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UNIDO / PPCL, India

MUSSOORIE PHOSPHATE ROCK PROJECT

14755

I. Prototype studies on production of nitrate / phosphate fertilizer by electric arc process (Final technology report)

II. Agronomic studies (Final agronomic report)

DP/IND/81/019

Battelle - Kettering Laboratory
Yellow Springs, Ohio USA

June, 1985

FINAL REPORT
for
UNIDO Project No. DP/IND/81/019
Activity Code: DP/02/32.1
Contract No. 83/26

"Investigation to use Mussoorie phosphate rock in the production of calcium nitrate/phosphate"

Battelle-C.F. Kettering Research Laboratory
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Yellow Springs, Ohio 45387, U.S.A.
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June 1985

SUMMARY

The basic objective of the work performed under this contract is to test the feasibility of employing a fertilizer production system developed at Battelle-C.F. Kettering Research Laboratory (BCFKRL) for the production of nitrogen/phosphorus fertilizer.

Low-grade phosphate rock from the Pyrites, Phosphates and Chemicals, Ltd (PPCL) mines of the Mussoorie region of India was used in the studies. As a first step in the BCFKRL process, nitrogen fertilizer is produced by combining the nitrogen and oxygen of air in an electric arc process to produce nitrogen oxides. The nitrogen oxides, when combined with water, produce nitric acid that is then reacted with phosphate rock to produce a fertilizer containing both nitrogen and phosphorus nutrients.

The work involved the design, development, construction and testing of a prototype nitrogen/phosphorus fertilizer production system at BCFKRL. Technology transfer of the BCFKRL process was expedited by the assignment of two scientists from the PPCL staff to the project. With the assistance of the PPCL staff, a prototype nitrogen/phosphorus fertilizer production system was installed in late 1983 in the village of Sirki near the city of Dehra Dun in north-central India. Work specified in the contract also included agronomic studies on the liquid nitrogen-phosphorus fertilizer produced by the BCFKRL process.

The technical feasibility of the BCFKRL system to produce nitrogen/phosphorus fertilizer from Mussoorie phosphate rock has been demonstrated by the prototype installation at Sirki. The agronomic efficacy of the liquid nitrogen/phosphorus fertilizer also has been demonstrated in field trials, as detailed in the agronomic section of this report.

ACKNOWLEDGEMENTS

Staff of the Battelle-Kettering Research Laboratory who contributed to prototype studies on production of nitrate/phosphate fertilizer from Mussoorie phosphate rock using the electric arc process are:

Mr. Donald R. Moles - Reactor Systems Engineer
Mr. Charlton K. McKibben - Electrical Systems Engineer
Dr. V. Ranga Rao - Contract Coordinator, Agronomist
Mr. Samuel M. Lough - Chemical Technician

Battelle-Kettering staff appreciate the guidance and support of the Pyrites, Phosphates and Chemicals Ltd. (PPCL) staff on this project. In particular, the guidance and support of Mr. T.N. Jaggi, Chairman and Managing Director of PPCL, Mr. B.V.M. Rao, Manager, Development of PPCL, Mr. R.K. Puri, Senior Manager, Engineering, PPCL and Mr. P.K. Awasthi, Senior Manager, Marketing, PPCL are acknowledged.

Mr. R.K. Puri provided on-site performance data. Mr. O.D. Thapar, University of Rookee, India, designed and supervised installation of the hydro-powered unit. Dr. Nand Ram, G.B. Pant University of Agriculture and Technology, Pantnagar, (U.P.), India, along with Dr. V. Ranga Rao and Mr. P.K. Awasthi, provided the data on the agronomic studies.

The contributions of the above scientists and their support staffs are gratefully acknowledged.

Richard W. Treharne
Contract Team Leader
Battelle-Kettering Research Laboratory

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Evaluation of Agronomic Effectiveness of Calcium Nitrate-Phosphate Liquid Fertilizer Produced by Kettering Arc Generator

PART I - FINAL TECHNOLOGY REPORT

Section A - Studies on Nitrate-Phosphate Fertilizer Production System at Battelle-Kettering Research Laboratory

I. INTRODUCTION:

Pyrites, Phosphates and Chemicals Ltd (PPCL), a Government of India Undertaking, owns and mines phosphate rock deposits in the Mussoorie region of India. The phosphate content of the Mussoorie rock is relatively low (17% to 24% P_2O_5). PPCL is investigating methods to enhance the efficacy of Mussoorie phosphate rock for fertilizer usage. Toward this objective, PPCL contacted Battelle-C.F. Kettering Research Laboratory (BCFKRL) to develop a prototype system, based on an electric arc process developed by BCFKRL, for the production of both nitrogen and phosphorus fertilizer using Mussoorie phosphate rock. A proposal entitled "Production of Calcium Nitrate-Phosphate Fertilizer from Low Grade Mussoorie Rock Phosphate" was submitted to United Nations Industrial Development Organization (UNIDO) on December 10, 1982 and the above designated contract was approved March 28, 1983.

Work performed under the terms of the above designated contract includes topics as stated in "Revised scope of work for study on Mussoorie rock" appended to the contract.

The topics specified, as quoted verbatim from the contract, are:

"1. A detailed description of the prototype unit tests and the conditions under which they were performed.

2. Interpretation of the test results as they pertain to system configuration and process efficiency.

3. A detailed description of the chemical and physical characteristics of the typical product.

4. Recommendations for alternate process strategies including N/P ratio control, product concentration, electrical interfacing, waste heat use, etc., and

5. Technical and economic aspects of scaling up the system."

This report addresses each of the above topics.

As a supplement to this report, a manual entitled "Kettering Fertilizer Production System Construction and Assembly Manual" is included. The supplement provides detailed information concerning the design and construction of the Kettering Fertilizer Production System.

II. BACKGROUND:

In 1976, the Battelle-C.F. Kettering Research Laboratory (BCFKRL) started development of a process to produce nitrogen fertilizer from renewable resources. As a first step in the Kettering Process, nitrogen oxides are produced in an electric arc discharge-in-air process. Basic reactions of the electric arc process are given by the following equations:

$$N_2 + O_2 \xrightarrow{\text{electric arc}} 2NO \qquad \Delta G = +41.4 \text{ Kcal/mol}$$

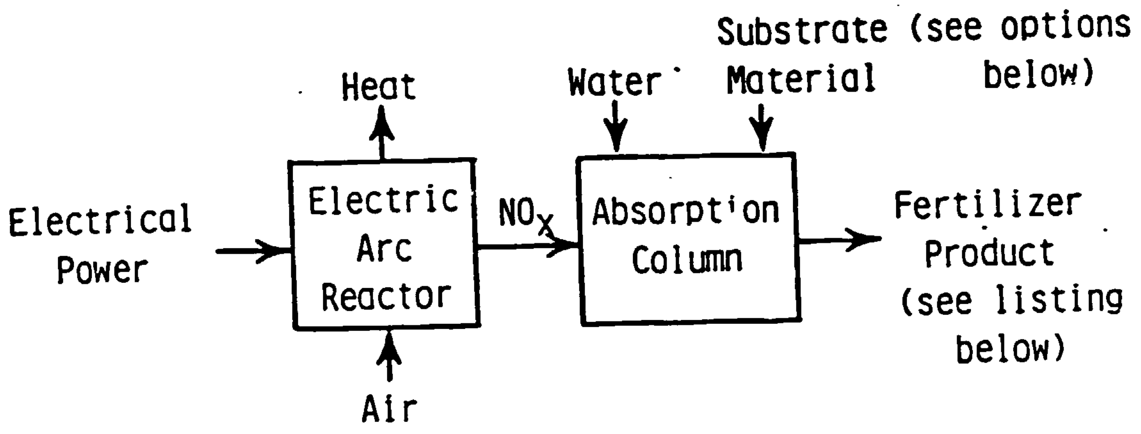
$$2NO + O_2 \longrightarrow 2NO_2 \qquad \Delta G = -16.6 \text{ Kcal/mol}$$

In the early part of this century, several types of systems were developed to produce nitrogen fertilizer using electric arc discharge processes (1-4). One of the most widely used electric arc processes was a process known as a "vortex stabilized arc" process developed by Schönherr (5).

The Kettering Process employs a modified form of a vortex-stabilized arc to produce nitrogen oxides and has been designed to meet the following objectives: 1) to produce fertilizer without the need for fossil fuel through the use of renewable resources and 2) to employ in the process technology appropriate for a developing country. The Kettering technology is adaptable to relatively small-scale applications and thus can be used to produce fertilizer at the site where needed. "On-site" production of fertilizer can eliminate costs normally associated with the transportation and distribution of commercially produced fertilizer. The process has been described in detail in several publications (6-11).

The Kettering Process involves three basic sub-systems namely: 1) the power source, 2) the electric arc reactor and 3) the absorption system. A flow diagram of the Kettering Process is shown in Figure 1.

Inputs to the electric arc reactor are electrical power and air. In the arc reactor, which is described in detail below, nitrogen oxides are produced and an appreciable quantity of heat also is produced as a by-product. As will be discussed later, the heat by-product also can be used productively. In the basic system, the nitrogen oxides produced in the electric arc reactor pass into an oxidation column where the ideal objective is to convert all of the nitrogen oxides to nitrogen dioxide. Conversion of nitric oxide (NO) to nitrogen dioxide (NO_2) is determined primarily by the availability of excess oxygen (from air) and by the "residency" time required for nitrogen oxide to be oxidized in the presence of air to nitrogen dioxide. Thus, the oxidation column is basically a large holding tank that serves to oxidize nitrogen oxide into the form of nitrogen dioxide which is very soluble in water.



Substrate — Fertilizer Product

1) Inert Packing → Dilute nitric acid in water
2) Limestone → Calcium nitrate in water
3) Phosphate Rock → Nitrate and phosphate in water
4) Wood Ashes → NPK fertilizer + trace elements in water

Figure 1. Flow diagram of several configurations of the BCFKRL fertilizer production process.

As a next step in the Kettering Process, nitrogen dioxide, along with other exit gases, passes into an absorption column where the nitrogen dioxide reacts with water to form a weak nitric acid. Depending upon the type of substrate material used in the absorption column, several types of fertilizer can be produced by the Kettering Process. If inert material is used in the absorption column, nitric acid in water solution is produced. Although not normally considered as fertilizer, weak nitric acid can serve as a source of nitrogen for plants. Preferably, however, weak nitric acid should be neutralized with some type of basic compound before application to plant life.

Limestone ($CaCO_3$) may be used in the absorption column in which case calcium nitrate in water solution is produced. Calcium nitrate is an excellent form of fertilizer that is relatively stable and may be applied at any time before or during the growing season.

Phosphate rock is another type of material that may be used in the absorption column. This report discusses a prototype system that uses Mussoorie phosphate rock from India in the absorption column. The advantage of using phosphate rock is that both nitrate and phosphate fertilizer may be produced using the same basic components of the Kettering Fertilizer Production System. Even relatively low grade deposits of rock phosphate, such as Mussoorie phosphate rock, can be used in the Kettering Process (12-14). Thus, the Kettering system is applicable in areas with deposits of rock phosphate not presently considered economically feasible for mining.

Another type of material that may be used in the absorption column is wood ashes. The use of wood ashes, which inherently contain phosphate, potassium and trace elements necessary for plant growth, has the potential of producing a complete N,P,K fertilizer plus essential trace element nutrients.

The several different choices for the types of substrate materials that may be used in the absorption column of the Kettering process, along with the resulting form of fertilizer as an end product, are summarized in Figure 1.

In April of 1983 a series of experiments were begun by BCFKRL staff and engineers of Pyrites, Phosphates and Chemicals aimed at the development of a system which would produce soluble nitrogen and phosphorus fertilizer from air, phosphate rock, water and a renewable source of electricity. These efforts culminated in the installation of a prototype system in India in the fall of 1983. This report is a review of the technical data compiled during the development of this hydro-driven prototype N/P production system installed with the assistance of Pyrites, Phosphates and Chemicals Ltd staff. near the vicinity of Sirki, India.

The remainder of this report is a discussion of the topics specified in the contract under the titles:

Prototype Tests
Interpretation of Results
Product Characteristics
Recommendations
Scaling Considerations

III. PROTOTYPE TESTS:

A. Objectives

1. To determine nitrogen recovery rates of the prototype system with Mussoorie phosphate rock as the reacting and absorbing medium.

2. To determine the ability of the system to solubilize phosphorus from the Mussoorie ore.

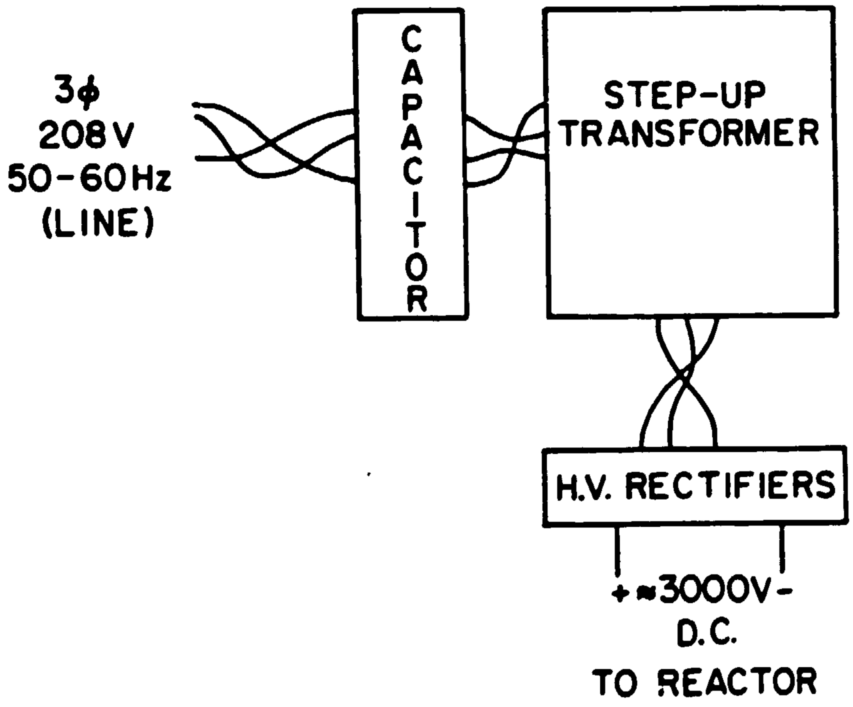
3. To optimize the system for nitrogen and soluable phosphate production.

B. Description of the Prototype System

The prototype used in this study is one that has been designed to produce calcium nitrate fertilizer from a calcium carbonate (limestone) substrate. The information derived previously from the study of a system using limestone served as the basis for the rock phosphate studies. The following is a detailed description of the prototype nitrogen generator system used in these studies. The description is broken down into three major subsystems: the power supply; the reactor assembly; and the absorption system.

1. The Power Supply

Figure 2 is a block diagram of the major components used in the prototype power supply. Power is provided to the transformer via the capacitor bank which serves to reduce current in the line. The transformer not only steps-up the three phase line voltage to the high voltage needed, but also performs the current limiting via a special ballast design described below. The high voltage is rectified to form high voltage direct current.



LINE OPERATED POWER SYSTEM

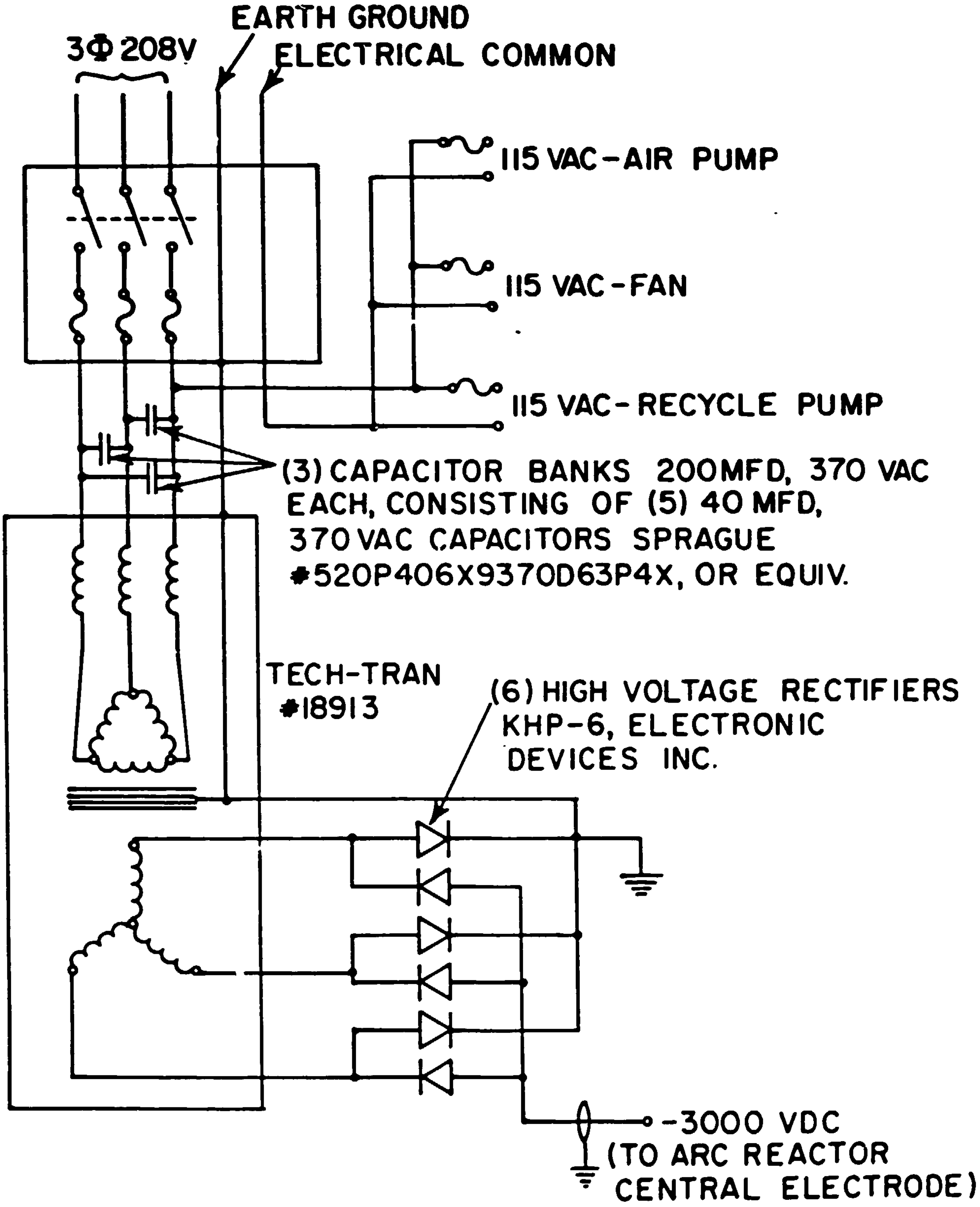
Figure 2

Transformer: The transformer was custom built to BCFKRL specifications for this application by Tech-Tran Corp., Rancoccas, New Jersey, U.S.A. This device performs three phase step-up from 208 vac, 50 Hz, line current to approximately 2200 vac (open circuit) on each phase. In addition, the transformer construction includes another set of windings in series with the primary called ballast windings. The purpose of the ballast windings is to limit current available on the secondary windings. The transformer weight is approximately 300 lbs, which should be considered when designing systems for remote locations where transportation will be a problem.

Capacitors: When driving an arc, the transformer generates considerable amounts of reactive current in the primary windings. A reactive electrical load possesses a low power factor because it produces large currents which are not in phase with voltage. Capacitors are used to absorb the out-of-phase current and thus prevent it from appearing in the line source. Capacitor banks are placed line-to-line across all three phases at the primary of the transformer. A total of 200 MFD. per phase is recommended for a 208 vac supply.

Rectifiers: Six rectifiers are configured as a standard three-phase, full- wave bridge. When connected to the three secondary terminals of the transformer, the bridge outputs provide approximately 3000 VDC (open circuit).

Full Schematic: Figure 3 shows the complete electrical schematic for the line powered system. Note that shutdown of the system is accomplished by interrupting line voltage to the transformer. Shutdown may be performed by an appropriate 3-pole switch, or by a suitable motor start relay. In the case where the relay is used, the relay coil windings may be incorporated into the interlock scheme. The use of 30 ampere line fuses on each of the three phases is highly recommended.



LINE POWER SYSTEM SCHEMATIC

Figure 3

Figure 4 is a photograph of the power system in a metal enclosure with the access door removed. The transformer is mounted inside the cabinet, with the frame of the transformer and the metal of the cabinet both connected to electrical (and earth) ground (see Figure 3, schematic). Ventilation has been provided at the sides and bottom of the cabinet.

The capacitors and rectifiers are mounted in the smaller enclosures and bolted to the main cabinet such that all of the exposed metal is maintained at ground potential for additional safety.

Figure 5 shows the internal configuration of the rectifier and capacitor boxes. The high voltage lead and ground cable exit the main cabinet through a grounded, plastic clad, water-tight conduit which terminates at the reactor.

2. The Reactor

Nitrogen fixation reactions occur in the arc reactor component of the Kettering Fertilizer Production Process. The reactor is basically a standard iron pipe about 3.8 centimeters in diameter and 1 meter long. The pipe serves as both the wall of the reactor and one electrode for an electrical arc discharge within the reactor. The second electrode, constructed from an iron rod 2.5 centimeters in diameter and 10 centimeters long is mounted concentrically in an air manifold at one end of the pipe. Air is injected through tangential air inlet ports of the manifold to create a vortex-shaped arc discharge when voltage is applied to the arc reactor.

Figure 6 shows a cross-section view of the assembled reactor complete with associated components such as the automotive-type spark plug used to initiate the arc when starting. The starting circuitry necessary to start the arc discharge is shown in Figure 7 and discussed in detail in the "Kettering Fertilizer Production System Construction and Assembly Manual" included as Appendix C of this report.

Figure 4

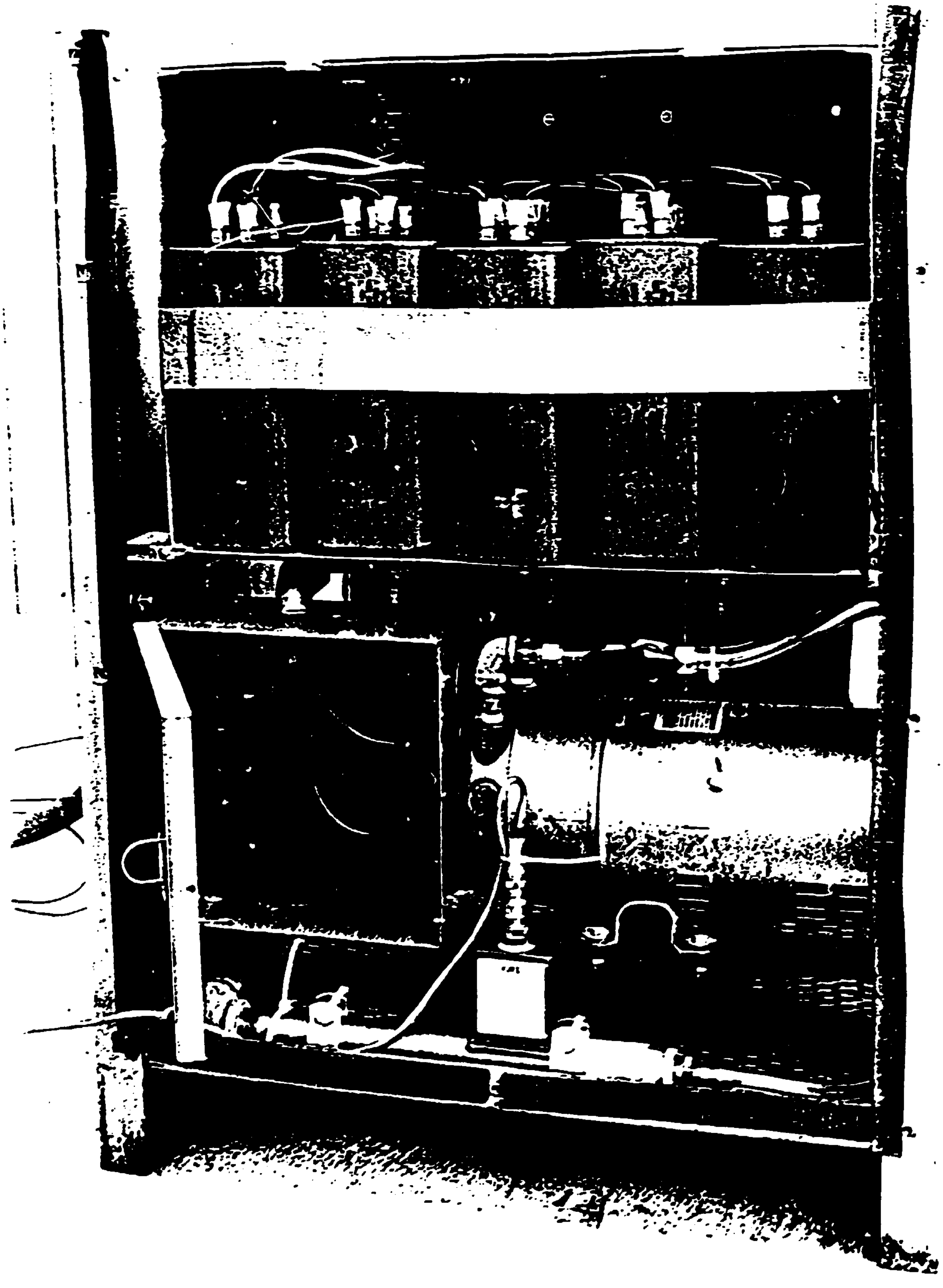
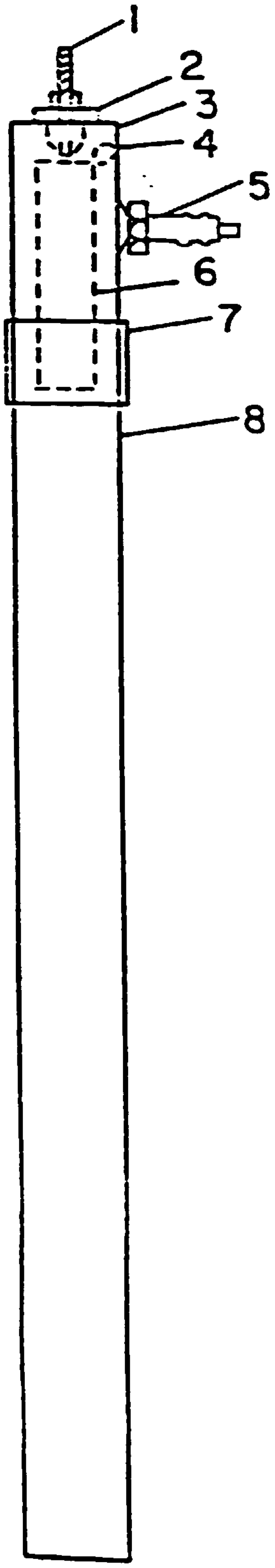


Figure 5



(1) Electrode support shaft/high voltage connection- This is a 1/4 inch diameter threaded rod (20 threads/inch), one nut and washer needed.

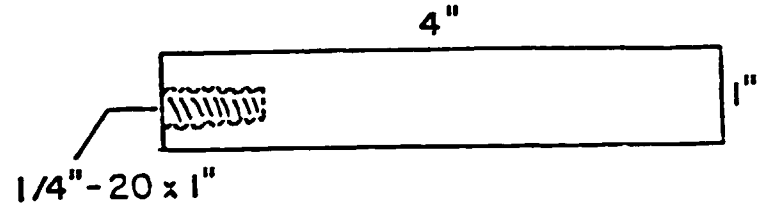
(2) Ceramic insulator- (2 piece), part # 9450, Herman H. Smith, Inc., Brooklyn, N.Y., USA, accommodates passage of support shaft through air manifold end piece to central electrode. Includes two fiber washers to seal at metal interface.

(3) Air manifold constructed from all steel material.

(4) Air inlet tube - 5/16 inch O.D., 0.27 inch I.D. steel tube integral to air manifold.

(5) Spark Plug - # BL13Y Champion, AC or similar, with extension removed (ground flush with rim). Modification show below:

(6) Central electrode - mild steel 1 inch diameter solid rod cut to 8 inch length. One end is center tapped to accommodate 1/4 inch support shaft with that end surface finished off square.



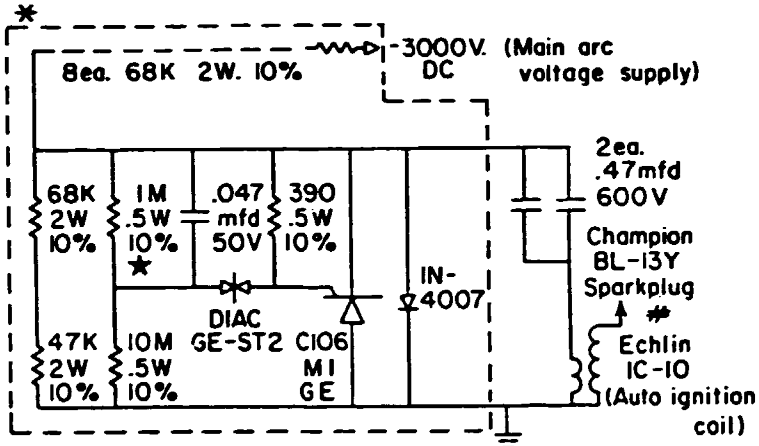
(7) Coupling - standard plumbing part to accommodate 1.5 inch pipe. This piece allows mating of the air manifold with the reactor tube, may also be incorporated into heat exchanger so as to provide support to the reactor.

(8) Reactor Tube - Standard plumbing 1.5 inch pipe cut to 24 inch length and threaded on both ends. This section of pipe serves as the grounded electrode and is easily replaceable.

REACTOR

Figure 6

NITROGEN FERTILIZER GENERATOR
ELECTRONIC STARTER CIRCUIT



LINE SYSTEM STARTER SCHEMATIC

Figure 7

3. The Absorption System

The gas leaving the reactor is a mixture of air and the oxides of nitrogen, e.g. NO_2 & NO. The nitrogen oxides constitute a small part (<2%) of the total flow. One of these oxides, NO_2, is readily soluble in water. The function of the absorption system is: 1) to convert as much of the insoluble nitric oxide to nitrogen dioxide as possible, and 2) to trap the nitrogen dioxide in solution as nitrate (NO_3).

Some of the basic reactions involved in these functions are shown below:

Reaction

1. $2NO + O_2 = 2NO_2$
2. $2NO_2 + H_2O = HNO_2 + HNO_3$
3. $4HNO_2 + 2NO = 2NO_2 + 2H_2O$

The oxidation of NO in air, reaction 1, is slow with its forward rate dependent upon the concentration of NO. The table below depicts this rate relationship.

OXIDATION RATE OF NITRIC OXIDE IN AIR

($20\%\ O_2$) at 20°C

NO Concentration (ppm)	Oxidation Time 25%	50%	90%
10,000	8.4 sec.	24 sec.	3.6 min.
1,000	1.4 min.	4 min.	36.0 min.
100	14.0 min.	40 min.	6.0 hours
10	2.3 hours	7 hours	63.0 hours
1	24.0 hours	72 hours	648.0 hours

It can be seen that the time required to completely oxidize NO in air to NO_2 is, for practical purposes, infinite. However, oxidation percentages exceeding 90% may be obtained in reasonable time periods if the NO concentration is greater than 10,000 PPM. For 90% oxidation, the time required for various NO concentration approximately is given by: Time (minutes) = 36,000/PPM (NO). Gases exiting the arc reactor contain nitric oxide in concentrations between 10,000 and 20,000 PPM. Thus for 90% oxidation a period between 1.8 and 3.6 minutes would be required.

Reaction #2 shows NO_2 and water reacting to form nitric and nitrous acids. Although nitric acid in weak solution may be used as a fertilizer directly, its low pH precludes its use in many applications. In addition, absorption efficiency is limited by the back reaction of nitrous acid (reaction #3). A preferable form of nitrogen fertilizer is a salt such as $Ca(NO_3)_2$, which has a slightly acidic pH and is highly soluble in water.

Figure 8 is a schematic cross-section of the prototype absorption system. Cooled gases from the reactor enter the top of the tall oxidation column and move slowly downward to exit above the waterline near the bottom of the column. The oxidation column is set in the reservoir in order that condensing water vapor and nitric acid are absorbed by the recirculating system without accumulating in the oxidation column.

The gases exiting the oxidation column enter the base of the absorption column just below the packing support plate. The gases pass through the holes in the plate and move upward through the wet packing material. On the surfaces of this material, the nitrogen dioxide is removed from the gas stream and imparted to the descending liquid as nitrate. A small percentage of the nitrogen dioxide exits the top of the absorption column along with air, carbon dioxide and water vapor. The aqueous nitrate-phosphate solution continues

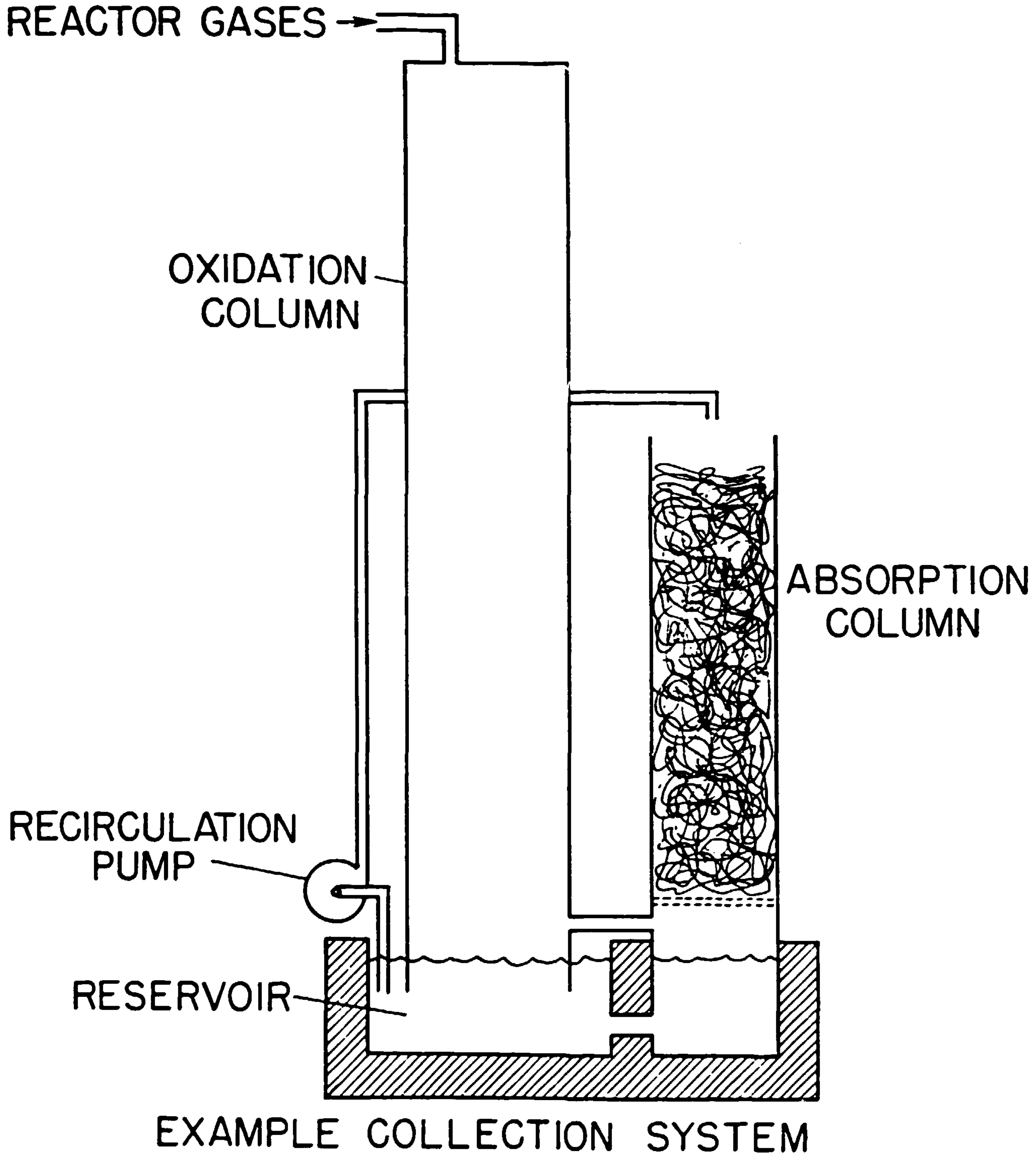

REACTOR GASES
OXIDATION COLUMN
ABSORPTION COLUMN
RECIRCULATION PUMP
RESERVOIR
EXAMPLE COLLECTION SYSTEM

Figure 8

down through the Mussoorie phosphate rock and support plate into the fines (residue) trap. The liquid moves from the trap through a small conduit to the local reservoir from which it is pumped back to the spray head at the top of the absorption column, thus completing its cycle.

C. Procedures and Test Conditions

Since the test system was located out-of-doors, no attempt was made to control gas inlet or liquid recycle temperatures, although these were recorded regularly as data items. Steps were taken to assure that rain water did not enter the process liquid. Observations were noted, however, in those cases where dilution from rain was suspected.

Two rock sizes were tested, primarily for their physical characteristics. The "large" rock had an average cross section of five (5) centimeters with a packed void space of approximately 50%. The "small" rock possessed an average cross section of two (2) centimeters and a void space of 43.7%. Both sizes of rock had the same composition. The analysis provided by International Fertilizer Development Center (IFDC) was as follows:

18.6% P_2O_5
43.8% CaO
15.4% SiO_2
1.7% Al_2O_3
4.0% Fe_2O_3
13.6% CO_2
1.4% MgO

The procedure of testing was the same for both the large and small rock, although the length of testing differed due to the length of time required for the column to attain a chemical equilibrium.

Because of the relatively large content of carbonates and other acid-neutralizing compounds in the rock phosphate, the column had to be operated for a long period of time before a "steady-state" condition could be attained. During this period of equilibration, the more reactive components of the rock phosphate were leached from the rock. Since it was known from previous experiments with a limestone substrate (15) that the nitrogen absorption efficiency of the column was a function of nitrogen concentration of the recycle liquid, it was necessary to run many small batchs of recycle liquid for short periods in order to record the column's performance across a range of nitrogen concentrations at various points in time as the column approached equilibrium. Typically, the recycle reservoir was filled with 70 liters of fresh water at the beginning of each batch. Then the unit was operated for a period of time, usually 48 hours, while the water was continuously recycled through the absorption column at a rate of 3 to 4 liters per minute and liquid samples were taken for nitrogen and phosphorus analysis. After the 48 hour period of operation the reservoir would be emptied and filled with fresh water and the process repeated.

Parameters monitored during each test included the following:

Parameter	Units	Method of measurement	Typical value
Power	KW	Analog multiplication & strip chart recorder	3.0
Energy	KWHR	Analog multiplication with Time Integration	Variable
Air Flow	L/Min.	Kurz 505-8 Electronic Mass Flow Meter	80
Liquid Recycle Rate	L/Min.	Volumetric/Time	3-4

Parameter	Units	Method of measurement	Typical value
Liquid Recycle Temperature	Deg. C	Platinum RTD	11.8 - 31.5
Process Gas NO_2 Content	% NO_2	Optical Density @ 354 NM	.89 - 1.72
Liquid pH	pH Units	Electronic pH Meter	.65 - 7.1
Recycle Liquid Nitrogen Content	G.N/L.	Cadmium Reduction Method & Absorbance @ 500 NM. or, Chemiluminescence Nitrogen Analyzer	0 - 31.2
Recycle Liquid Phosphorus	G.P/L.	Ascorbic Acid Method & Absorbance @ 700 NM	0 - 13.7
Recycle Liquid Iron Content	G.Fe/L.	1-10 Phenathroline & Absorbance @ 510 NM.	0 - 3.2

Two series of tests were performed. The first series had the absorption column packed with large rock and was comprised of three tests or "batches" with a variable number of samples taken per batch. The second series had the column packed with small rock and consisted of seventeen (17) batches also with a variable number of samples taken during the course of each batch.

During both series, the packing height of the absorption column was maintained at 175 centimeters by periodic additions of the appropriate size rock. Additionally, air flow rates and reactor power levels were maintained at their nominal values during the course of each series.

The analytical procedures used in the determination of nitrogen, phosphorus, and iron in the liquid test samples were standard and acceptable techniques, the details of which are provided in Appendix A of this report.

D. Data

Table 1 presents in tabular form the data from the large rock series. As was mentioned previously, this was a limited series consisting of three (3) test batches, A through C,

Tables 2 and 3 present the data from the small rock series in batches D through V.

The following is a discussion of the column headings including any calculations used to derive the various data items.

BATCH - Labeled A through V in the order in which they were performed.

SAMPLE - Labeled 1 to n in the order in which they were taken at various intervals.

DATE - Month/Day, 1983

TIME - 24 hour notation

ESTIMATED PIT VOLUME - The liquid reservoir volume was determined from the starting and ending volumes. Intermediate values were interpolated based upon the time interval.

GRAMS N/L. - Based directly upon the results of the appropriate analytical procedure.

GRAMS P/L. - Based directly upon the results of the appropriate analytical procedure.

TOTAL GRAMS PIT N - A multiplication of Estimated Pit Volume and G.N/L.

TOTAL GRAMS PIT P - A multiplication of Estimated Pit Volume and G.P/L.

CUMULATIVE HOURS - Hours elapsed since beginning of series.

KWHR CONSUMED - A direct reading from a high-voltage Watt-Hour meter designed and constructed at BCFKRL.

Data Showing Collection of 'N', Evolution of 'P' from Mussourie Rock Phosphate (5 cm Size used in Absorption Column), pH of Solution Fertilizer and Consumption of Power in Production of N/P Fertilizer by Arc Process at BCFKRL, Yellow Springs, Ohio, USA during 143 Hrs.

