sup>

Plant capacity - 200 tons/stream day Capital investment - 6,050,000 \$/ton

Materials		\$
Natural Gas* (1,040 Btu/scf)		6.67
Catalysts		0.80
K <sub>2</sub> CO <sub>3</sub>		0.01
Others		0.11
Total		7.59
<u>Utilities</u>		
Fuel Gas \$0.30/10 <sup>6</sup> Btu*		6.03
As electric power at 8 mill/kwh As electric power at 1 mill/kwh	\$47.00 \$ 5.86	
Electricity \$0.008/kwh		1.78
Water		0.21
		8.03
Labor, supervision, maintenance		7.73
Depreciation, taxes, insurance		13.97
Total cost per ton		37.32

<sup>\*</sup>Natural gas at  $30 \frac{e}{10^6}$  Btu equivalent to 1.03 mill/kwh  $(10^6 \text{ Btu} = 2.93 \times 10^2 \text{ kwh})$ 

all utility energy was electric, a power cost of 1 mill/kwh instead of 8 mills/kwh would reduce the total power cost from \$47.00 to \$5.86 per ton of ammonia (Table 12).

From Electrolytic Hydrogen. Electrolysis of sea water or the fresh water from a sea water distillation plant should also be considered as a source of hydrogen for ammonia production. Ullmann<sup>8</sup> has estimated that hydrogen might be produced by electrolysis of water for about twice the cost of hydrogen from natural gas reformers, i.e. \$1.00/10<sup>3</sup> scf or \$0.85 if a \$0.17 credit for oxygen production is included for electrolysis vs \$0.38-0.51/10<sup>3</sup> scf for hydrogen from natural gas reformers. Thus ammonia produced from electrolytic hydrogen would be up to twice as expensive as that from natural gas. Ammonia and nitric acid now sell for \$0.056 and \$0.177 per pound of nitrogen. Almost all industrial nitric acid is now made by catalytic oxidation of ammonia. Hence, an increase of \$0.056 per pound of nitrogen as ammonia as a raw material to produce nitric acid would increase the cost of the nitric acid by approximately the same amount, i.e. from \$0.177 to \$0.233. The price of ammonium nitrate correspondingly increases roughly 50%.

# 4.1.3 Urea Synthesis

Urea is increasing in importance as a fertilizer because it is an easily shipped solid with a high (46%) nitrogen content and because of its easy application and low solubility in water. Its use has tripled since 1949 and its price is competitive with ammonium nitrate, i.e. \$0.10 for nitrogen as urea vs \$0.104 for nitrogen as ammonium nitrate (Table 11). Many processes are in use for urea synthesis but all use ammonia and carbon dioxide as raw materials. The steps in the Du Pont of process are:

- (1) Autoclave NH<sub>3</sub> + CO<sub>2</sub> + H<sub>2</sub>O at 200°C and 400 atms pressure to form ammonium carbamate.
- (2) Hydrolyze ammonium carbamate to urea.
  About 24% of the ammonia is converted and the remainder is recycled.

As in the case of ammonia, little reduction in price is expected from the use of cheap electrical power in areas where natural gas is available.

# 4.1.4 Oxamide Synthesis 10

TVA has described oxamide (CONH<sub>2</sub>) as an example of the ultimate in nitrogenous fertilizer but adds that production is uneconomical on a competitive basis. Oxamide is (1) non-explosive, (2) non-toxic, (3) non-hydroscopic, (4) has high (31.8%) nitrogen content and (5) is practically insoluble in water. The particle size actually determines the rate of dissolution in soil. The present process involves oxidation of hydrogen cyanide to cyanogene and then hydrolysis with concentrated hydrochloric acid.

# 4.2 Phosphates

Natural phosphates consisting of fluorapatite (3 Ca3(PO<sub>4</sub>)·CaF<sub>2</sub>) and hydroxy-apatite (3 Ca3(PO<sub>4</sub>)·Ca(OH)<sub>2</sub>) are of little value as fertilizer. The basis of phosphate fertilizer manufacture is to free the phosphate of fluoride and form water soluble compounds from which plants can absorb H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Superphosphate is the principle phosphate fertilizer and along with triple superphosphate constitutes 67% of the world's phosphate fertilizer.<sup>2</sup>

# 4.2.1 Superphosphate

Superphosphate is made by treating finely ground rock phosphates with 77% sulfuric acid to volatilize the fluoride and form soluble calcium phosphate and gypsum (CaSO<sub>4</sub>). The product contains 16-20%  $P_2O_5$ .