A	B	Date	Time	Est.Pit Volume	Grams N/Liter	Grams P/Liter	Total G Pit N	Total G Pit P	KW-Hr. Consume	Avg.Batch Air Flow	Avg.Batch NO_2 %	Avg. N Prod.	Column Eff. %	Elapsed Hours	N/P Ratio	Cum. Hrs.	Cum. KW-Hr. Hrs.	pH of Solution Fertilizer
A	1	5/23	12:00	70	0	0	0	0	0					0	0	0	0	7.8
	2	5/24	10:00	66.4	7.4	.04	491.4	2.7	58.9			771		22	185			3.6
	3		16:00	65.4	10.6	.08	693.3	5.2	75.7		GN/HR=35.0	981		28	132			3.5
	4	5/25	8:40	62.6	15.4	.192	964.0	12.0	124.9			1566		44.7	80			2.1
	5		12:25	62	16.6	.234	1029.2	14.5	136.3	85.7	1.09% NO_2	1699	61%	48.5	71	48.5	136.3	2.0
B	1	5/25	15:30	70	.64	.02	44.8	1.4	0					0	32			7.0
	2		16:00	69.9	.78	.01	54.5	.7	1.53			18.4		.5	78			3.3
	3		21:10	69.0	2.03	.065	140.1	4.5	16.8			209		5.67	31			2.5
	4	5/26	9:00	67.0	8.1	.24	542.7	16.1	52.4		GN/HR=36.9	645		17.5	34			2.0
	5		16:00	65.8	10.4	.327	684.2	21.5	72.9			903		24.5	32			1.8
	6	5/27	9:05	62.8	16.0	.543	1005.5	34.1	123.6			1534		41.6	30			1.6
	7		14:00	62	20.1	.65	1246.2	40.3	138.4	84.7	1.16% NO_2	1714	73%	46.5	31	95	274.7	---
C	1	5/31	9:00	70	1.1	.01	77.0	.7	0					0	110			6.7
	2		13:00	69.4	2.3	.065	159.7	4.5	11.3			139		4.0	35			2.1
	3		16:00	69.0	3.9	.122	269.0	8.4	19.9			243		7.0	32			2.0
	4		21:00	68.3	5.4	.195	368.8	13.3	34.6		GN/HR=34.7	416		12.0	28			1.9
	5	6/1	9:00	66.5	10.8	.394	718.2	26.2	70.0			832		24.0	27			1.7
	6		16:00	65.5	13.0	.562	851.2	36.8	90.8			1074		31.0	23			1.6
	7	6/2	9:00	63	19.0	.845	1197.0	53.2	140.8	84.3	1.10% NO_2	1663	72%	48.0	23	143	415.2	1.4

Column A = Batch
Column B = Sample

Table 1

Data Showing Collection of 'N', Evolution of 'P' from Mussourie Rock Phosphate (2 cm Size used in Absorption Column), pH of Solution Fertilizer and Consumption of Power in Production of N/P Fertilizer by Arc Process at BCFKRL, Yellow Springs, Ohio, USA during 868.1 Hrs.

A	B	Date	Time	Est.Pit Volume	Grams N/Liter	Grams P/Liter	Total G Pit N	Total G Pit P	KW-Hr. Consume	Avg.Batch Air Flow	Avg.Batch NO_2 %	Avg. N Prod.	Column Eff. %	Elapsed Hours	N/P Ratio	Cum. Hrs.	Cum. KW-Hr. Hrs.	pH of Solution Fertilizer
D	1	6/2	14:45	70.0	.031	.0014	2.2	.1	0					0				7.1
	2		16:45	69.7	.17	.0053	11.9	.4	5.2			55.4		2				3.8
	3		21:15	69.1	3.4	.0137	234.9	1.0	17.5			180		6.5				4.0
	4	6/3	9:15	67.4	12.3	.038	829.0	2.6	51.15		GN/Hr=27.7			18.5				3.95
	5		16:00	66.4	14.4	.064	956.2	4.3	70.81					25.25				3.85
	6	6/4	9:00	64.0	19.4	.138	1241.6	8.8	120.33		Avg.MV=39.4			42.25	141			3.20
	7		16:20	63	18.7	.193	1178.1	12.2	141.64	82.80	.89% NO_2	1373	86%	49.58		49.58	141.6	2.80
E	1	6/6	9:40	70.0	.5	.002	35	.1	0					0				7.25
	2		16:00	68.9	3.0	.062	206.1	4.3	18.29		GN/Hr=38.8	246		6.33				7.10
	3	6/7	9:00	66.1	9.4	.203	621.3	13.4	67.47			905		23.3				3.25
	4		16:00	65.0	14.0	.289	910.0	18.8	87.97		Avg. MV=49.4	1177		30.3	52			2.40
	5	6/8	9:40	62	22.0	.425	1364	26.4	140.06	82.06	1.26% NO_2	1864	73%	48.0		97.58	281.7	2.25
F	1	6/8	11:15	70.0	1.6	.031	112	2.2	0					0				6.25
	2		16:00	69.5	4.1	.117	285	8.1	13.86		GN/Hr=42.4	201		4.75				2.40
	3	6/9	9:00	67.7	11.4	.269	771.8	18.2	64.45		Avg. MV=52.5	922		21.75				2.00
	4		16:00	67.0	14.6	.357	978.2	23.9	85.5			1218		28.75				1.90
	5	6/10	11:15	65	21.2	.511	1378	33.2	142.44	82.19	1.38% NO_2	2034	68%	48.0	42	145.6	424.1	1.70
G	1	6/13	9:30	70.0	.85	.004	59.5	.3	0		GN/Hr=36.3			0				6.95
	2		16:00	68.8	3.0	.065	206.4	4.5	19.06		Avg. MV=47.0*	236		6.5				2.40
	3	6/14	16:00	64.3	12.5	.225	803.8	14.5	88.95			1108		30.5				1.80
	4	6/15	9:30	61	18.7	.251	1140.7	15.3	137.61	82.59	1.17% NO_2	1744	65%	48.0	75	194	561.7	1.70
H	1	6/15	15:00	70	2.0	.013	140	.9	0					0				6.0
	2	6/16	9:00	67.4	7.9	.159	532.5	10.8	48.92		GN/Hr=35.2	634		18.0				1.9
	3		16:00	66.4	11.0	.212	730.4	14.1	68.03		Avg. MV=46.6	880		25.0				1.8
	4	6/17	9:00	63.9	17.3	.264	1105.5	16.9	115.07			1479		42.0				1.7
	5		15:00	63*	19.4	.297	1222.2	18.7	131.91	81.04	1.16% NO_2	1690	72%	48.0	65.3	242	693.6	1.6
J	1	6/20	10:15	70.0	1.0	.001	70	.1	0					0				5.4
	2		16:00	69.0	3.4	.042	234.6	2.9	16.45		GN/Hr=36.3	209		5.75				2.1
	3	6/21	9:30	66.1	9.3	.179	614.7	11.9	66.55		Avg. MV=47.2	844		23.25				1.75
	4		16:00	65.0	12.5	.241	812.5	15.7	83.50			1080		29.75				1.7
	5	6/22	10:15	62	18.0	.261	1116.0	16.2	129.61	81.97	1.18% NO_2	1742	64%	48.0	69	290	823.2	1.6
K	1	6/22	14:15	70.0					0					0				4.5
	2	6/23	9:00	68.1					53.87		GN/HR=43.7	819		18.75				1.7
	3		16:00	67.3					73.89		Avg.MV=53.9	1124		25.75				1.7
	4	6/24	9:00	65.6					124.35			1866		42.75				1.6
	5		14:15	65	17.8	.449	1157	29.2	138.88	81.49	1.43% NO_2	2096	55%	48.0	40	338	962.1	1.5
L	1	6/27	9:00	70.0					0					0				6.4
	2		16:00	69.3		.066		4.5	19.70		GN/HR=34.4	241		7.0				2.0
	3	6/28	9:00	67.5		.303		21.0	70.02		Avg.MV=45.9	825		24.0				1.7
	4		16:00	66.8		.414		27.7	88.64			1066		31.0				1.6
	5	6/29	9:10	65	19.1	.590	1241.5	38.3	142.54	80.93	1.13% NO_2	1656	75%	48.17	32	385.8	1104.6	1.5

Column A = Batch
Column B = Sample
*Final Pit volume lost, average value used

Table 2

Data Showing Collection of 'N', Evolution of 'P' from Mussourie Rock Phosphate (2 cm Size used in Absorption Column), pH of Solution Fertilizer and Consumption of Power in Production of N/P Fertilizer by Arc Process at CFKRL, Yellow Springs, Ohio, USA during 868.1 Hrs.

A	B	Date	Time	Est.Pit Volume	Grams N/Liter	Grams P/Liter	Total G Pit N	Total G Pit P	KW-Hr. Consume	Avg.Batch Air Flow	Avg.Batch NO_2 %	Avg. N Prod.	Column Eff. %	Elapsed Hours	N/P Ratio	Cum. Hrs.	Cum. KW-Hrs. Hrs.	pH of Solution Fertilizer
M	1	6/29	14:00	70.0		.065		4.6	0		GN/HR=46.1			0				5.4
	2	6/30	9:00	67.2		.685		46.0	57.1		Avg.MV=56.1	875		19.0				1.6
	3	7/1	8:30	63.8		.920		58.7	127.52			1958		42.5				1.4
	4		14:00	63*	19.1	1.07	1203.3	67.4	144.12	81.34	1.51% NO_2	2211	54%	48.0	18	433.8	1248.7	1.3
N	1	7/5	13:45	70.0					0					0				5.7
	2	7/6	9:00	67.2		.776		52.2	60.03		GN/HR=43.9	846		19.25				1.6
	3		16:00	66.2		1.24		82.3	80.88		Avg.MV=52.1	1153		26.25				1.4
	4	7/7	9:00	63.7		1.90		120.9	133.15			1900		43.25				1.3
	5		13:45	63	20.2	2.36	1272.6	148.6	147.48	83.19	1.41% NO_2	2108	60%	48.0	9	481.8	1396.2	1.2
P	1	7/11	11:10	70.0		.035		2.51	0					0				6.3
	2		16:00	69.2		.287		19.9	14.03		GN/HR=50	242		4.83				1.6
	3	7/12	10:00	66.2		1.36		90.3	68.61		Avg.MV=58.2	1142		22.83				1.4
	4		16:00	65.2		1.78		115.9	86.41			1442		28.83				1.25
	5	7/13	11:10	62	19.2	2.59	1190.4	160.4	143.29	82.46	1.62% NO_2	2440	49.6%	48.0	4.3	529.8	1539.5	1.15
Q	1	7/13	13:45	70.0		.336		23.5	0					0				2.5
	2	7/14	9:00	67.3		1.73		116.4	58.49		GN/HR=38.2	736		19.25				1.4
	3		16:00	66.3		2.81		186.0	79.58			1004		26.25				1.1
	4	7/15	9:45	63.7		3.85		245.2	134.28		Avg.MV=50.3	1682		44.0				1.0
	5		14:45	63*	21.0	4.37	1323	275.4	149.35	78.89	1.29% NO_2	1874	71%	49.0	4.8	578.8	1688.8	0.9
R	1	7/18	9:45	70.0					0					0				4.7
	2		16:10	69.1					19.38		GN/HR=46.8	301		6.42				1.4
	3	7/19	9:00	70.6*					71.43			1089		23.25				1.2
	4		16:00	69.6*					92.55		Avg.MV=58.1	1416		30.25				1.1
	5	7/20	9:45	67	15.88	5.22	1064	349.7	147.89	80.91	1.54% NO_2	2248	47%	48.0	3.0	626.8	1836.7	1.0
S	1	7/20	11:15	70.0					0					0				2.0
	2		14:10	69.5					14.93		GN/HR=43	125.5		2.92				1.3
	3	7/21	9:30	66.3					69.47			956		22.25				1.1
	4		16:00	65.2					88.73		Avg.MV=56.4	1246		29.0				1.0
	5	7/22	11:00	62	18.1	7.17	1122.2	444.9	148.80	77.02	1.49 % NO_2	2063	54%	48.0	2.5	674.8	1985.5	0.9
T	1	7/22	12:00	70.0					0					0				1.8
	2	7/23	9:00	66.9*					65.17		GN/HR 39.4	827		21.0				1.1
	3		16:00	65.9*					86.10		Avg.MV=46.9	1103		28.0				0.95
	4	7/24	12:00	77	17.0	7.83	1309	602.8	147.98	75.75	1.39% NO_2	1890	69%	48.0	2.2	722.8	2133.5	1.00
U	1	7/25	10:15	70.0	2.7	.757	189	53.0	0					0	3.6			2.45
	2		16:00	69.2	5.4	1.7	373.7	117.6	17.06			218	85%	5.75	3.2			1.4
	3	7/26	9:00	66.6	11.4	4.4	759.2	293.0	67.20		GN/HR=38	865	66%	22.75	2.6			1.2
	4		16:45	65.5	12.0	5.8	786	380.0	88.96			1160	52%	30.5	2.1			1.1
	5	7/27	9:00	63.1	18.2	7.8	1148.4	492.2	136.60			1777	54%	46.75	2.3	769.5	2270.1	1.0
	6		16:00	62.1	19.8	9.4	1229.6	583.7	156.85		Avg.MV=45	2044	51%	53.75	2.1			0.9
	7	7/28	9:00	59.6	25.6	11.5	1525.8	685.4	208.62			2690	50%	70.75	2.1			0.8
	8		16:00	58.5	25.5	12.7	1491.8	743.0	229.03			2956	44%	77.75	2.0			0.7
	9	7/29	9:00	56	31.2	13.7	1747.2	767.2	284.6	76.58	1.32% NO_2	3602	43%	94.75	2.3	817.5	2418.1	0.65
V	1	7/29	14:10	70.0					0					0				1.95
	2		16:00	69.8					5.56		GN/HR=51.7	95		1.83				1.60
	3		21:00	69.2								353		6.83				1.30
	4	7/30	16:30	66.9					84.59		Avg.MV=57.3	1358		26.3				1.0
	5	7/31	7:30	65.1								2133		41.3				1.0
	6		16:45	64	19.1	9.79	1222.4	626.3	161.71	80	1.72% NO_2	2613	47%	50.58	1.95	868.1	2579.8	0.9

Column A = Batch
Column B = Sample
*Final Pit volume lost, average value used

Table 3

AIR FLOW - An average of the sample readings taken from the electronic mass flow meter in liters of air per minute.

AVERAGE BATCH NO_2% - An average of the sample readings taken from a ultraviolet optical density monitor after the application of a calibration formula. Grams N/Hr. was calculated from the percentage of NO_2 in the gas at the outlet of the oxidation column assuming standard temperature and pressure via the formula:

$$\text{Grams N/Hr.} = (((\%NO_2/100) * 14)/22.4) * \text{Air Flow} * 60$$

AVERAGE N PRODUCTION - A multiplication of the average G.N/Hr. and the elapsed hours.

COLUMN EFFICIENCY - from the following formulae:

$$\text{Column Efficiency} = \frac{\text{Final Total Pit N}}{\text{Final average N production}} * 100$$

ELAPSED HOURS - Cumulative hours elapsed since the beginning of the test (batch).

N/P RATIO - Division of the total grams pit N by the total grams pit P (both expressed by weight in their elemental form).

CUMULATIVE KWHR - Cumulative energy expended since the start of the series.

pH of FERTILIZER SOLUTION - pH of the undiluted sample with an electronic pH meter.

IV. INTERPRETATION OF RESULTS

The reactive component of the gas stream produced by the nitrogen generator is NO_2, nitrogen dioxide. Upon entering the absorption column, NO_2 gas reacts with the water on the wet surfaces of the packing substrate, in this case the rock phosphate, to form nitric acid. The nitric acid, in turn, reacts with various components of the phosphate rock. The reaction with one of these components, the apatite complex, serves to solubilize phosphorus, the other possible reactions tend to reduce the availability of the nitric acid to solubilize phosphorus. The major component of the Mussoorie phosphate rock which competes with the apatite complex for the nitric acid is calcium carbonate.

Figure 9 depicts the changes in the constitution of the liquid samples taken at the end of 48 hours for small rock samples D through V. This graph shows the competition of calcium carbonate for the nitric acid. Clearly the amount of nitrogen needed to evolve a given quantity of phosphorus in the first batch, (batch D) represented by the point in the upper left-hand corner of the graph, is much higher than in subsequent batches. Additionally, the right-hand portion of the curve, especially at 600 hours and above, indicates a leveling-off of the N/P ratio or, in other terms, that chemical equilibrium has been attained. This leveling-off is important in the sense that the N-P content of the solution up to this point is not indicative of production rates of the equilibrated column. The N/P ratio of 2:1 attained after 600 hours of operation of the system is representative of the production rates expected from this column under extended operating conditions. For the conditions as described previously, and with small periodic additions of rock of similar size and composition, minor deviations are expected from this ratio.

Figure 10 is a plot of the cumulative soluble phosphorus as a function of the cumulative kilowatt-hours expended during the small rock series. As in Figure 9, the equilibration period is apparent from the shape of the curve. The interval bounded by samples D through K yields a slope equal to .14 grams P/KWHR, while the interval S through V, which represents the column after it has attained equilibrium, yields a phosphorus evolution rate of 3.24 grams

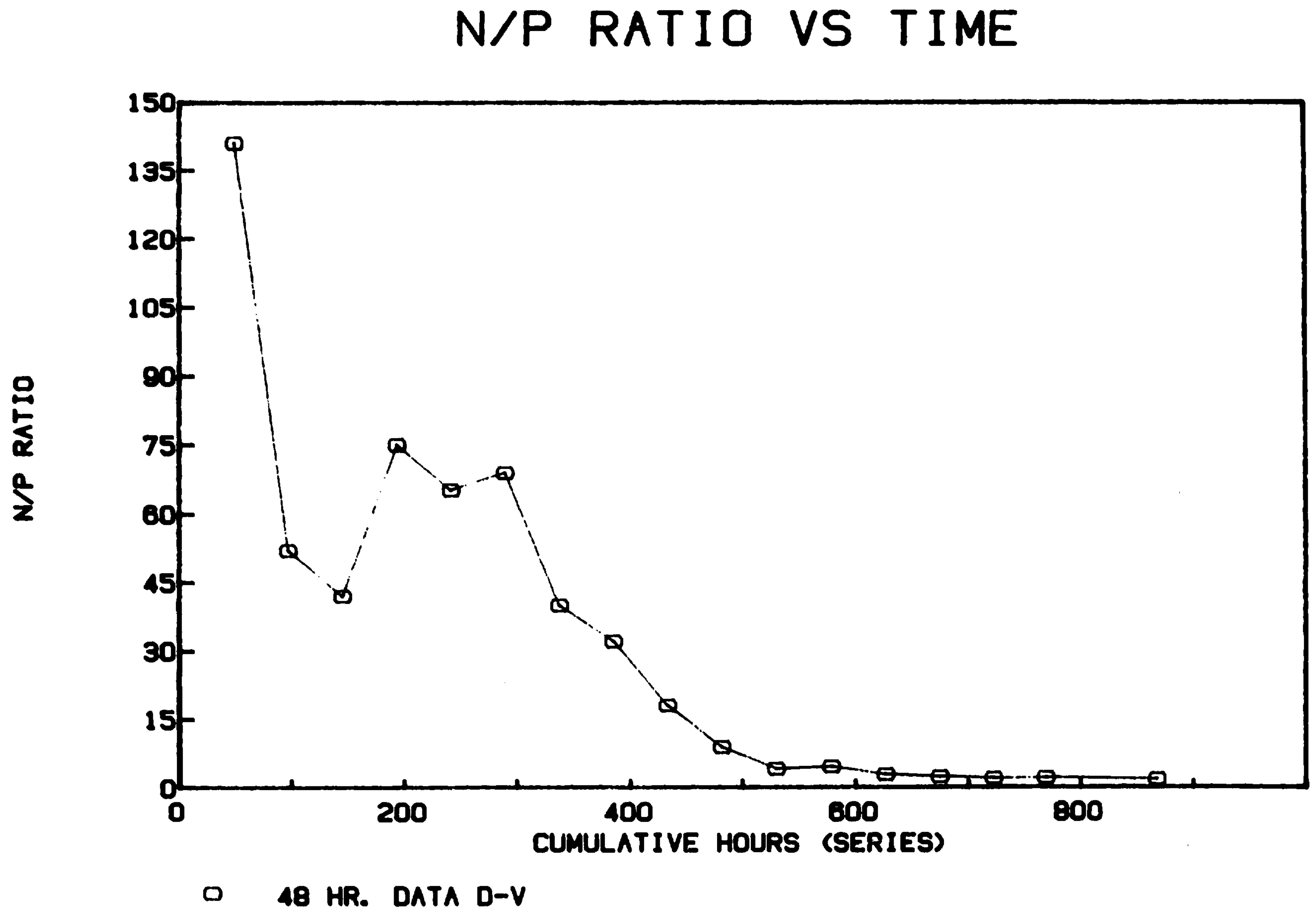
N/P RATIO VS TIME
N/P RATIO
150
135
120
105
90
75
60
45
30
15
0
0
200
400
600
800
CUMULATIVE HOURS (SERIES)
48 HR. DATA D-V

Figure 9

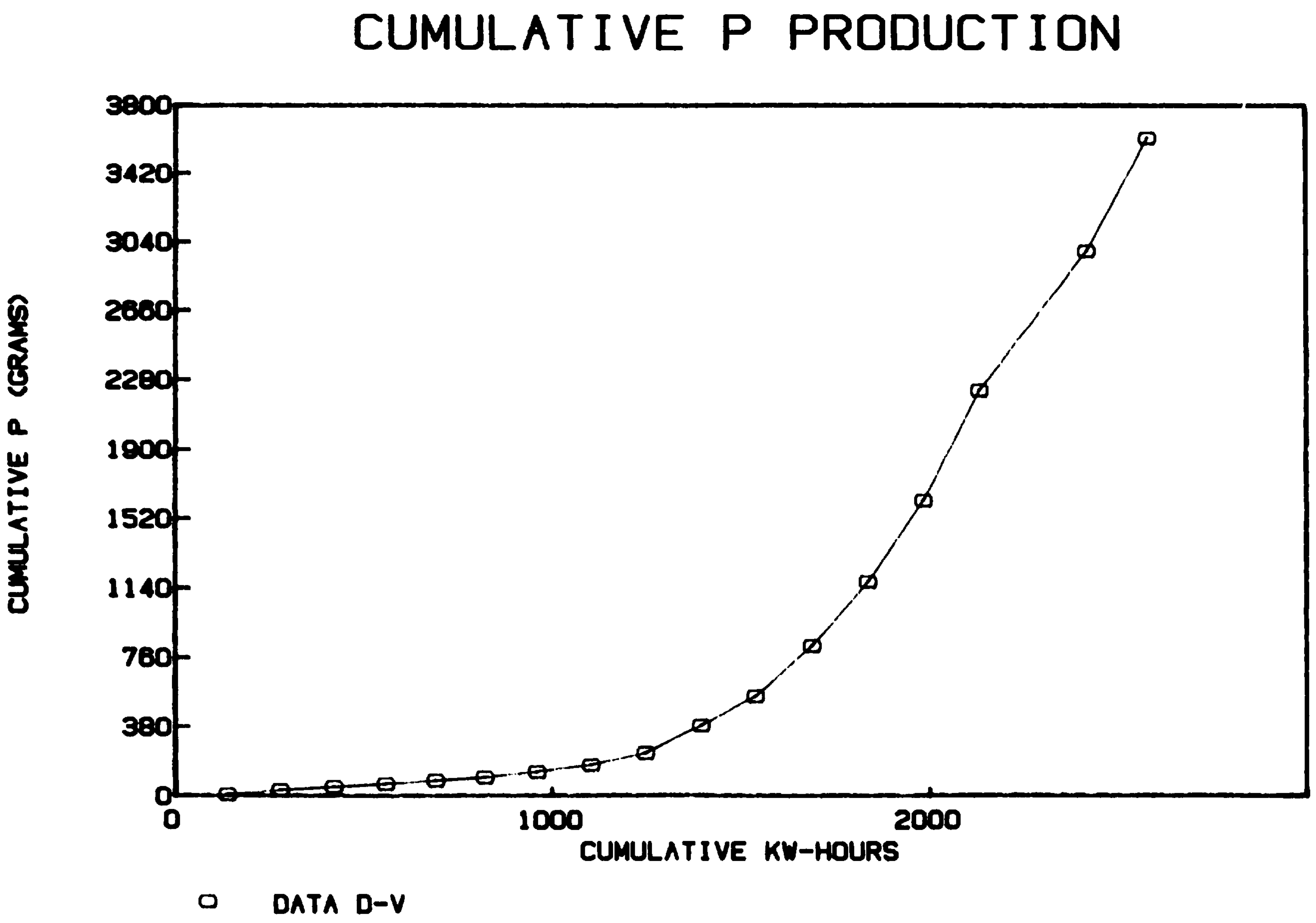

CUMULATIVE P PRODUCTION
CUMULATIVE P (GRAMS)
3800
3420
3040
2660
2280
1900
1520
1140
760
380
0
0
1000
2000
CUMULATIVE KW-HOURS
DATA D-V

Figure 10

P/KWHR. This latter rate should represent the rate of phosphorus evolution in the operational mode, at least within the range of nitrogen concentrations encountered during a typical 48 hour test (i.e., 0 to 20 grams N/L). However, since the nitrogen dioxide molecule must be trapped by the absorption system before it can react to solubilize phosphorus, the rate of phosphorus evolution is inextricably tied to the nitrogen absorption efficiency of the column. As mentioned previously, the column's absorption efficiency is inversely proportional to the nitrogen concentration of the recycle liquid.

Figure 11 depicts the column's nitrogen absorption efficiency versus nitrogen concentration of the recycled liquid during a single 96 hour batch (U) performed after the column reached equilibrium. The general conclusion to be made from this graph is that more favorable production rates may be obtained by maintaining low nitrogen concentrations. Though some variability exists in the data, the graph suggests that a nitrogen absorption efficiency between 60% and 70% may be obtained by limiting nitrogen concentrations below 10 grams N per liter.

Figure 12 shows the change in average column efficiency over time during the small rock series. It appears that, in addition to nitrogen concentration, the column efficiency might also be affected by the relative carbonate content of the rock. Although the downward trend is apparent, it is unclear from this graph as to whether or not this trend would continue with extended operation.

Figure 13 depicts the final pH (48 hour) of each batch of the small rock series versus time (or their chronological order). It is interesting to note that the six samples, Q through V, all have pH values less than, or equal to 1.0 and represent, when totaled, 85% of the phosphorus production for the entire series. This calculation suggests that maximum P production occurs at

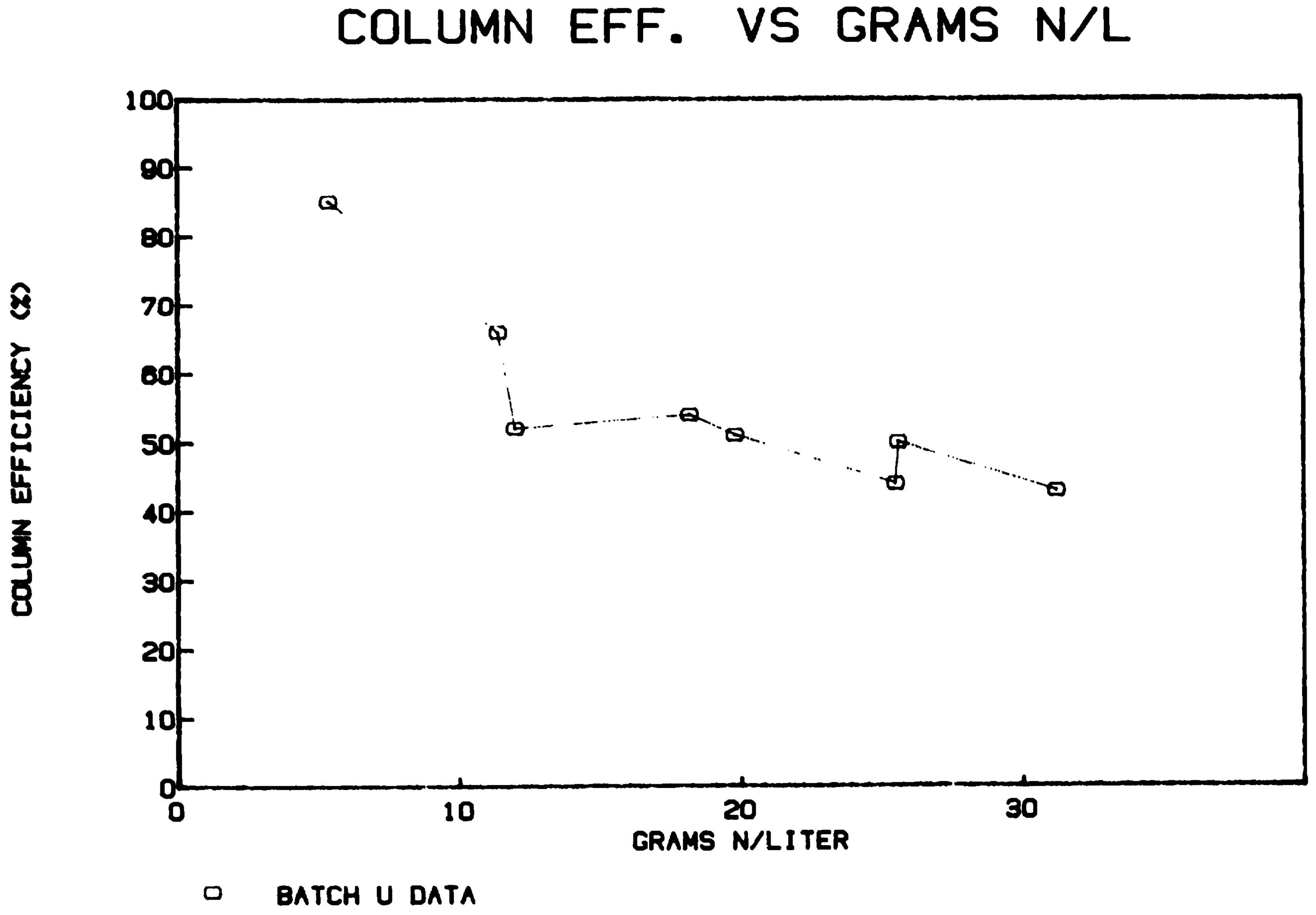
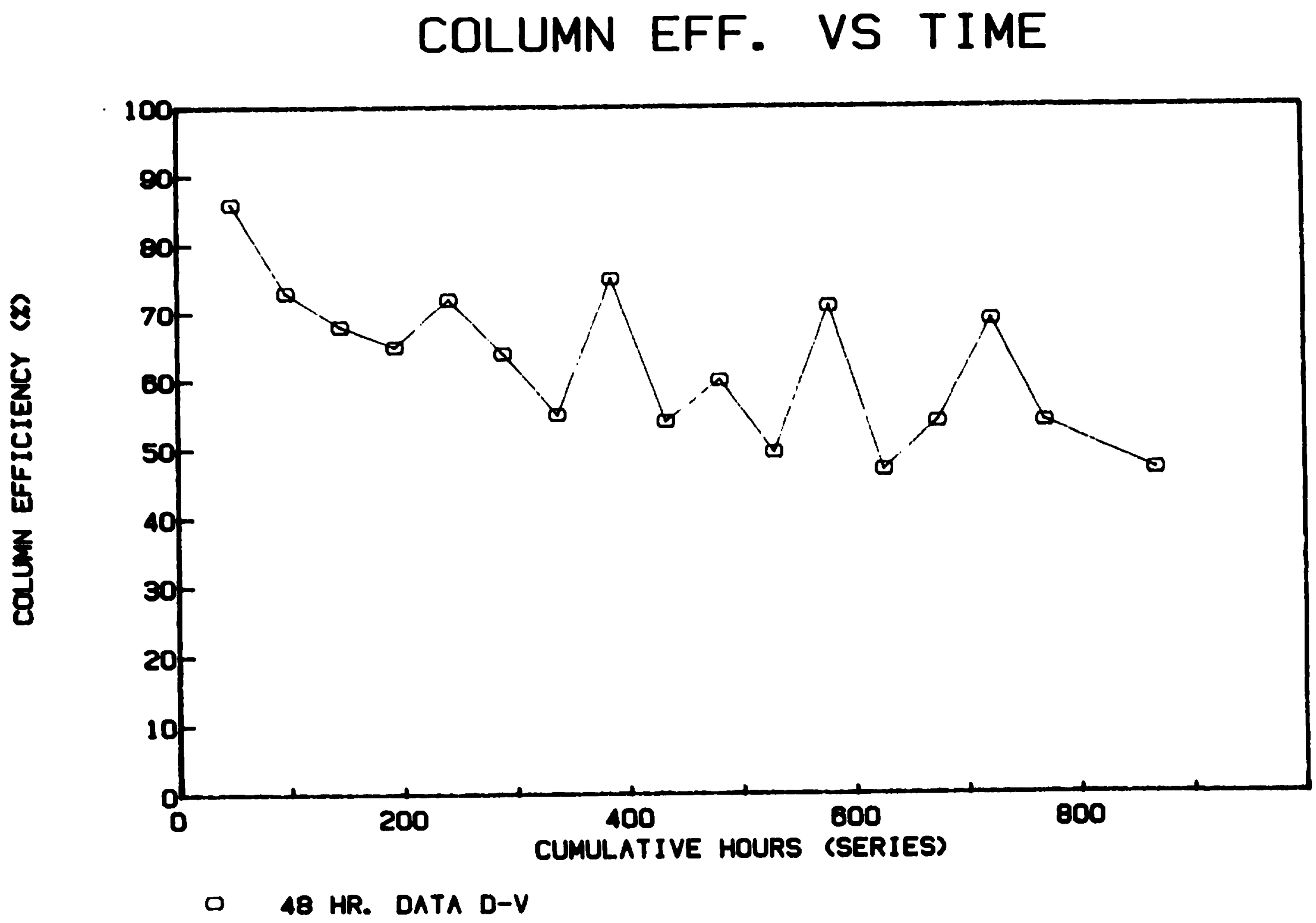

COLUMN EFF. VS GRAMS N/L
COLUMN EFFICIENCY (%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
GRAMS N/LITER
BATCH U DATA

Figure 11



COLUMN EFF. VS TIME

Figure 12

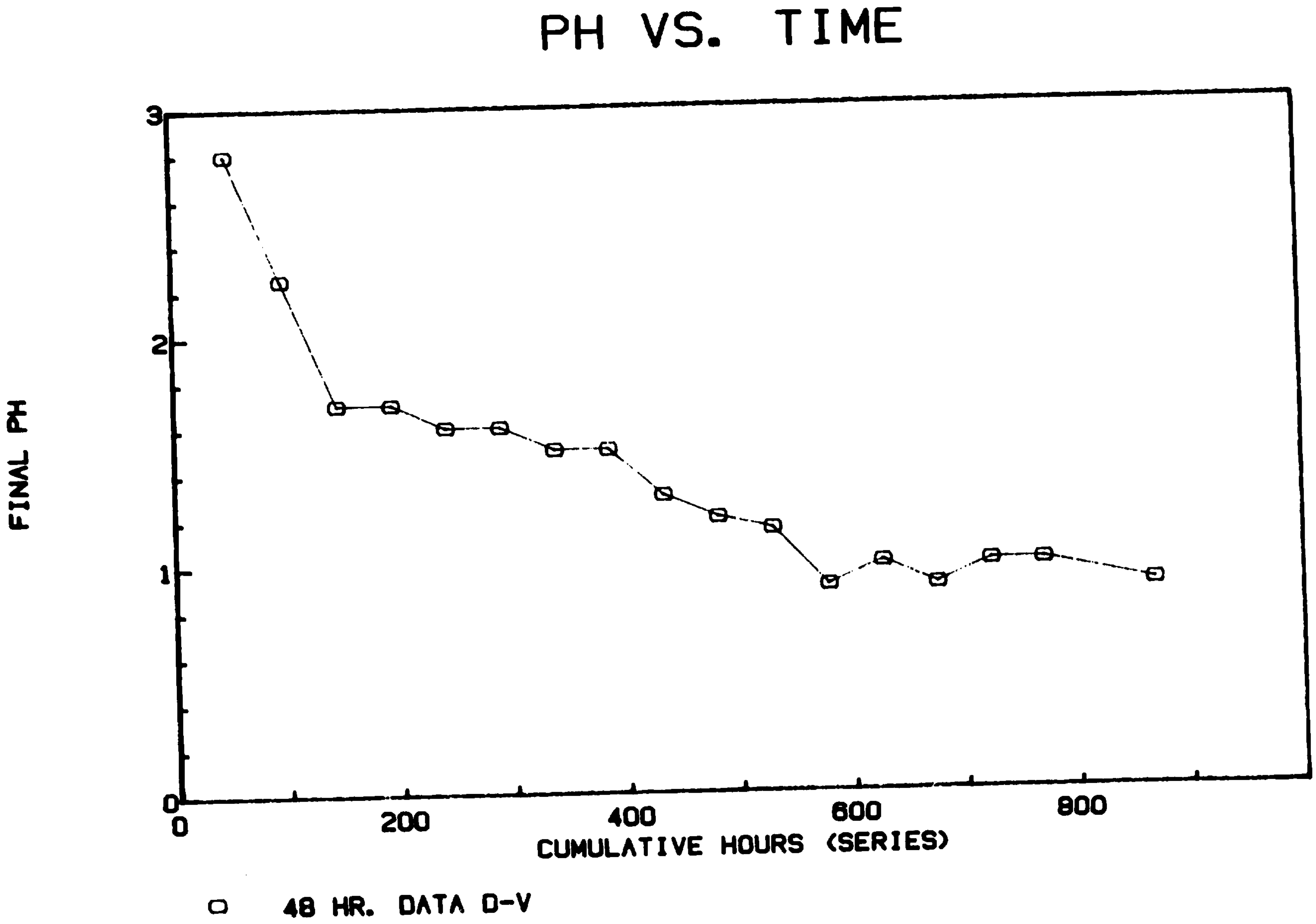

PH VS. TIME
FINAL PH
3
2
1
0
0
200
400
600
800
CUMULATIVE HOURS (SERIES)
○ 48 HR. DATA D-V

Figure 13

a pH of less than 1.0 which was confirmed in another experiment conducted after the column had reached equilibrium and the recirculation experiments of the small rock series had been concluded. The "fresh water" test had the absorption column packed with the same rock used in the small rock series, undisturbed from the previous recirculation experiments. The absorption column was flushed with fresh water for 24 hours at a rate of four liters per minute in order to remove any residual nitrogen and/or soluble phosphorus. The next step was to operate the system without recirculation for a period while fresh water was being introduced at the top of the absorption column at a rate of four liters per minute. After a steady state was attained, a sample of the liquid from the bottom of the absorption column was taken for analysis. This liquid, which had made one pass through the absorption column, had a pH of 3.0, a nitrogen content of .15 G.N/L and a phosphorus content of .005 G.P/L. These values yield a N/P ratio of approximately 30, much higher than the equilibrated column produced during recirculation (multi-pass) tests. Production rates for the two parameters were calculated to be 11.8 G.N/KWHR and .4 G.P/KWHR for nitrogen and phosphorus respectively. The rate of .4 G.P/KWHR can be compared to the rate of 3.24 G.P/KWHR mentioned previously for the equilibrated column with recirculation.

At least two conclusions may be drawn from the fresh-water, or single-pass, test. First, it may be concluded that the lowering of pH obtained by passing fresh water through the column at the rate described is insufficient to solubilize phosphorus to any significant degree. This means that the system must be operated in a recirculation mode if significant quantities of phosphorus are to be solubilized. Secondly, it is concluded that the process liquid cannot be buffered (e.g., by the addition of limestone to the column packing or to the reservoir) to yield a higher pH product without reducing the phosphorus yield.

In summary, the data have shown that:

1. Under the conditions previously described, Mussoorie rock phosphate can be used as the substrate in a nitrogen generating system to produce, after a suitable equilibration period, soluble phosphorus at the rate of approximately 3.24 grams P/KWHR.

2. Under the same conditions, nitrogen (N) is collected at a rate approximately twice that of phosphorus (by weight), i.e. approximately 7.5 grams N/KWHR (as determined by computing the average of the last six samples in the small rock series).

3. A pH of 1.0, or less, in the process liquid is optimum for the solubilization of phosphorus to occur.

4. Nitrogen absorption efficiency may be enhanced by maintaining lower (<10 G.N/L.) nitrogen concentrations in the process liquid.

5. With all other factors being equal, rock phosphate of approximately 2 cm dimension is preferable to 5 cm rock since the smaller size rock presents greater absorption area in the collection column. Very small rock, such as powdered rock, however, is not suitable since very finely ground rock can block the absorption column.

6. In order to maintain high NO_x absorption efficiency, phosphate rock normally is replenished at the top of the collection column as it is consumed. However, our laboratory studies have demonstrated that virtually all of the phosphate can be extracted by nitric acid from Mussoorie phosphate rock. One rock sample studied yielded a fertilizer product with an N/P ratio of 2.94:1. See Appendix C.

Additional discussion of system performance is included in the "Recommendations" section of this report.

V. PRODUCT CHARACTERISTICS

The characteristics of the fertilizer produced by this process are dependent upon factors such as the type of phosphate rock used and the extent of recirculation or concentration of the fertilizer product. Product concentrations as high as 37.2 grams N per liter for nitrogen and 13.7 grams P per liter for phosphorus were recorded during this study. For purposes of defining a "typical" product, we can predict that a solution containing 20 grams N per liter should contain approximately 10 grams phosphorus (23 grams P_2O_5) and 3.2 grams iron per liter. Furthermore, it should possess a pH between .7 and 1.0 and a specific gravity of 1.093 at 60° Fahrenheit.

In addition to containing nitrogen, N, and phosphorus, P, the liquid fertilizer product from the Kettering Process also contains other nutrients obtained from Mussoorie phosphate rock that are essential for plant growth. For example, a small amount of potassium, K, (approx. 100 ppm) and many trace elements necessary for plant growth such as iron calcium and magnesium are present in the liquid fertilizer product.

A severe test of the efficacy of any liquid fertilizer product is to grow plants hydroponically using the liquid fertilizer product as the only source of nutrients for the plant growth. Hydroponic tests were performed using properly diluted liquid fertilizer product from the Kettering Process. Satisfactory growth of plants (lettuce) hydroponically was observed but additional potassium apparently is needed to provide outstanding growth. Field trials, described in the Agronomic Report (Appendix D) confirmed the efficacy of the fertilizer produced in the Kettering Process.

VI. RECOMMENDATIONS

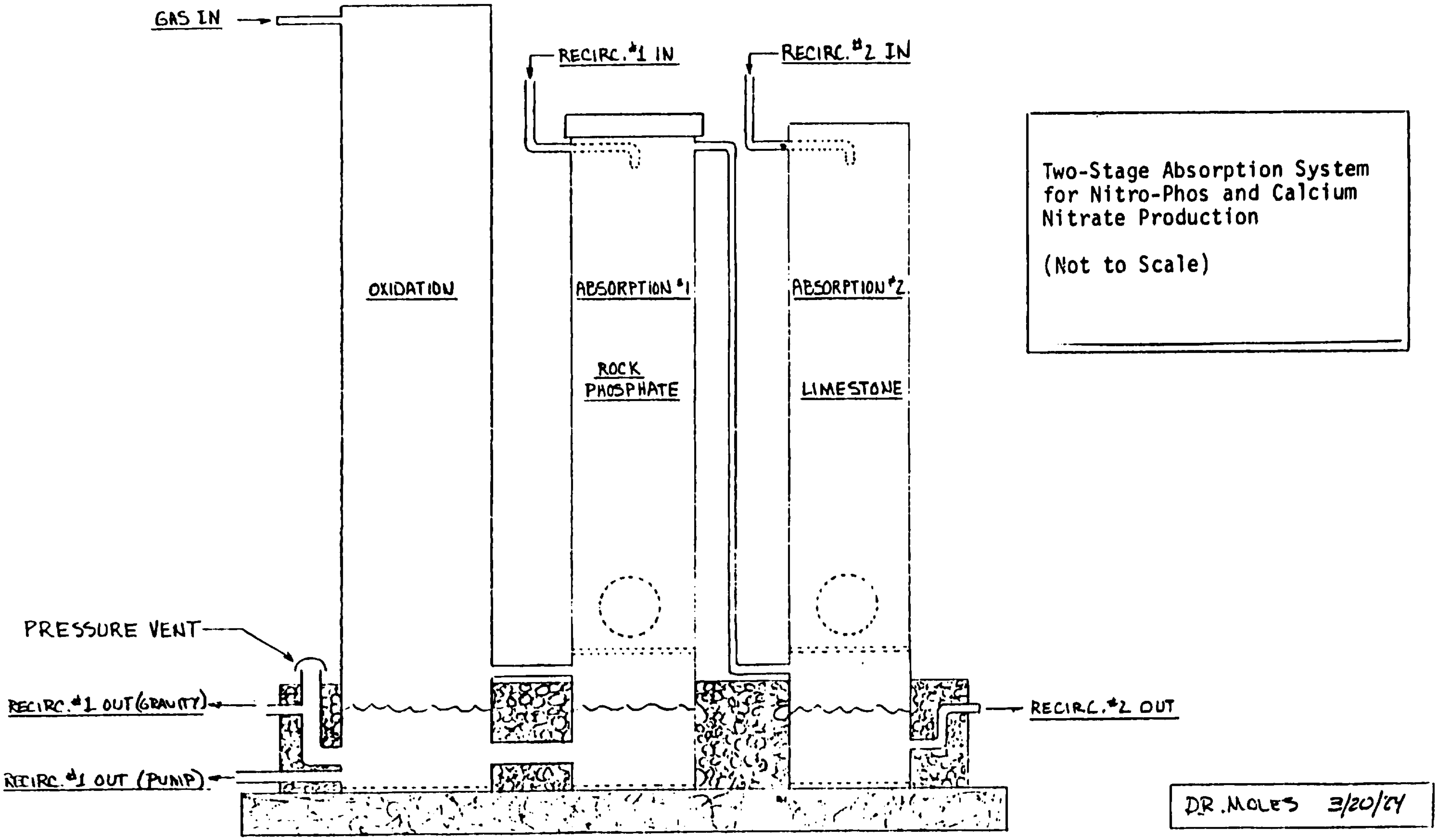
Alternate Process Strategies

The prototype system installed at Sirki was designed and developed to demonstrate the basic principles, capabilities and limitations of the Kettering Fertilizer Production System as applied to the production of N-P fertilizer from Mussoorie phosphate rock. All objectives of the project, as specified under terms of the contract, were fulfilled within the time frame allotted. Certain recommendations and improvements for subsequent installations are made below based on knowledge gained from experience with this first prototype/installation.

Two Stage Absorption -

Results of preliminary tests performed at BCFKRL, subsequent to the installation of the field system in India, indicate that, with a modification to the absorption system, several process parameters of the nitro-phos generating system may be improved. The modification, as shown in figure 14, involves the addition of a second absorption column and recirculation system downstream from the first, or primary, absorption stage. The second absorption would be packed with limestone, rather than rock phosphate. The purpose of this second column would be to "scrub" the output gases of the first (phosphate rock) column, thereby capturing a greater percentage of the total nitrogen produced by the system. The benefits to be obtained from this "two-stage" absorption strategy go beyond simply enhancing total system performance.

By virtue of its higher operating pH (approx. 4.0), the second absorption stage has a much greater potential for removing (absorbing) NO_2 than does the first stage. By operating the two stages in tandem, the first stage is relieved of the task of having to remove a high percentage of the process NO_2.



Two-Stage Absorption System for Nitro-Phos and Calcium Nitrate Production

(Not to Scale)

DR. MOLES 3/20/74

Figure 14

This strategy allows much greater latitude in the concentration of the nitro-phos product in the first stage. If this technique is employed, much higher concentrations of nitrogen and phosphorus may be produced than the concentrations which were recommended in order to maintain high column efficiency. Additionally, by separating the two recirculation systems, an indirect form of N/P ratio control is obtained. Although the N/P ratio of the first stage process liquid is fixed, the applied nitrogen can be increased from the second stage calcium nitrate reservoir. Our preliminary tests indicate that the two-stage system can absorb more than 90% of the total nitrogen oxides produced in the electric arc process, thereby improving the process economics.

Although not essential to demonstrating the principles of the Kettering Process, it is recommended that a second stage absorption column be added to the Sirki prototype installation, if improved efficiency for this test installation is desired.

Dry Fertilizer Process -

A liquid fertilizer has certain advantages such as providing immediate availability of nutrients to stimulate plant growth. However, dry fertilizer products are more commonly used and therefore often preferred. The Kettering Fertilizer Production Process can be modified to produce a dry fertilizer product, if desired. One modification to yield a dry fertilizer involves combining the liquid N-P fertilizer product with finely ground Mussoorie phosphate rock to obtain a slurry mixture. This slurry then can be dried by solar evaporation of by using heat from the nitrogen generator itself to obtain a dry product. The calcium nitrate component of the liquid fertilizer used is very hydroscopic in its dry form, hence caking of the slurry can occur if excess liquid fertilizer is used. However, light grinding will restore the caked powder to its original form. Sealing of this product in a moisture proof bag creates a good dry fertilizer with improved characteristics. The advantages of this alternate process when fully developed could be:

1. a dry fertilizer is produced,
2. the Mussoorie phosphate rock powder is partially acidulated,
3. the physical properties of the Mussoorie Phos powder are improved to reduce dust in handling and
4. nitrogen is added to the final product.

As a specific example, we have found that a typical liquid fertilizer product (∿10 gm N and 5 gm P per liter) from the Kettering Process when mixed with about an equal portion of powdered Mussoorie phosphate rock yields a promising fertilizer product after being air dried. The resulting partially acidulated, dry fertilizer product not only has a higher level of available N and P than untreated Mussoorie phosphate rock but also has less dust and a "richer" black appearance that could further enhance its marketability.

System Integration

Waste Heat Utilization -

A large percentage (98%) of the energy input to the Kettering Process appears as heat. If a suitable heat exchanger is utilized, a large part of this heat can be captured as "high-grade" heat which could dramatically improve the overall economics of the Kettering Process. In small-scale applications, such as the 3 kilowatt prototype presently being tested near Dehra Dun, India, reclamation of the waste heat in this form may not be profitable. However, in larger-scale systems (say above 10 KW) the larger quantities of heat could be used in such diverse applications as producing steam for various manufacturing processes, sterilization of food in canning operations, concentrating cane syrup, or even electrical power generation. If desired, the heat also could be used to drive a refrigeration system using the absorption refrigeration technique. Studies currently are being conducted at Cornell University, Ithaca, New York to develop the refrigeration concept.

It is recommended that, when planning scale-up of the Kettering Process, careful consideration be given to take maximum advantage of this heat by-product.

Electrical Interfacing -

Although the Kettering Process may be powered by conventional utility power, preferably it is powered by a renewable energy source such as hydro-electric power, wind-electric power or solar photovoltaic power.

At present day (1984) costs, hydro-electric power generally is the least costly source of power - particularly in areas where only relatively simple civil works structures are required to provide the source of water power. Cost of less than $1,000 (U.S.) per kilowatt of installed hydro-electric power are attainable in many areas. Further reduction in the effective cost of hydro-electric power can be obtained if only "off-peak" hydro-electric power is used to power the Kettering Fertilizer Production Process.

In relatively high (say >20 kilometers per hour) average wind speed areas, wind-electric power may be feasible. For the production of fertilizer, stand-by power with its associated costs of batteries etc. is not required so that wind-electric systems costing less than $2,000 per installed kilowatt can be obtained (16).

Solar photovoltaic systems, at the present time, are a very costly form of energy with costs ranging between $5,000 and $10,000 per installed peak kilowatt. However, solar photovoltaic costs are falling rapidly and solar electric systems costing less than $1,000 per peak kilowatt are predicted within ten years (17).

Though the capital costs of implementing the process can be quite low, the overall costs of producing the fertilizer product are to a large degree dependent upon the cost of the electrical power to run the process. As mentioned above, one option which deserves consideration involves operation of the Kettering Fertilizer Production System to absorb "off-peak" electricity produced in small hydroelectric installations. This may be especially appropriate in India where the load factor for such installations is often quite low. The Kettering Process is ideally suited for "off-peak" power use since it can be turned on and off frequently without suffering process degradation and the process also can be operated at various power levels.

Presently, a plan is being created by Pyrites, Phosphates and Chemicals Ltd. in cooperation with the Alternate Hydro Energy Center, Roorkee University. This plan incorporates the Kettering Process, along with several other processes, in a highly integrated resource utilization scheme.

VII. SCALING CONSIDERATIONS

Technical Considerations -

The basic design of the Kettering System is adaptable to being scaled up or down in production capacity. In fact, the reactor used in the present prototype N-P production system is a scaled-down version of a 1000 KW Schönherr furnace (5) operated in Norway at the turn of this century. Individual consideration of the operating ranges of the system components are outlined below.

1. Power supply: The 3 KW power supply used in the installation in India, and also in the testing of the prototype at BCFKRL, is of a fixed ballast design. This means that the transformer used has been designed to operate at a fixed power level with the ballast controlling the current in the secondary of the transformer. Virtually any output level can be obtained by re-design of the transformer.

2. Reactor: A reactor similar to the one used in the prototype system has been operated satisfactorily at power levels ranging from 1.0 to 8.0 KW; thus indicating the reactor possesses a considerable range within which it can operate without major modification.

3. Absorption System: This part of the fertilizer production system would be more sensitive to changes in scale. In configurations requiring greater volumes of gas to be processed, the absorption system, as it exists presently, would require extensive alteration. However, for configurations where the NO_2 percentage alone would be affected, the present design would be adequate over a range up to approximately 10 KW, especially if the two-stage design is employed.

Economic Considerations -

The economics of scaling the process, either up or down, would be more heavily influenced by capital and operating expenses than by changes in process efficiency. Basic process efficiency with the reactor prototype installed at Sirki should remain constant, or nearly so, over a wide range of production capacities.

Small-scale systems, such as the installation at Sirki, may be economically viable only in areas where one or more of the following factors prevail: 1/the delivered cost of fertilizer to that area is high and/or 2/

low cost electric power such as "off peak" hydroelectric power is available and/or 3/ productive use can be made of the heat generated by the process and/or 4/ farmers in the area desire to be independent of outside sources of fertilizer. Any combination of the above factors could favor small-scale systems such as at Sirki.

If scaling-up is considered, captial costs will increase in absolute terms primarily due to the larger power supply required. However, in relative terms the capital costs per unit of production capacity would be much less in large-scale systems than in the present prototype system at Sirki.

It is expected that operating expenses, other than power costs, also will be reduced substantially per unit of production capacity in large-scale systems. Electricity costs and the pay-back associated with waste-heat recovery will play a major role in determining the final cost of the fertilizer product.

VIII. FUTURE DIRECTIONS

Although not part of the work specified under terms of this contract, preliminary experiments performed during the course of investigations on this contract indicate that it is technically feasible to produce P_2O_5 directly from Mussoorie phosphate rock by electrical (ohmic) heating of the rock. It was discovered that Mussoorie phosphate rock possesses electrical semi-conductor properties that permit heating the rock to fusion temperatures when an electrical current is caused to pass through the rock. A system has been proposed to PPCL in which an N-P fertilizer product can be produced by combining the electric arc process described in this report with a process in which phosphorus is driven from Mussoorie phosphate rock by electrical heating of the rock. The proposed system is believed to offer sufficient application potential that a research effort to develop these findings to a practical design stage is being recommended to PPCL and UNIDO.

IX. SUMMARY

A small-scale system has been developed for the co-generation of soluble nitrogen and phosphorus fertilizer using a renewable energy resource. A prototype N-P fertilizer production system has been installed and is now operating near Dehra Dun, India from power derived from an irrigation canal (see figure 15) in the village of Sirki, India.

Agronomic testing of the fertilizer produced by this system shows that the fertilizer product, when properly applied, provides positive results. The "Final Agronomic Report" is appended to this report.

The development of this prototype N-P fertilizer production system is the result of collaborative efforts between Battelle-C.F. Kettering Research Laboratory, Yellow Springs, Ohio, U.S.A. and Pyrites, Phosphates and Chemicals Ltd., New Delhi, India.

Figure 15

Two views of the Nitrogen-Phosphorus Production System installed at Sirki, India. The absorption system is visible along with the fertilizer storage reservoirs. The electrical components were placed inside the building. The prototype system was powered by a small-scale hydro-electric generator.

Figure 16

Two scientists from Pyrites Phosphates and Chemicals Limited (PPCL) worked with Battelle-C.F. Kettering Research Laboratory (BCFKRL) researchers to construct and test a nitrogen-phosphorus fertilizer production system and to develop testing procedures for the N-P fertilizer product.

Top: Mr. R.K. Puri, Sr. Manager Engineering of P.P.C.L. and Mr. C.K. McKibben, Research Associate of BCFKRL.

Bottom: Mr. P.K. Awasthi, Sr. Marketing Manager of P.P.C.L. and Mr. D. Moles, Research Associate of BCFKRL.

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PART I - FINAL TECHNOLOGY REPORT

SECTION B - PERFORMANCE OF ELECTRIC ARC FERTILIZER PRODUCTION SYSTEM AT SIRKI VILLAGE NEAR DEHRADUN (U.P.), INDIA

PERFORMANCE OF ELECTRIC ARC FERTILIZER PRODUCTION SYSTEM AT SIRKI VILLAGE NEAR DEHRADUN (U.P.), INDIA

INTRODUCTION

The Pyrites, Phosphates and Chemicals Ltd. (A Government of India undertaking) through the sponsorship of the United Nations Industrial Development Organization (UNIDO) has entered into a contract with Battelle-C.F. Kettering Research Laboratory of Yellow Springs, Ohio, USA to demonstrate the production of calcium nitrate-phosphate fertilizer from low grade Mussoorie rock phosphate using Kettering's electric arc fertilizer production system. The University of Roorkee, India, joined the collaboration by providing and installing a Micro-hydel system to provide energy for this process and the Irrigation Department of the State of Uttar Pradesh cooperated by providing cost free supply of water and space required for this work in the remote village of Sirki, near Dehradun, Uttar Pradesh State in India (Fig. 1).

Before installation of electric arc fertilizer production system at Sirki, tests were carried out on the prototype system at Battelle-C.F. Kettering Research Laboratory (hereinafter abbreviated as BCFKRL) in Yellow Springs, Ohio, USA. In the tests conducted at BCFKRL, low grade rock phophate (Mussoorie rock) from Pyrites, Phosphates & Chemicals Limited's (hereinafter abbreviated as PPCL) Maldeota Mines (near Dehradun) India, was used. The results obtained by the studies conducted at BCFKRL were encouraging and subsequently it was decided to install two units in remote villages in India to gain experience on performance evaluation, and product output.

OBJECTIVES

The main objectives of the studies conducted at the Sirki fertilizer unit installation are:

i) To gain first hand on site operational experience in the remote Sirki village near Dehradun, India.

ii) To gain experience in operation of the fertilizer unit by renewable source of energy, in this case a 6 KW Micro-hydel unit.

iii) To evaluate the production of soluble P from low grade rock phosphate from Maldeota Mines near Dehradun, India.

iv) To study production of fertilizer by using other substrate materials like limestone, limestone and rock phosphate mixture, gluconite etc.

v) To evaluate economic viability of the fertilizer produced by this unit as compared to conventional fertilizer.

vi) To optimize the system for nitrogen and soluble phosphate production.

vii) To produce requisite quantity of fertilizer for carrying out greenhouse pot experiments as well as actual experiments for evaluation of agronomic effectiveness of fertilizer produced by the unit.

LOCATION

The site for installation of first fertilizer unit was selected in the village of Sirki in the district Dehradun of Uttar Pradesh State in India. Sirki is about 14 kms. from Dehradun city and is connected to Dehradun by road, which is partially paved. The site is behind the Sirki colony of Maldeota Mines of PPCL and is about 11 kms. from the mines. An irrigation canal locally known as Bandal Canal is in close proximity to the installation site and carries water throughout the year for supplying water for irrigation purpose in the area and therefore this site was ideally suited for installation of the Micro-hydel Unit. For most of the time, in the area, the quantity of water flowing through the canal is more than 10 cusecs. In summer months the flow may reduce to about 6 cusecs if the winter snow fall in the hills has been sparse or in rainy season if the area gets less than the normal rain fall in the region. The canal system is operated and maintained by the Canal Division of the Irrigation Department of Uttar Pradesh State. The department agreed to collaborate and extend all the necessary help in designing the weirs and pen-stock system, tail stock system etc. for the Micro-hydel Unit and ensured a supply of water cost free throughout the life of the experimental and developmental work at the Unit site at Sirki. Also land for construction of physical facilities for installation of fertilizer unit as well as the Micro-hydel set was provided. The Micro-hydel Unit was designed and installed by Alternate Hydro-Energy Centre at the University of Roorkee, India. Sirki Colony of PPCL has utility power available. Therefore, for operation of fertilizer unit, the utility power could be tapped very easily and used in case of operational problems with the Micro-hydel Unit.

PPCL has sufficient technical personnel at the mine site which is in close proximity to the fertilizer unit site, to take care of electrical as well as mechanical problems if these are encountered during the operation of the fertilizer unit as well as the Micro-hydel Unit.

Considering the above points, Sirki was selected for installation of the fertilizer unit for carrying out all the experimental and developmental studies under the terms of the contract with UNIDO.

INSTALLATION OF FERTILIZER PRODUCTION UNIT

Two (2) units were received from BCFKRL, USA in the month of September, 1983. The installation work, including its civil work, was immediately undertaken by the PPCL engineer (Mr. Raj Puri) who spent three months at BCFKRL studying the unit. The basic unit description and assembly are described in detail in the first part of the technology report. The salient features of the installation at Sirki site are given below:

i) Electric high voltage transformer, arc reactor, air and liquid pumps and associated electrical switches were all housed in a small room (1.8M x 3.7M). For proper ventilation two windows were provided. Also openings covered with wire netting have been provided on all four side walls near the roof for rapid dissipation of the heat from the hot water from the reactor drum. The main door of the room was electrically inter-locked to facilitate shutting down the unit when the door was opened. This has been done with a view to eliminate chances of any person coming in contact with high voltage on the transformer secondary. An overall view of the installation is shown in Figure 2. In the rear is the Bandal irrigation canal diversion built for the hydrotubbine and the brick colored shed where the electric arc unit is installed at the ground level and the hydroturbine is installed in the basement (Figs. 2-4).

ii) The oxidation and absorption columns along with the fertilizer pits were constructed in the open. This has been done with a view to facilitate dissipation of NO_2 fumes and to reduce inhalation of NO_2 fumes by personnel working on site. A view of the installation along with the fertilizer storage reservoirs are shown in Figure 3.

iii) In the prototype unit installed at BCFKRL, the fertilizer pit below the oxidation column was of 70 liters capacity, with the result that fertilizer had to be removed after every 48 hours of running of the unit. Keeping this difficulty in mind, at Sirki, one additional pit (secondary pit) has been added having interconnection with the oxidation column pit so that up to 300 liters of fertilizer could be prepared in one run. The plan of the fertilizer pit along with the oxidation and absorption columns is given in Figure 5.

iv) The installation work was completed in the beginning of October, 1983 and the plant was commissioned soon after the arrival of BCFKRL engineers Mr. Donald R. Moles and Mr. Charlton K. McKibben.

v) The plant was actually put on continuous run from 28 October 1983 onwards.

INSTALLATION OF MICRO-HYDEL UNIT ALONG WITH ITS CIVIL WORKS

The Micro-hydel Unit has been designed and developed by Alternate Hydro Energy Centre, University of Roorkee, Roorkee, India. PPCL has purchased the unit and accessories from the University of Roorkee. Layout plan of the civil works is given in Figure 6 and an illustration of turbine in Figure 4. A number of factors were taken into account while designing the system to interface the fertilizer production unit which have been detailed in the following sections.

Hydrological Studies

Water in the Bandal feeder is available throughout the year and used for irrigation. The flow discharge data were readily available from the irrigation department in Dehradun, UP., which ensured the constant flow discharge for almost throughout the year to be 10 cusecs. The head available at the site is 3.5 meters. Therefore the available power is 7.5 KW. Accordingly a 7.5 KVA generator has been installed.

Civil Features

The civil features consist of a suitable diversion structure, power channel, which may involve suitable augmentation capacity of the water channel so as to meet to the installed capacity of the power house.

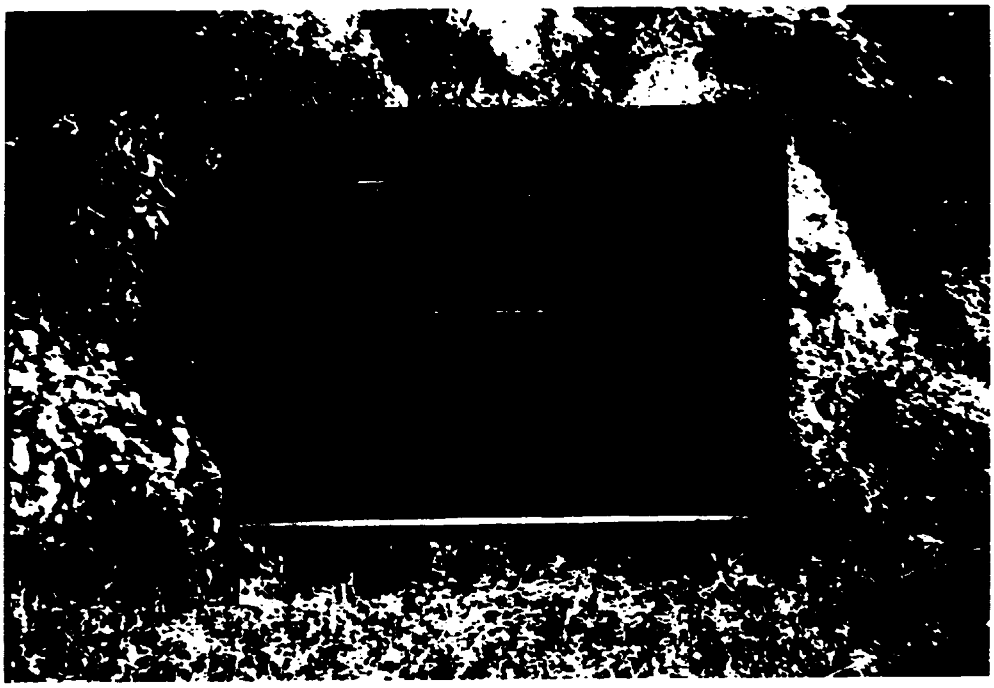
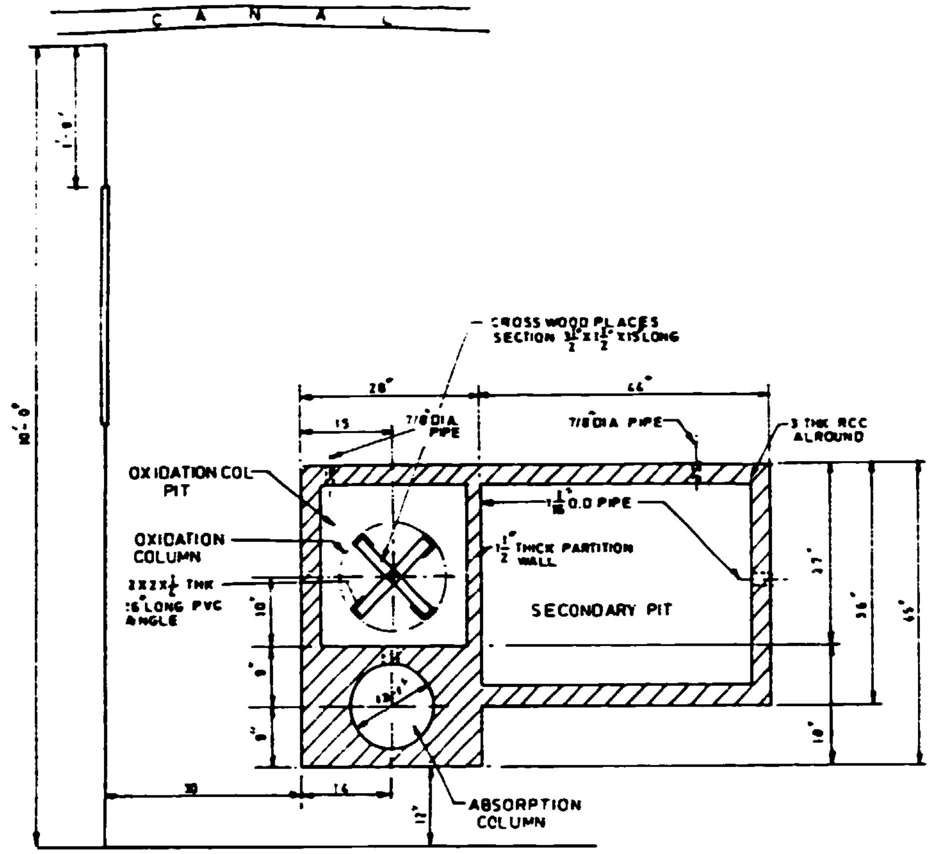


Fig. 1. A sign at the installation site in the Village of Sirki, near Dehradun, India.

Fig. 2. An overall view of the installation site showing in the rear the Bandal irrigation canal diversion built for the hydroturbine and red brick shed where the electric arc unit is installed.

Fig. 3. The absorption column and the storage pit are located outside and the arc generator and associated electrical equipment inside the red brick shed approachable through the door.

Fig. 4. A close-up view of the hydroturbine, located in the basement of the shed.



PLAN

FIG. 5:- OXIDATION & ABSORPTION COLUMN & SECONDARY PITS AT SIRKI VILLAGE.

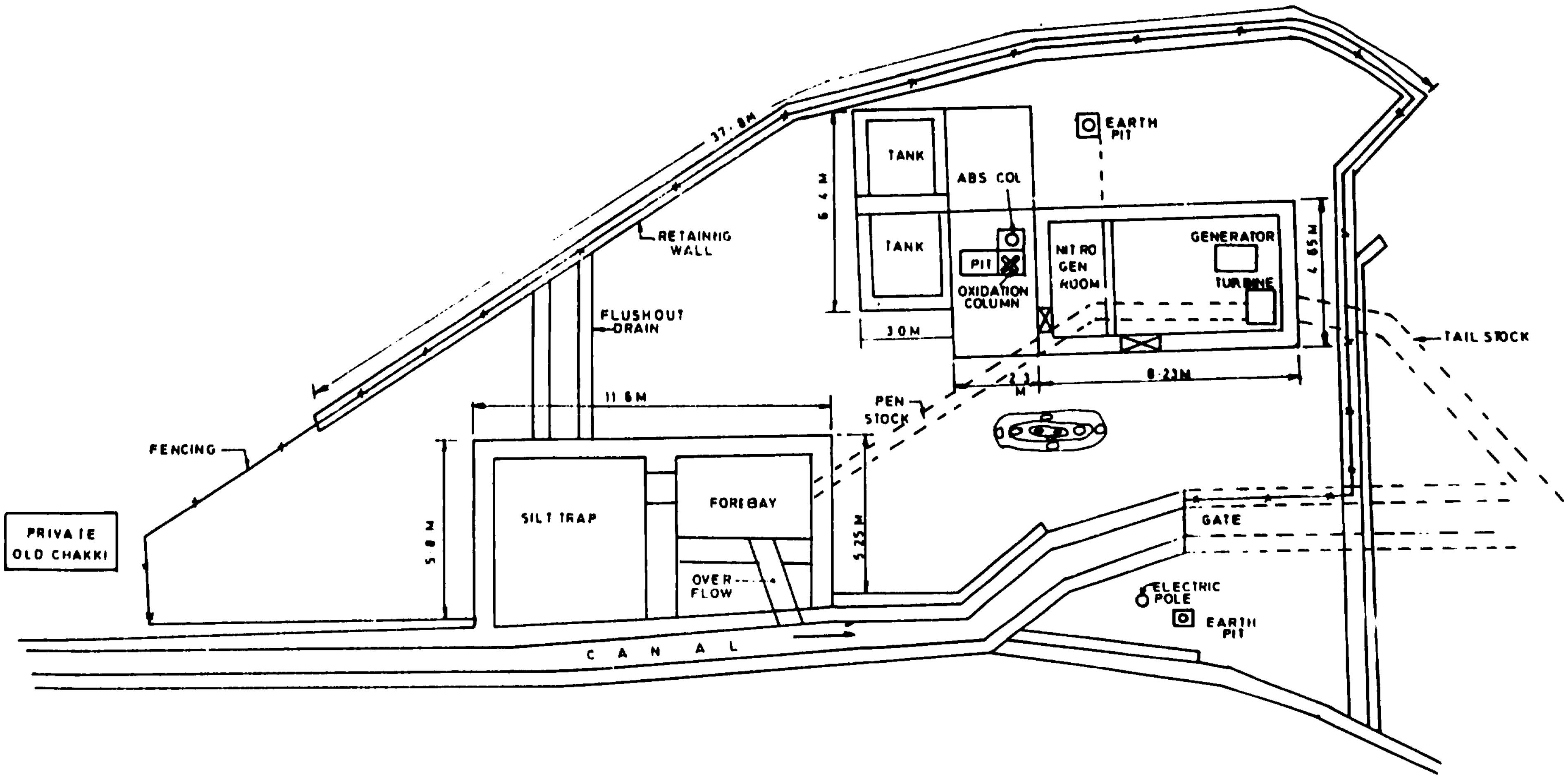


FIG. 6:- NITRO-PHOS/HYDRO-GENERATOR SET OF 6 KWH AT SIRKI VILLAGE

Diversion structure is provided at the point of origin of the power channel from the main irrigation canal. A water channel is designed to handle the required discharge of water to the power house. The existing feeder has been used and as such no extra diversion or the power channel construction was needed, except that the existing feeder was reinforced for safety, being of old construction. Adequate desilting arrangement has been made by constructing the desilting tank and by providing a trash rack arrangement. A suitable forebay has been designed which delivers water to the turbine for about 4 minutes, in order to overcome the problems which may arise in fluctuation of water flow. A penstock of 35 centimeter diameter and 20 meter in length of steel conduit of adequate thickness has been provided (Fig. 6).

Electro-Mechanical Equipment

Instead of using a conventional turbine, a propeller pump of 2 meters head and 11.5 cusec discharge has been used to work as turbine by matching the reverse characteristics of the pump. The turbine was coupled to a 7.5 KVA 3 phase 50 c/s alternator.

Electronic Controller

A conventional hydro mechanical governor has been replaced by an electronic controller which maintains the constant electrical load on the generator by diverting the surplus power to low priority loads. Details of the controller are provided in Figures 7 and 8. The electronic controller described has been developed in the Alternate Hydro Energy Centre, University of Roorkee, Roorkee. The controller has been developed for a micro-hydro power station having a synchronous generator up to the capacity of 10 KVA. It has been successfully run and tested on a synchronous generator made by Kirloskar Electric Co., Ltd, Poona, India, having the following specifications.

Volts	415	Hz	: 50
KVA	7.5	RPM	: 1500
Current	10.4 Amps	Phase	: 3
Extn.	250 V.	2.1 Amps	
Power Factor	0.8		

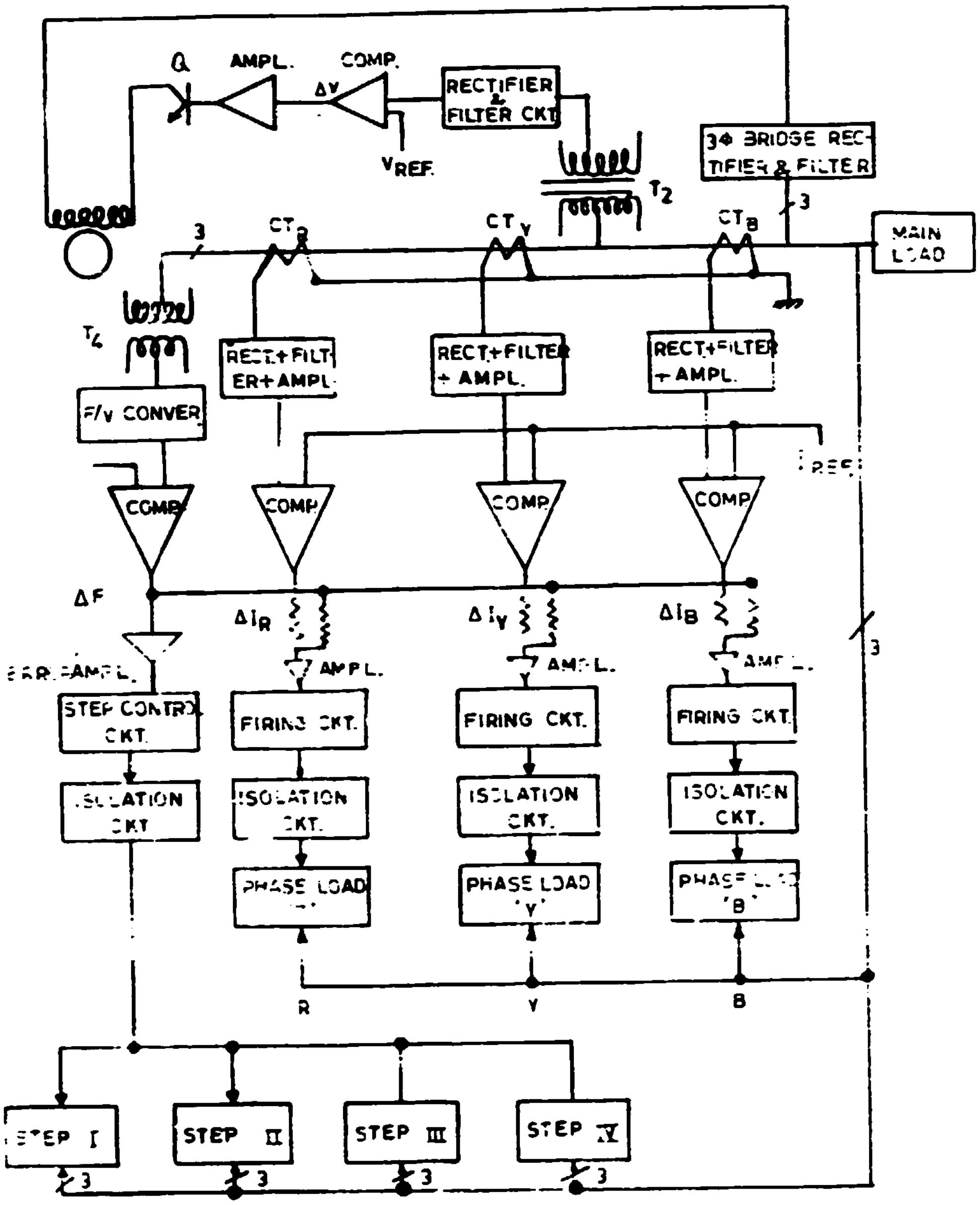


FIG.7 - CONTROL-SCHEME

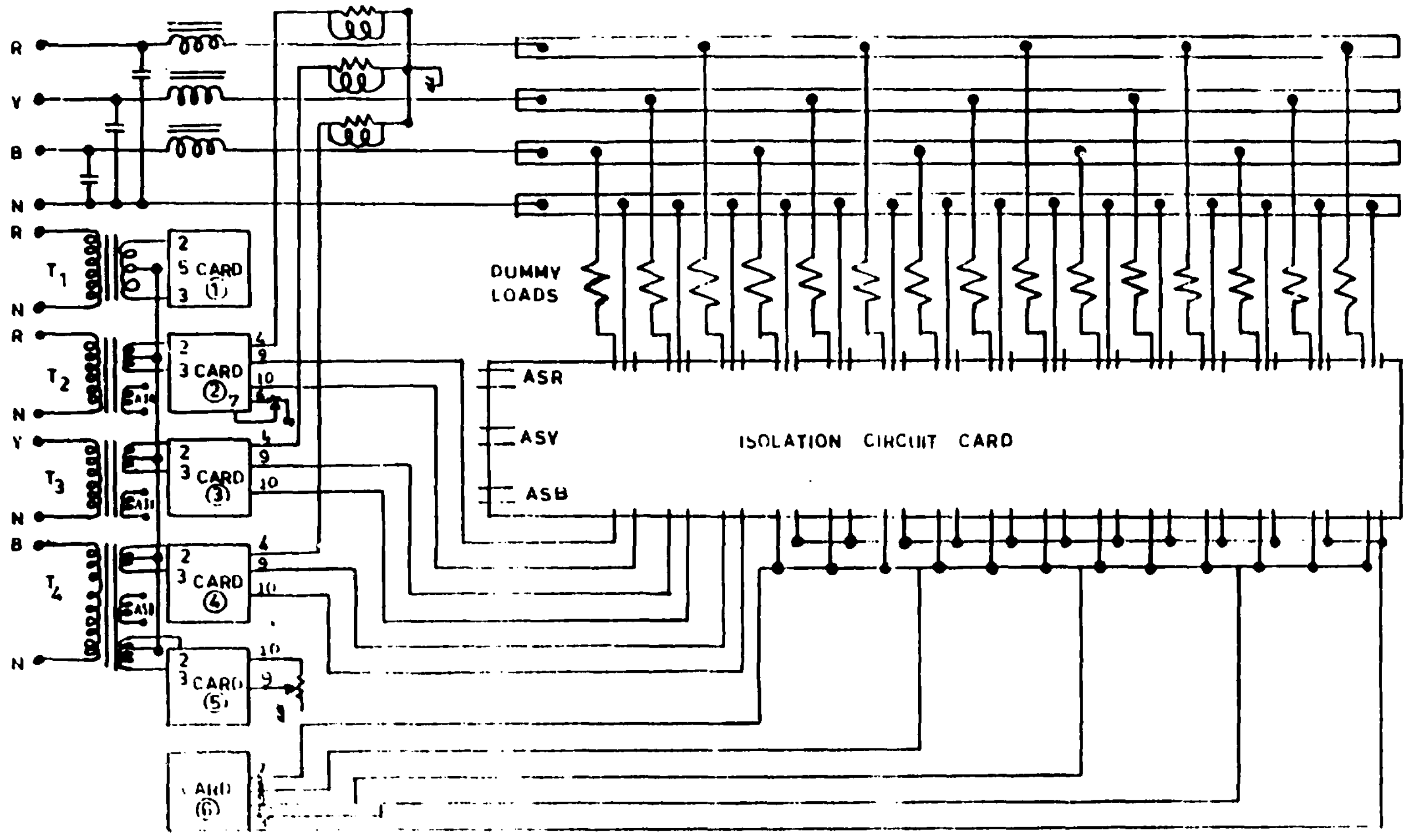


FIG. 8. POWER CIRCUIT DIAGRAM OF THE CONTROL CABINET

It has been established that for a constant head and constant discharge a properly selected pump used in reverse mode is most cost effective. Constant head and constant discharge mean constant power input to the pump (used as turbine) which will give constant shaft power to rotate the generator. This ultimately means that constant mechanical power is available as input to the generator. If the output load (electrical load) on the generator is also kept constant, the system will remain stable. The electronic controller keeps the electrical load on the generator constant, thereby eliminating the need for a mechanical governor. It diverts the surplus power preferentially to a number of useful loads. The conditions under which the governed system is stable have been tested on the synchronous generator as specified above.

Operation

The magnitude of the main load (mostly the priority load) on the generator is variable from zero load to full load. The difference in power output available at the generator terminals and the main load should be diverted to an auxiliary load system (less priority load). This auxiliary load should be a variable load so that the surplus power not being utilized in the main load may be transferred to the variable load. One way to control the magnitude of power flow into the auxiliary loading system is by varying the biasing of the grid of a thyristor (by control of firing angle). It is necessary that the auxiliary load has a power rating equal to that of the generator power rating. The use of thyristors to obtain 0 to 100% variation in auxiliary loads leads to serious problems of distortion in supply voltage and current wave forms, harmonic generation and radio frequency interference for all firing angles except 0° and -180°. These problems will be maximum when the firing angle is 90°. Therefore, the above problem will exist if the total variation in auxiliary load is to be taken care of through the thyristor firing alone. The problems may be overcome to a great extent if the capacity of the auxiliary load to be varied by adjustment of firing angle is reduced. This can be achieved by providing a discrete load together with a variable load, so that when the variable load has reached a limit, power may be diverted to a discrete auxiliary load through thyristors firing at 0° crossing. Hence there should be two types of auxiliary loads.

1. Variable load which may be used as a fine control.
2. Discrete load which may be used as coarse control.

Therefore it may be stated that at all times the generator output = main load + variable auxiliary load + discrete auxiliary load. For simplicity, the variable auxiliary load has been named as "phase load" and the discrete auxiliary load as "step load".

Selection of Phase Load and Step Load

For selecting the capacity of the phase and step load the following two points should be considered:

(1) The phase load should always be more than the permissible unbalance loading which may occur in the system.

(2) The individual step load should always be less than the phase load. Otherwise, if the step load is more than the phase load the system may oscillate.

Having auxiliary loads of two types (i.e. phase and step load) facilitates the use of components of lower rating which are easily available as compared to the higher rating components. Auxiliary loads may be used at a number of distinct useful destinations. Reduced distortion in voltage and current wave forms, harmonics and radio frequency interference are obtained with the use of phase and step loads.