# 4.2.2 <u>Triple Superphosphate</u>

Triple superphosphate can be made two ways. Both produce products containing 55-60%  $P_2O_5$ .

- (1) Treat low or high grade rock phosphates with concentrated sulfuric acid to produce phosphoric acid. Then use the phosphoric acid to leach high grade phosphate rock.
- (2) Electrolyze a mixture of silica, coke, and low grade phosphate rock in a special electric furnace to volatilize pure phosphorus. The condensed phosphorus is converted to phosphoric acid which is then used to leach high grade phosphate rock.

# 4.2.3 Calcium Metaphosphate

Calcium metaphosphate is made by volatilizing phosphorus from an electric furnace (as above) and burning the phosphorus to form  $P_2O_5$  vapor. Rock phosphate treated with this vapor is converted to a product containing 60-65%  $P_2O_5$ .

The TVA has pioneered the development of the electrolytic methods for producing high analysis superphosphates. TVA data <sup>11</sup> shows that about 4,500 kwh are required per short ton of P<sub>2</sub>O<sub>5</sub> or 2.25 kwh/lb P<sub>2</sub>O<sub>5</sub> for either triple superphosphate or calcium metaphosphate. Since triple superphosphate sells for \$0.051/lb P<sub>2</sub>O<sub>5</sub> (Table 11), the power cost, at 4 mill/kwh for TVA is \$0.009/lb P<sub>2</sub>O<sub>5</sub> or 17.7% of the selling price. The use of 1 mill power would reduce the price to only \$0.044/lb P<sub>2</sub>O<sub>5</sub> (on a direct proportion basis), a reduction of 13%.

Schurr and Marshak <sup>12</sup> considered the effects of atomic power on phosphate production as follows: Would atomic power be cheap enough to make the electric smelting of phosphate rock in Florida competitive with the sulfuric acid process for double superphosphate production? Costs for production of superphosphates by the electrical or sulfuric acid routes are essentially the same, \$30/ton P2O5, excluding costs for power and sulfuric acid,i.e. 2.3 tons of 50° Baumé (62.7% acid) vs 4,670 kwh, respectively, per ton of P2O5. Table 13 shows the relation between sulfuric acid and electrical power.

Table 13. Comparison of Sulfuric Acid and Electrical Costs for Production of Superphosphate

(From Schurr and Marschak) 12

	The electricity
If the price of	rate which will equalize
sulfuric acid (50° Be.)	production costs is
is (dollars per ton)	(mills per kwh)
<b>6.</b> 50	3.2
<b>7.00</b>	3.4
<b>7.5</b> 0	3.7
8.00	4.0
8.50	4.2
9.50	4.7
10.00	4.9

In 1946, atomic power rates of about 3.5-4.0 mills/kwh were required to equal the cost using sulfuric acid. Since the elemental phosphorus produced by the electrolytic method could be shipped cheaper than the sulfuric acid produced superphosphate, an additional saving accrued (Sec 6.0). It was estimated <sup>12</sup> that at 3.5 mill/kwh power, \$7.50/ton 50° Be acid, a production price of \$50.00, a final selling price of \$125/ton P2O5, and transportation of the product 500 miles, only a 4% reduction in the price would accrue vs superphosphate produced with sulfuric acid. However, on the same basis, but using the 1 mill atomic power assumed for the present survey, the reduction in selling cost amounts to 16%, a substantial decrease.

# 4.2.4 Complex Fertilizers

Complex fertilizers are made by leaching phosphate rock with nitric acid followed by a variety of treatments to make an acceptable fertilizer. The presence of both nitrogen and phosphate in one product is very desirable but the physical qualities of the highly hygroscopic product containing calcium nitrate makes the crude products undesirable for fertilizer. Generally ammonia is added to form dicalcium phosphate and ammonium nitrate. The addition of a sulfate, phosphate or carbonate salt precipitates the remaining calcium. Since these processes require large amounts of ammonia and sulfate or carbonate in addition to nitric acid, they may be less practical for use at an integrated atomic energy fertilizer plant than a process developed by the Nassen Laboratories. <sup>13</sup> In the Nassen process, nitric acid is used to leach phosphate rock and lime or limestone added to neutralize the product and precipitate dicalcium phosphate. The filtrate is evaporated and the calcium nitrate calcined to produce lime for recycle and nitrogen oxide gases which are absorbed in water to form nitric acid for recycle. In this process only the phosphate rock need be shipped to the proposed integrated atomic production site (Sec 7.0).