Utilization

It is anticipated in the near future to utilize power generated from the hydro unit for lighting the near-by Sirki village (2.5 KW) and the balance of the power shall be used in a 3.5 KW nitrogen fertilizer arc generator. At present only the arc generator is running on the load.

UTILITY POWER INSTALLATION

To operate this experimental and developmental fertilizer unit, in the case when Micro-hydel power is not available, arrangements for running the unit with utility power supply have been made by tapping 415 Volts, 3 phase electric power line near Sirki Colony of PPCL.

FERTILIZER UNIT PERFORMANCE

Solubilization of Low Grade Mussoorie Rock Phosphate

Initially, about 250 Kg of Mussoorie rock pieces of 12 to 15 mm size were packed in the absorption column, 175 cms. in height. This absorption column packing height was maintained by periodic addition of a small quantity of rock phosphate pieces throughout the duration of the test. The air flow level was adjusted to about 80 liters per minute and the liquid pump recycle rate was adjusted to about 4 liters per minute. From the fertilizer generated during a complete run, 13 samples, 9 for phosphorus and 4 for nitrogen, were collected. The plant was operated for 447 hours. The results of the analysis done on the samples drawn is given in Tables 1 and 2.

Table 1. Determination of Phosphorus Contents in the Solution

Sl. No.	Sample No.	P_2O_5 sample collected after the plant run in hrs (cumulative)	P_2O_5 in gms per liter
1.	P1 (fresh water)	0	0.000
2.	P2	2	0.112
3.	P3	12	0.635
4.	P4	64	1.569
5.	P5	110	2.428
6.	P6	264	2.575
7.	P8	310	3.120
8.	P10	386	9.184
9.	Final sample	447	13.359

Table 2. Determination of Nitrogen in the Solution

Sl. No.	Sample No.	Nitrogen sample collected after the plant run in hrs (cumulative)	Nitrogen in gms. per liter
1.	4 N	64	4.25
2.	7 N	195	19.00
3.	9 N	256	42.00
4.	Final sample	447	62.50

The above results for P_2O_5 and nitrogen were obtained by using a hand held colorimeter (DR-100, HACH, USA).

KWH readings were taken from a high voltage watt-hour meter, which showed that the average KW during the complete run was 3.3.

Figure 9 is the plot of the cumulative soluble phosphorus (in terms of P_2O_5) as a function of the cumulative hours of running of the fertilizer unit. As seen from the graph, the equilibrium period is evident from the shape of the curve. It may be seen that at point A the liberation of P (in terms of P_2O_5) in the solution is only 0.002 gms. per hour, but at point B it is 0.1145 gms. per hour. Because of the relatively large content of calcium and magnesium carbonates and other acid neutralizing compounds in the rock, the column had to be run for longer periods before the equilibrium was achieved. After "steady state" equilibrium is achieved, phosphate is leached readily from the rock. From the graph it may be seen that equilibrium position is attained after about 400 hours.

A total of 6 batches of fertilizer containing nitrogen and soluble phosphorus were produced by using rock phosphate in the absorption column, once the stage of equilibrium was achieved. During these 6 batches, the level of the rock phosphate in the absorption column was maintained by suitable addition of appropriate size of rock phosphate. Details of the results obtained are given in Table 3.

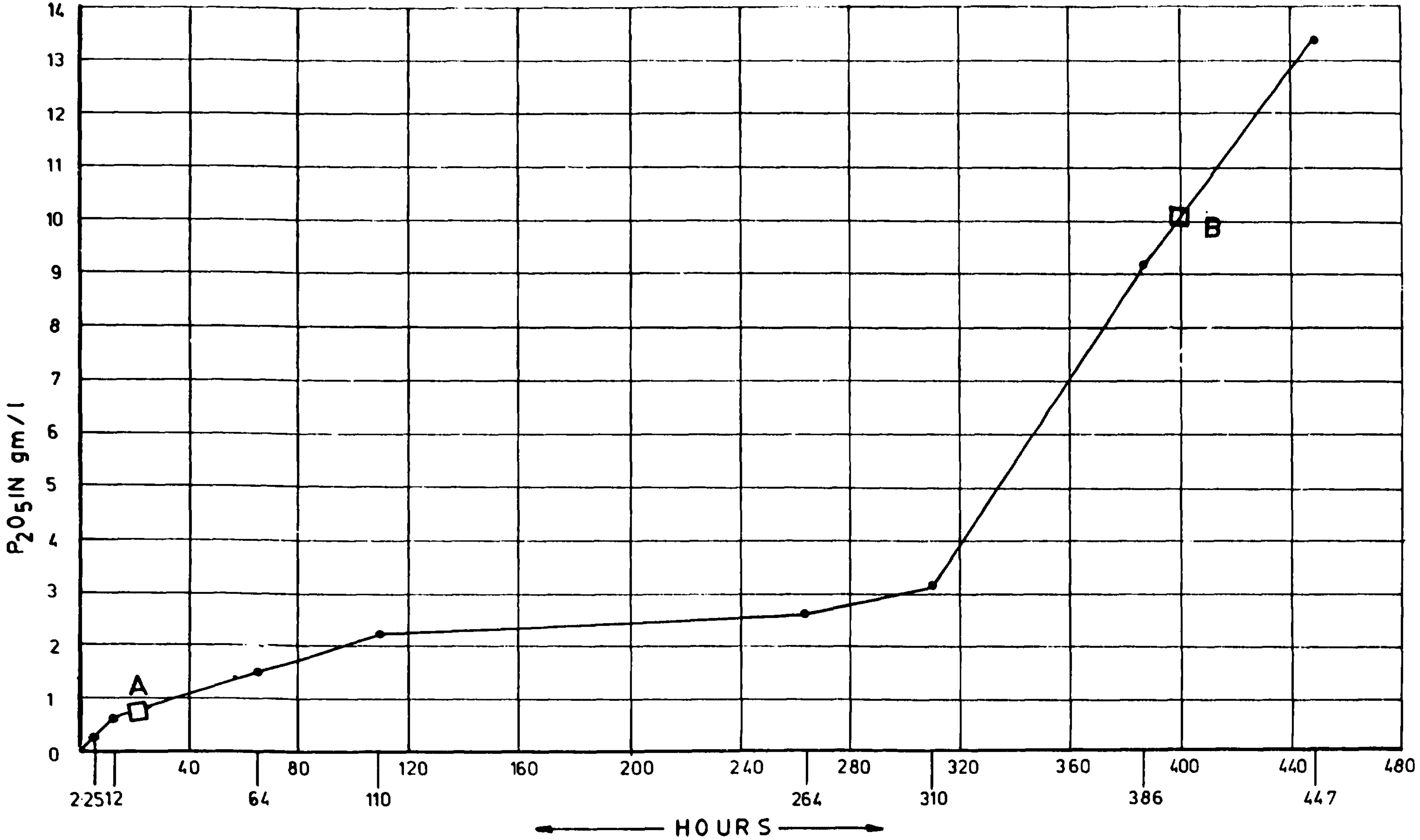


Fig. 9 GRAPH SHOWING RELATIONSHIP BETWEEN HOURS AND PHOSPHORUS PENTOXIDE GRAMS PER LITRE

Table 3. Test Results of Fertilizer Produced by Using Mussoorie Rock Phosphate in Absorption Column after State of Equilibrium bas been Achieved

Sl. No.	Unit run in hrs	Quantity of fertilizer produced	N in gms' ltr of solution	P_2O_5 in gms/ltr of solution	Ratio of $N:P_2O_5$	Total nutrient ($N+P_2O_5$) in gms/hr
1.	270	280	40	25.65	1.56	68.08
2.	230	280	40	24.60	1.65	79.25
3.	225	280	42	27.60	1.52	86.40
4.	248	280	43	26.17	1.64	78.00
5.	245	280	42	25.88	1.64	78.06
6.	184					

Average nutrient ($N+P_2O_5$) in gms/hr = 79.07

Consumption of Rock Phosphate

We have prepared 1680 liters of calcium nitrate phosphate fertilizer where 12 mm rock phosphate chips were used in the absorption column. Initially 200 kg. rock was filled in the column and small additions were made to keep the level of the rock in the absorption column constant. After about 1000 working hours, the liquid pump stopped working and on examination it was found that most of the rock pieces in the absorption column have been reduced to a very small size and became a slurry that blocked passage of the recycle fluid from the absorption column. The whole absorption column was emptied of the rock phosphate and fresh rock phosphate was filled. Out of the spent rock phosphate, only 50 kg. could be collected and the balance had to be thrown away as it had become a slurry.

The P_2O_5 percentage of the original rock phosphate which was filled in the absorption column was 19%. Upon analysis the percentage of P_2O_5 of "spent" rock phosphate remaining in the column the P_2O_5 percentage had improved to 24%. This demonstrated that this method delivered soluble 'P' in the fertilizer solution and that the rock phosphate in the absorption column is slowly upgraded due to removal of calcium and magnesium carbonates from the original rock thereby improving the P_2O_5 percentage of the rock phosphate.

These observations show that this method can be used for upgrading the rock phosphate ore. It is expected that out of 200 kgs. material filled at the initial filling and about 20 kgs. material used for replenishment, about 100 kg. of (rock pieces + powder recovered from the slurry) beneficiated rock can be produced. This can be a useful source of P for application in the fields for crop growth. Experiments will be conducted during 1985 to determine the appropriate dosages and methods of application of the left over slurry, by conducting agronomic trials designed for this purpose.

Operational Experience

The fertilizer unit has worked for a period of 11 months at the time of compiling this report. During this period of 11 months it has been operated for a total number of 2222 hours and a total of 2612 liters of fertilizer have been produced.

During the period of operation of the fertilizer unit no major maintenance problems or breakdowns have been experienced. The list of minor breakdowns and replacement of the parts done during this complete period are given below:

i) Reactor Tube

During the operation one reactor tube burst and was replaced. On removing the burst tube it was seen that burned powder from the electrode deposited at the bottom of the reactor blocking eventually the passage and causing the tubes to burst due to excessive heat. This is an isolated case and if regular cleaning of the reactor tube is done it will be possible to avoid such a problem.

ii) Electrodes

A total of 4 electrodes have been replaced during the operation of 2222 hours. Original length of the electrode is 10 cm. When its length reduced to about 5 cm it was replaced.

iii) Insulator

During the operation 4 insulators burst and needed to be replaced. The design of the insulator needs some modifications to extend the life of the insulators.

iv) Starting Circuit

When the fertiliz .nit was run on utility power, it was found that occasionally the starting circuit did not operate and the arc did not start. The arc had to be started with external help. One of the reasons for non-starting of the arc may be due to low voltage of the utility power supply but this could easily be rectified. With hydel power this problem was not seen.

From the operational experience, it is seen that this fertilizer unit can very easily be operated on a day to day basis even by un-skilled persons after two weeks of initial training. Serious mechanical or electrical troubles were never experienced.

Production of Fertilizer using Limestone, Limestone and Rock Phosphate Mixture and Gluconite Columns

The fertilizer produced by the unit was calcium nitrate phosphate by using Mussoorie rock phosphate in the absorption column. The basal dose of nitrophos solution applied in pot and field trials did not contain all the nitrogen required for plant growth. Additional calcium nitrate liquid fertilizer was produced by using limestone, in the absorption column.

From the 5 test results which are given in Table 4, it may be seen that in the case of limestone column where concentration of nitrogen in the solution is high, column efficiency is reduced. From this it is very clear that nitrogen absorption efficiency of the column is a function of nitrogen concentration in the fertilizer liquid. If the nitrogen concentration in the fertilizer solution is more than 50 gms/liter, the nitrogen absorption efficiency of the column is reduced.

When limestone chips and rock phosphate chips are placed together in the absorption column, the liberation of P from the rock phosphate was very little. As the limestone neutralizes the acid gradually elevating the pH to 4.5, the P from the rock phosphate is no longer dissolved, resulting in very little soluble P in the solution.

In additional studies, the absorption column was filled with gluconite (containing potassium) rock pieces of approximate size of 3 cms. Two studies were undertaken. The results of the two studies conducted on two lots of gluconite are detailed below:

Lot No.	Hrs run	Quantity produced	N in gms per liter	K in gms per liter	N in gms produced/hr
1.	195	80	115	7.5	47.2
2.	177	120	80	5.0	54.2

Table 4. Test Results Using Limestone Alone and Limestone and Rock Phosphate Mixture in Absorption Column

Lot No.	Quantity of fertilizer in liters	Hours run	Substrate material in the absorption	Av.KW consumed by the unit per hour	Nitrogen produced in gms/ltr	P_2O_5 produced in gms/hr	Nitrogen produced in gms/hr	Phosphorus produced in gms/hr
1.	60	71	200 kg of 12mm (Approx) size limestone	3.25	70	-	59.154	-
2.	72	102	200 kg of 12mm (Approx) size limestone	3.20	75	-	52.83	-
3.	60	140	120 kg of limestone + 80 kg rock phosphate	3.22	102.50	2.2	48.05	0.010
4.	260	177	150 kg limestone + 50 kg rock phosphate	3.20	52.25	1.5	66.10	0.004
5.	280	286	200 kg limestone (large pieces)	3.25	55.00	-	53.81	-

From these two results it is very clear that reactivity of weak solution of nitric acid on gluconite rock is slow and very little K can be obtained in the fertilizer solution along with N. The analysis of the potassium was performed using a flame photometer Wadia Institute of Himalayan Geology, Dehradun, India.

For better evaluation more experiments using different sizes of gluconite and running the unit for longer periods are essential. Experiments are being planned to evaluate and optimize the release of K from gluconite. Also, Mussoorie rock phosphate and gluconite mixtures will be used in the absorption column to get a complete NPK fertilizer.

FERTILIZER STORAGE AND TRANSPORTATION

Storage

A total of 2612 liters of fertilizer have been produced from this unit. We have stored it all in 40 liter plastic jerry cans. These jerry cans have been found to be quite good and cheap for storage and the acidity of fertilizer solution (pH 0.5-0.7) did not cause any damage to the plastic even after 6 months of storage. A storage pit of 3000 liters capacity is also ready for storing the fertilizer on site next to the absorption column of the unit.

Transportation

Thirteen hundred liters (900 liters of calcium nitrate phosphate and 400 liters of calcium nitrate) of fertilizer have been sent to G.B. Pant University of Agriculture, Pantnagar (U.P.) about 200 miles from the production site. All of this was sent in 20/40 liter jerry cans. For transportation of fertilizer, plastic jerry cans have been found very useful and economical as these can be reused.

DIFFERENCE BETWEEN THE UNIT INSTALLED AT SIRKI AND THE PROTOTYPE UNIT ON WHICH INITIAL TESTS WERE CARRIED OUT AT BATTELLE-C.F. KETTERING RESEARCH LABORATORY

Basically the major items like transformer, rectifiers, reactor unit, air and water pumps are exactly the same as in the prototype unit installed at BCFKRL. The following are the main differences:

i) In the Sirki fertilizer unit, there are two tanks for recycled liquid in place of the one tank with approximate capacity of 70 liters used at BCFKRL. The total capacity of these two tanks at Sirki is 300 liters. With this capacity any quantity of fertilizer, between 50 to 300 liters can be produced in one run.

ii) Electric supply available for operation of prototype unit installed at BCFKRL was 220 volts, 3 Ph., 60 cycle, whereas, the supply voltage of the utility power, as well as the generated voltage of Micro-hydel unit, at Sirki are 415 volts, 3 Ph., 50 cycle. As such, all the electrical components were specially ordered to suit this voltage.

SECOND UNIT INSTALLATION

Two units were received from BCFKRL, USA. One was installed at Sirki and the other has been sent to Alternate Hydro Energy Centre, University of Roorkee. The second unit is under installation and is expected to be ready by the end of October 1984. Alternate Hydro Energy Centre is in the process of installing a number of 200 KW and larger capacity Micro-hydel units in India and desires to use 20 such units (60 KW capacity), or a lesser number of larger, scaled-up units with total input capacity of 60 KW, at these projects. All these Micro-hydel projects will have hybrid systems controlled by a microprocessor controller. In these systems, electricity will be supplied primarily to a main rural load and when it is surplus to the rural load requirement, it will automatically be switched over to the hydrid system loads including nitro-phosphate fertilizer units and other similar loads. PPCL and the University of Roorkee would collaborate in this project with technical collaboration from BCFKRL subject to the availability of funding. The main objectives are:

i) Carrying out experiments for optimizing the production of nitrogen and soluble phosphorus from this unit.

ii) Studying the possibility of scale-up of the unit to 10 KW size.

iii) Studying the possibility of running 20 such units by using one common transformer for all of the 20 units and using one common oxidation and one common absorption column for five such units.

iv) Studying the consequent improvement in the performance of the above mentioned batch of units as compared to the performance of a single unit.

v) Studying the possibilities of usefully utilizing the heat from the arc reactor tube.

ECONOMICS OF PRODUCING LIQUID NITRO-PHOSPHATES FROM ARC REACTOR USING HYDRO POWER

An attempt is made to evaluate the economics of producing liquid nitro-phosphate fertilizer from the arc reactor based on the experience obtained from the existing prototype unit. The economics are, however, based on a unit of 3 kW. It is envisaged that the economics will considerably improve in case the unit is scaled-up along with development of a system to recover excess heat generated during the arc reaction. Further research and development work should be focused on this aspect.

The economics are predominantly influenced by the order of investment for the electric power supply and are relatively independent of the investment for the arc generator. The economics are estimated for:

A) The existing prototype unit and

B) An ideal system based on a micro-hydel unit located at another suitable place.

A. Economics of Existing Prototype Unit

As mentioned earlier, the present system is powered by a Micro-hydel unit developed exclusively for the purpose. It may be noted that the investment towards the present Micro-hydel unit had been excessive for the first prototype. For future installations the investment is expected to be considerably less.

a)	No. of working hours/day	... 22
b)	No. of work days/year	... 330

c) Average data collected

i)	Total average nutrients $(N+P_2O_5)$ produced/hr	... 79 gms
ii)	Total nutrients produced/year = 79x22x320	... 556.1 Kg
iii)	Average power consumed by the fertilizer unit/hr	... 3.25 K
iv)	Power consumed by fertilizer unit in one year 3.25x22x320	...22880 KWH
v)	Cost of utility power per unit	...Rs. 0.62
vi)	Total number of electrical units (KWH) produced by Micro-hydel unit taking 95% efficiency = 0.95x10x22x320	...66880 KWH
vii)	Revenue earned by selling surplus power to Sirki village @ Rs. 0.62/unit	...Rs. 27,280/-
viii)	Surplus power available from Micro-hydel unit after supplying to fertilizer unit 66880-22880	...44000 KWH

1. Capital Costs

a) Micro-hydel Unit (10KW)

- Generator and turbine	... Rs. 50,000
- Civil works for water diversion, system and penstock etc.	...Rs. 115,000
	Rs. 165,000

b) Fertilizer Unit (indigenous costs)

- Equipment and hardware including electrical components	..Rs. 15,000
- Civil works	...Rs. 5,000
	...Rs. 20,000
Total of a + b	...Rs.185,000

2. Operating Costs

a) Variable costs

		In Rs.
- Rock phosphate	: 0.5 ton	140
- Limestone	: 0.5 ton	60
- Cost of replaceable parts like electrodes etc.		1,000
		1,200

b) Fixed Costs

- Salaries		5,400
- Maintenance		1,000
- Depreciation of:		
i) Hardware @ 8%	: Rs.5,200	
ii) Civil works @ 2%	: Rs.2,400	7,600
		14,000
	Total of a + b	15,200

Profitability

- Revenue expected from surplus power 44,000 KW power/yr @ 0.62	: 27,280
- Revenue from fertilizer sale 556.1 kg of nutrient (P_2O_5+N)	: 3,890
Total Revenue	:Rs.31,170
Total profit (Revenue-Cost) (31,170-15,200)	Rs. 15,970

i.e. 8.63% of return on total investment

Approximately 10.5 Indian rupees = One US Dollar

B. Economics of an Ideal System Based on Micro-hydel Unit Located at Another Suitable Place

In this case it is envisaged that a two stage absorption column will be used for fertilizer production and the anticipated investment of Rs.70,000/- is sufficient for all the civil works of the Micro-hydel unit.

1.	Total nutrient produced/hr in double absorption column unit	- 90 gms/hr
2.	Total nutrients/year	- 633.6 kgs
3.	Revenue from fertilizer sale (P_2O_5 + N)	- Rs.4,435
4.	Revenue from surplus power (from the previous page)	- 27,280

As the civil work cost is only Rs. 70,000 the
depreciation of civil work will be - Rs. 1,500
Total operating costs will be - Rs.14,300
Total revenue (27,280 + 4435) - Rs.31,715
Total profit (31,215 - 14300) - Rs.17,415
(i.e. 15.1% return on total investment)
Approximately 10.5 Indian rupees = One US Dollar

This system is ideal for remote hilly or coastal locations where fertilizer transport cost can be quite high. In our economic assessment we have not given any weightage for saving in transport cost which could significant in remote areas.

Also, a special subsidy needs to be provided by the Government for encouraging such fertilizer units which need only water and air as raw materials. The power required to support this process can be produced by renewable sources of energy such as wind, water or solar.

Similar units or scaled-up units, will be ideal for operation in a hybrid system along with the rural load, at Micro-hydel units of capacities in the range of 200 KW and above. In such cases, the rural load is only for 4-6 hours a day and there is surplus power available from Micro-hydel system for the remaining hours of the day. This surplus power can be very usefully utilized for operating a batch of such fertilizer units. In such cases, interest and depreciation as well as operating cost is minimal as the operator will always be there for operation of 200 KW Micro-hydel system. In such cases the fertilizer produced could be economical, when all these factors are taken into consideration.

SCALE-UP PREDICTIONS FOR CONSEQUENT IMPROVEMENT IN PERFORMANCE

The basic design of the fertilizer unit can very easily be scaled-up or scaled-down.

The unit can very easily be scaled-up to 6 KW by changing the transformer and changing the capacity of the ballast for controlling the current of the secondary of the transformer. As far as the reactor is concerned, this can also be easily adapted up to 6 KW capacity. For larger capacities, like 10 KW, more experimental developmental work is needed. The present absorption system is sufficient for 10 KW capacity. Nitrogen absorption efficiency of the column also will improve if a two stage system is adopted.

For scaling-down the unit to 1.5 KW capacity, no modifications are required except changing the ballast capacity needed on the secondary of the transformer. After experimentation, a smaller transformer and other suitable small components can be designed to reduce the cost.

USE OF ALTERNATIVE RENEWABLE SOURCES LIKE WIND AND SOLAR ENERGY FOR POWERING THE FERTILIZER UNIT

Wind Electric Generators

The expertise in manufacturing high capacity wind electric generators in India is very limited. At the moment, only small 1.5 KW wind electric generators are manufactured in India. These wind electric generators are primarily meant for battery charging and for water lifting. Our requirement is for a 3.5 KW, 3 Ph, 415 Volts, supply wind generator. The system should be capable to supply a total load of about 6 KW at the time of starting.

The calcium nitrate-phosphate fertilizer unit is best suited for isolated locations as the farmer can become self sufficient, not having to transport fertilizer as he presently does, because the fertilizer can be produced for his use at the site itself. If the locations are situated in the coastal areas, where wind velocity is sufficient, wind electric generator power supported fertilizer units could be ideal.

It is suggested that one wind electric generator of suitable capacity should be imported and installed in a coastal area along with a fertilizer unit for experimental purposes to collect operational data from such a unit. BCFKRL could provide technical collaboration for such a project.

Solar Photo Voltaic Power

The Government of India had given importance for development of solar photo voltaic power and a separate Department of Non-Conventional Energy Sources has been established recently. The solar modules manufactured in India to suit our requirement are still very costly. Estimates from Central Electronics, Sahibabad, UP, India show that a solar module to suit the requirement for a 3 KW fertilizer unit would be approximately US$ 40,000.

SUMMARY

A prototype system for the production of fertilizer using an electric arc process has been field tested in India. Production of nitrogen and phosphorus fertilizer has been studied using low-grade Mussoorie rock phosphate as the phosphorus source. Technical feasibility of the process has been demonstrated using hydro-electric energy as the power source. Performance of the system has been satisfactory with only minor equipment and operating problems encountered during the first year of tests. The nitrogen and phosphorus fertilizer produced in the prototype system have been analyzed chemically and demonstrated to be effective in agronomic field trials using maize as a test crop. Preliminary studies on the feasibility of extracting potassium from gluconite rock also have been explored.

Economics of the process can be favorable if surplus or "off peak" power is used particularly in large scale hydro-electric systems. Productive uses of heat generated in the process also could enhance the economic viability of the process. It is suggested that the application potential of the system in India could further be extended by using wind electric power as an alternate enrgy source for the process.

PART II - FINAL AGRONOMIC REPORT

EVALUATION OF AGRONOMIC EFFECTIVENESS OF CALCIUM NITRATE PHOSPHATE LIQUID FERTILIZER PRODUCED BY KETTERING ARC GENERATOR

EVALUATION OF AGRONOMIC EFFECTIVENESS OF CALCIUM NITRATE PHOSPHATE LIQUID FERTILIZER PRODUCED BY KETTERING ARC GENERATOR

INTRODUCTION

The Pyrites, Phosphates and Chemicals Ltd. (a Government of India undertaking referred to in the text as PPCL) and the United Nations Industrial Development Organization (UNIDO) have sponsored a project on "Production of Calcium Nitrate Phosphate Liuqid Fertilizer from Low Grade Mussoorie Rock Phosphate" to the Battelle-C.F. Kettering Research Laboratory (BCFKRL) in Yellow Springs, Ohio, USA. BCFKRL's arc generator produces a weak nitric acid solution which, when passed through a column of rock phosphate, results in calcium nitrate-phosphate liquid fertilizer. Two arc generators have been supplied to PPCL by BCFKRL, one of which was installed in the remote village of Sirki near Dehradun (U.P.), India. The process dynamics, the fertilizer output and the on-site performance of the generator in India are described in the technology report. The agronomic effectivensss of the fertilizer produced at Sirki was tested at the G.B. Pant University of Agriculture and Technology at Pantnagar (U.P.), India by the scientists from Pantnagar University with assistance from BCFKRL and PPCL scientists.

During the year 1984 pot experiments were conducted using soils from Pantnagar and Dehradun with maize and wheat as test crops. Since field experiments were proposed in both Pantnagar and Dehradun, the objective of the pot experiments in these soils was essentially to provide some base data. One field experiment with spring maize was conducted at Pantnagar during 1984. The results of pot and field trials are reported in this report. Subsequent field trials are proposed by PPCL in Dehradun and elsewhere in India during the cropping season of 1984-85.

OBJECTIVES

The principal objectives of this study were:

1. To study the agronomic effectiveness and suitability of calcium nitrate-phosphate liquid fertilizer produced by BCFKRL's arc generator as a source of nitrogen and phosphorus for crop production in pot and field trials conducted in India.

2. To find out appropriate methodologies for applying calcium nitrate-phosphate liquid fertilizer keeping in view the needs and practices of Indian farmers.

EXPERIMENTAL METHODS

I. Soil Characteristics

Soils used for pot experiments were collected from Pantnagar and Dehradun. Pot and field experiments were conducted at the G.B. Pant Agriculture University in soils low in nitrogen and phosphorus. In Pantnagar, soils for pot experiments were collected from the field experimental site and in Dehradun from a farmer's field. The physico-chemical characteristics of the soils from Pantnagar and Dehradun are listed in Table 1.

Table 1. Physico-chemical characteristics of the soils from Pantnagar and Dehradun

Soil Characteristics	Location	
	Pantnagar	Dehradun
Texture	clay loam	loam
pH	7.90-8.20	7.50-7.80
Organic Carbon (%)	0.88	1.01
Total N (%)	0.08	0.09
Available P_2O_5 (Kg/ha)	40	96
Available K_2O (Kg/ha)	87	114

II. Characteristics of Liquid Fertilizer

The calcium nitrate-phosphate liquid fertilizer produced by arc generator was used to provide all the nitrogen and phosphorus required for basal application. Additional nitrogen was supplied as liquid calcium nitrate which was produced by passing weak nitric acid produced by arc generator through a column of limestone. The concentration of total nitrogen in calcium nitrate phosphate fertilizer ranged from 0.8 to 4.5% and that of P from 0 to 1.4% depending on the batch of fertilizer. The pH of the liquid calcium nitrate-phosphate fertilizer was found to be 0.5-0.7 and that of calcium nitrate fertilizer 4.8-5.0. For comparison with the liquid fertilizer, urea was used as a nitrogen source and triple super phosphate as the phosphorus source in both pot and field experiments.

III. Small Pot Experiments

The nitrophos solution originating from the arc generator is highly acidic (0.5-0.7 pH). The small pot experiments were conducted to evaluate the impact of the low pH of the fertilizer solution on the seed germination and shoot and root growth of the seedlings, under controlled environment conditions.

The experiments were conducted in 1 Kg. plastic pots containing 800 g of dry and previously sieved soils. Fertilizer solution was thoroughly mixed with the soil and the soil moisture brought to field capacity. Two crops, maize (var Kanchan) and wheat (var Sonalika) and two soils, Pantnagar (pH 8.0) and Dehradun (pH 7.8) were used. Four seeds were planted in each plastic pot. pH of the soil was monitored before sowing and after 25 days when the experiment was terminated after growth characteristics of the shoot and roots were observed.

We have estimated that the first 15 cms of soil in a hectare will approximate (varying from soil to soil) to 2100 tons of soil (1 hectare = 100M X 100M or 10,000 cm X 10,000 cm. Bulk density of 1 cm of soil will be 1.4 gms. The first 15 cms of the soil in an hectare would, therefore, weigh 10,000 X 10,000 X 1.4 X 15 g or 2,100 tons.) Based on the nitrogen and P content of the solution (averaging 2 g of N and 1 g of P_2O_5 for 100 ml) we have estimated that we would need an application of 5,000 litres (100 kg N and 50 kg of P_2O_5) of this solution to meet average crop demand of nitrogen and P required for cultivation in a hectare. Five thousand litres of fertilizer solution in 2,100 tons of soil (soil in the first 15 cm of an hectare) will correspond to 0.238 ml in 100 g of soil (or 0.24% of solution on soil weight basis). Therefore, the concentration of fertilizer solutions used on a soil weight basis were: 0, 0.25, 0.5, 1.0, 2.0 and 5.0. The highest concentration tested (5%) was nearly 20 times that of the optimal fertilizer dose required. This was done to reflect the effect of repeated application of such a fertilizer solution (for example year after year) on soil pH as well as on plant growth. We recognize that long term incubation studies are more appropriate for such a study but in the time frame available we hoped some relevant information could be obtained from these laboratory experiments.

IV. Large Pot Experiments

a) Wheat.

Pot experiments with wheat were conducted with both soils, in which liquid fertilizer (calcium nitrate-phosphate) was compared with standard fertilizer. The standard fertilizer consisted of solid urea and triple super phosphate to supply nitrogen and phosphorus, respectively. The liquid and standard fertilizers were compared at three levels of N and P addition and four methods of fertilizer application. A uniform dose of 50 ppm K was applied through muriate of potash in all the treatments.

The treatments included two types of fertilizers, 3 rates of N and P and 4 methods of applications as listed below:

Types of fertilizers:
1. Liquid fertilizer - F_1
2. Standard fertilizer - F_2

Rates of N and P.
1. 120 ppm N + 32 ppm P - T_1
2. 60 ppm N + 16 ppm P - T_2
3. 30 ppm N + 8 ppm P - T_3

Method of application:
1. Mixing in soil - M_1
2. Injection into the soil,
   5 cm below the seed - M_2

3.	Half N and full dose of P as basal + rest N in two equal splits with irrigation.	- M_3
4.	Half N and full dose of P as basal + rest N in two equal splits as foliar spray	- M_4

The treatments were triplicated in a completely randomized design. The various treatment combinations included in the pot experiments with wheat are given below:

Treatment No.	Treatment Combinations
1.	Control
2.	$F_1T_1M_1$
3.	$F_1T_1M_2$
4.	$F_1T_1M_3$
5.	$F_1T_1M_4$
6.	$F_1T_2M_1$
7.	$F_1T_2M_2$
8.	$F_1T_2M_3$
9.	$F_1T_2M_4$
10.	$F_1T_3M_1$
11.	$F_1T_3M_2$
12.	$F_1T_3M_3$
13.	$F_1T_3M_4$
14.	$F_2T_1M_1$
15.	$F_2T_1M_2$
16.	$F_2T_1M_3$
17.	$F_2T_1M_4$
18.	$F_2T_2M_1$
19.	$F_2T_2M_2$
20.	$F_2T_2M_3$
21.	$F_2T_2M_4$
22.	$F_2T_3M_1$

Treatment No.	Treatment Combinations
23.	$F_2T_3M_2$
24.	$F_2T_3M_3$
25.	$F_2T_3M_4$

Seven kilograms of previously sun-dried and sieved soil was filled in each plastic pot (7 kg) and the required amounts of fertilizers were applied as per above treatments. Seven seeds of wheat variety Sonalika were sown on December 22, 1983 and after germination four uniform plants in each plastic pot were maintained. Plants were irrigated when required. Remaining amounts of fertilizers were applied at 45 and 80 days after sowing through irrigation and foliar spray as calcium nitrate liquid fertilizer. Standard agronomic practices were adopted during the growth period. Harvesting was done on May 2, 1984 and grain and straw yields per pot were recorded.

b. Spring Maize

This pot experiment was conducted with only Pantnagar soil. The methodology of the experiments and treatment combinations were similar to that of wheat experiment with the difference that foliar spray treatment was substituted by application of fertilizer through irrigation in four equal splits. Potassium was applied uniformly at the rate of 50 ppm K through muriate of potash in all the treatments.

The treatments included 2 types of fertilizers, 3 rates of N and P and 4 method of fertilizer application along with a control.

Types of fertilizers:

1. Liquid fertilizer - F_1
2. Standard fertilizer - F_2

Rates of N and P:

1. 120 ppm N + 32 ppm P - T_1
2. 60 ppm N + 16 ppm P - T_2
3. 30 ppm N + 8 ppm P - T_3

Methods of application:

1. Mixing in soil - M_1
2. Injection into the soil at 5 cm below the seed - M_2
3. Half N and full dose of P as basal + remaining half N in two equal splits with irrigation (Irrigation I) - M_3
4. Half N and full dose of P as basal + remaining half N in four equal splits with irrigation (Irrigation II) - M_4

Fertilizers as per treatments were applied in each plastic pot containing 7 kgs of processed soil. Five seeds of maize variety Kanchan were sown on February 28, 1983 in each pot and after germination 3 uniform maize plants per pot were retained. Plants were watered when needed. Remaining nitrogen was applied along with irrigation water at 20 and 40 days after sowing in case of two equal splits and at 20, 30, 40 and 50 days after sowing in case of 4 equal splits. Plants were harvested on April 28, 1984 and at the time of harvesting, dry matter yield was recorded.

III. Field Experiment with Spring Maize

This experiments was conducted at Pantnagar in a plot having 40 kilogram of available P_2O_5 (Olsen's method) and 0.08% of total N. The soil was of clay loam texture with a pH of 7.9. In this experiment, two types of fertilizers, liquid (calcium nitrate-phosphate) and standard were compared at 3 rates of N and P applied by 3 methods. Standard fertilizer consisted of solid urea and triple super phosphate to supply N and P, respectively.

Types of fertilizers:

1. Liquid fertilizer - F_1
2. Standard fertilizer - F_2

Rates of N and P:

1. 40 Kg N + 20 Kg P_2O_5/ha - T_1
2. 80 Kg N + 40 Kg P_2O_5/ha - T_2
3. 120 Kg N + 60 Kg P_2O_5/ha - T_3

Methods of application:

1. Mixing in soil - M_1
2. Furrow placement at 5 cm below the seed - M_2
3. Side placement at 5 cm depth and 10 cm away from the seed row - M_3

Following treatment combinations were triplicated in a randomized block design. The various treatment combinations included in the field experiments with maize are given below:

Treatment No.	Treatment Combinations
1.	Control
2.	$F_1T_1M_1$
3.	$F_1T_1M_2$
4.	$F_1T_1M_3$
5.	$F_1T_2M_1$
6.	$F_1T_2M_2$
7.	$F_1T_2M_3$
8.	$F_1T_3M_1$
9.	$F_1T_3M_2$
10.	$F_1T_3M_3$
11.	$F_2T_1M_1$
12.	$F_2T_1M_2$
13.	$F_2T_1M_3$
14.	$F_2T_2M_1$
15.	$F_2T_2M_2$
16.	$F_2T_2M_3$
17.	$F_2T_3M_1$
18.	$F_2T_3M_2$
19.	$F_2T_3M_3$

Gross plot size for each treatment was 4 X 2 square meters. Half amount of N and full amounts of P and K were applied as basal dressing. In mixing method of application of fertilizers, liquid fertilizer was sprinkled with the help of a sprayer while standard fertilizer was broadcasted on the soil surface. Subsequently, they were uniformly mixed with the soil with the help of a spade. In case of furrow placement, fertilizers were applied in slightly deeper furrows opened for the purpose of sowing and after fertilizer application the furrows were covered loosely with soil. For side placement, deeper side rows at a distance of 10 cm from the main row were opened and fertilizers were applied in them.

A distance of 60 cm between rows was maintained. Seeds of maize variety Kanchan were planted at a distance of 25 cm within a row. All sowing was completed on March 28, 1984. After sowing, the seeds in the row were covered with soil. Irrigation was done when ever required. Standard agronomic practices were followed throughout the growing season. Remaining half dose of nitrogen was applied in between the rows in two equal splits at 30 and 70 days after sowing.

Plant population in each plot was recorded. Crop was grown till maturity and was harvested on June 30, 1984. Dry matter yield of maize stover and plant height were recorded for each plot. The grain setting in the cobs was very poor because of extremely high temperatures prevailing during May-June 1984. Therefore, only the data for dry matter yield and plant height were recorded for each plot.

RESULTS

I. Small Pot Experiments

In small pot experiments, the effects of increasing concentrations (0, 0.25, 0.5, 1.0, 2.0 and 5.0% on a soil weight basis) of calcium nitrate-phosphate liquid fertilizer, on several plant growth parameters (Figs. 1 and 2) was examined as described below.

i) Seed germination: Both wheat and maize seeds germinated well in Pantnagar and Dehradun soils without any significant difference in germination rates between 0 and 2% of fertilizer solution. At the 5% level, germination and emergence declined drastically suggesting acid toxicity. At 0.25% concentration (supplying optimal levels of N and P) the germination was as good as the treatment without any liquid fertilizer added.

Table 2. Germination (%) of Wheat and Maize

Concentration of Fertilizer Solution (%)*	Maize		Wheat	
	Pantnagar**	Dehradun**	Pantnagar	Dehradun
0	100	100	88	100
0.25***	88	100	100	83
0.5	100	88	100	88
1.0	100	88	100	75
2.0	88	63	100	88
5.0	12	25	63	12

Germination at 5% concentration of liquid fertilizer significantly different from other concentrations.

*On soil weight basis.

**Soils from two locations where field experiments were proposed.

***Level corresponding to 100 Kg N and 50 Kg of P_2O_5/hectare.

ii) Shoot fresh weight: There were significant differences in the fresh weight of shoots at different concentrations. Increases in shoot weights above controls were observed at 0.25% concentration in both wheat and maize in Dehradun and Pantnagar soil. However, the increases were prominent in wheat up to 1% concentration in Dehradun as well as Pantnagar soil. On the other hand in maize shoot weights declined sharply above 0.5% concentration and shoots exhibited increasing acid toxicity symptoms, as the concentration of fertilizer solution was increased. Wheat plants exhibited less pronounced acidity symptoms even at the higher concentrations of fertilizer solution.

Table 3. Mean Fresh Weight of Shoots (g/plant)

Concentration of Solution (%)	Maize		Wheat	
	Pantnagar	Dehradun	Pantnagar	Dehradun
0	1.57	1.25	0.50	0.30
0.25	1.21	1.50	0.75	0.48
0.5	0.75	0.94	0.88	0.47
1.0	0.60	1.07	0.75	0.60
2.0	0.50	0.83	0.34	0.29
5.0	0.20	0.15	0.08	0.16
LSD (0.05)	0.25	0.20	0.21	0.24

iii) Root fresh weight. The fresh weight of roots in maize showed a gradual decline with increasing concentration of fertilizer solution in both the soils. However, root fresh weights in wheat showed a significant increase up to 1% in both the soils. The decline was rapid above 2% concentration.

Table 4. Mean Fresh Weight of Roots (g/plant)

Concentration of Fertilizer Solution (%)	Maize		Wheat	
	Pantnagar	Dehradun	Pantnagar	Dehradun
0	2.20	2.09	0.67	0.76
0.25	2.00	2.43	0.78	1.00
0.5	1.40	1.92	0.68	0.87
1.0	1.40	1.54	0.75	0.80
2.0	0.65	1.00	0.45	0.47
5.0	0.73	0.60	0.32	0.40
LSD (0.05)	0.34	0.28	0.10	0.18

iv) Plant height. Plant height with 0.25% fertilizer solution showed a tendency for increase over unfertilized soils for both wheat and maize. In maize the decline in height corresponded with increasing concentration of liquid fertilizer beyond 0.25%. In wheat the increase in plant height was noticed until 1% concentration and at 5% there was a sharp decline.

Table 5. Mean Height* of Plants (cms)

Concentration of Fertilizer Solution (%)	Maize		Wheat	
	Pantnagar	Dehradun	Pantnagar	Dehradun
0	21.8	21.1	24.9	23.6
0.25	22.5	23.9	28.0	26.3
0.5	17.8	20.2	31.0	25.2
1.0	12.5	21.6	29.5	27.2
2.0	11.6	16.0	23.8	19.0
5.0	5.6	5.5	10.7	11.3
LSD (0.05)	1.2	1.6	2.4	2.6

*Height of longest leaf in a plant

v). Number of leaves per plant. While in maize a gradual decline in the number of leaves was noticed in both Pantnagar and Dehradun soils, an increase in the number of leaves was noticed in wheat up to 1% of fertilizer concentration. At 2% and above, the number of leaves declined sharply.