A cost estimate for the Nassen process (Table 14) shows a production cost of 0.03/lb  $P_2O_5$  if it is assumed that all lime is recycled and no credit is taken for its sale. This price is competitive with the current selling price of about 0.05/lb  $P_2O_5$  (Table 11). Two sources of energy are used, natural gas for heat at a rate equivalent to  $\sim 1 \, mill/kwh$  and power at a rate of 10 mills/kwh. The use of 1 instead of 10 mill/kwh would decrease

the total cost per pound of P<sub>2</sub>O<sub>5</sub> by only ~5% in areas where natural gas is available as a supplemental heat source. In areas where natural gas is not available, the use of 1 mill/kwh power for both heat and power would permit production at the same cost whereas the total power-fuel cost alone would be impossibly high, \$0.064/lb P<sub>2</sub>O<sub>5</sub> at 10 mills/kwh.

Table 14. Dicalcium Phosphate, Fertilizer Grade (36% P<sub>2</sub>O<sub>5</sub>)

(From Nassen and Parks) <sup>13</sup>

Investment: \$4,500,000.00  For: Phosphate-plant, nitric acid recovery and make-up acid un	nit
Product: 394 tons/day = 14,200 units P2O5 (1 unit = 20 lb)	
Feed: 450 tons/day	
Daily Operating Cost: Raw Materials: Phosphate rock 450 tons at \$5.15/ton Limestone 125 tons at \$2.00/ton Nitric Acid (make-up) 25 tons at \$40.00/ton	\$2318.00 250.00 1000.00
Utilities: Fuel 5000 x 10 <sup>6</sup> Btu at \$0.35/10 <sup>6</sup> Btu Power 40,000 kwh at \$0.01/kwh Water	1750.00 400.00 60.00
Labor: Operators and helpers (192 man-hr) Maintenance (64 man-hr) Supervision (32 man-hr)	442.00 147.00 112.00
Other Expenses: Supplies Taxes, insurance Plant overhead	80.00 120.00 360.00
Depreciation: 10% per year of \$4,500,000.00, per day	1350.00
	\$8389.00
Factory cost/lb P2O5	0.03
(Possible credit: for 120 tons lime at \$10.00)	(\$1200.00)

# 4.3 Potassium

Potassium fertilizers are obtained from salt beds located principally in Germany, France, the United States, and Canada. Potassium chloride is the most important

fertilizer and is obtained mainly from sylvinite (KCI + NaCI) by a fractional crystal-lization process over the temperature range  $20\text{--}110^{\circ}\text{C.}^{2}$  Potassium sulfate accounts for only about 12% of world consumption. Potassium nitrate is an excellent duopurpose fertilizer but an economical production method does not exist at present. The oceans contain about 1 lb  $\text{K}_2\text{O}/245$  gal or 1,600 tons of potassium per cubic mile of water and represent an inexhaustible supply at a multipurpose production plant. Certain economies, such as in pumping costs and in cost of heat for temperature adjustments, should be obtained for potassium production from sea water in conjunction with a sea-water distillation plant.

The Dutch and Norwegians have pilot planted a process for recovery of potassium from sea water by precipitation of the insoluble potassium salt of dipicrylamine. <sup>14</sup>

Treatment of the precipitate with nitric acid forms potassium nitrate and insoluble dipicrylamine. The latter is recycled and reused. Details of the process are not available but apparently the process proved to be uneconomical. The use of cheap nitric acid and process heat from a multipurpose reactor may make the process economical. A particular advantage of this process is that shipment of raw materials or chemicals is not required other than replacement of amine lost in processing.

Salutsky and Dunseth <sup>15</sup> have described a process for the recovery of potassium from sea water by the precipitation of magnesium-potassium phosphate (MgKPO<sub>4</sub>). Recovery of 90% of the potassium was obtained when phosphate equivalent to the magnesium and calcium content of sea water was added and the pH adjusted to 9.5 with caustic. The product, probably a mixture of potassium, magnesium, and calcium phosphates, contained 4-5% K<sub>2</sub>O after dehydration. An advantage of this process in a multipurpose plant is the use of phosphoric acid produced in the plant. A disadvantage is the need to ship in caustic to adjust the pH to 9.5. Electrolysis of sea water would produce caustic but also chlorine, probably an undesirable product at a multipurpose plant. A second advantage of this process is the possibility of the combined recovery of potassium during the removal of evaporator scaling elements calcium and magnesium as described below.

The above work was carried out on contract from the Office of Saline Water to find methods for preparing fertilizer during the removal of calcium and magnesium from sea water to prevent scaling during distillation. As a distillation pretreatment process, phosphoric acid and ammonia are added to sea water to precipitate MeNH4PO4·XH2O where Me is principally magnesium or calcium. The final dried fertilizer in this case contains 7% N, 44% P2O5, 21% MgO and 5% CaO and a fraction (not specified) of the potassium present in sea water (total of 37 tons of fertilizer/10<sup>6</sup> gal sea water). Less ammonia is required if sodium hydroxide is used to neutralize the phosphoric acid. Some effort is warranted to optimize this process both for recovery of potassium and removal of scaling elements.

# 5. TOTAL POWER REQUIREMENTS FOR FERTILIZER PRODUCTION

Since cheap power is available from atomic energy only if large amounts of power are produced, it is of interest to estimate the total power required to produce the world's supply of fertilizer.

Nitrogen. The power required to make all of the nitrogen fertilizer used in the United States and in the world at the present time and in the year 2000 are shown in Table 15. For the arc process it was assumed that 7.3 kwy was required/metric ton. Actually only ~3% of this energy is used to make nitrogen oxides and a large fraction of the waste heat could go into the distillation of sea water (see Sec 4.1.1). Table 15 shows that the nitrogen requirements for the United States and the world can be met with five and seventeen 5,000 Mw<sub>e</sub> (30,000 Mw<sub>h</sub>) reactors, respectively, in 1961 but by the year 2000 twenty-six and one hundred additional reactors, respectively, will be required. Similarly, if the hydrogen is produced electrolytically to make ammonia 7 and 26 additional 5,000 Mw<sub>e</sub> reactors are required in the United States and the world, respectively, by the year 2000.

Phosphate. The power required to make all of the phosphate fertilizer used now in the United States and in the world and that predicted for the year 2000 is shown in Table 16. In 1961, the production in the United States and the world would use 0.3

Table 15. Power Requirements for Nitrogen Fixation

			Year 1961	:		Yea	Year 2000	
	Nitrogen (106 m tous)	rogen	Power	er	±Z,	Nitrogen	Power	
		rons/ yr)	Α E.	(m warts)	E   0		m wat	rs)
	رز  اد	World	0.5	World	U.S.		U.S.	World
Arc Process <sup>a</sup>	3.27	12	23.8×10 <sup>3</sup>	$87.5 \times 10^3$	21.9	80	160×10 <sup>3</sup>	584×10 <sup>3</sup>
No. 5,000 Mwe Reactors	ŀ	;	5	17	;	ł	31	117
Ammonia								
Natural Gas Processb	3.27	12	3.06×10 <sup>3</sup>	$11.2 \times 10^{3}$	21.9	80	20.4×10 <sup>3</sup>	75×10 <sup>3</sup>
No. 5,000 Mwe Reactors	į 1	;	9.0	. 2	ł	;	4	15
Electrolytic Process <sup>c</sup>	3.27	12	6.2×10 <sup>3</sup>	22.8×10 <sup>3</sup>	21.9	80	$41.6 \times 10^{3}$	150×10 <sup>3</sup>
No. 5,000 Mwe Reactors	į	!	-	4	ļ	ł	œ	30

<sup>a</sup>7.3 kwy/metric ton; uses only 3% of total energy for NO production.

b Uses natural gas for raw material but assumes use of electrical power in place of natural gas now used as fuel (Table 12). <sup>C</sup>Uses electrolytic hydrogen for raw material and other power as in (b). Assumes: 1 vol of natural gas  $(CH_4) \approx 2$  vol of hydrogen (H2); electrolytic H2 obtained for 150 kwh/1,000 scf as calculated by Ullmann.<sup>8</sup>