Table 6. Mean Number of Leaves per Plant

Concentration of Fertilizer Solution (%)	Maize		Wheat	
	Pantnagar	Dehradun	Pantnagar	Dehradun
0	4.6	5.0	4.3	3.9
0.25	4.1	4.8	4.6	4.6
0.5	3.9	4.3	5.0	4.4
1.0	3.9	4.4	4.8	4.5
2.0	3.4	4.0	3.9	3.4
5.0	2.3	2.0	2.4	2.5
LSD (0.05)	0.48	0.42	0.3	0.46

The results from Tables 2-6 with various plant growth parameters showed that wheat responded better to the fertilizer solution due probably to more tolerance of this crop to acid fertilizer solution. In maize there was a general decline in plant growth with increasing concentration of fertilizer solution, particularly above 0.25% concentration.

vi). Soil pH change. The pH of the soil samples with different concentrations of fertilizer solutions were taken at the beginning (0 days) and end (25 days) of experiment. The pH was elevated after 25 days consistently with both the soil types showing that the calcareous soils of Dehradun and Pantnagar have enough buffering capacity to absorb the acidity of fertilizer solution as well as elevate the pH with time.

Table 7. pH of the Soil soon after Mixing with Fertilizer Solution and 25 days after (25 d)

Concentration of Solution (%)	Pantnager		Dehradun	
	0 d	25 d	0 d	25d
0	8.20	7.85	7.80	7.71
0.25	8.00	7.62	7.80	7.52
0.5	7.70	7.55	7.60	7.50
1.0	7.20	7.40	7.20	7.30
2.0	6.70	7.05	6.60	7.10
5.0	6.00	6.50	5.80	6.50
LSD (0.05)	0.25	0.20	0.18	0.23

II. LARGE POT EXPERIMENTS

A. Wheat in Pantnagar Soil

i). Wheat grain yield. At lower fertilizer dose level (30N + 8P) grain yield resulting from the application of solid or liquid fertilizers did not differ. At higher dosages general toxic effects due to the application of acid fertilizer resulted in lower grain yields. Also, heavy rains during the cropping period inundated the pots and, as a result of this, the water logging in liquid fertilizer applied pots caused a cumulative harmful effect on plants. Dose responses were, however, clear with the solid fertilizer. Heavy rains also resulted in the washing off of the foliar applied fertilizer.

Table 8. Effect of Fertilizer Dosage and Method of Application on the Grain Yield (grams/pot) of Wheat Grown in Pots Containing Pantnagar Soil.

Method of Application	FERTILIZER DOSAGE* 30N + 8P Liquid	Solid	60N + 16P Liquid	Solid	120N + 32P Liquid	Solid	Mean
Mixing	12.9	12.6	5.6	15.8	0.2	17.1	7.9
Injection	11.9	13.8	8.8	19.4	1.1	19.3	12.4
Irrigation	9.9	13.1	8.8	11.9	0.9	15.9	10.1
Foliar spray	12.6	12.3	12.1	13.1	1.3	15.3	11.1
Mean	11.8	13.0	8.8	15.1	0.9	16.9	
Control (unfertilized)	2.93						

*See Experimental Methods

C.D. 5%
Type of fertilizer x dosage of fertilizer = 2.0
Type of fertilizer x method of application = 2.3

ii). Wheat straw yield. The results for the wheat straw yield showed a similar pattern to that of grain yield. Liquid and solid fertilizers performed equally at two levels of fertilizer application (30N + 8P, 60N + 16P), but at higher levels liquid fertilizer yielded poorly. Fertilizer dose response was prominent with solid fertilizers. The lowest dose of liquid fertilizer application (30N + 8P) resulted in a significant increase in both wheat grain and straw yields.

Table 9. Effect of Fertilizer Dosage and Method of Application on the Dry Weight of the Straw of Wheat Grown in Pots Containing Pantnagar Soil.

Method of Application	FERTILIZER DOSAGE 30N + 8P		60N + 16P		120N + 32P		Mean
	Liquid	Solid	Liquid	Solid	Liquid	Solid	
Mixing	21.1	16.4	14.8	19.7	4.1	26.9	17.1
Injection	24.9	25.6	19.7	27.9	11.1	22.9	22.0
Irrigation	18.1	18.4	19.9	20.7	9.6	24.4	18.5
Foliar spray	18.1	16.9	16.7	17.9	10.2	21.4	16.9
Mean	20.6	19.3	17.8	21.6	8.8	23.9	
Control (unfertilized)	12.73						

C.D. 5%

Type of fertilizer x dosage of fertilizer = 2.8

Type of fertilizer x method of application = 2.8

B. Wheat in Dehradun Soil

i) Wheat grain yield. Both the liquid and solid fertilizers responsed equally well at 30N + 8P and 60N + 16P. Foliar spray of liquid fertilizers was damaging at higher concentrations.

Table 10. Effect of Fertilizer Dosage and Method of Application on the Grain Yield (grams/pot) of Wheat Grown in Pots Containing Dehradun Soil.

Method of Application	FERTILIZER DOSAGE 30N + 8P		60N + 16P		120N + 32P		Mean
	Liquid	Solid	Liquid	Solid	Liquid	Solid	
Mixing	11.1	12.8	10.8	14.9	5.1	15.1	11.6
Injection	10.9	8.8	11.6	13.4	0	14.9	9.9
Irrigation	11.6	12.4	13.1	11.6	9.8	10.1	11.4
Foliar spray	9.3	10.8	8.6	12.6	0.2	14.1	6.9
Mean	10.7	11.2	11.0	13.1	3.8	13.5	
Control (unfertilized)	9.8						

C.D. 5%

Type of fertilizer x dosage of fertilizer = 1.5

Type of fertilizer x method of application = 1.7

ii). Wheat straw yield. Straw yields were comparable at 30N + 8P and 60N + 16P for both liquid and solid fertilizers. Among methods of application foliar spray was highly detrimental.

Table 11. Effect of Fertilizer Dosage and Method of Application on the Dry Weight of Straw (grams/pot) of Wheat Grown in Pots Containing Dehradun Soil.

Method of Application	FERTILIZER DOSAGE 30N + 8P Liquid	 Solid	 60N + 16P Liquid	 Solid	 120N + 32P Liquid	 Solid	Mean
Mixing	24.7	18.6	17.0	15.7	15.1	21.2	18.7
Injection	23.4	24.7	16.1	28.2	8.3	26.7	21.2
Irrigation	17.7	20.9	16.6	20.1	11.4	17.9	17.4
Foliar spray	14.4	16.9	14.4	13.4	7.6	17.2	14.0
Mean	20.1	20.3	16.0	19.4	10.6	20.8	
Control (unfertilized)	15.6						

C.D. 5%
Type of fertilizer x dosage of fertilizer = 2.7
Type of fertilizer x method of application = 3.1

C. Pot Experiments with Spring Maize

Only dry weight of straw was taken into consideration to evaluate plant growth. Foliar spray treatment was discontinued based on the experiences with the wheat pot experiments.

There was no significant differences in methods of application. At the lowest concentration (30N + 8P) liquid fertilizer appeared to be equal to or better than solid fertilizers and both fertilizers resulted in higher dry matter yield than unfertilized controls. The straw yields were better at higher concentrations of solid fertilizers.

Table 12. Effect of Fertilizer Dosage and Method of Application on the Dry Weight (grams/pot) of Straw of Maize Grown in Pots Containing Pantnagar Soil.

Method of Application	FERTILIZER DOSAGE 30N + 8P Liquid	30N + 8P Solid	60N + 16P Liquid	60N + 16P Solid	120N + 32P Liquid	120N + 32P Solid	Mean
Mixing	24.3	24.3	22.3	26.3	17.3	28.7	19.1
Injection	23.0	20.0	20.7	23.7	17.3	28.7	22.2
Irrigation I	22.3	22.0	17.3	27.7	15.0	31.7	22.7
Irrigation II	22.3	21.7	19.3	26.0	20.3	30.7	23.4
Mean	23.0	22.0	19.9	25.9	17.5	30.0	
Control (unfertilized)	13.33						

C.D. 5%
Type of fertilizer x dosage of fertilizer = 2.9
type of fertilizer x method of application = 2.9

III. FIELD EXPERIMENTS WITH SPRING MAIZE

i) Plant population. In furrow application because the seeds are in close proximity with the liquid fertilizer poor germination resulting in poor population sizes were noticed. However, mixing and side application resulted in good germination and even with increase in concentrations of liquid fertilizer seed germination was not effected.

Table 13. Effect of Fertilizer dosage and method and of Application on the Plant Population of Maize Grown in Field Plots at Pantnagar.

Method of Application	FERTILIZER DOSAGE* 40N + 20P Liquid	40N + 20P Solid	80N + 40P Liquid	80N + 40P Solid	120N + 60P Liquid	120N + 60P Solid	Mean
Mixing	70.7	71.3	65.3	76.3	53.4	82.0	69.8
Furrow	60.3	70.7	27.3	65.0	7.3	55.0	47.6
Side	83.7	74.0	70.1	81.0	70.3	80.3	76.6
Mean	71.6	72.0	54.2	74.1	43.7	72.4	
Control (unfertilized)	64.7						

*See Experimental Methods

C.D. 5%
Type of fertilizer x dosage of fertilizer = 10.7
Type of fertilizer x methods of application = 10.7

ii) <u>Stover yield</u>. Stover yields in fertilizer treatments were significantly higher in comparison to unfertilized plots. Unfertilized plots (not receiving N and P) showed symptoms of N and P deficiency (Figs. 3, 4). Despite irrigation, extreme hot conditions prevailing curtailed the plant growth in general, though treatment differences and patterns are evident. Both mixing and side application of liquid fertilizer showed good stover fields (Figs. 5-8). Liquid fertilizer at the lowest dose (40N + 20P) gave yields equivalent to solid fertilizer at the highest dose (120N + 60P). At 80N + 40P dose both fertilizers showed equal dry weights using mixing and side application (Fig. 9). Furrow application resulted in better dry matter yield for solid fertilizer (Fig. 10).

Table 14. Effect of Fertilizer Dosage and Method of Application on the Stover Yield (Kg/ha) of Maize Grown in Field Plots at Pantnagar.

	FERTILIZER DOSAGE						
Method of Application	40N + 20P		80N + 40P		120N + 60P		Mean
	Liquid	Solid	Liquid	Solid	Liquid	Solid	
Mixing	1183	780	1153	1030	770	1120	1006
Furrow	500	620	373	760	350	850	576
Side	1040	800	1120	1040	850	1050	983
Mean	908	733	882	943	657	1007	
Control (unfertilized)	710						

C.D. 5%
Type of fertilizer x dosage of fertilizer = 2.11
Type of fertilizer x method of application = 2.11

DISCUSSION OF RESULTS

The nitrophos solution resulting from the arc generator process described in the previous section is an acidic solution with pH of 0.5 to 0.7. Small pot experiments with maize and wheat using soils from Dehradun and Pantnagar have clearly demonstrated that at optimal fertilizer dose requirement for plant growth, using liquid fertilizer presented no problems as seen from seed germination, shoot and root growth data. The above neutral soils of Dehradun and Pantnagar seem to have adequate buffering capacity.

The large pot experiments conducted with wheat using Dehradun and Pantnagar soils were basically designed to give some base data for field experimentation regarding methods of application and dose responses. The frequent water logging of pots due to heavy non-seasonal rains did not reveal any clear differences between methods. The foliar spray method was discontinued in further experiments because of the poor crop growth. Overall, lower doses of liquid fertilizer were as effective as solid fertilizers in all the plant growth parameters studied.

Adequate precautions were taken to prevent water logging in subsequent pot experiments conducted with maize. Liquid fertilizer at two lower dosage levels gave significantly higher yields compared to unfertilized controls. Data from maize pot experiments was, however, not conclusive enough to focus on a particular method of application for field experimentation.

The emphasis in the field experiment with maize was placed on comparing the three methods of application at three levels of fertilizer dosage. Mixing and side application were found to be the best methods. Liquid fertilizer at the dosage level of 40N + 20P gave stover yields equivalent to 120N + 60P of solid fertilizer with both mixing and side methods of application indicating that liquid fertilizers are more readily available for plant growth.

Thus, based on pot and field experiments, it can be concluded that the liquid nitro-phos fertilizer at lower dosage levels is equally effective as solid fertilizers in neutral and above neutral soils of Dehradun and Pantnagar.

LIMITATIONS OF THE PRESENT EXPERIMENTATION AND AND THE NEED FOR FURTHER AGRONOMIC EVALUATION

I. Planting Season

The project schedule did not match very well with the planting season in India and therefore led to conduction of unseasonal pot and field experiments, further limited by single season experimentation. The pot trials with wheat were affected by unusual heavy rains and consequent water logging. The field trials conducted with spring maize were subjected to a serious hot, dry spell with highest temperatures recorded in India since the last two decades. The plots were irrigated twice a week and despite irrigation severe environmental conditions curtailed plant growth as seen from the poor stover yields and very low grain yield (not presented). Nevertheless, treatment differences were significant and some trends in methods of application and fertilizer dosages were clear.

II. Product Concentration

Until the equilibrium is reached, the concentration of the product from the electric arc process is variable, the concentration building up as the number of hours of operation increase and as a result of this lower N and P levels are frequently seen in the initial batches of fertilizer produced. This is particularly true when low grade Mussoorie rock phosphate is used in the absorption column. High level of calcium carbonate present in the Mussoorie rock phosphate is first consumed by acid produced by the arc generator before phosphorus in the rock begins to dissolve (Tables 15, 16).

Pot experiments were conducted at the University of Agricultural Sciences at Pantnagar from the first batch of fertilizer produced at the unit site in Sirki Village. The analysis at this university consistently read the nitrogen values at 8g N/litre of solution. However, as seen from Table 15, subsequent batches of fertilizer produced at Sirki and analysed by hand-held Hack colorimeter, gave four times the values reported at Pantnagar. Three batches of fertilizer produced at Sirki were independently analyzed at three different laboratories in the USA (Table 17) and show trends similar to that seen in Table 15.

Table 15. Analysis of Nitrogen Content in the Fertilizer Solution before the State of Equilibrium has been Achieved, as Determined at Sirki Using a Hand-Held Hack Colorimeter.

Sample No.	No. of hours run (cumulative)	Nitrogen (grams/litre)
1	64	4.25
2	195	19.00
3	256	42.00
4	447	62.50

Table 16. Analysis of Nitrogen Content in the Fertilizer Solution After the State of Equilibrium has been Achieved as Determined at Sirki using a Hand-Held Hack Colorimeter.

Sample No.	No. of hours run (cumulative)	Nitrogen (grams/litre)
1	270	40
2	230	40
3	225	42
4	248	43
5	245	42

Table 17. Comparison of Analysis for Nitrogen (grams N/litre) at Three Different Laboratories in the USA of Three Batches of Fertilizer Produced at Unit Site at Sirki before the State of Equilibrium is Attained.

Batch	Kettering	Ohio Dept. of Agric.	IFDC
1	40.6	43.2	42.9
2	29.9	29.8	29.7
3	24.1	27.5	25.7

The initial batches of fertilizer with low nitrogen content provided to Pantnagar for pot and field experimentation has led to extensive application of the acidic calcium nitrate phosphate liquid fertilizer to meet the N and P dosage required for basal application. This may explain the lower yields at higher dosage of liquid fertilizer in large pot experiments due possibly to extensive acidity. An additional point in support of the concentration problem is the data for stover yield of maize. Liquid fertilizer at 40N + 20P and 80N + 40P level yielded equivalent to that of solid fertilizer at 120N + 60P.

Clearly, these descrepancies prove the point for further experimentation. Based on the observations and the experiences during the first season experimentation it is recommended:

1) All batches of liquid fertilizer be bulked to maintain a uniform concentration of fertilizer. The concentration of N and P levels in the liquid fertilizer should be analyzed at 2-3 agricultural research institutions in order to confirm the values and based on these values to ensure that the plants receive precise and comparable doses of liquid and solid fertilizers.

2) The severe drought and high temperature conditions existing during field experimentation with spring maize were unusual for realizing the normal yield of maize. In order to establish the agronomic effectiveness of the liquid fertilizer and confirm the method of application recommended in this report, at least two more field experiments should be conducted on two different locations during a regular cropping season.

SUMMARY AND CONCLUSIONS

Calcium nitrate-phosphate liquid fertilizer is produced by using the Kettering arc generator fertilizer production system and Mussoorie rock phosphate. The process dynamics and the on-site performance of the generator in India are described in the technology report. The agronomic effectiveness of the fertilizer produced has been studied by conducting pot and field trials at the G.B. Pant University of Agriculture and Technology, Pantnagar (U.P.), India. The objective of this study was to evaluate agronomic effectiveness of calcium nitrate-phosphate liquid fertilizer by comparing it with the solid fertilizers such as urea (as N source) and triple superphosphate (as P source) commonly used by Indian farmers, and recommend suitable methods of application appropriate to Indian farming practices.

Wheat and maize crops, in two different soils (Pantnagar and Dehradun), at three dosage levels and four methods of application were studied in pot trials. A field trial was conducted with spring maize using three levels of fertilizer doses and three methods of application. Solid and liquid fertilizers were compared except in small pot experiments.

Calcium nitrate-phosphate liquid fertilizer produced by the Kettering process is acidic with a pH of 0.5-0.7. Small pot experiments were designed to study the i) effects of acidity ii) and the effects of fertilizer on plant growth. These experiments have clearly demonstrated that in both wheat and maize, using liquid fertilizer presented no problems for plant growth as seen from the seed germination, shoot and root growth data up to a concentration of 0.25% of liquid fertilizer on a soil weight basis corresponding to 100 Kg N and 50 Kg of P_2O_5/ha. Shoot and root growth, as well as the plant height, improved in maize at this concentration, compared to unfertilized control pots. In maize a decline in plant growth was noticed above 0.5% concentration and acid toxicity symptoms were seviour at 1%. However, wheat plants showed improvement in growth up to a concentration of 1% and acid symptoms appeared only above 2% concentration, suggesting that wheat is tolerant to acidity to a much higher degree than maize. The above neutral soils from Dehradun and Pantnagar appear to have sufficient buffering capacity as evidenced by elevation of soil pH during twenty-five days of the experimental period, especially at concentrations above 0.5%. The observations suggest that the application of optimal doses of calcium nitrate-phosphate solution of pH 0.5-0.7, may not alter the soil pH or even effect maize and wheat growth. However, properly designed, long term field experiments should be conducted to evaluate the impact of application year after year of large quantities of acid solution as a fertilizer source on shifts in soil pH, nutrient balance as well as crop yields.

Large pot experimental data with wheat showed that the lower doses of liquid fertilizer were as effective as the solid fertilizer for all plant growth parameters studied. Foliar spray of liquid fertilizer appeared to be quite toxic to leaves, particularly at the highest dose. Large pot experiments with maize showed that liquid fertilizer was as effective as solid fertilizer at the two lower levels of dosage used.

Three application methods were compared at three levels of fertilizer in field trials conducted with spring maize. Mixing and side application were found to be the best methods for liquid fertilizer application. Furrow application of liquid fertilizer resulted in poor seed germination, resulting in fewer plants and considerably reduced yields. Liquid fertilizer at 40N + 20P and 80N + 40P gave stover yields equivalent to that of solid fertilizer at 120N + 60P indicating that liquid fertilizers are more readily available for plant growth.

There were a number of limitations for this experimentation, chief among which are the i) unseasonal plantings for pot and field trials imposed by the tight project schedule and, ii) product concentration problems. It is recommended that all batches of liquid fertilizer be bulked to achieve uniform product concentration, to ensure that plants receive precise doses of N and P in the field experiments. As in any fertilizer evaluation trials, more than one season field trials are necessary to arrive at definite conclusions and make definite recommendations.

Fig. 1A-C. Wheat plants grown in pots receiving 0 (A), 0.25 (B) and 0.5% (C) of liquid calcium nitrate phosphate solution on a soil weight basis. Two pots on the right hand side contain soil from Pantnagar and two on the left soil from Dehradun. Note the improved plant growth in 0.25 and 0.5%.

Fig. 2A-C. Maize plants grown in pots receiving 0 (A), 0.25 (B) and 0.5% (C) of liquid calcium nitrate phosphate solution on a soil weight basis. Two pots on the right hand side contain soil from Pantnagar and two on the left soil from Dehradun. Note the improved plant growth in 0.25 and 0.5%.

Fig. 3. (above) PPCL, BCFKRL and Pantnagar University scientists examining the crop response to liquid calcium nitrate phosphate fertilizer. Note the symptoms of N and P deficiency (small plants yellow in color) in the maize crop in the unfertilized control plots.

Fig. 4. (right) Unfertilized control plots show nitrogen deficiency symptoms.

Fig. 5. (right) A plot showing liquid fertilizer applied by mixing method at a dosage level of 40 KgN and 20 Kg of P_2O_5 (/ha). Notice that the plants are showing greener and more vigorous plants than unfertilized controls.

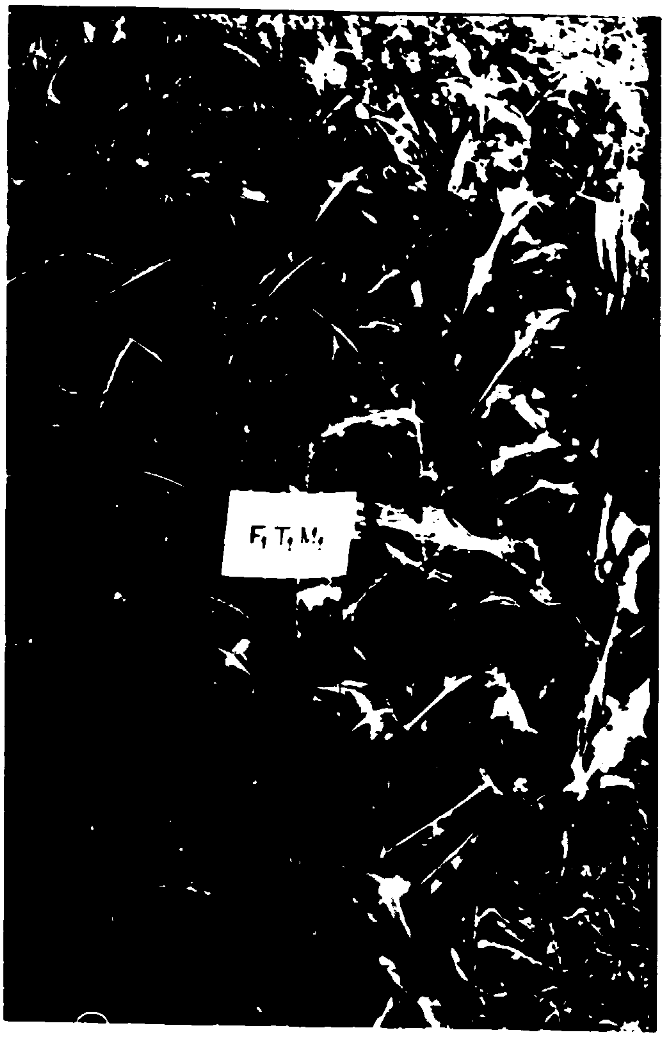


Fig. 6. (below) Same dose of liquid fertilizer but using side application method, also showing more greener and vigorous plants.

Figs. 7 and 8. Both the mixing (Fig. 7) and side application methods (Fig. 8) show good plant growth response at 120 KgN + 60 Kg P_2O_5 (/ha) of liquid fertilizer.

Fig. 9. (right) Urea and triple superphosphate (solid fertilizer) at 80 KgN + 40 Kg P_2O_5 (/ha) level using side application method. The plant growth is similar to liquid fertilizer at same dose and method of application (figure not shown).

Fig. 10. (below) Urea and triple superphosphate at 120 KgN + 60 Kg P_2O_5 (/ha) level using furrow placement method. Liquid fertilizer application using this method retarded germination resulting in poor plant populations (picture not shown).

APPENDIX A

ANALYTICAL PROCEDURES

ANALYTICAL TECHNIQUES

Phosphorus -

The HACH PhosVer III Phosphate Reagent Method was used for all phosphorus assays made for this study. This test is used in determining orthophosphate or "reactive" phosphorus in solution. It is a modification of the molybdenum blue procedure with all reagent combined in a single powder pillow. The sample unknown is diluted an appropriate amount with demineralized water after which an aliquot is taken and mixed with the reagent from a PhosVer III powder pillow. The acidic ammonium molybdate reacts with orthophosphate to produce a yellow phosphomolybdate complex. Ascorbic acid then reduces the complex giving an intense molybdenum blue color. This color is measured spectrophotometrically using a 1 cm cell at 700 nm. The PO_4^{-3} concentration is then determined from a calibration curve which relates absorbance with PO_4^{3-} concentration. A sample calibration is given below using a Cary model 118 spectrophotometer.

ASSAY FOR PHOSPHORUS AS PO_4^{3-}, USING THE HACH PHOS VER III PHOSPHATE REAGENT.

1. Preparation of Standard PO_4^{3-} Solution.

   a. KH_2PO_4 (FW 136.09) dried overnight at 100°C.

   b. Solution containing 143.2 mg KH_2PO_4/liter of water made up. This solution contains 100 mg/l PO_4^{3-}.

   c. The 100 mg/l solution was diluted 50 ml to 1000 ml to give a 5 mg/l PO_4^{3-} solution.

   NOTE: All glassware should be acid washed with 1-2 M HCl before starting the experiments.

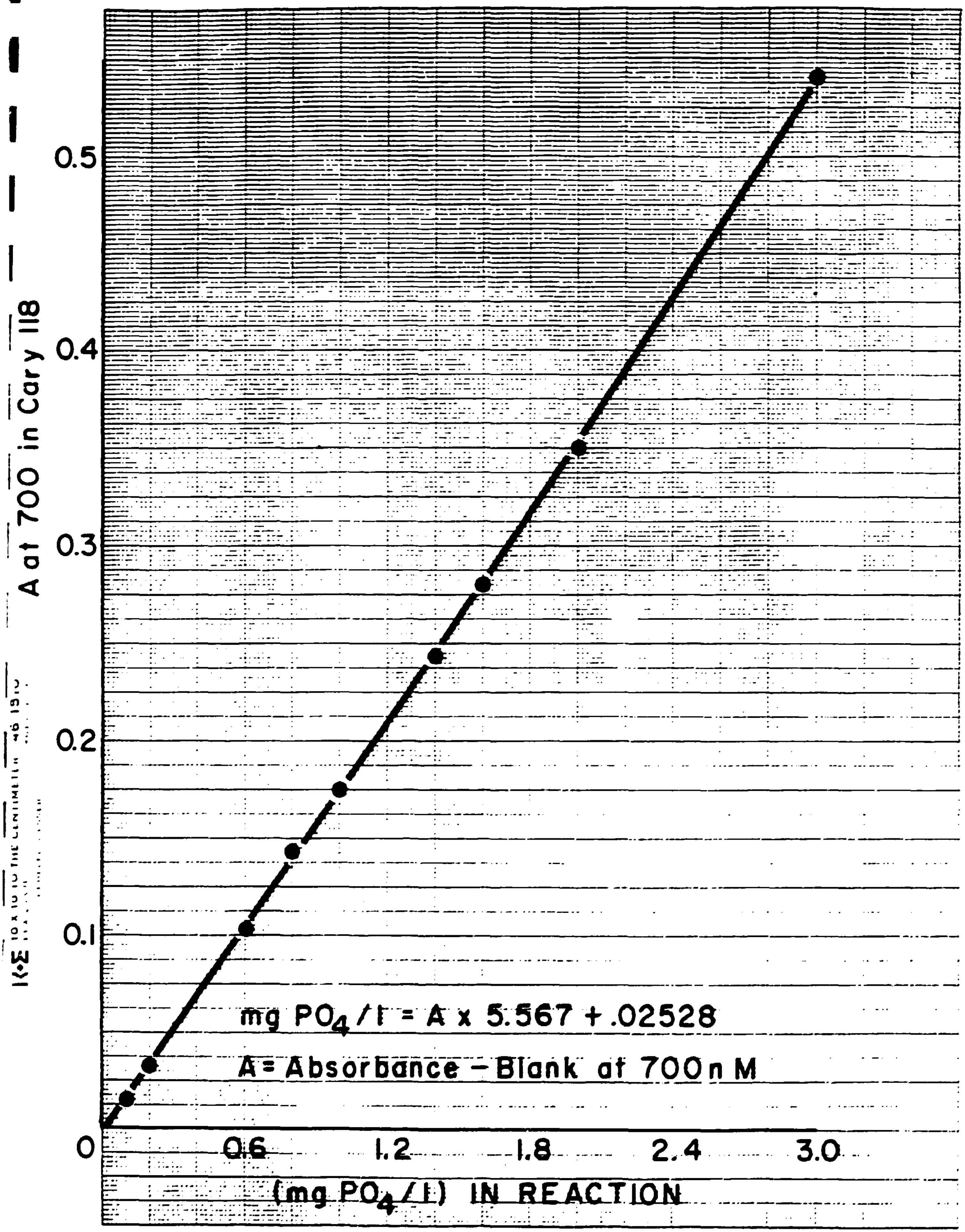
2. Standard Curve.

   Solution was appropriately diluted (see Table) to 25 ml with water. The Phos Ver III pillow (25 ml size) was added to sample, shaken to dissolve and allowed to stand for five min. Absorbance then read using a 1 cm cell in Cary 118 at 700 nm.

   Data plotted on Graph, which includes a least-squares fit.

Table. Standard PO_4^{3-} curve (25 ml pillows).

#	PO_4^{3-} (ml)	H_2O	PO_4^{3-} (mg/l)	A700	AVG.A	Corrected A-BLANK A700
1	-	25	0	0.035	0.0355	-
2	-	25	0	0.036		
3	0.5	24.5	0.1	0.051	0.049	0.0135
4	0.5	24.5	0.1	0.050		
5	0.5	24.5	0.1	0.047		
6	1.0	24	0.2	0.070	0.068	0.0325
7	1.0	24	0.2	0.068		
8	1.0	24	0.2	0.067		
9	3.0	22	0.6	0.138	0.140	0.105
10	3.0	22	0.6	0.140		
11	3.0	22	0.6	0.142		
12	4.0	21	0.8	0.180	0.177	0.142
13	4.0	21	0.8	0.174		
14	4.0	21	0.8	0.176		
15	5.0	20	1.0	0.211	0.210	0.175
16	5.0	20	1.0	0.209		
17	5.0	20	1.0	0.211		
18	7.0	18	1.4	0.280	0.279	0.244
19	7.0	18	1.4	0.277		
20	7.0	18	1.4	0.279		
21	8.0	17	1.6	0.317	0.316	0.280
22	8.0	17	1.6	0.315		
23	8.0	17	1.6	0.315		
24	10.0	15	2.0	0.386	0.385	0.350
25	10.0	15	2.0	0.385		
26	10.0	15	2.0	0.384		
27	15.0	10	3.0	0.580	0.574	0.539
28	15.0	10	3.0	0.578		
29	15.0	10	3.0	0.565		


A at 700 in Cary 118
0.5
0.4
0.3
0.2
0.1
0
0.6
1.2
1.8
2.4
3.0
(mg PO4 / l) IN REACTION
mg PO4 / l = A x 5.567 + .02528
A = Absorbance − Blank at 700 n M
K•E 10 X 10 TO THE CENTIMETER 46 1510

Nitrogen -

Two methods of nitrogen determination were used during this study. The first is a modification of the cadmium reduction method using gentisic acid in place of 1-naphthylamine. All the reagents have been combined into a single powder called NitraVer V Nitrate reagent. The test registers both nitrates and nitrites in solution. The test is susceptible to interference from ferrous ions in concentration of 1mg/L or greater (see following test report). For samples containing more than this amount of iron a chemiluminescent nitrogen determination was used. For this second technique, samples were diluted appropriately with demineralized water and microliter quantities were injected into an Antek model 720 Digital Nitrogen Analyzer. In this technique the injected samples are pyrolyzed in oxygen at 1000°C to form NO which in turn reacts with ozone in a reaction which gives off light. The quantity of light given off is then proportional to the amount of nitrogen in the sample. This technique registers all forms of nitrogen (except N_2).

NITRATE ANALYSIS BY THE HACH NITRO VER V REAGENT EFFECTS OF ADDED IRON AND THE CHELATING AGENT Na_2EDTA.

1. Reagent Used

(a). Stock KNO_3 solution - 10.1178 gm KNO_3/l (pH 6.6), equivalent to 1401 mg/l N. A 1/10 dilution in demineralized water of this stock solution was used for all assays.

(b). Stock Fe solution - 114.712 mg Fe/l (≡ 0.002 M) made up, using stock of Fe wire dissolved in HCl, in demineralized water.

(c). EDTA solution - 0.002 M solution of Na_2 salt, made up using 0.336 gm EDTA (disodium salt) in 500 ml of demineralized water.

2. Procedure Used

All reactants were added to 10 ml Hach cell, followed by the Nitro Ver V pillow contents. The mixture was mixed with a Vortex mixer for 1 min. The sample was allowed to stand for exactly 5 min. and readings were taken on both the Hach DR-100 colorimeter and the Cary 118C at 500 nm. It was determined that, after 5 min., the readings were stable for at least an additional 5 min.

The order of addition of reagents was as follows:

1st-NO_3^- solution
2nd-Fe (if used)
3rd EDTA (if used)
4th-Water to a total volume of 10 ml.
5th-Nitro Ver V pillow contents.

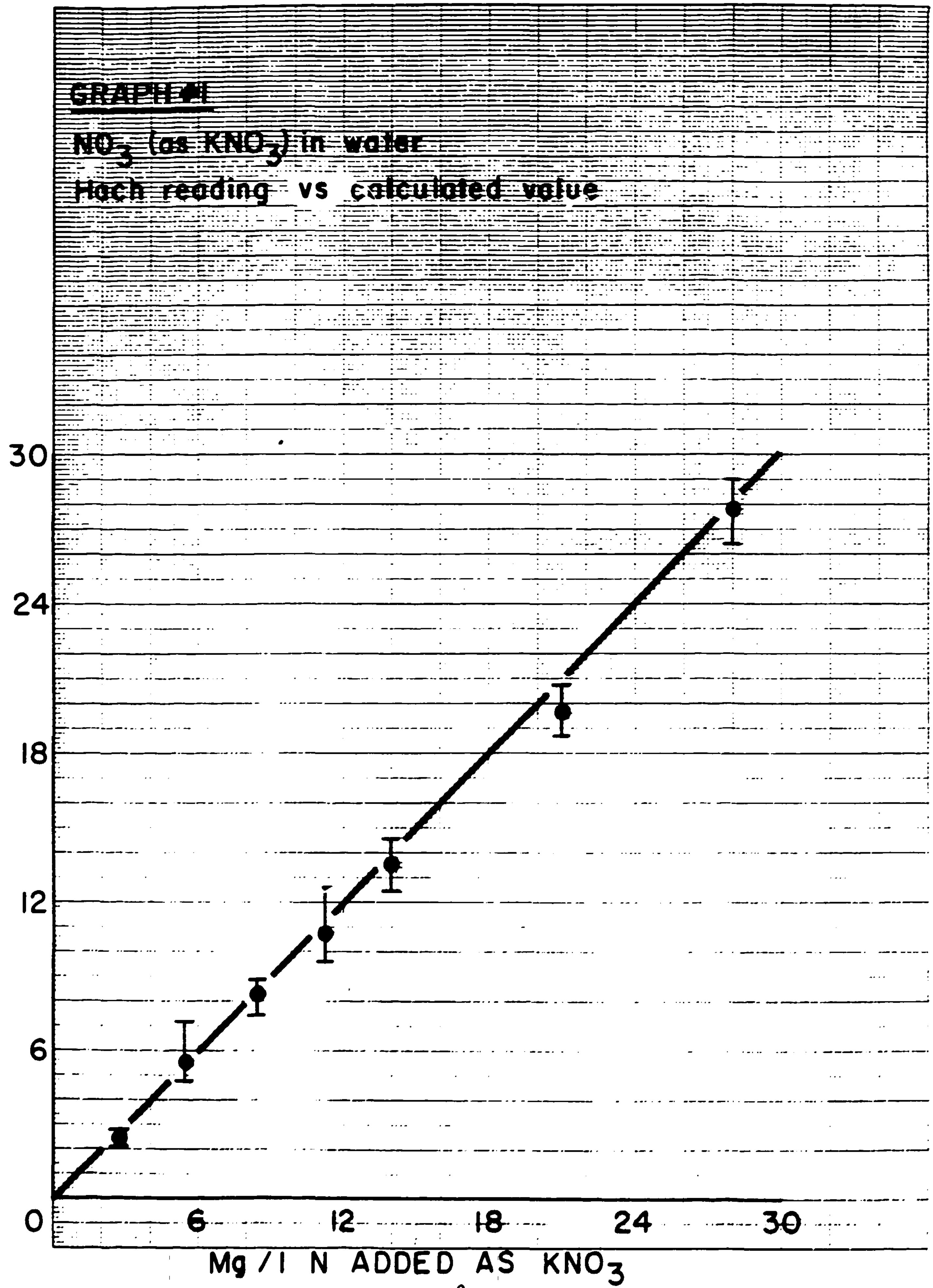
3. Comparison of Hach and Cary Values Using the Standard Nitrate Solution.

This experiment attempted to determine if the Hach colorimeter would give reproducible and accurate results. A blank containing no nitrate was run using only 10 ml of H_2O + Nitro Ver V reagent as described above. This blank gave a 1.5 mg/l N reading on the Hach scale and an A(500) of 0.068 on the Cary 118C. This background value was very reproducible and has been subtracted from all of the measurements listed in the following Table (#1).

TABLE 1

Sample #	NO$_3^-$ Sol. (ml)	A(500)	(mg/l N) Hach	Avg. Hach	Calc (mg/l N)
1	0.2	.024	2.3	2.33	2.8
2	0.2	.030	2.5		
3	0.2	.020	2.2		
4	0.4	.085	7.1	5.67	5.6
5	0.4	.051	4.9		
6	0.4	.054	5.0		
7	0.6	.079	7.5	8.15	8.4
8	0.6		8.8		
9	0.8	.104	10.7	10.8	11.2
10	0.8	.107	12.5		
11	0.8	.103	10.4		
12	0.8	.106	9.6		
13	1.0	.121	14.5	13.7	14
14	1.0	.137	14.5		
15	1.0	.125	12.3		
16	1.0	.120	14.5		
17	1.0	.152	12.7		
18	1.5	.156	20.7	19.67	21
19	1.5	.172	20.5		
20	1.5	.176	18.5		
21	1.5	.169	19.0		
22	2.0	.213	26.5	27.88	28
23	2.0	.216	27.5		
24	2.0	.218	28.5		
25	2.0		29.0		

The results are plotted in Graph # 1.


GRAPH #1
NO3 (as KNO3) in water
Hach reading vs calculated value
30
24
18
12
6
0
6
12
18
24
30
Mg / l N ADDED AS KNO3

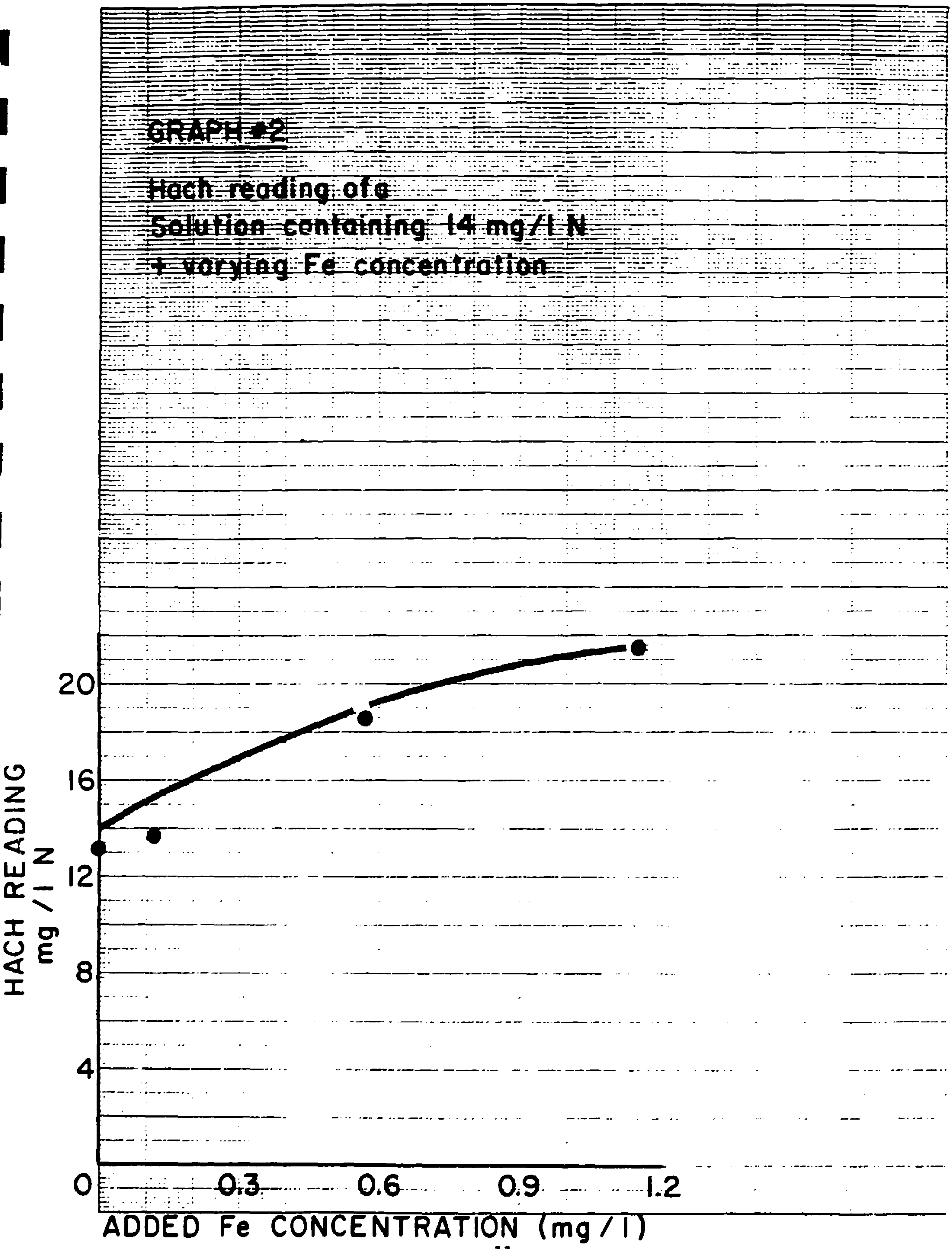
4. Effect of Added Fe on NO_3^- Assay by Hach Method.

Each reaction contained 14 mg/l N (1.0 ml KNO_3 solution) plus varying amounts of the stock Fe solution. From this data in Table # 2 and Graph # 2, it seems that Fe at 0.57 mg/l or greater affects the Hach analysis for NO_3^-.