Table 16. Power Requirements for Phosphate Production

		*	Year 1961			<b>&gt;</b>	Year 2000	
	P <sub>2</sub> O <sub>5</sub>	20 <sup>2</sup>	Po	Power	P <sub>2</sub> O <sub>5</sub>	5	Pov	Power
	E)	ons/yr)	(m)	(m watts)	(m tons/yr)	ns/yr)	м ш)	(m watts)
	U.S. World	World	U.S.	World	U.S.	World	U.S.	World
Electrolytic Process <sup>a</sup>	3.2	8.0 <sup>b</sup>	1.5×10 <sup>3</sup>	3.75×10 <sup>3</sup>	21.6	54	10×10 <sup>3</sup>	25×10 <sup>3</sup>
(Superphosphate or metaphosphate)								·
No. of 5,000 Mw <sub>e</sub> Reactors	;	;	0.3	0.75	ł	ł	7	5

<sup>a</sup>2.25 kwh/lb P<sub>2</sub>O<sub>5</sub><sup>11</sup> (Sec 4.2.3).

b<sub>Estimate</sub> for 1959.

and 0.75 of one 5,000  $\rm Mw_e$  reactor, respectively. In the year 2000 approximately 2 and 5 additional 5,000  $\rm Mw_e$  reactors would be required, respectively.

Potassium. The minimum power requirements for potassium production from sea water were estimated based on the amount of nitric acid required, i.e. stoichiometrically equivalent to potassium. Other data is not available. At least 2 and 6 additional 5,000 Mwe reactors would be required by the year 1960 for the United States and world, respectively (Table 17).

## 6. TRANSPORTATION

In a multipurpose, ocean-side plant for production of fertilizer and water distillation, the economics of transportation are principally concerned with phosphates. Nitrogen and potassium would be recovered on site from the air and ocean and hence would be shipped out in the most concentrated form consistent with the economics of production. Unless the multipurpose plant could fortuituously be located close to both the ocean and phosphate deposits (as in Florida, North Africa or Southern Arizona) and where cheap irrigation water is needed, the problem of shipping the raw material (phosphate rock) to the plant vs the type of product produced is unique to phosphate among the 3 fertilizer types. The detailed problems associated with a plant for production of the three fertilizer types, but not located at ocean-side in conjunction with production of fresh water, is beyond the scope of this paper. The economic aspects of transportation and atomic power costs on phosphate fertilizer production have been surveyed by Schurr and Marschak 12 along with many other industries. Their conclusions are quoted extensively below.

The economics of shipping phosphate fertilizers from a multipurpose water distillation plant are of interest since more fertilizer will probably be produced than can be used in the immediate area in which the water is used for irrigation. Generally, triple superphosphate plants are located near raw materials to minimize shipping costs. Triple superphosphate (40–50% P<sub>2</sub>O<sub>5</sub>) contains about 1.5 times the P<sub>2</sub>O<sub>5</sub> content of phosphate rock. Since it takes about 1.5 tons of rock and about 1/4 ton of sulfur (about 1 ton of 70% sulfuric acid) to produce 1 ton of superphosphate, the total weight

Table 17. Power Requirements for Potassium Production

		Year	Year 1961			Year 2000	2000	
	K <sub>2</sub> O	0_	P	Power*	K <sub>2</sub> O	0	Pov	Power*
	(m to	tons/yr)	<u>ъ</u> )	(m watts)	(m to	ns/yr)	× ш)	(m watts)
	S.U	World	U.S.	World	U.S.	World	ร <sub>์</sub> ว	World
Dipicrylamine process	2.8	7	1×10 <sup>3</sup>	4.8×10 <sup>3</sup>	19	47	13×10 <sup>3</sup>	32×10 <sup>3</sup>
No. 5,000 Mw <sub>e</sub> reactors	1	ł	0.2		¦	ł	ო	7

\*Based on nitric acid required; 1 mole HNO3=1 mole K.

Electrolytic fixation process (Table 15).

of raw materials is 75% more than the product. Hence, it is cheaper to ship the final concentrated product to the market rather than the raw materials (Table 18). The saving is even greater, where phosphorus is produced electrolytically. In this case (column (3) Table 18), the estimated shipping costs for the raw materials to produce superphosphate at a plant closer to the market is about 0.5 that of the sulfuric acid process.

This analysis indicates that production of elemental phosphorus may be the more economical process for a multipurpose plant. Since the electrolytic production of phosphorus from phosphate rock also requires the use of coke as a reducing agent, the cost of shipping in coke must be considered. Hence it may be best to produce only complex phosphate fertilizers which require only nitric acid (produced at the plant) and phosphate rock (Sec 4.2.4). In this case a balance must be made between the cost of coke shipped in vs cost of shipping out the complex fertilizer containing both nitrogen and phosphorus. The cost of shipping in rock fertilizer is common to all processes and should not constitute a significant problem since cheap ocean transportation can be used similar to that used at present for both phosphate rock and bauxite (aluminum ore). About 4,465,000 tons of phosphate rock were exported from the United States in 1960-61 compared to a total world production of 40.1 million tons.

# 7. DISCUSSION OF INTEGRATED PRODUCTION FLOWSHEETS

Integrated flowsheets for production of nitrogen, phosphate, and potassium fertilizers are presented in Fig. 2. Many combinations are possible using the production methods discussed in previous sections of this report. Figure 2 shows an optimization based on the parameters listed in Section 2, particularly in terms of minimization of chemicals to be shipped in or by-products to be shipped out. In this combination, the raw materials are air, sea water, and phosphate rock. Phosphate rock is the only raw material or chemical to be shipped in large quantities other than the product fertilizers. Both arc fixation of nitrogen to form nitric acid and electrolytic hydrogen production to form ammonia are shown. Catalytic production of nitric acid from ammonia is also shown. A detailed cost evaluation is required to choose between these routes. Neither route requires shipment in of raw materials but oxygen may be an excess by-product of

Table 18. Transportation Requirements and Costs of Superphosphate Fertilizer by Different Concentrations and Different Production Processes<sup>a</sup>

	H)	(From Schurr and Marschak) 12	Marschak) 12		
(1)	(2)	Repr	(3) Representative costs	(4)	(5) Representative cost
Final Product (P2O5 content in parentheses)	Major raw materials consumed per ton of final products (in approximate amounts)		materials required per ton of final product 500 miles by rail	of transporting final product 500 miles	of P <sub>2</sub> O <sub>5</sub> in form of final product 500 miles by rail <sup>b</sup>
Ordinary superphosphate (16% to 20%)	Phosphate rock Sulfur	1/2 ton 1/8 ton	2,50	5.85	32.50
Double superphosphate by sulfuric acid process (40% to 50%)	Phosphate rock Sulfur	1-1/2 tons 1/4 ton	7.00	5.85	12.19
Double superphosphate from elemental phosphorus (40% to 50%)	Elemental phosphorus Phosphate rock	283 lb 900 lb	3.75	5.85	12.19

All of the figures are approximate. They are based mainly on data in "Transportation Costs as They Affect New Phosphorus Industries in the West," by Roscoe E. Bell and Donald T. Griffith, Western Phosphate Fertilizer Program, June 1947; and "Transportation Costs of Sulphur," by Roscoe E. Bell, Pacific Northwest Coordination Committee, April 1948. Both reports have been issued as mimeographed releases of the U.S. Department of the Interior. The freight rates used throughout were in effect prior to July 1, 1946.

<sup>b</sup>Column (4) divided by the average P2O5 content of the final product.

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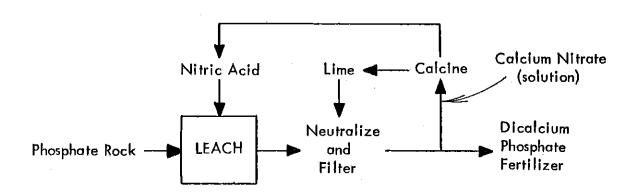
# SEA WATER DISTILLATION REACTOR Heat Electricity Fresh Water

# NITROGEN FIXATION Water Nitrogen Calcium Nitrate **ELECTRIC ARC** Nitric Acid Oxide Scrubbers Fertilizer Lime Ammonium Nitrate **Fertilizer** ELECTROLYSIS Fresh Water Hydrogen Ammonia Fertilizer (caustic) Catalyst N<sub>2</sub> **→** Urea Fertilizer Catalyst -> Nitric Acid $O_2$ Oxygen (by-product)

Fig. 2. Multipurpose Agricultural Atomic Reactor Station for Distillation of Sea Water and Production of Fertilizer.