TABLE # 2

#	KNO_3 (mg/ l N)	Fe (mg/l)	A500	Hach (mg/l N)	Avg. Hach (mg/l N)
1	0	0	.067	1.3	12.9
2	14	-	.188	12.0 *	
3	14	-	.188	13.8 *	
4	14	11.4	.345	>30	> 30.0
5	14	1.14	.219	20.0 *	20.5
6	14	1.14	.223	21.0 *	
7	14	0.57	.216	19.0 *	18.75
8	14	0.57	.218	18.5 *	
9	14	0.114	.185	13.0 *	13.5
10	14	0.114	.183	14.0 *	

* These values have been corrected for the 1.3 mg/l N in the blank.



GRAPH #2

Hach reading of a
Solution containing 14 mg/l N
+ varying Fe concentration

5. Relief of the Effect by EDTA and Effect of EDTA alone.

This experiment attempts to complex the Fe with EDTA, so that the interference by Fe in the Hach-NO_3^- reaction is minimized. The added Fe concentration was 1.1 mg/l, at least twice the concentration shown to influence the Hach reading in Section 4 above. The solutions of Fe and EDTA are both 0.002 M. The NO_3^- content is 14 mg/l in all reactions in these 3 sets of experiments.

TABLE 3

Sample #	KNO_3 (mg/l N)	Fe (mg/l)	EDTA (ml)	EDTA/Fe ratio	A500	Hach (mg/l N)	
1	14	0	0		.186	12.4	12.6
2	14	0	0		.191	12.4	
3	14	0	0		.191	13.0	
4	14	1.1	0		.230	18.0	18.5
5	14	1.1	0		.228	19.0	
6	14	1.1	0.1	1:1	.204	15.0	15.5
7	14	1.1	0.1	1:1	.216	16.0	
8	14	1.1	0.5	5:1	.190	12.5	12.75
9	14	1.1	0.5	5:1	.188	13.0	
10	14	1.1	1.0	10:1	.158	8.0	8.5
11	14	1.1	1.0	10:1	.150	9.0	
12	14	0	0		.193	13.5	
13	14	1.1	0		.232	17.9	
14	14	1.1	0.1	1:1	.214	16.0	
15	14	1.1	0.5	5:1	.196	14.0	
16	14	1.1	1.0	10:1	.157	7.8	
17	14	1.1	0.5	5:1	.192	13.0	
18	14	0	0.5		.194	13.8	
19	0	0	0		.063	1.5	

The results of these experiments indicate:

(a). that, at levels of Fe equal to about 1 mg/l, its effect on the Hach nitrate test can be eliminated completely by adding 5 equivalents of EDTA for each equivalent of Fe, i.e., 5-times the Fe concentration is 1 X 10^{-4} M EDTA in these experiments (see # 1-11 and # 12-16);

(b). that EDTA at these levels has no effect on the nitrate test (see # 17-19); and

(c). that EDTA levels of 10-times the Fe concentration, i.e., 2 X 10^{-4} M EDTA concentration, do affect the nitrate results with the EDTA possibly complexing some of the cadmium in the Nitro V reagent.

6. Conclusions

(a). An Fe analysis is in order before running the nitrate test. If iron is present, the sample should be diluted so that the iron concentration is 1 mg/l or less, then EDTA should be added to 5-times the molar concentration of the iron. If the iron level is appreciably higher, additional experiments need to be run to determine the effect of increased levels of EDTA relative to Nitro Ver V reagent.

(b). The color reagents should be mixed vigorously for exactly one minute using a Vortex mixer.

(c). The color development should be for 5 minutes, then the sample read in the Hach colorimeter.

(d). A blank of distilled water plus one Nitro Ver V pillow should be run and this value should be substracted from each reading.

(e). The round 10 ml cells from Hach seem to give a slightly different readings, depending on which way they are placed in the colorimeter.

HACH TOTAL IRON ASSAY (FERRO VER REAGENT).

1. Standard Curve.

A solution containing 114.712 mg/l Fe (iron wire in HCL) was diluted 17.35 ml to 1 L to give a solution containing 2 mg/l Fe (pH 3.3). All reactions contained standard Fe solution diluted to a total of 10 ml with demineralized water. Ferro Ver reagent added and mixed by shaking.

Sample #	Vol. Std. (ml)	Calculated (mg/l)	Hach Reading	A510 Cary 118	Corrected A (A510-Blank)
1	10	2.0	2.0	0.494	0.426
* 2	10	2.0	2.0		
3	8	1.6	1.61	0.431	0.363
* 4	8	1.6	1.60		
5	6	1.2	1.21	0.358	0.290
* 6	6	1.2	1.21		
7	4	0.8	.79	0.239	0.171
* 8	4	0.8	.80		
9	2	0.4	.40	0.145	0.077
* 10	2	0.4	.42		
11	1	0.2	.24	0.117	0.049
* 12	1	0.2	.23		
13	0.5	0.1	.13	0.091	0.023
* 14	0.5	0.1	.15		
15	0	0	.03	0.068	--

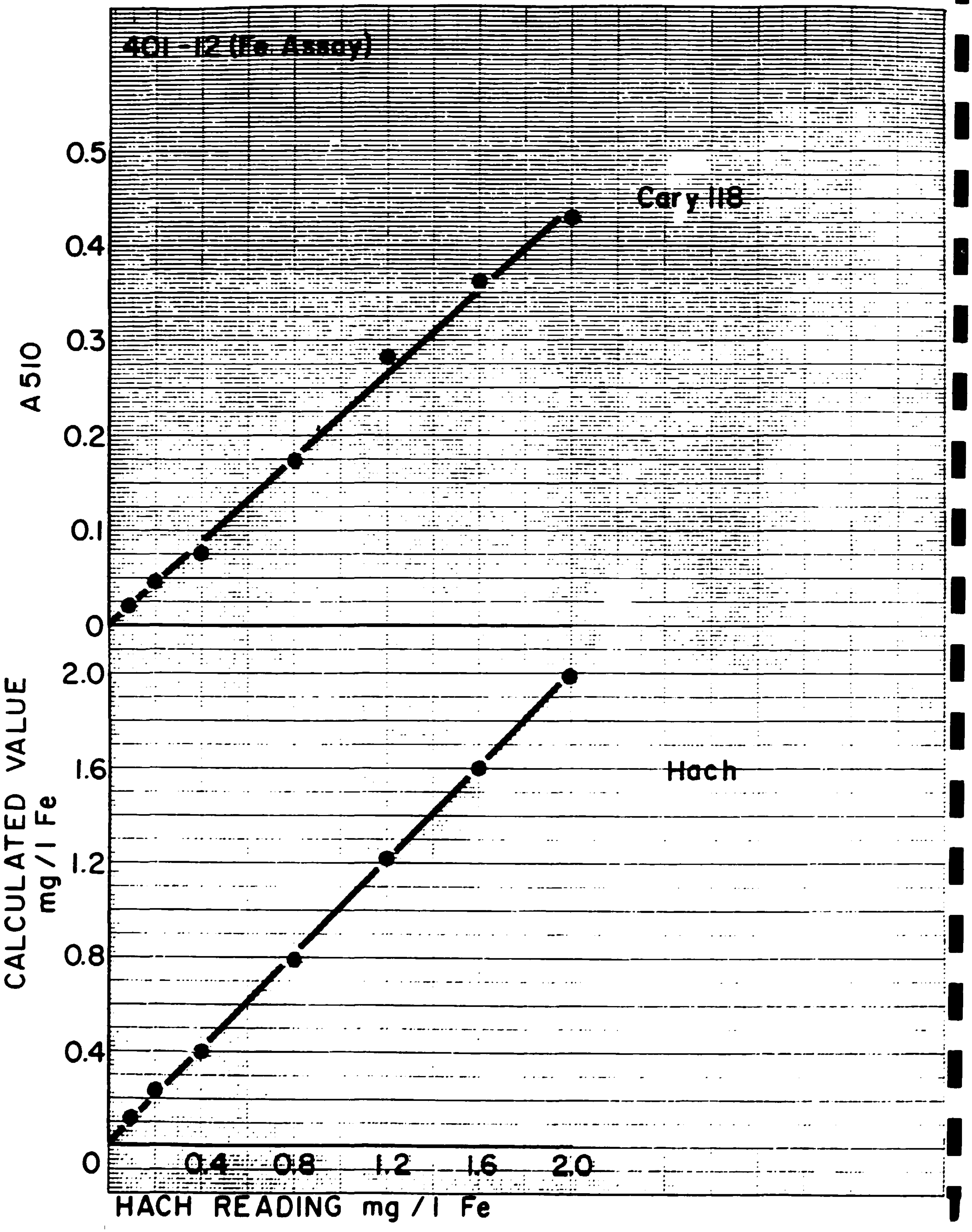
* The even number samples were not new samples but were the same samples read after ca. 30 min. Samples were read on Hach, then Cary 118, then Hach again to determine if color was stable. Color was stable from 3 to 30 min.

2. Other Observations.

(a). It was found that the pH could be as low as 3.3, but not significantly lower to give an accurate reading on the samples.

(b). The samples from the reactor must be diluted 1 to 100 or a precipitate will form when adjusting the pH to 3.

(c). This pH adjustment is very important, because a sample at pH 2.2 gave only about 50% of the iron concentration (56 vs 110 mg/l) determined at pH 3.3.


401-12 (Fe Assay)
Cary 118
Hach
A 510
0.5
0.4
0.3
0.2
0.1
0
CALCULATED VALUE mg / l Fe
2.0
1.6
1.2
0.8
0.4
0
0.4
0.8
1.2
1.6
2.0
HACH READING mg / l Fe

APPENDIX B

Preliminary Tests on Mussoorie Rock Sample

Preliminary Tests On Mussoorie Rock Sample

Donald R. Moles
Charles F. Kettering Research Laboratory
Yellow Springs, Ohio 45387

September 15, 1982

This report outlines briefly the results of a preliminary solubility test on the 1 kg Mussoorie rock sample, sent to us by Pyrites, Phosphates and Chemicals Ltd.

PURPOSE:

The purpose of the experiment was twofold:

1. to determine if the phosphorus-containing Mussoorie rock could be solubilized with nitric acid,
2. to determine the yield of "reactive" (ortho-) phosphate per unit of nitrogen (as HNO_3) applied under the conditions described.

PROCEDURE:

To each of two 1000 ml flasks a 25.0 g sample of the ground Mussoorie rock was added along with 1000 ml distilled water. Each flask was equipped with a magnetic stir bar and mixed continuously over the course of the experiment.

To one of these flasks, the test flask, discrete additions of reagent grade nitric acid (70.5% HNO_3) were made; the other flask remained a control. After each acid addition orthophosphate concentration was monitored until the P levels stabilized. The stable P concentration then was logged as data along with its corresponding N level as calculated. Stepwise additions of acid continued until no further increase in P concentration was observed. Orthophosphate levels were determined colorimetrically at 700 nm via the ascorbic acid method. (APHA standard methods #223F, 13th ed., 1971.)

DATA/RESULTS:

The Mussoorie rock sample shipped to us contains, as stated on the label, 21.5% by weight the equivalent of P_2O_5. This translates into a phosphorus content of 9.38%. Thus for the 25.0 g sample size used in the experiment each flask was expected to contain 2.35 grams phosphorus. The control flask orthophosphate level remained very low over the two week course of the experiment, with P concentrations averaging less than 10 mg/liter and exhibiting no trend. Figure 1 is a graph of the data obtained from the test flask. It depicts the equilibrium orthophosphate levels obtained in response to step additions of nitric acid. Since the test flask volume changed only slightly with sample taking and acid additions, the gP/liter axis also reflects, approximately, the absolute solubilized phosphorus content (grams P). Equilibrium orthophosphate concentration in the test flask showed no increase after a total of 7.35 grams N had been added with a final absolute orthophosphate content of 2.5 grams (after volume correction). These values yield a final N/P ratio of 2.94:1.

DISCUSSION:

The shape of the curve in Figure 1 supports what might be expected from the acidulation process; that is, that initially acid neutralizing substances (CaO, Na_2O, MgO) are competing with the phosphorus containing compounds for the acid protons, thereby diminishing the amount of P solubilized per unit acid. The slopes of the lines below and above the 2 grams N point on the X axis represent N/P ratios of approximately 5:1 and 1.8:1, respectively.

The final value of phosphorus content in solution, 2.5 grams, is slightly higher than the 2.35 grams expected in the sample.

CONCLUSIONS:

Nitric acid can be used to solubilize phosphorus in Mussoorie rock. Furthermore, N/P ratios on the order of 3:1 may be expected under the conditions previously described.

Testing of the Mussoorie rock phosphate in an absorption column is necessary in order to determine its feasibility of use in the Kettering nitrogen/phosphorus fertilizer production system.

MUSSOORIE ROCK TEST

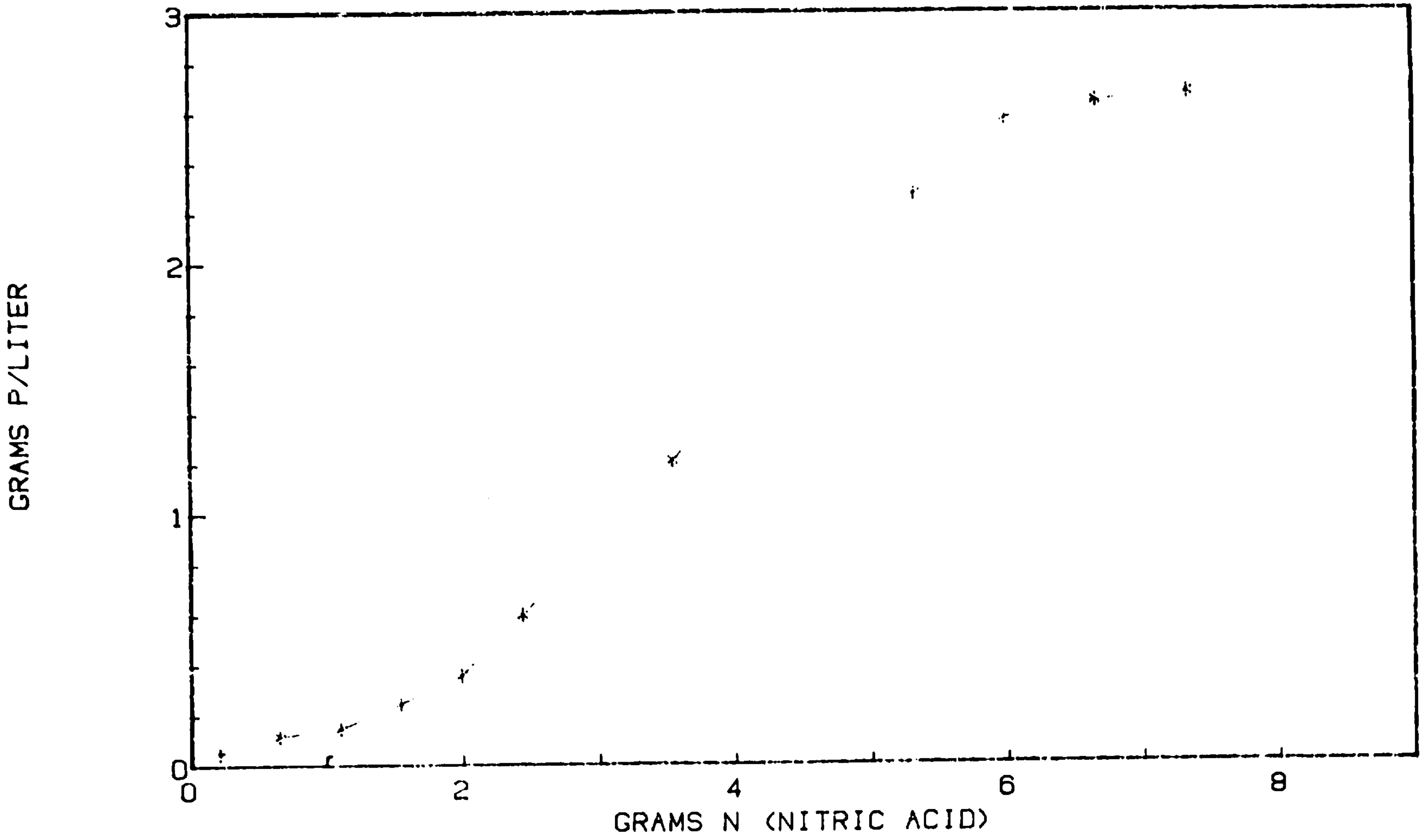


Figure 1

D.R.M. 9/10/82

APPENDIX C

KETTERING FERTILIZER PRODUCTION SYSTEM

CONSTRUCTION AND ASSEMBLY MANUAL

Kettering Fertilizer Production System

Construction and Assembly Manual

Charles F. Kettering Research Laboratory
150 East South College Street
Yellow Springs, Ohio 45387, U.S.A.

September 1983

Notice

Information concerning the Kettering fertilizer production system contained in this manual is the exclusive property of the Charles F. Kettering Research Laboratory (CFKRL) and may not be used without the expressed, written consent of CFKRL. Portions of the information contained in this manual are covered under U.S. Patents Nos. 4,010,897 and 4,256,967 with other patents, foreign and domestic, pending.

Safety Warning

Construction, assembly and use of the Kettering fertilizer production system involves certain safety risks. Construction should be attempted only by qualified personnel approved and trained by the Charles F. Kettering Research Laboratory (CFKRL). CFKRL assumes no liability involved in the construction, assembly or use of the Kettering fertilizer production system. Neither does CFKRL warrant the accuracy or adequacy of any information contained in this manual.

Kettering Fertilizer Production System

Introduction

The Kettering fertilizer production system has been developed by the Charles F. Kettering Research Laboratory (CFKRL) to produce fertilizer from renewable resources. Unlike present day commercial processes for fertilizer production, the Kettering process does not require natural gas or any other type of fossil fuel as a feedstock for the process.

In the Kettering fertilizer production system, air, water, a source of electrical power, and preferably, a neutralizing agent, such as limestone, are required as inputs to the process. Electrical power to drive the process may be obtained from any renewable energy source such as hydro-power, wind-power or solar energy; thereby circumventing the need for fossil fuel at any stage of the process.

This manual is prepared exclusively for the use of qualified technicians selected by CFKRL to expedite transfer of this technology - particularly to developing countries with limited fossil fuel reserves. Certain legal restrictions are involved with unauthorized use of this information. Also, safety factors must be considered when using this technology. Accordingly, written approval must be obtained from the Charles F. Kettering Research Laboratory before using any of the information contained in this manual.

Background

Present day commercial processes for the production of nitrogen fertilizer in the form of ammonia or derivatives of ammonia, like urea, require some type of fossil fuel as a source of hydrogen for the process. A widely used and efficient process for the production of nitrogen fertilizer, known as the Haber-Bosch (1) process, requires natural gas as a feedstock for the process. In addition to natural gas, the Haber-Bosch process requires high technology and large capital investment costs. Consequently, many nations, particularly developing countries lacking fossil fuel reserves, are dependent upon imported fertilizer to meet their needs.

In 1976, the Charles F. Kettering Research Laboratory started development of a process to produce nitrogen fertilizer from renewable resources. As a first step in the Kettering process, nitrogen oxides are produced in an electric arc discharge-in-air process. Basic reactions of the electric arc process are given by the following equations:

$$N_2 + O_2 \xrightarrow{\text{electric arc}} 2NO \qquad \Delta G = +41.4 \text{ Kcal/mol}$$

$$2NO + O_2 \longrightarrow 2NO_2 \qquad \Delta G = -16.6 \text{ Kcal/mol}$$

The formation of nitric oxide (NO), given by the first equation, occurs in nature during lightning discharges which can "fix" the inert nitrogen of air into an oxidized form of nitrogen usable in certain forms as fertilizer for plant life.

In the early part of this century, several types of systems were developed to produce nitrogen fertilizer using electric arc discharge processes (2-5). One of the most widely used electric arc process was a process known as a "vortex stabilized arc" process developed by Schönherr (6). All of these early electric arc processes, however, were abandoned when the Haber-Bosch process was developed based on abundant and then relatively inexpensive sources of natural gas as a feedstock for the production of fertilizer.

The Kettering process employs a modified form of a vortex-stabilized arc to produce nitrogen oxides and has been designed to meet the following objectives: 1) to produce fertilizer without the need for fossil fuel through the use of renewable resources and 2) to employ in the process technology appropriate for a developing country. The Kettering technology is adaptable to relatively small-scale applications and thus can be used to produce fertilizer at the site where needed. "On-site" production of fertilizer eliminates costs normally associated with the transportation and distribution of commercially produced fertilizer. The process has been described in detail in several publications (6-11).

The Kettering process involves three basic sub-systems namely: 1) the power source, 2) the electric arc reactor and 3) the absorption system. A flow diagram of the Kettering process is shown in Figure 1.

Inputs to the electric arc reactor are electrical power and air. In the arc reactor which is described in detail below, nitrogen oxides are produced and an appreciable quantity of heat also is produced as a by-product. As will be discussed later, the heat by-product also can be used productively. In the basic system the nitrogen oxides produced in the electric arc reactor pass into an oxidation column where the ideal objective is to convert all of the nitrogen oxides to nitrogen dioxide. Conversion of nitric oxide (NO) to nitrogen dioxide (NO_2) is determined primarily by the availability of excess oxygen (from air) and by the "residency" time required for nitrogen oxide to be oxidized in the presence of air to nitrogen dioxide. Thus, the oxidation column is basically a large holding tank that serves to oxidize nitrogen oxide into the form of nitrogen dioxide which is very soluble in water.

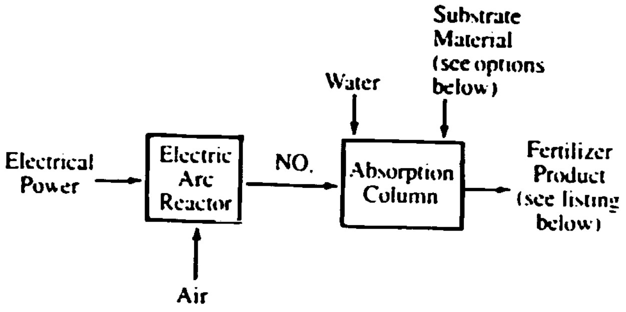
As a next step in the Kettering process, nitrogen dioxide, along with other exit gases, passes into an absorption column where the nitrogen dioxide reacts with water to form a weak nitric acid. Depending upon the type of substrate material used in the absorption column, several types of fertilizer can be produced by the Kettering process. If inert material is used in the absorption column, nitric acid in water solution is produced. Although not normally considered as fertilizer, weak nitric acid can serve as a source of nitrogen for plants. Preferably, however, weak nitric acid should be neutralized with some type of basic compound before application to plant life.

Limestone ($CaCO_3$) may be used in the absorption column in which case calcium nitrate in water solution is produced. Calcium nitrate is an excellent form of fertilizer that is relatively stable and may be applied at any time before or during the growing season.

Phosphate rock is another type of material that may be used in the absorption column. The advantage of using phosphate rock is that both nitrate and phosphate fertilizer may be produced using the same basic components of the Kettering fertilizer production system. Even relatively low grade deposits of rock phosphate can be used in the Kettering process (12). Thus, the Kettering system could be applicable in areas with deposits of rock phosphate not presently considered economically feasible for mining.

Another type of material that may be used in the absorption column is wood ashes. The use of wood ashes, which inherently contain phosphate, potassium and trace elements necessary for plant growth, is an attractive possibility that has the potential of producing a complete N,P,K fertilizer plus essential trace element nutrients.

The several different choices for the types of substrate materials that may be used in the absorption column of the Kettering process, along with the resulting form of fertilizer as an end product, are summarized in Figure 1.



Substrate	*Fertilizer Product*
1) Inert Packing	Dilute nitric acid in water
2) Limestone	Calcium nitrate in water
3) Phosphate Rock	Nitrate and phosphate in water
4) Wood Ashes	N-P-K fertilizer + trace elements in water

Figure 1 — Flow diagram of several configurations of the Kettering fertilizer production process.

Construction Details

The nitrogen fertilizer generator (NFG) system is broken down into three functional "sub-systems", namely: 1) the power source, 2) the reactor, and 3) the absorption or collection system. Although all three of these subsystems work together to produce nitrate fertilizer, they can, for the most part, be assembled separately and later linked together to form the total NFG system. In some instances where construction may overlap into another sub-system it will be noted in the "Assembly Section" of that sub-system.

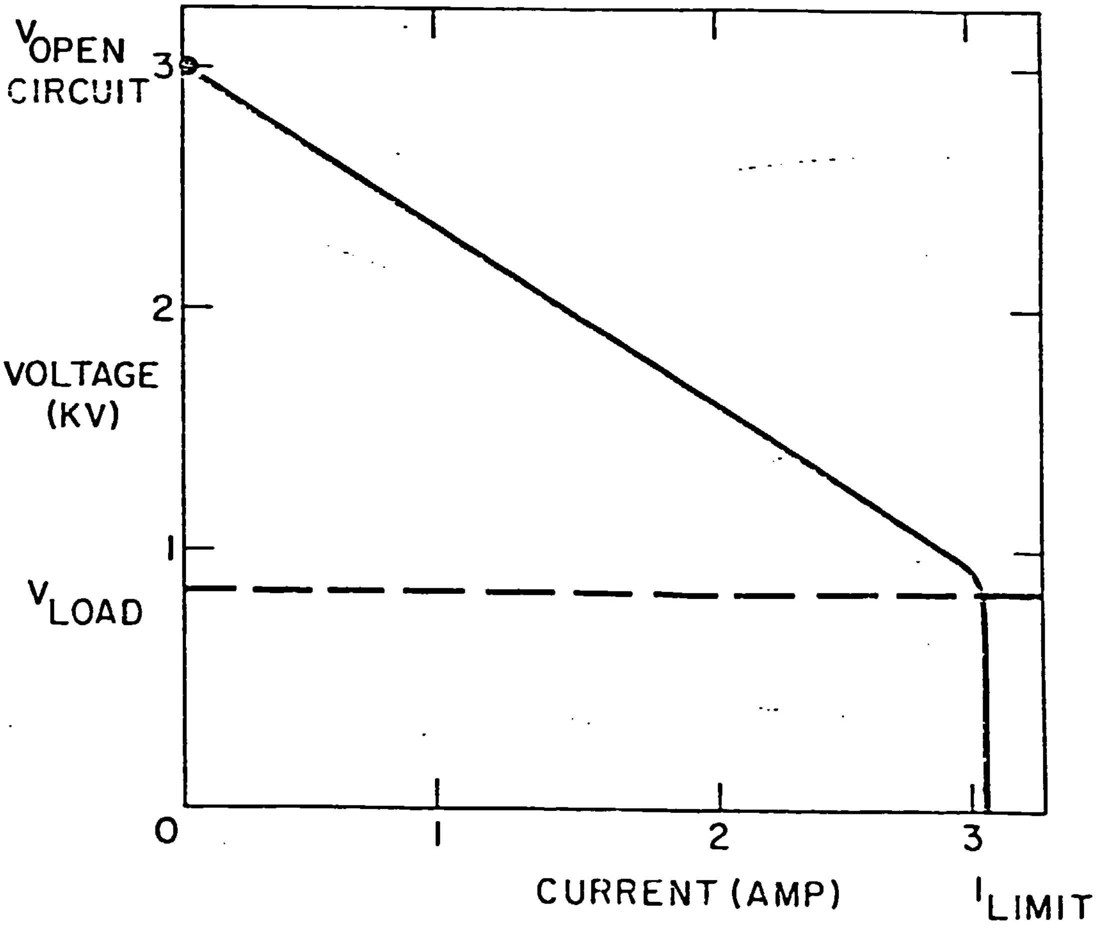
Because of the numerous alternative materials and components available, no single construction plan is appropriate. Accordingly, construction plans in this section are divided into two categories for each sub-system, the "ideal" and the "example". The "ideal" category attempts to convey the essential operating characteristics of that group of components or sub-system. In this way the reader may elect to implement his own hardware to accomplish the function. The "example" category presents a detailed description of components and their assembly as they have been used in laboratory tests and field trials in the U.S.

The discussion of components centers on their function in that sub-system and is augmented by drawings, graphs and schematics. If further information is required for a component, the reader is referred to the appropriate appendix. Lastly, the assembly section deals with the problems of mounting, interconnections, modifications to manufactured items, etc.

A. Power System

1. Ideal power system characteristics.

Because the arc is a unique electrical load, the power supply for the arc reactor is somewhat unique. Since the arc tends to consume as much power as is supplied to it, the power supply must be designed to limit current. Thus, the ideal power supply for the reactor is one that will provide sufficient voltage to maintain a plasma while limiting the current. In the following figure (2) the ideal current/voltage relationship is shown. Note that the



IDEAL V-I CHARACTERISTICS
FIG. 2

voltage is high under open circuit conditions (No Load) and drops to V_{load} as the current approaches I_{limit} and drops more precipitously for further increases in current. V_{load} corresponds to the desired operating voltage for the arc, I_{limit} corresponds to the current at which the magnetics of the power supply begin to saturate. The combined quantities of V_{load} and I_{limit}

determine the steady-state power consumed by the system. We have arbitrarily set this value nominally at 3 Kw. The desired operating voltage is approximately 1000 volts which in turn defines I_{limit} to be about 3 amperes.

The reactions that fix nitrogen occur on the surface of the arc, therefore, it is advantageous to create as large an arc surface as possible. This means that the arc will extend down the reactor tube some distance ($\sim$45 cm). Extension of the arc can be accomplished by higher voltages since arc length increases with arc voltage. The power supply must minimally support the desired arc length at the power level required. Empirical data show that at least 1000 volts is necessary to sustain a 45 cm. arc at atmospheric pressure.

Briefly it should be mentioned that direct current (DC) is the preferred mode of voltage. Although alternating voltage can drive an arc satisfactorily, its implementation presents a set of problems not discussed in this manual. In this discussion, it is sufficient to say that direct current provides us with a more stable arc and is more accommodating when utilizing multi-phase devices.

In summary, the following table lists the most important characteristics of the ideal power system. The power supply:

1. should have current limiting (or ballasted) design, such that short circuit current is in the range between 3.0 and 3.5 amperes.
2. should be capable of supplying 3 Kw power to the arc under continuous operation.
3. should have nominal voltages: 3000 VDC at 0 amps (starting conditions), 1000 VDC at 3 amps (operating conditions).
4. Must be capable of operating into dead short indefinitely.

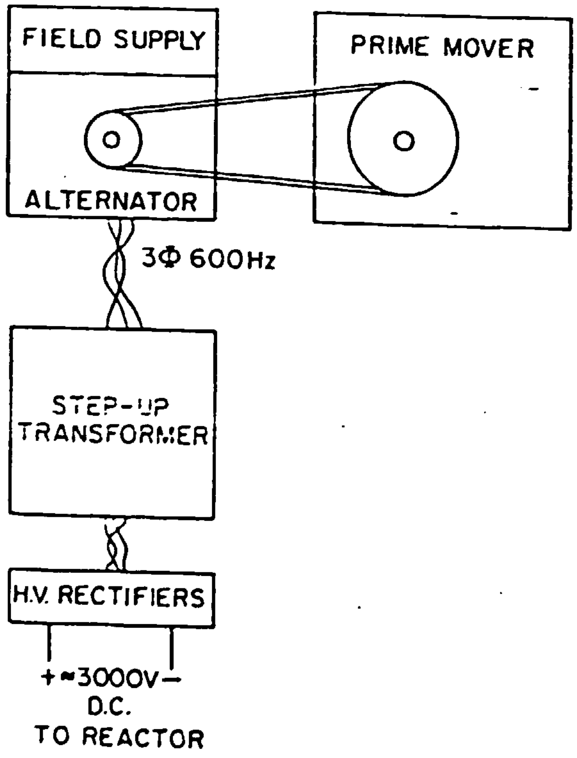
5. Should provide negative voltage as the "high voltage connection".
6. Must provide a low voltage, nonhazardous scheme for shutting down high voltage.
7. Should provide some indication of arc operation.
8. Must be safe!!

2. Example power systems.

Two types of power systems will be discussed in this section. The "mechanically driven" type assumes that the user has at his disposal a hydro-turbine, windmill, engine, or some other means of drive in the form of a rotating shaft. The "line driven" example refers to a "utility" form of alternating current of constant voltage and frequency.

A. Mechanically Driven Power System

Figure 3 shows in block form the major components of this type supply and their relationship to each other. Basically, power is coupled from the



MECHANICAL POWER SYSTEM
Figure 3

prime mover to the shaft of an alternator which provides low voltage, three phase power to a step-up transformer, that in turn, creates high voltage. The high voltage is rectified to combine the 3 phases and form direct current. The high-voltage DC is connected to the electrodes of the arc reactor.

1. Components.

Alternator: A heavy duty marine type alternator, model E100/32, made by Electrodyne can be used as a power source. This alternator can produce about 3200 watts, does not require brushes and has durable bearings. The mechanical to electrical conversion efficiency is adequate. Figure 4 shows a cut-away of the alternator as obtained from the factory.

The unit as purchased produces 32 volts DC with voltage regulation at currents up to 100 amps. The regulator and rectifiers are removed from the unit. This "stripped-down" version, when turned at 5000 RPM, produces three phase AC voltage at 600 Hz. to drive the primary of the transformer. The open circuit voltage is 90 VAC (line to line) and drops to approximately 30 VAC under full load (3200 watts).

The field winding also requires replacement. The standard E100/32 alternator is supplied with a 32 volt field coil. The 32 volt coil is replaced with an Electrodyne 12 volt coil and additional circuitry which allows the alternator to operate without an external field supply. A detailed description of this circuitry is supplied in Figure 5.

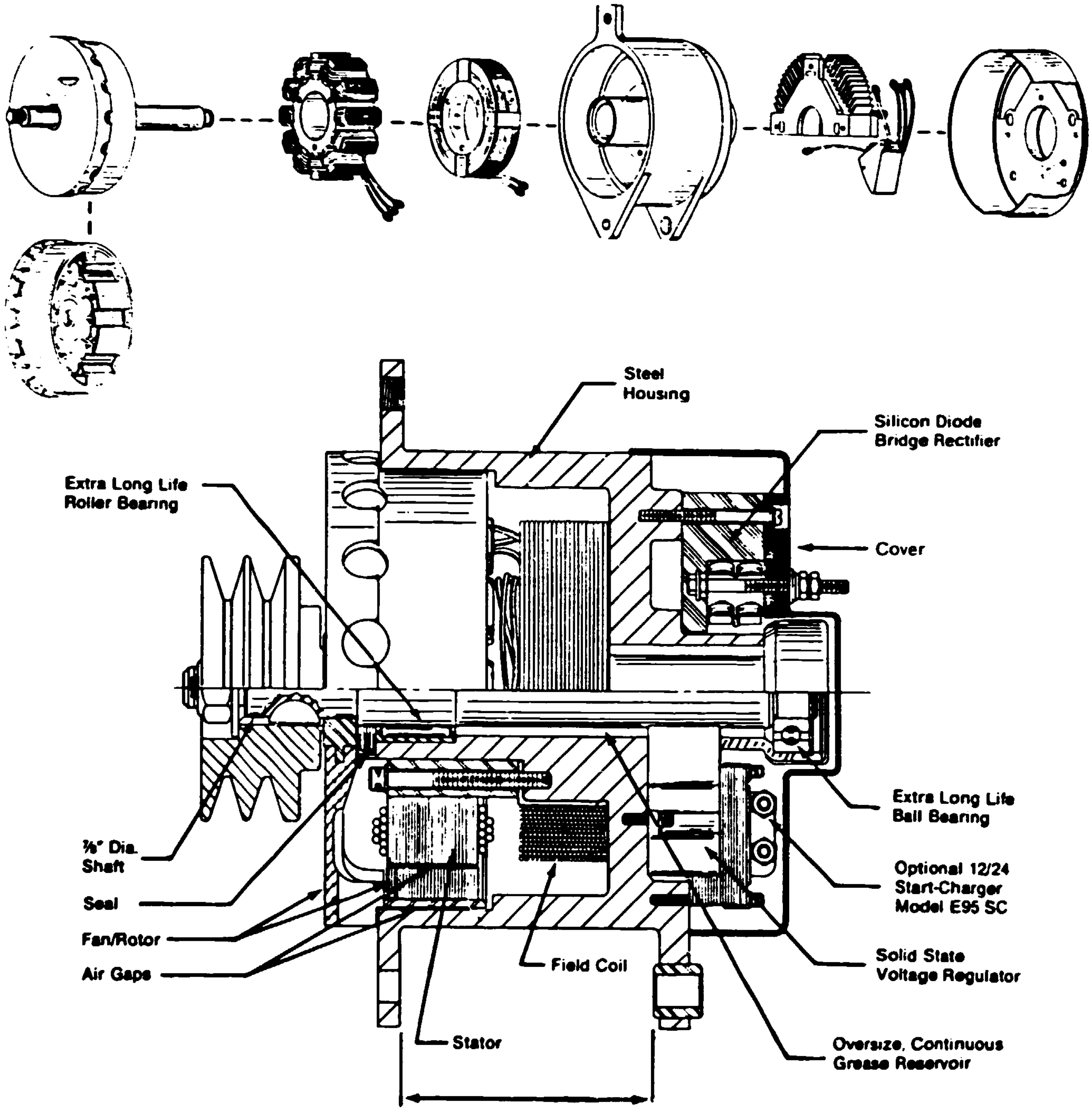
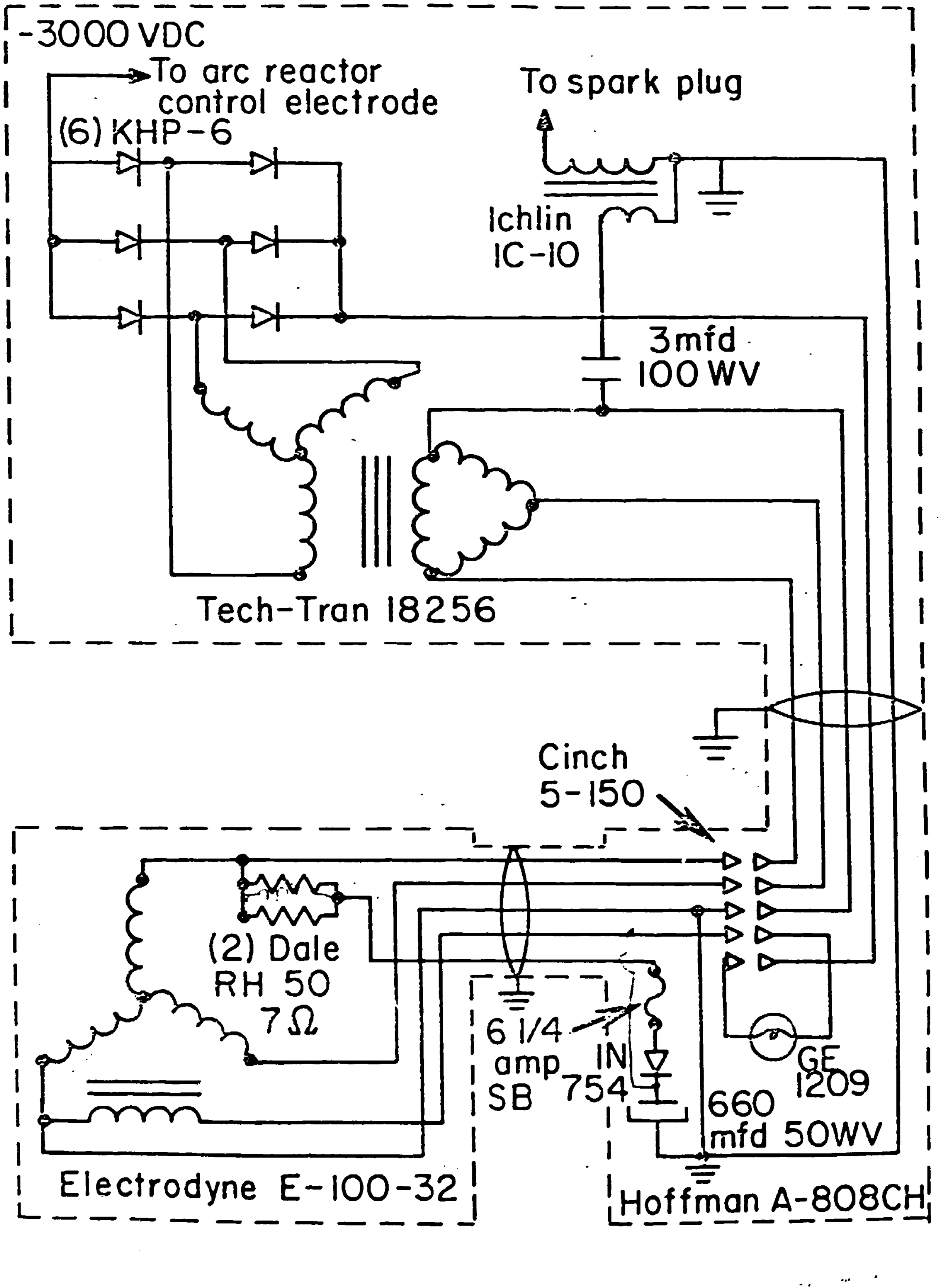

Steel Housing
Silicon Diode Bridge Rectifier
Extra Long Life Roller Bearing
Cover
Extra Long Life Ball Bearing
⅞" Dia. Shaft
Optional 12/24 Start-Charger Model E95 SC
Seal
Fan/Rotor
Solid State Voltage Regulator
Air Gaps
Field Coil
Stator
Oversize, Continuous Grease Reservoir
Compatible with SAE-J180, RCCC-101 Recommended Mounting Practice

Figure 4

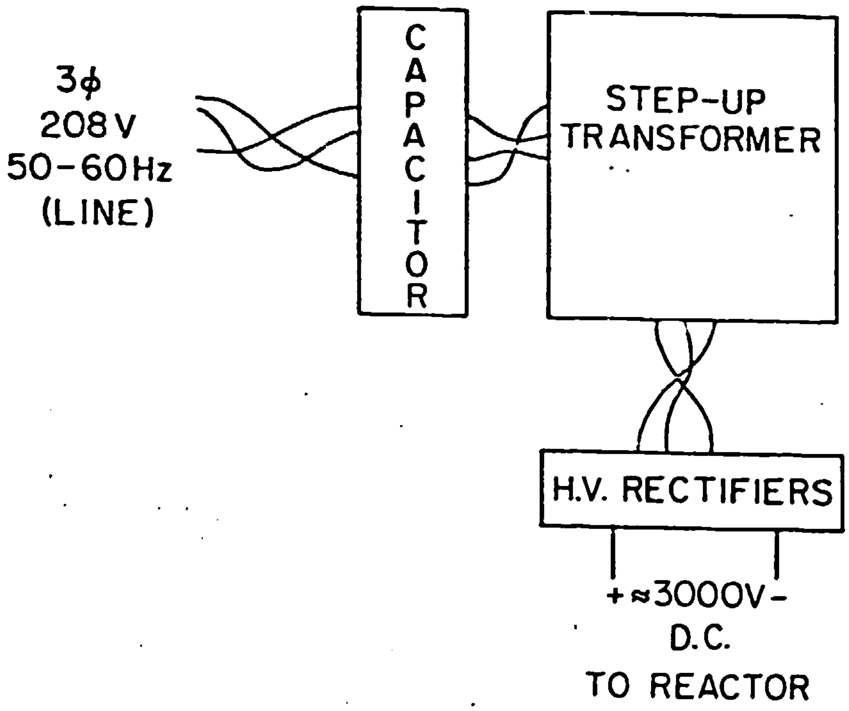


MECHANICAL POWER SYSTEM SCHEMATIC

Figure 5

B. Line Driven Power System

Figure 6 is a block diagram of the major components used in the line driven system. Line power is provided to the transformer via the capacitor bank which serves to reduce current in the line. The transformer not only steps up the three phase line voltage to the high voltage needed, but also performs the current limiting via a special ballast design described below. The high voltage is rectified in the same manner as in the mechanical system to form high voltage direct current.



LINE OPERATED POWER SYSTEM

Figure 6

1. Components.

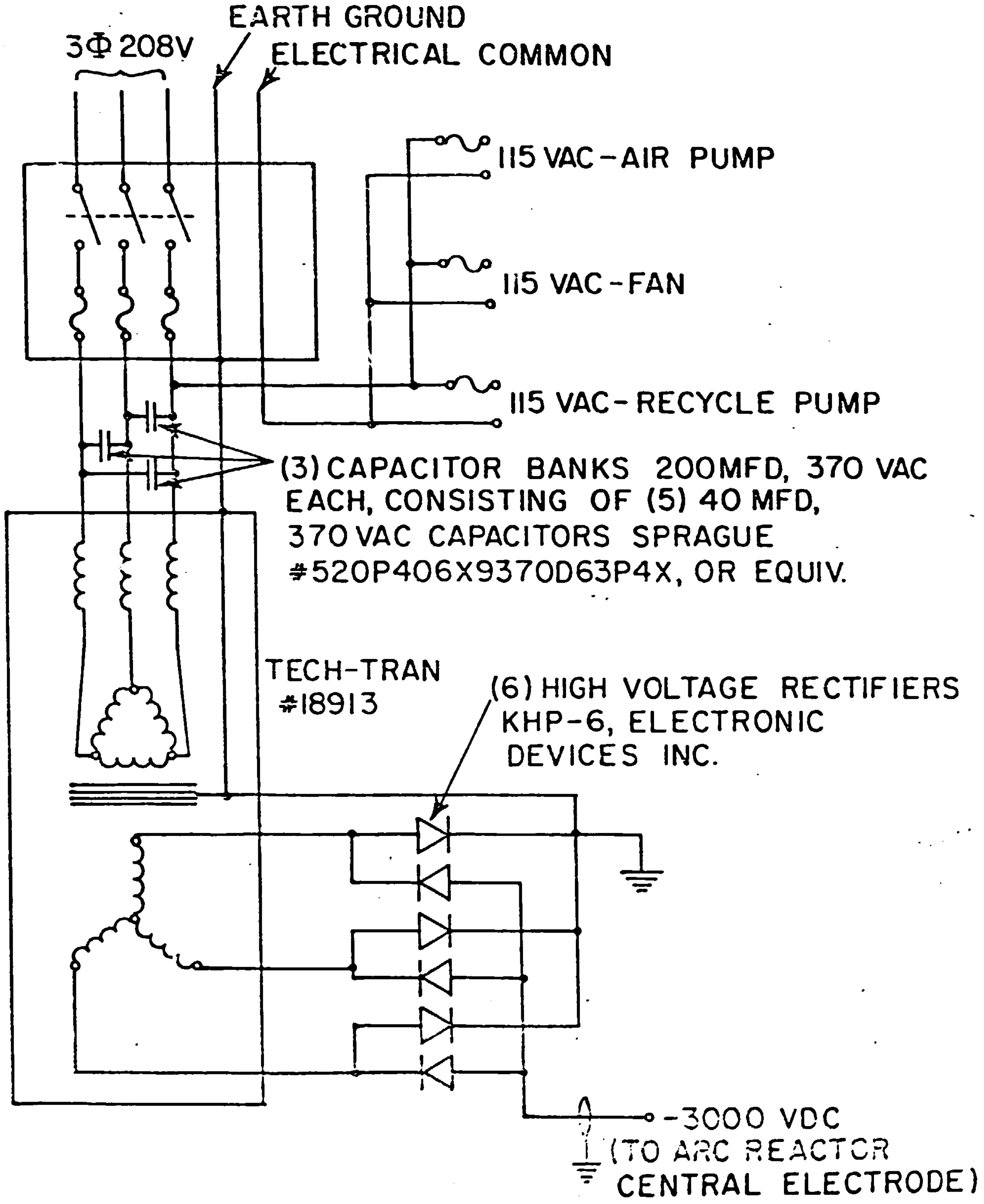
<u>Transformer</u>: The transformer was custom built to CFKRL specifications for this application by Tech-Tran Corp., U.S.A. This device performs the conventional three phase step-up from 208 vac, 60 Hz, line current to

approximately 2200 vac (open circuit) on each phase. But in addition, the transformer construction includes another set of windings in series with the primary called ballast windings. The purpose of the ballast windings is to limit current available on the secondary windings. The transformer weight is approximately 300 lbs, which should be considered when designing systems for remote locations where transportation will be a problem.

Capacitors: When driving an arc, the transformer generates considerable amounts of reactive current in the primary windings. A reactive electrical load possesses a low power factor because it produces large currents which are not in phase with voltage. Capacitors are used to absorb the out-of-phase current and thus prevent it from appearing in the line source. In the example system, capacitor banks are placed line-to-line across all three phases at the primary of the transformer. A total of 200 MFD. per phase is recommended for a 208 vac supply.

Rectifiers: Rectifiers are the same type as those used in the mechanically driven system. The six rectifiers are configured as a standard three phase full wave bridge. When connected to the three secondary terminals of the transformer, the bridge outputs provide approximately 3000 VDC (open circuit).

Full Schematic: Figure 7 shows the complete electrical schematic for the line powered system. Note that shutdown of the system is accomplished by interrupting line voltage to the transformer. Shutdown may be done by the appropriate 3-pole switch, or a suitable motor start relay. In the case where the relay is used, the relay coil windings may be incorporated into the interlock scheme. The use of 30 amp line fuses on each of the three phases is highly recommended.



LINE POWER SYSTEM SCHEMATIC

Figure 7

2. Assembly.

Figure 8 is a photograph of the line system in a metal enclosure with the access door removed. The transformer is mounted inside the cabinet, with the frame of the transformer and the metal of the cabinet both connected to electrical (and earth) ground (see Figure 8, schematic). Note that ventilation has been provided at the sodes and bottom of the cabinet.

The capacitors and rectifiers are mounted in the smaller enclosures and bolted to the main cabinet, such that all of the exposed metal is maintained at ground potential.

Figure 9 shows the internal configuration of the rectifier and capacitor boxes. The high voltage lead and ground cable exit the main cabinet through a grounded, plastic clad, water-tight conduit which terminates at the reactor.

B. Reactor System Construction

1. Ideal reactor system characteristics.

This group of components perform what is essentially the primary function of the NFG system, i.e. the fixation of nitrogen. The reactor components and their functions are discussed below.

Air supply: The air supply is the source of the chemical "feedstock" for the process, namely air. It must be capable of providing steady flow rates from 70 to 100 liters/minute over long periods of time into back-pressures less than 3 psig. The air supply must also provide a safety release for pressures greater than 3 psig. to protect system components. Additionally, a means of adjusting the flow rate is needed to allow the operator to "tune" the system.

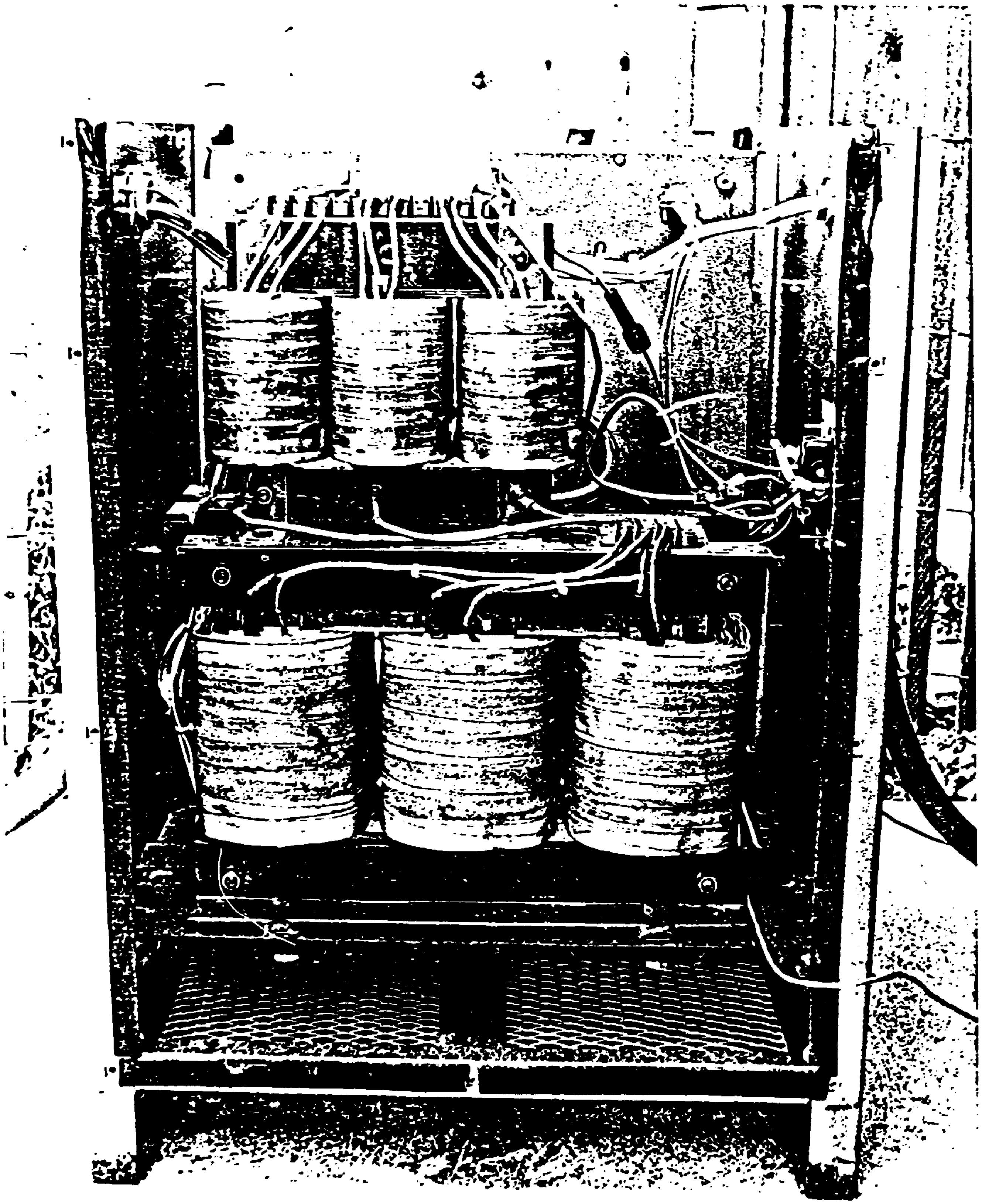


Figure 8

Figure 9

Reactor: The reactor is where the nitrogen-fixing reactions occur. The function of the reactor is to heat incoming air to temperatures exceeding 2000 degrees centigrade. Because of the high temperatures involved, certain parts of the reactor erode or sluff off metal, therefore accommodations must be made to replace these "consumable" parts. These parts, ideally, should be inexpensive, simple to fabricate, and accessible to the operator.

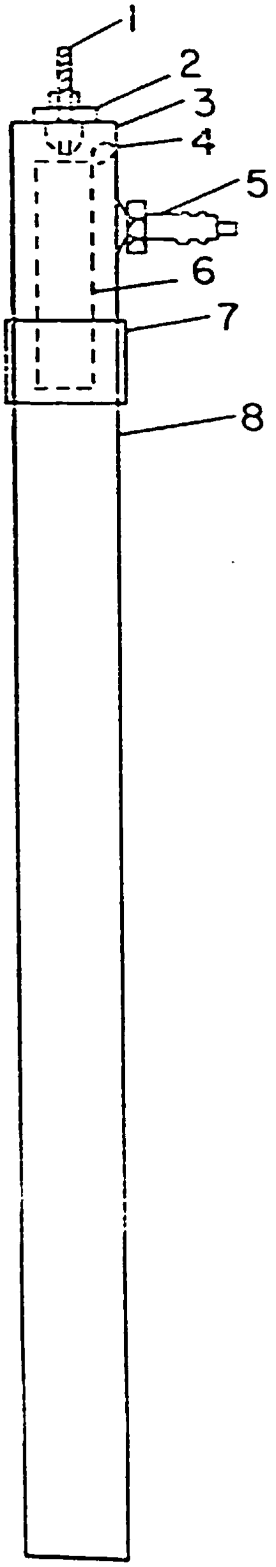
Ideally, the reactor will be integrated into a heat absorption scheme that would allow the heat to be used in a profitable way while maintaining exit gas temperatures below 70 degrees centigrade. The entire reactor assembly can be constructed from readily available materials and requires only modest machining capabilities.

In terms of operation, the reactor must be air-tight, present minimal back pressure (<1 psig), and maintain a stable arc plasma for long periods of time. The reactor also should possess good isolation between the electrodes. More importantly only grounded metal surfaces are exposed on all external parts of the arc reactor for electrical safety.

Starter: The power supply is responsible for providing the power to sustain the arc, but another set of components called the "starter" circuit is responsible for the initiation of the arc. In the course of its operation the reactor will be turned on and off occassionally by the operator. Also, due to differences in the way the electrodes wear, the arc may spontaneously extinguish. In order to assure constant operation, a means of automatically re-initiating the arc should be implemented. The starting device should be reliable and consume little power when the arc is present.

2. Example reactor system.

The following is a discussion of the components found to perform adequately in the reactor system.



(1) Electrode support shaft/high voltage connection- This is a 1/4 inch diameter threaded rod (20 threads/inch), one nut and washer needed.

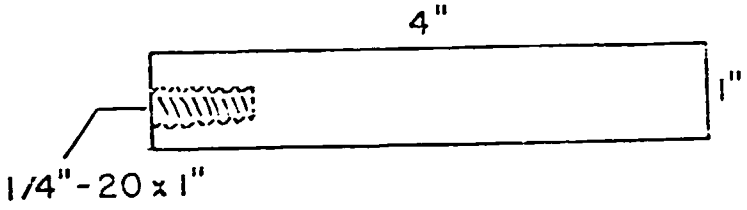
(2) Ceramic insulator- (2 piece), part # 9450, Herman H. Smith, Inc., Brooklyn, N.Y., USA, accommodates passage of support shaft through air manifold end piece to central electrode. Includes two fiber washers to seal at metal interface.

(3) Air manifold constructed from all steel material.

(4) Air inlet tube - 5/16 inch O.D., 0.27 inch I.D. steel tube integral to air manifold.

(5) Spark Plug - # BL13Y Champion, AC or similar, with extension removed (ground flush with rim). Modification show below:

(6) Central electrode - mild steel 1 inch diameter solid rod cut to 8 inch length. One end is center tapped to accommodate 1/4 inch support shaft with that end surface finished off square.



(7) Coupling - standard plumbing part to accommodate 1.5 inch pipe. This piece allows mating of the air manifold with the reactor tube, may also be incorporated into heat exchanger so as to provide support to the reactor.

(8) Reactor Tube - Standard plumbing 1.5 inch pipe cut to 24 inch length and threaded on both ends. This section of pipe serves as the grounded electrode and is easily replaceable.

REACTOR

Figure 10

Air supply: For stable operation the reactor requires an air supply capable of supplying 70-100 liters/minute (2.5 - 3.5 cf./min.) at 210-350 grams /sq. cm (3-5 psig.). For this purpose, a rotary vane pump performs satisfactorily. A GAST model = 0440-P107A air pump is recommended for the mechanically coupled system. This pump delivers 90 liters/min. at 350 grams/sq. cm. For the line-powered system a Gast model 0522-P102-6180DX is recommended. Either of these pumps, in conjunction with a 1/2 inch ball valve and felt filter, comprise a satisfactory air supply.

Reactor: The reactor is composed of basically three pieces: the air manifold; the coupling; and the reactor tube. These parts are made from standard plumbing components. Standard metal working tools are required, e.g. mill, lathe, drill press and brazing equipment.

Figure 10 shows a cross section of the assembled reactor complete with associated parts.

Starter: Two types of starter circuits have been developed. Both are totally electronic and require no moving parts. The first was designed to be used in conjunction with the mechanically driven power system and is driven by the alternators stator windings. The schematic of this circuit is shown below:

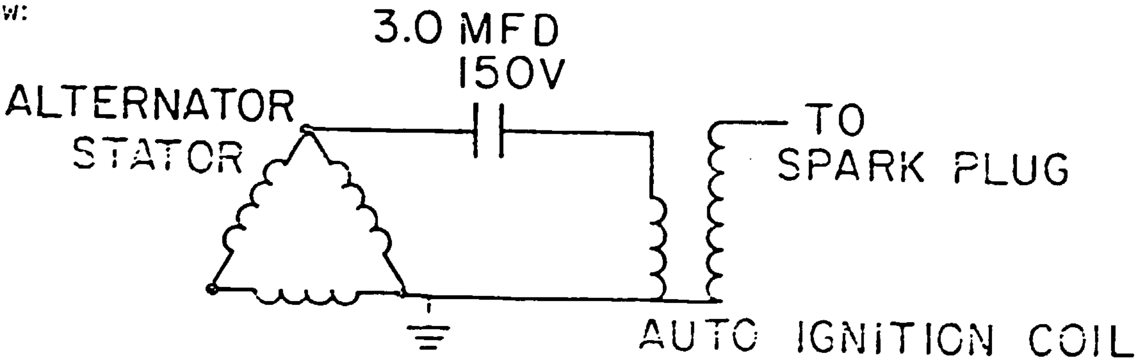
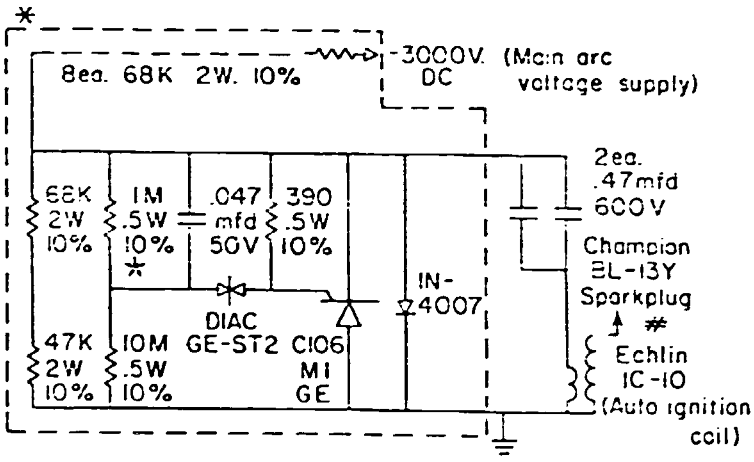


Figure 11

The 600 Hz. stator voltage is coupled through a 3 Mfd. 150 volt, non-polarized capacitor to the ignition coil (Model = IC-10, Echlin) which has its output connected directly to the spark plug. When the arc is present, the stator voltage is sufficiently low (30 volts) to prevent sparking at the spark plug. However, when the arc is extinguished, the stator voltage climbs to nearly open circuit potential (90 volts), which, after passing through a step-up transformer, is sufficient to cause the air to breakdown in the region between the central electrode and the spark plug tip. This action then causes current to flow from the power system through the newly created plasma. The formation of the arc drives the stator voltage down thereby "turning off" the ignition circuit.

The second starter circuit utilizes different parts but works on the same basic principle in that the change in voltage associated with the presence of the arc controls its operation. The schematic is given below in Figure 12 and a detailed parts list is provided in the appendix.



LINE SYSTEM STARTER SCHEMATIC

Figure 12

The circuit is basically an oscillator with its output controlling a silicon controlled rectifier that switches high voltage DC from the power system through the automotive ignition coil. This circuit design can be used with either of the power systems discussed earlier.

Assembly -

Air supply: In the case where the air pump is driven from the same shaft as the mechanically driven power supply, precautions should be taken to assure that proper pump speed is maintained and that the drive train is adequately rated to the power level involved. Figure 13 depicts one such configuration where the air pump is belt driven from the alternator shaft. Where this arrangement is employed, the valve and filter should be mounted external to the pump/alternator housing to permit safe and easy access to the valve. The inlet to the filter should be arranged such that rain or condensed moisture cannot enter the pump. If the pump is to be motor driven, as would be the case in a line system, the pump and motor may be mounted inside the power system enclosure as shown in Figure 9.

Metal tubing (> 3/8 inch O.D., copper or steel) may be used to conduct air from the pump to the air manifold of the reactor. Non-metallic tubing, such as rubber or tygon, may be employed if adequate heat exchange is performed at the pump outlet.

Reactor: It is assumed in this discussion that the air manifold has been constructed to the specifications (see Appendix) and that the miscellaneous reactor parts (e.g. support shaft, insulator, etc.) have been obtained.

Assembly of the reactor should begin with the air manifold. The manifold, as it comes from the machine shop, should be inspected for conformity to specifications and cleaned to remove metal burrs, flux, etc., especially in the region of the air inlet tube. The electrode support shaft should then be threaded into the end of the central electrode until it seats. As the next step, an asbestos washer is positioned over the shaft and slid up the shaft to meet the bottom of the electrode. The inside member of the

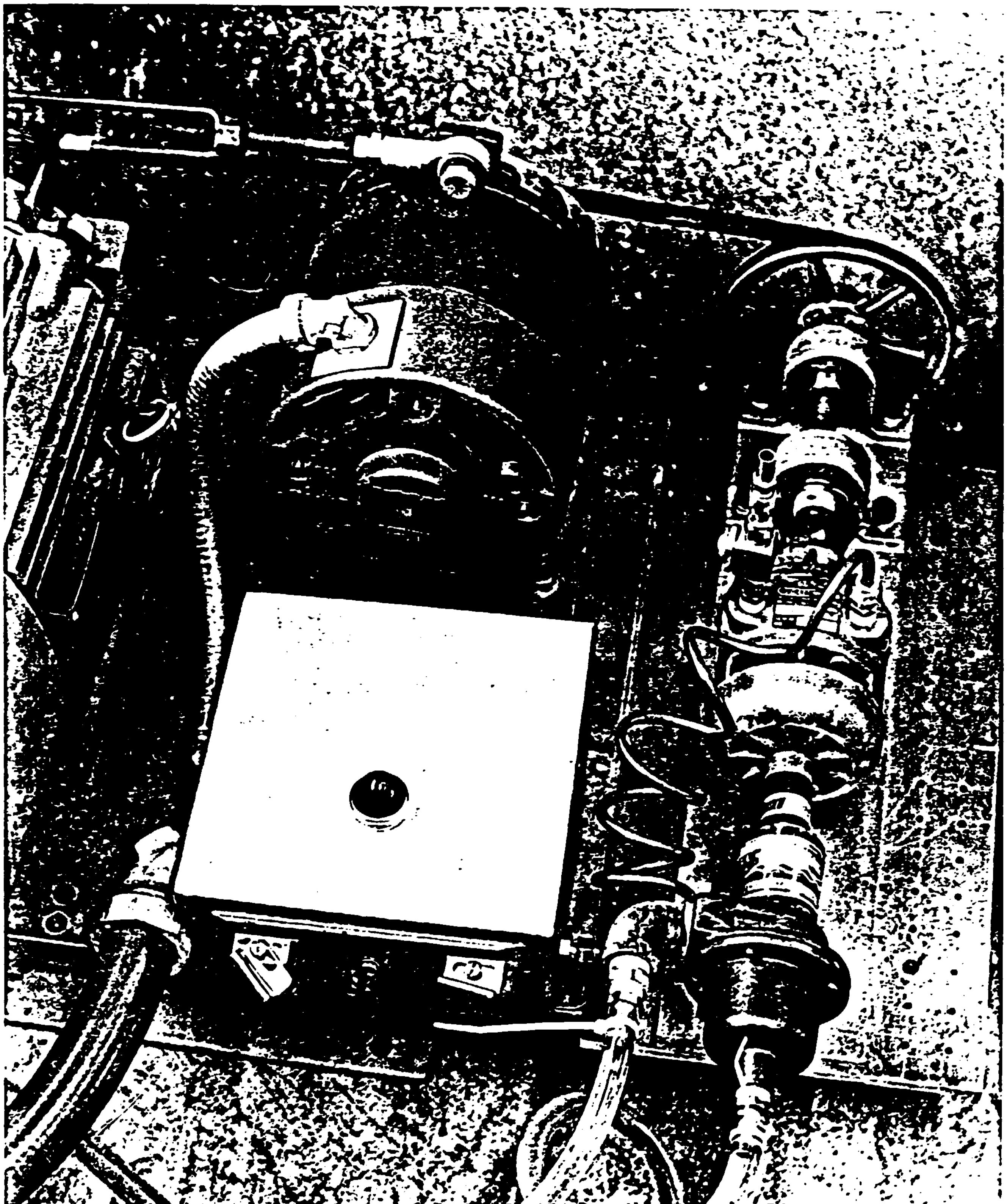


Figure 13

ceramic insulator is put on the support shaft, followed by the fiber washer as shown below in Figure 14.

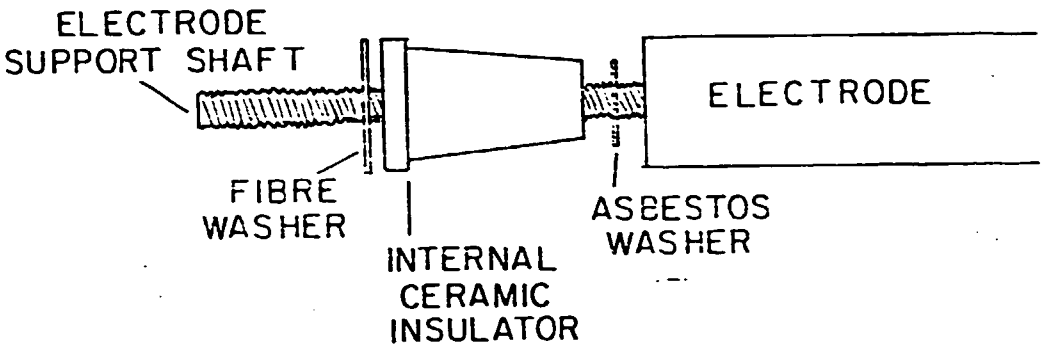


Figure 14

Set the electrode on a flat surface such that the support shaft points up and then center the washers on the insulator. Bring the air manifold down over the support shaft to rest on the fiber washer now inside the manifold. Align the hole in the end of the manifold with the hole in the inside ceramic piece, then add the remaining fiber washer, ceramic outer member, metal washer, and nut, in that order as shown below in Figure 15.

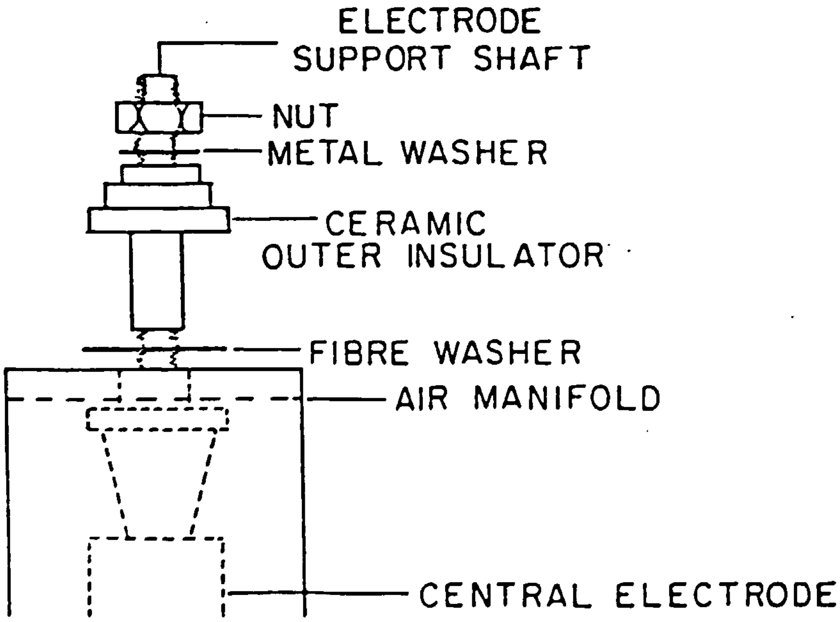


Figure 15

Do not over tighten this nut! Tighten sufficiently to hold all members firmly. At this point the base of the central electrode should appear in middle of the view obtained by looking down the air-expanded inlet tube.

Next, the modified spark plug may be screwed into place, again, do not overtighten. The tip of the plug (inside the manifold) should remain about 0.187 inches (48 mm) from the nearest edge of the central electrode. Also, the central electrode, when viewed from the open end of the manifold, should appear in the center of the opening. With the application of some high temperature pipe sealant, the manifold is ready to be threaded into the coupling. But first, the problem of reactor mounting must be addressed.

Heat exchanger: This example heat exchanger provides a solid mount for the reactor, a safe enclosure for the electrical components and a continuous supply of hot water to the user, if desired. The heat exchanger is built from two steel 55 gallon, open-head drums. The two drums are combined in such a way that two compartments are formed, one contains water, the heat exchange medium, and the other forms an enclosure for the electrical parts. Figures 16 and 17 show the heat exchanger during various stages of construction.

The electrical components mounted in the lower compartment of the heat exchanger differ depending upon which power system is employed. The following examples show component layouts for both line and alternator driven systems. Both descriptions have the basic reactor parts configured in the same fashion as described previously. The systems differ primarily in the location of the high voltage transformer and the type of starter used.

The alternator-driven reactor system encloses all of the high voltage components in the lower compartment of the heat exchanger. As shown in Figure 16 the three phase, 600 Hz, step-up transformer, high voltage

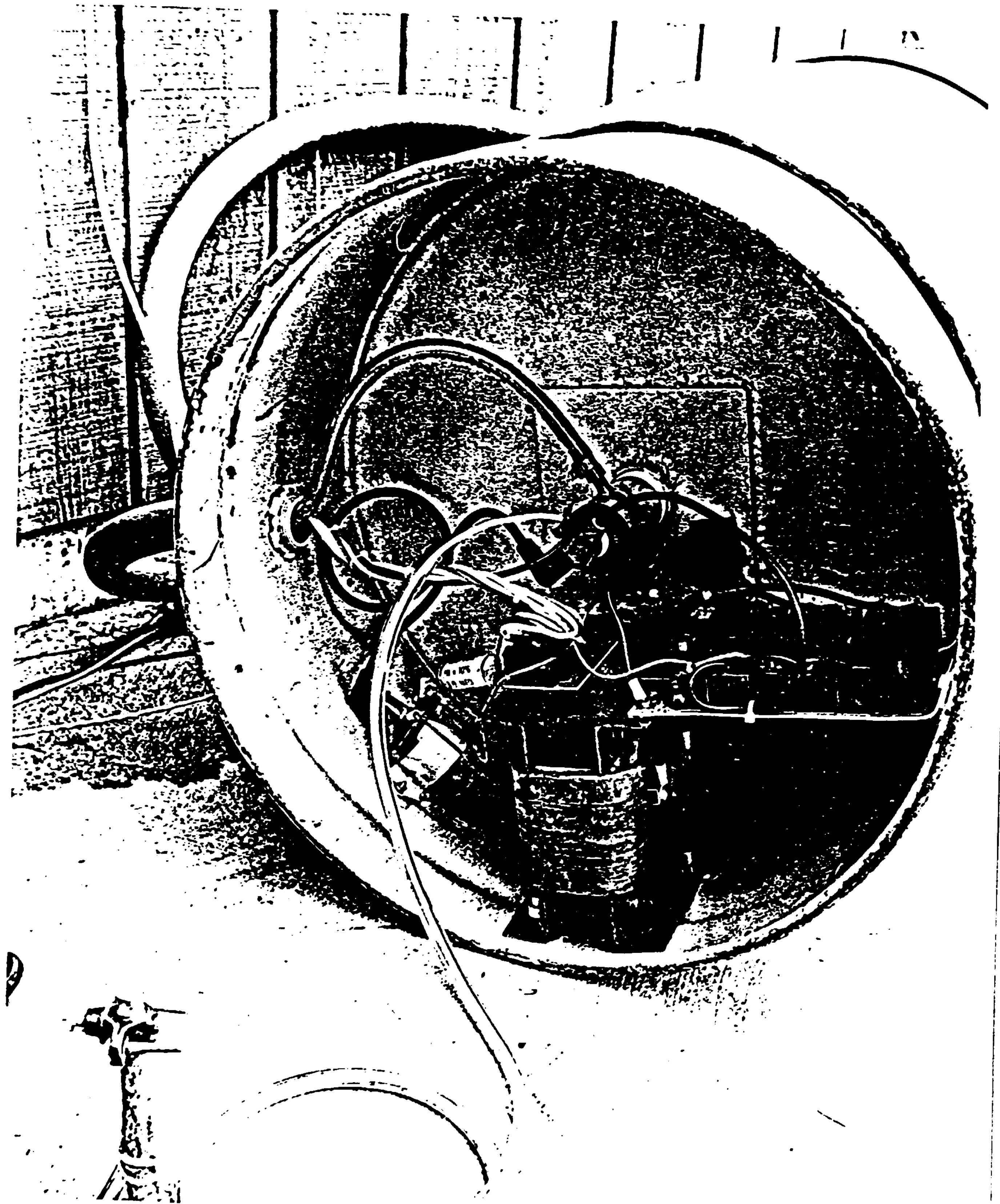


Figure 16

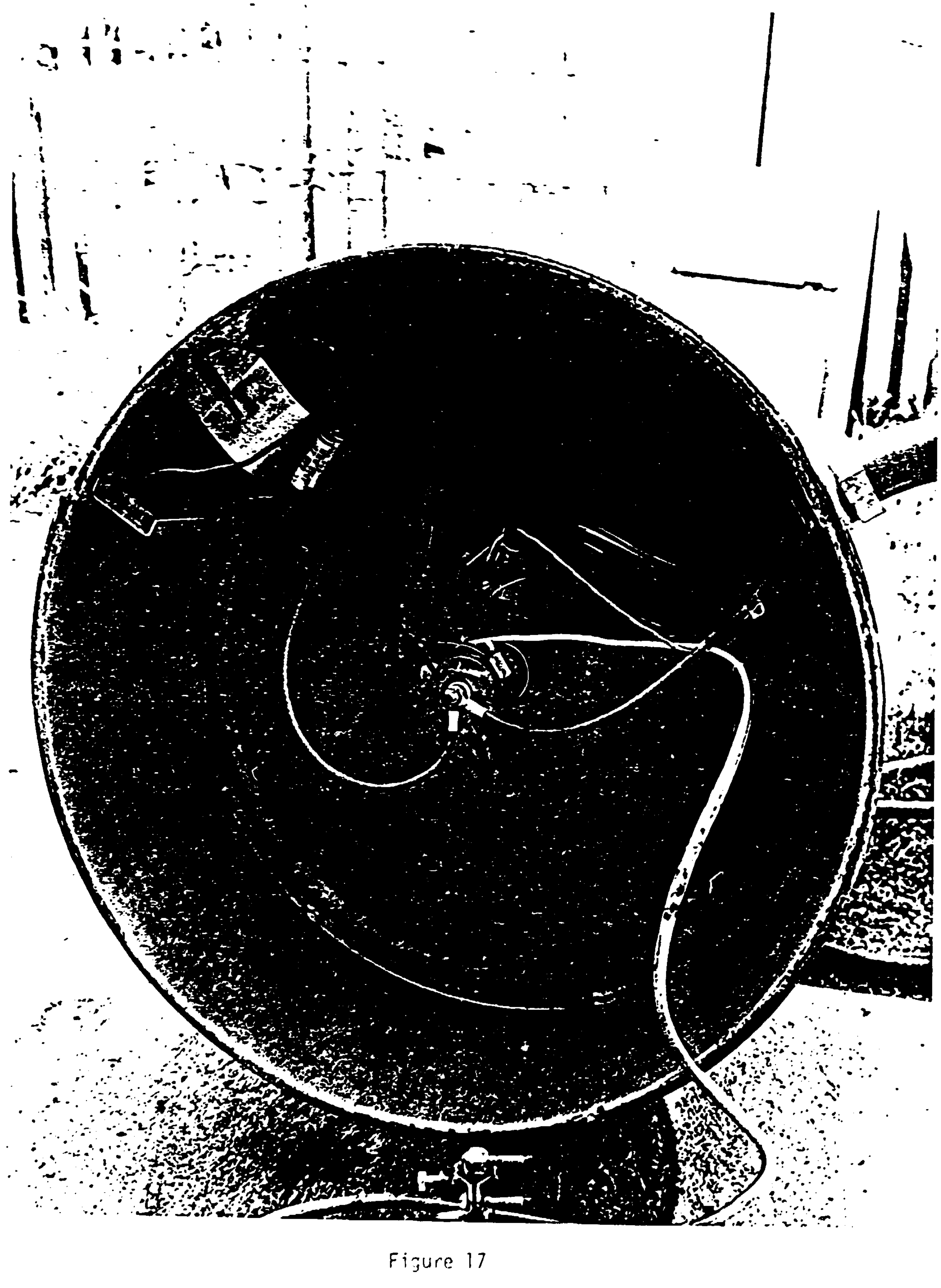


Figure 17

rectifiers and starter circuit are all mounted in this lower chamber. The plastic-clad metal conduit contains a ground wire, the three phase stator leads, the field current return lead, and a flexible air line. The metal sheath of the conduit is also grounded and maintains good chasis contact at both ends. When uprighted the components inside the lower compartment have a ground clearance of 1 inch or more.

Figures 8, 9 and 17 show the mounting of the components used in conjunction with the line powered system. In this example, the high voltage lead is brought into the lower compartment via the plastic-clad metal conduit along with the ground lead and flexible air line. Before the reactor/heat exchanger assembly may be positioned, a platform or pad should be prepared. Since the total unit, filled with water, weighs in excess of 400 lbs. (180 Kg), a solid surface is required. Figure 18 shows the form of the recommended concrete pad.

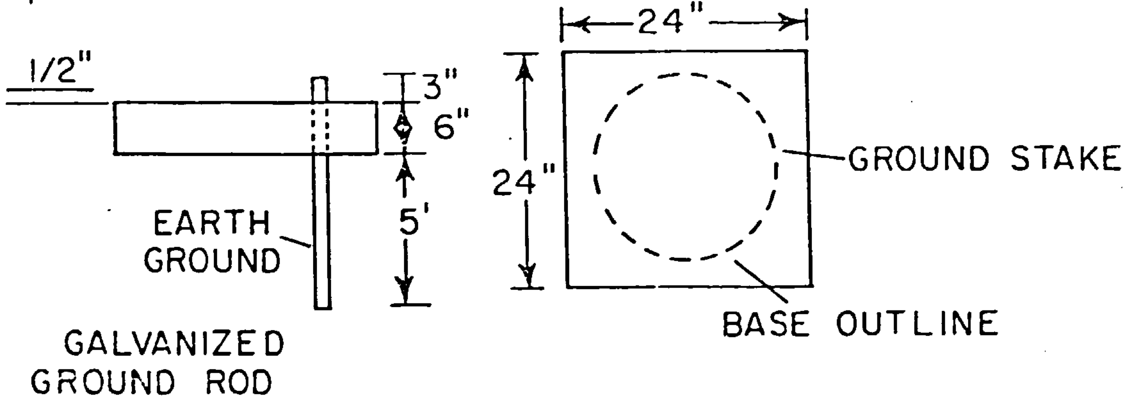


Figure 18

The top surface of the pad is slightly convex to assure drainage and the pad itself should be above ground for the same reason. Before the concrete is poured an electric ground stake is driven at least 5 feet (1.5 meters) into the earth with approximately 3 inches remaining above what would be the top surface of the pad. The flat surface of the stake is such that later it may be bolted to the interior surface of the lower compartment of the heat exchanger. This extra ground rod is added as a safety measure and should not be omitted. With the pad installed, the drum may be set upright and the ground stake bolted to the drum wall. At this point, the user has the option of adding a "hot plate" to the end of the reactor tube as shown in Figure 22, or terminating the reactor tube into a water-cooled gas exit line. (Hot plate details in the appendix.)

The reactor gases exit the heat exchanger via the 1/2 inch (12mm) O.D. copper tube which penetrates the wall of the water chamber just below the upper rim. When constructed in this way the drum lid may be used to keep foreign material from contaminating the water and to prevent excess evaportion of coolant water.

C. Collection System

1. Ideal system characteristics.

The gas leaving the reactor is a mixture of air and the oxides of nitrogen, e.g. NO_2 & NO. The nitrogen oxides constitute a small part (<2%) of the total flow and are of no benefit to the user in their gaseous state. Only one of these oxides, NO_2, is readily soluble in water. The function of the collection system is: 3) to convert as much of the insoluble nitric oxide to nitrogen dioxide as possible, and 2) to trap the nitrogen dioxide in solution as nitrate (NO_3).

Some of the basic reactions involved in these functions are shown below:

Reaction

1. $2NO + O_2 = 2NO_2$
2. $2NO_2 + H_2O = HNO_2 + HNO_3$
3. $4HNO_2 + 2NO = 2NO_2 + 2H_2O$
4. $2HNO_3 + CaCO_3 = Ca(NO_3)_2 + CO_2 + H_2O$

The oxidation of NO in air, reaction 1, is slow with its forward rate dependent upon the concentration of NO. The table below depicts this rate relationship.