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# PHOSPHATE PRODUCTION



# POTASSIUM PRODUCTION

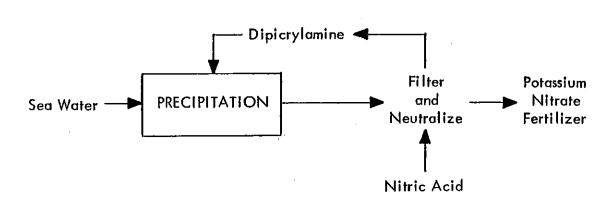
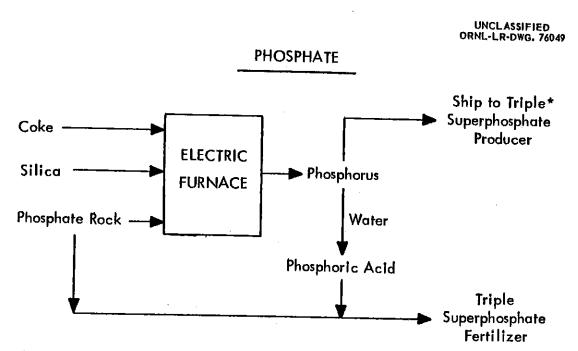


Fig. 2. (Continued) Flowsheets for Production of Fertilizer.



\*low shipping cost to market

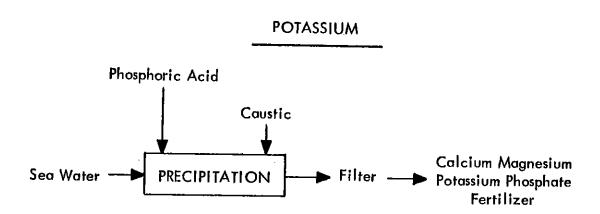


Fig. 2. (Continued) Alternative Flowsheets for Production of Fertilizer.

the electrolysis of water if it is not consumed in the production of nitric acid by oxidation of ammonia. An advantage of the arc process is the possibility of cheap fixation of nitrogen, if the 97% of the power not used in fixation can be efficiently used for water distillation (Sec 4.1.1). A disadvantage of the arc process is the poor quality of fertilizer (hygroscopic) produced when nitric acid is reacted with lime. Formation of this product is probably required since all the nitric acid produced by the arc process (in the absence of an ammonia process) may not be consumed in preparing KNO3 from sea water or in replacing acid lost in leaching phosphate rock.

Probably the best combination is to make both ammonia and nitric acid and produce solid ammonium nitrate. If the production of nitric acid via the ammonia route is cheaper than by arc fixation, the latter could be eliminated. Considerable research should be done on improving the efficiency of the arc process by the use of modern electronic techniques. The recovery of potassium by precipitation with dipicrylamine followed by solubilization in nitric acid has the advantages of using nitric acid produced at the site complex and the recycle of dipicrylamine. Little has been published on the efficiency of the process, however.

Two alternative methods are also shown in Figure 2. The electrolytic production of phosphorus has the disadvantage of requiring the shipment of coke to the plant. It is assumed that siliceous materials can be found on all sea shores. The particular advantage of this method is the low cost of shipment of a concentrated product (phosphorus) which can be converted to triple superphosphate fertilizer close to the market.

Coprecipitation of potassium-calcium-magnesium phosphates from sea water by the addition of phosphoric acid and sodium hydroxide (to pH 9.5) has the advantage of removing the scale producing elements (Ca, Mg) and at the same time forming an acceptable fertilizer containing phosphate and potassium. However, sodium hydroxide must be shipped in. Further study is warranted to increase the yield of potassium using ammonia rather than sodium hydroxide as the precipitant.

# 8. ADDITIONAL SURVEY OR RESEARCH AND DEVELOPMENT WORK REQUIRED

- (1) Evaluation of the combined economics of arc fixation of nitrogen and distillation of sea water.
- (2) Research and development work to increase the efficiency of the arc process through modern electronics, gas absorption, and heat exchange systems.
- (3) Determine the economics of recovery of potassium from sea water by either the dipicrylamine or phosphate precipitation processes. Additional research and development effort is probably required to obtain the necessary data.

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