OXIDATION RATE OF NITRIC OXIDE IN AIR

(20% O_2) at 20°C

NO Concentration (ppm)	Oxidation Time 25%	50%	90%
10,000	8.4 sec.	24 sec.	3.6 min.
1,000	1.4 min.	4 min.	36.0 min.
100	14.0 min.	40 min.	6.0 hours
10	2.3 hours	7 hours	63.0 hours
1	24.0 hours	72 hours	648.0 hours

It can be seen that the time required to completely oxidize NO in air to NO_2 is, for practical purposes, infinite. However, percentages exceeding 90% may be obtained in reasonable time periods if the NO concentration is greater than 10,000 PPM. For 90% oxidation, the time required for various NO concentration is given by approximately: Time (minutes) = 36,000/PPM (NO). Gases exiting the arc reactor contain nitric oxide in concentrations between 10,000 and 20,000 PPM. Thus for 90% oxidation a period between 1.8 and 3.6 minutes would be required.

Reaction #2 shows NO_2 and water reacting to form nitric and nitrous acids. Although nitric acid in weak solution may be used as a fertilizer directly, its low pH precludes its use in most applications. In addition, absorption efficiency is limited by the back reaction of nitrous acid (reaction #3). A preferable form of nitrogen fertilizer is a salt such as

$Ca(NO_3)_2$, which has a slightly acidic pH and is highly soluble in water. $Ca(NO_3)_2$ may be formed in an absorption column packed with $CaCO_3$ via reaction #4.

In summary the collection system should possess at least the following characteristics:

(1) Provide sufficient residency volume to oxidize at least 90% of the incoming nitric oxide to nitrogen dioxide.

(2) Absorb NO_2 on an acid-neutralizing medium with a transfer efficiency exceeding 90% over the range of the conditions involved.

(3) Be constructed of nitric acid resistant materials to provide longevity to system components commensurate with other power and reactor system parts.

(4) Provide sustained satisfactory performance in a variety of environmental and operational circumstances.

(5) Present no health hazard to those who would operate or otherwise work near it for prolonged periods.

(6) Be constructed from inexpensive and available materials.

2. Example collection system.

Figure 19 is a schematic cross-section of the example collection system. Cooled gases from the reactor enter the top of the tall oxidation column and move slowly downward to exit above the waterline near the bottom of the column. The oxidation column is set in the reservoir in order that condensing water vapor and nitric acid may be absorbed by the recirculating system without accumulating in the oxidation column.

The gases exiting the oxidation column enter the base of the absorption column just below the packing support plate. The gases pass through the holes

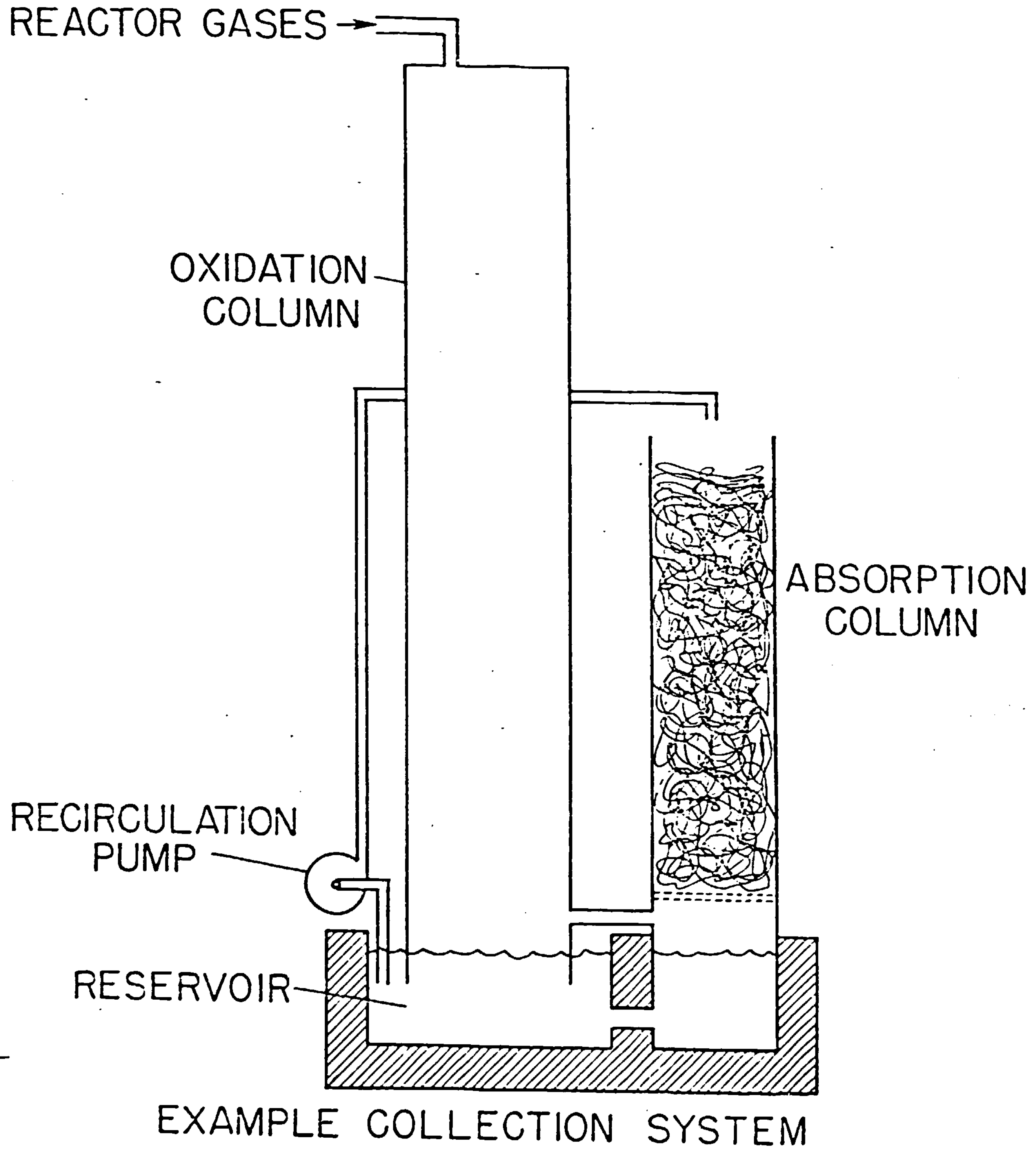

REACTOR GASES
OXIDATION COLUMN
ABSORPTION COLUMN
RECIRCULATION PUMP
RESERVOIR
EXAMPLE COLLECTION SYSTEM

Figure 19

in the plate and move upward through the wet packing material. On the surfaces of this material, the nitrogen dioxide is removed from the gas stream and imparted to the descending liquid as nitrate. A small percentage of the nitrogen dioxide exits the top of the absorption column along with air, carbon dioxide and water vapor. The aqueous nitrate solution continues down through the packing and support plate into the fines (residue) trap. The liquid moves from the trap through a small conduit to the local reservoir from which it is pumped back to the spray head at the top of the absorption column, thus completing its cycle.

A. Components

1. Oxidation column.

From prior discussion it should be recalled that the oxidation column is basically an empty vessel of relatively large volume through which the reactor gas must pass so that it may oxidize to form the water-soluble product, nitrogen dioxide. The example system uses a 16 inch (40.6 cm.) diameter PVC tube 10 feet (3.05 meter) long to perform this function. The PVC tube is commercially sold in the U.S. as fumehood ducting material. It is lightweight, being of a lighter gauge than PVC pipe, and is chemically inert to nitric acid and the oxides of nitrogen.

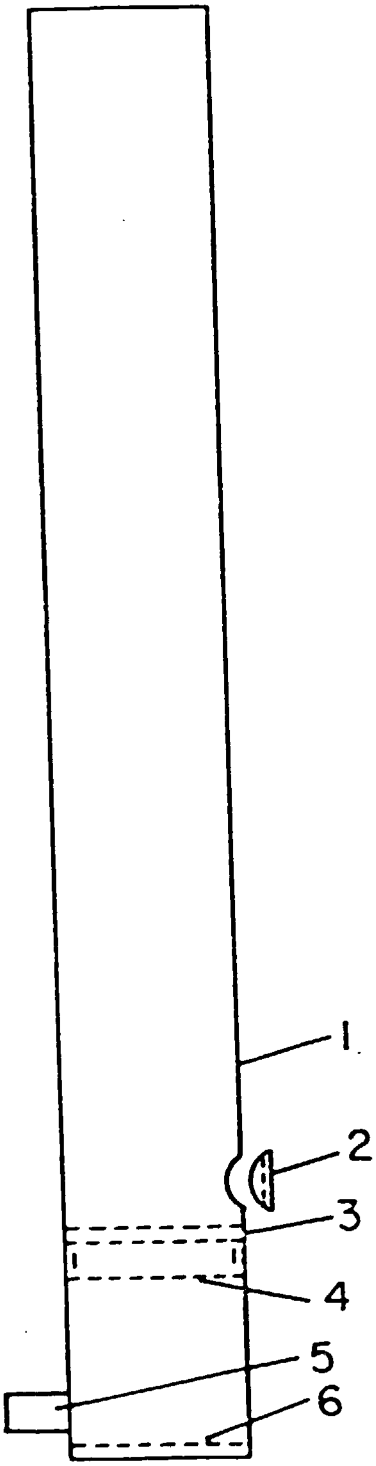
To a 10 foot section of this tube is added a 1/2 inch thick plug of PVC. The plug is chemically welded to one end of the tube which then becomes the top of the oxidation column. A hole is drilled into the plug to accommodate the fittings necessary to allow the reactor gas to enter the top of the column. Another hole is made on the lower side of the column which serves as the gas exit.

The oxidation column is supported from the top by a steel pipe mast which has its base set in concrete. The bottom of the column is supported by PVC extruded angle material also embedded in the concrete floor of the reservoir. The appendix contains the details of this column's construction.

2. Absorption column.

The example absorption column is constructed from a 9 foot (2.7 meter) section of PVC schedule 40 pipe. Because this column must contain the heavy packing media a heavier gauge (.437 inch wall) is used. To this piece of pipe a substantial number of alterations must be made (see appendix for construction details). Figure 20 defines the parts of the column.

A 4 inch (10 cm) clean-out hole is cut in the side of the column just above where the support plate will be positioned. Unused portions of the 12 inch (30.5 cm) pipe may be used to fashion a clean-out hole cover, as well as the support plate bracket. This bracket must support the weight of the packing and is glued to the inside wall of the column, whereas the support plate is not glued to the bracket but rests upon its upper edge. This mounting allows the plate to be removed when the system is cleaned. The support plate is constructed from 1/2 inch (12.7 mm) PVC sheet material cut to a diameter slightly less than the inside diameter of the absorption column and drilled with many holes (0.187 inch, each). The bottom of the column is fitted with a plug also of PVC which protects the concrete from the erosion which would take place if it were exposed to the acidic fertilizer solution for long periods. A hole is drilled slightly above the floor of the column to accommodate a short section of 1.5 inch (3.8 cm) PVC pipe through which recycle liquid will return to the reservoir. This PVC pipe should be glued to the column and protected while the concrete is being poured. Another hole in



ABSORPTION COLUMN

Figure 20

the side of the column just below the support plate serves as an entry for the gases leaving the bottom of the oxidation column. Lastly, a hole near the upper edge of the column supports the tubing which conducts recycle liquid to the spray head.

3. Reservoir/support/recirculation.

At the base of the two columns is a concrete structure which performs two functions. First, the concrete is formed in such a way as to create a small holding volumn, termed the local reservoir, of liquid beneath the oxidation column. The height of liquid in this reservoir is above the bottom edge of the column by several inches. Under normal operating conditions the back pressure created by the absorption column is less than one (1) inch of water. Should this pressure increase due to downstream blockages, water inside the bottom of the oxidation column would be displaced thereby protecting the oxidation column from over-pressurization. Secondly, the concrete structure surrounds the base of the absorption column to provide a rigid support. Figure 21 is a photograph of this structure. Its construction consists of two stages, beginning with the floor, which includes the setting of the mast and oxidation supports into the concrete. After the floor has hardened, the walls

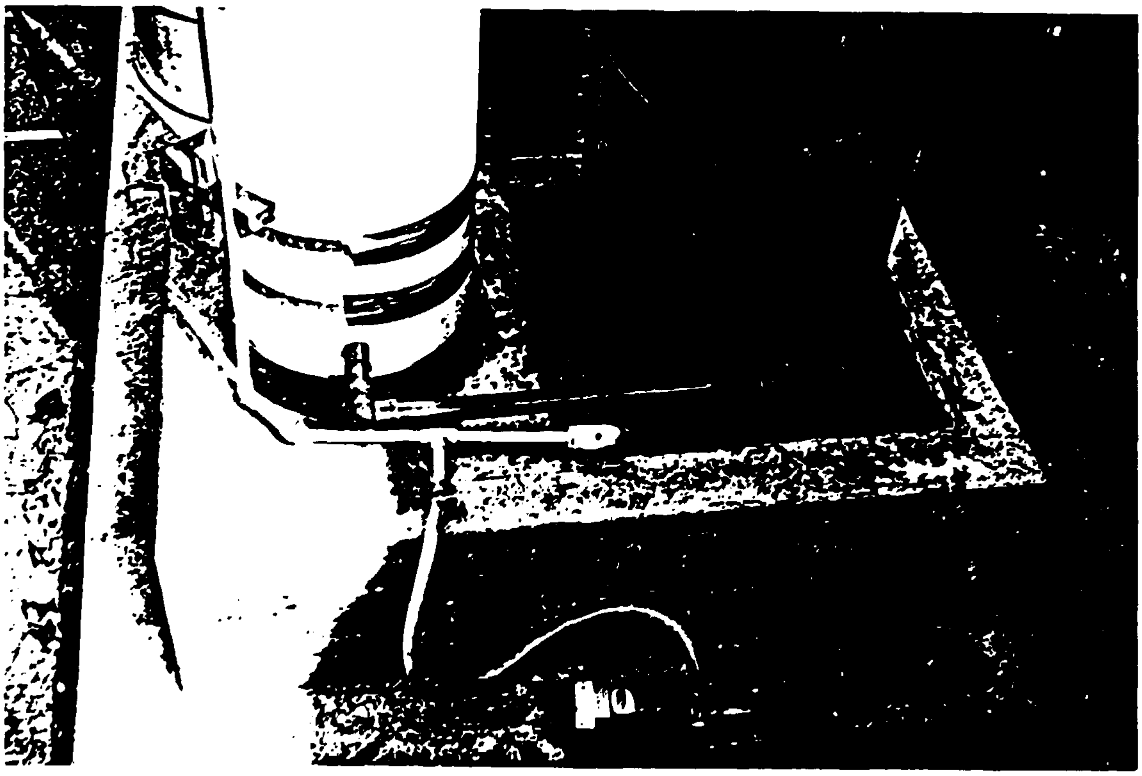


Figure 21

of the reservoir and the absorption column support are poured as one piece. The structure should be constructed below ground in temperate climates in order the help prevent freeze damage.

For the recirculation system, the reservoir is fitted with two short sections of PVC pipe which penetrate the walls of the reservoir. One of these sections is located near the floor and thus may be used in draining the reservoir; the other section is positioned at the upper edge and may be used as an overflow. Either or both of these sections can be used in various ways to connect the reservoir with other fertilizer facilities or, as in the case of this example, to connect the reservoir with the recirculation pump which returns the liquid to the top of the absorption column.

B. Assembly

Figure 22 is a photo of the completed example collection system constructed above ground. Three features should be noted at this point; the tall dark oxidation column, the shorter light colored absorption column, and at the bottom of each, the concrete reservoir/support.

Assembly of the collection system assumes that the oxidation and absorption columns are constructed according to the drawings provided. Only construction "tips" are provided in this regard, with the remainder of this section being devoted to construction of the reservoir, positioning of the columns and their interconnections.

1. Oxidation column.

The construction of the oxidation column requires that the ends of the 16 inch diameter duct material be finished off square and the top end fitted with a plug which is glued or sealed with a PVC weld. Furthermore, the outside of

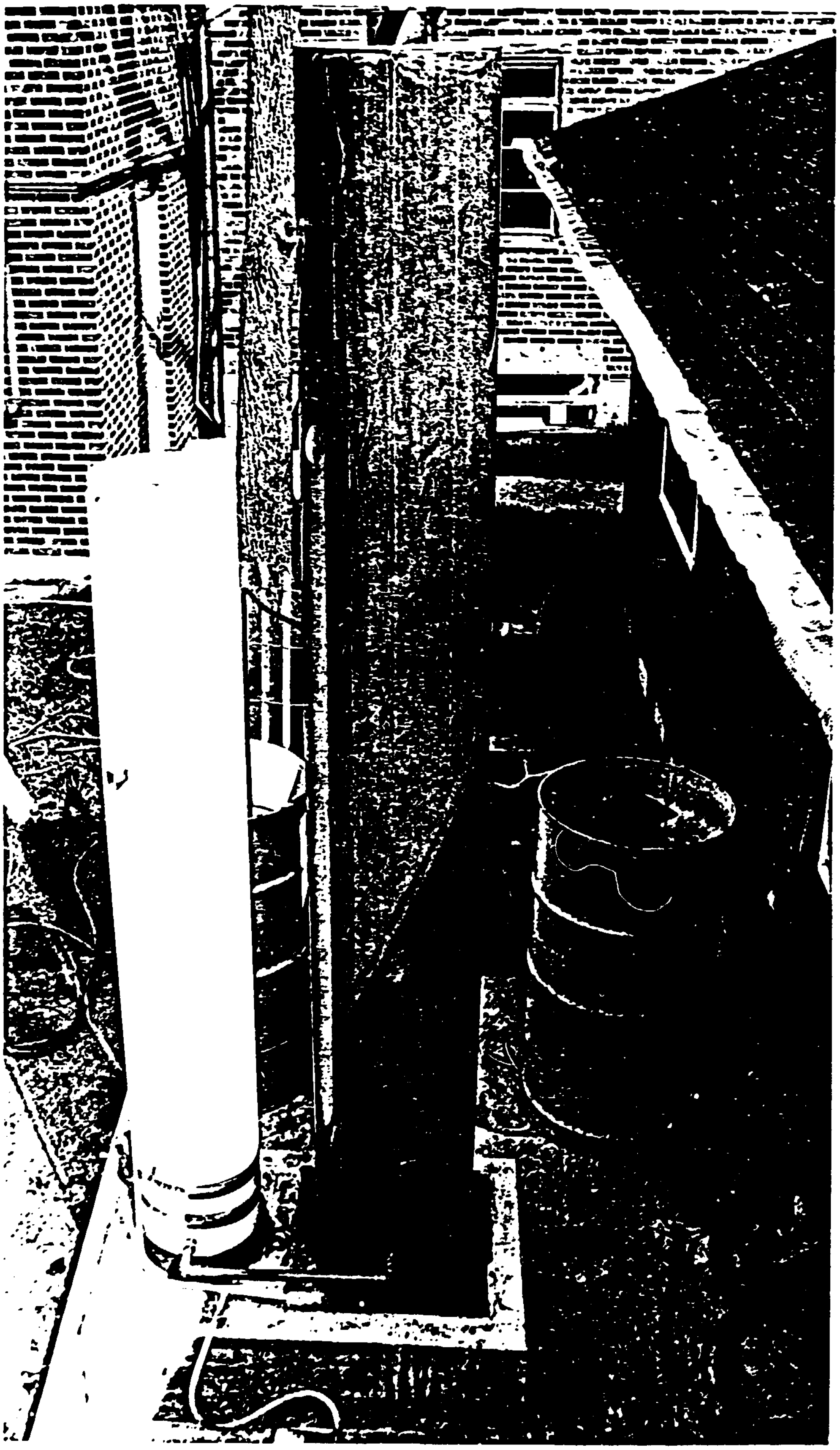


Figure 21

this plug should have glued to it a PVC spacer which has been tapped so that it may be attached to the mast arm as in Figure 23. Gas inlet fittings also appear in this figure. Construction details for the oxidation column are contained in the Appendix.

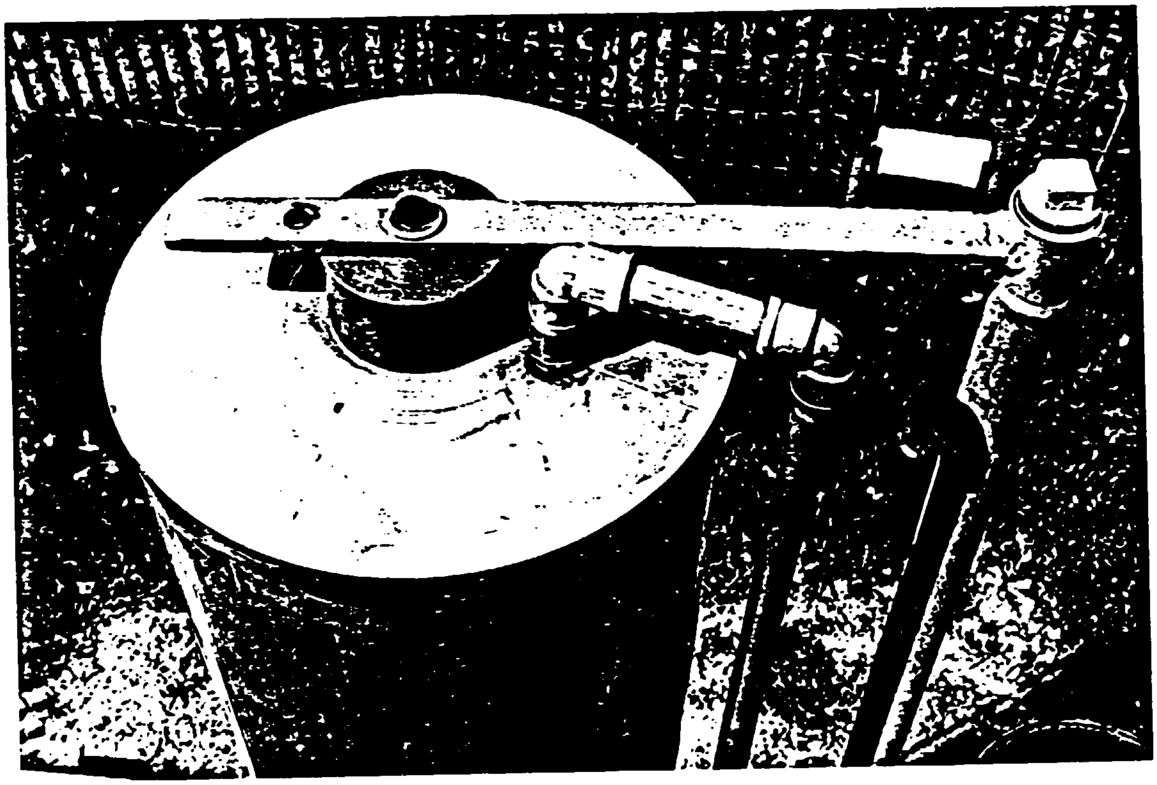


Figure 23

2. Absorption column.

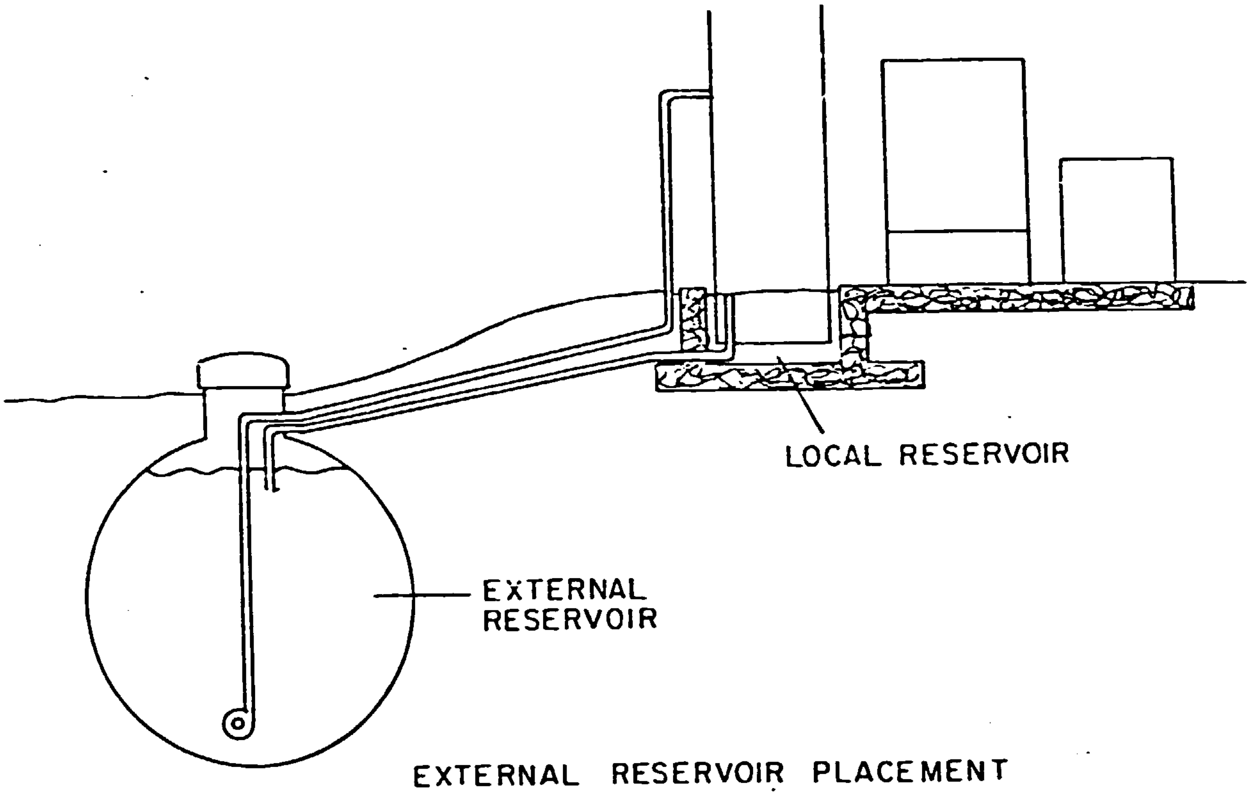
Although the absorption column itself is only 7 feet, 3 inches (2.3 M) in length, a total of 9 feet (2.7 M) of the 12 inch inside diameter (30.48 cm) is required for its construction because short sections of the pipe are needed for the fabrication of the support plate bracket and clean-out hole cover. Therefore, no less than 9 feet (2.7 M) of this pipe should be obtained.

The bottom edge of this pipe should be finished off square prior to being fitted with a plug (a butt connection is also acceptible). The sequence of assembly is also somewhat critical for this column in that the support plate bracket is more easily installed before the mounting of the floor piece and after the cutting of the clean-out hole.

The support plate bracket is made from a short (approximately 2 inch) section of the 12 inch diameter pipe which has had one end squared. When a 3.25 inch (8.3 cm) wide piece has been removed from one side, the "C" shaped bracket may be compressed to slide inside the column with the squared edge toward the top of the column. The bracket is glued into place and squared with the column before the glue has set. This provides a firm ledge on which the support plate will rest when the column is uprighted. The cutting of the clean-out hole and cover is non-critical, except to say that they should be round in order to maintain the structural integrity of the pipe. After the short, 1.5 inch (3.8 cm) I.D. PVC pipe has been installed in the side of the column, it is ready to be positioned on the concrete pad where the reservoir/support is to be constructed. For details of the absorption column refer to the Appendix.

3. Reservoir/support structure.

Prior to the construction of the reservoir support structure some consideration should be given to the vertical placement of the local reservoir with respect to other reservoir(s) to be used in the system, especially if a gravity return is desired from the local reservoir. Figure 24 depicts one possible arrangement. After the plans for placement have been finalized, excavation may begin. If the reservoir is to be below ground, the earth must be removed to a depth of approximately 16 inches (40.6 cm) and refilled with 2



EXTERNAL RESERVOIR PLACEMENT

Figure 24

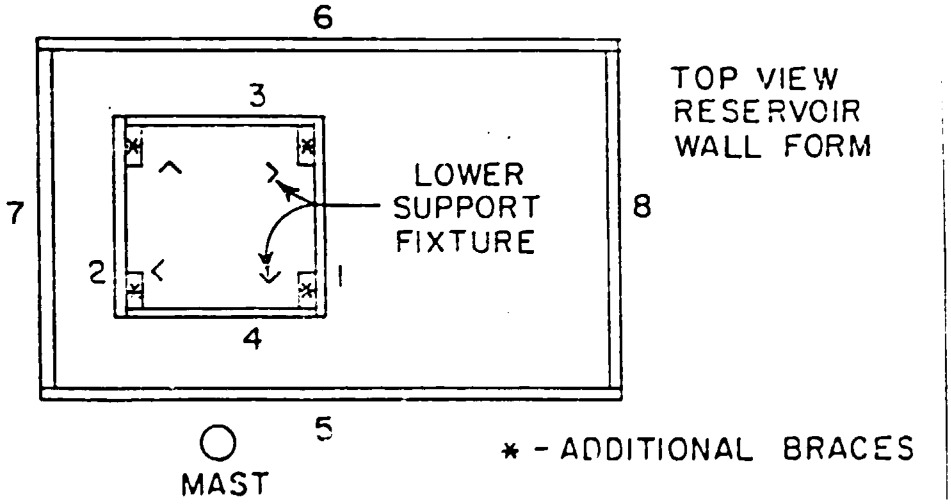
inches (5 cm) of small gravel to form a level surface upon which the forms will be set. A 6 inch (15.2 cm) hole must be dug an additional 3 feet (∿1 M) in depth to accommodate the mast. Refer to the appendix for placement of the mast.

Next, the oxidation columns lower support should be constructed. Four sections of 2 inch (5.1 cm) PVC extruded angle material are cut to lengths of 16 inches (40.6 cm) each. A wooden frame in the shape of an "X" is made to hold the PVC members. The PVC pieces are attached to the wooden frame such that opposing pieces possess an outside dimension equal to the inside diameter of the oxidation column.

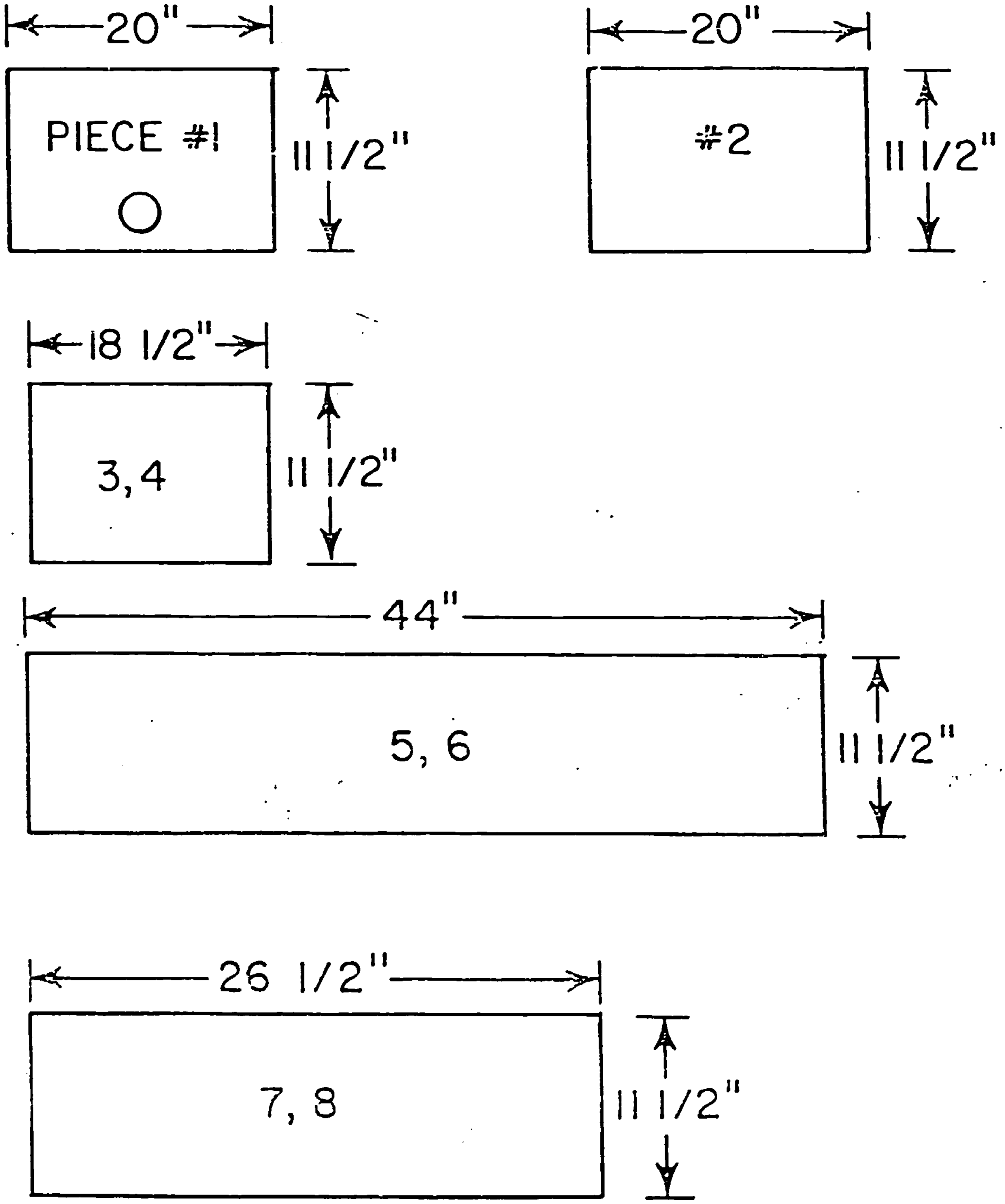
The mast consists of a 1.5 inch (3.8 cm) I.D. galvanized standard plumbing pipe 14 ft. (4.3 M) in length, threaded on one end. It may be set in the hole dug for it. Center the mast in the hole and fill the hole half way with coarse gravel. Level the mast while tamping the gravel to hold it in place until the concrete is poured. The mast arm is constructed from a pipe coupling (to match the mast diameter) and length of 1/2 inch (12 Mm) thick steel strap material.

The forms for the 4 inch (10.2 cm) thick reservoir floor may be prepared, positioned, staked and leveled. The top edge of the forms should be approximately 10 inches (25.4 cm) below the ground level. Next, the wooden frame lower support fixture can be positioned inside the floor forms. The support fixture, wooden side down, should be pushed down into the gravel such that the top of the wooden part of the fixture rests at least 3 inches (7.6 cm) below the top of the floor forms. After the fixture has been staked and leveled the reservoir floor is ready to be poured.

After the concrete has been poured and before it has set up, the mast and column support fixture should be checked for level and adjustments made if necessary. When the floor has hardened, the forms for the reservoir walls and absorption column support may be set into place. Dimensions for the various form pieces are given in Figure 26, all pieces are numbered to indicate their final position. Assembly of the forms is shown in Figure 25 below. Pieces



FORM PLACEMENT
Figure 25



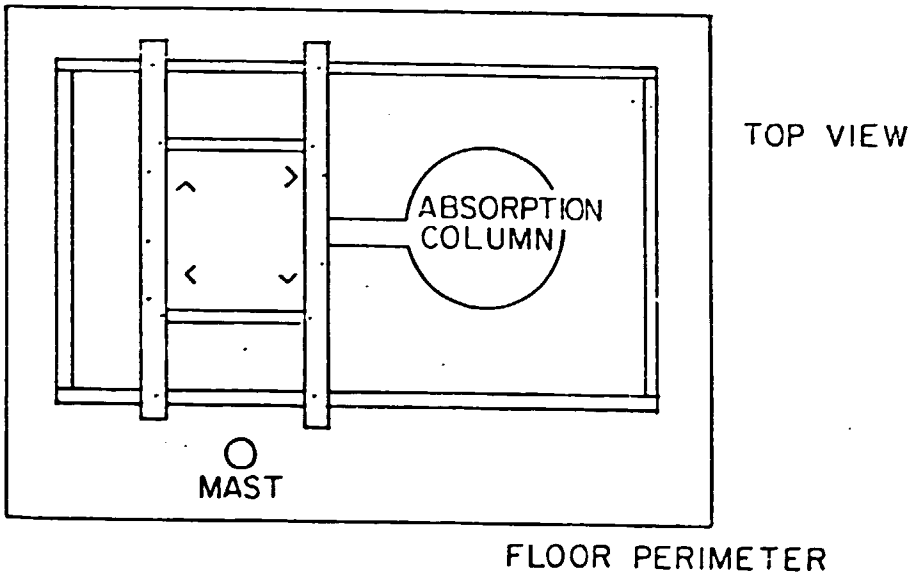
ALL MATERIALS ARE 3/4" THICK

FORM DIMENSIONS

Figure 26

1, 2, 3 and 4 should not be nailed together, as this would make their removal difficult. Rather, they should be braced by additional wood pieces inside the reservoir as noted in figure above. These braces are attached to pieces 1 and 2 only. Pieces 3 and 4 are held in place by the weight of the concrete when it is poured.

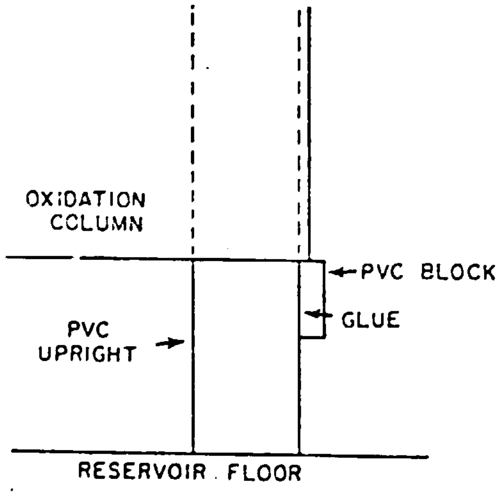
After the inside forms have been centered and squared with respect to the lower support fixture and mast, the outside forms are positioned so as to create three reservoir walls of equal thickness. The inside and outside forms should be tied together with narrow wood strip braces nailed from the top as shown below in Figure 27. Additional strength may be given to the outer forms by bracing them externally to the floor forms if they are still in place. The absorption column is centered inside the forms and its 1.5 inch diameter pipe mated with the hole in reservoir form #1. The reservoir drain and overflow pipes may now be installed. Holes are drilled through the outer and inner forms to accommodate these short sections of PVC pipe.



BRACE AND COLUMN PLACEMENT

Figure 27

The absorption column should be level; if not, it should be shimmed under its base until it is level in both planes. The concrete, when poured, should be somewhat thin in order to form a good seal with the floor, with care taken not to disturb the placement of the forms. When the concrete has cured the forms may be removed. The inside walls and the floor of the reservoir should be cleaned and sealed with an acid resistant coating such as PVC paint.
The oxidation column then may be set into place. Place the column over the lower support fixture such that the PVC pieces protruding from the floor slide smoothly into the bottom of the column. Let the column rest upon the floor of the reservoir. Next, dope the coupling of the mast arm and screw a pipe plug tightly into one end. Screw the mast arm loosely onto the top of the mast so that the arm is aligned with the center of the oxidation column below. Now raise the column from below until the PVC spacer atop the column touches the bottom of the mast arm. Temporarily shim the column at this height. Level the column in both planes, adding shims as needed. When level, re-position the mast arm over the spacer and mark where the arm should be drilled to accommodate the spacer bolt. Drill the arm and tighten it back on the mast. Bolt the mast arm to the top of the column spacer. Prepare small PVC blocks

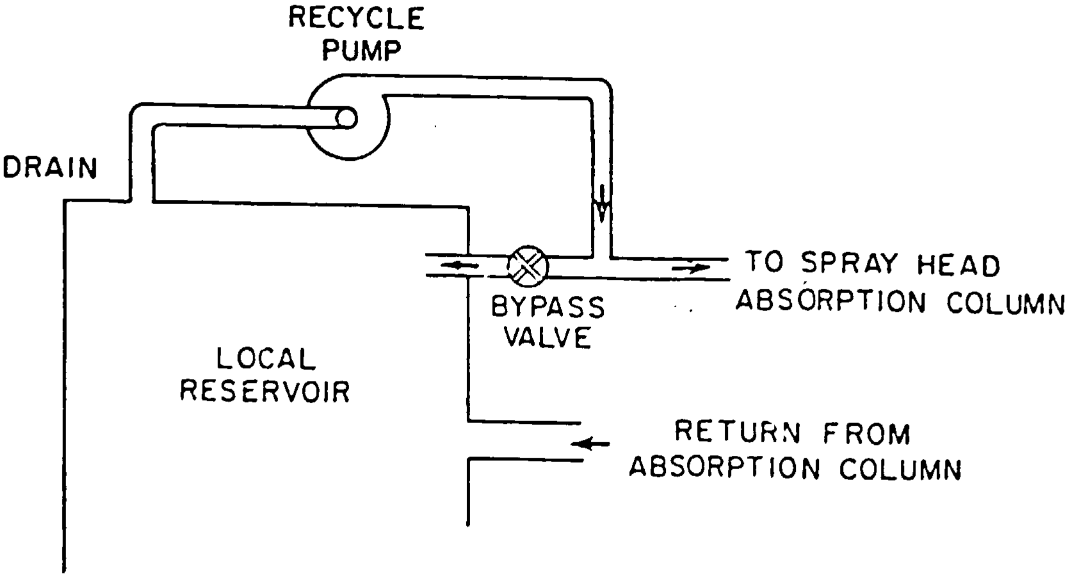


SUPPORT BLOCKS
Figure 28

and glue them to the uprights of the lower support as shown below in Figure 28.

The collection system is now ready for the interconnections to be installed. First the connection from the arc reactor will be considered. The gases leaving the reactor/heat exchanger do so via some form of metal tubing or pipe. These gases will have, in the case of the water cooled reactor, temperatures in the range of 100 degrees centigrade. For air cooled systems these temperatures may be even higher. Accommodations must be made to lower the temperature below 70 degrees, the temperature at which PVC deforms. Some form of metal conduit, preferably corrosion resistant, will be needed for this function. In the example system 1/2 inch O.D. strainless steel tubing is used to conduct the reactor gases to the oxidation column. The length of tubing involved in this transfer is adequate to perform the additional heat exchange required in a water-cooled system. From this point the interconnections may be made using 3/4 inch I.D. PVC pipe and fittings.

Plumbing of the recirculation pump depends upon the strategy involved. The example system schematic, Figure 29, depicts the situation where the



SCHEMATIC, EXAMPLE RECIRCULATION SYSTEM

Figure 29

recycle liquid is pumped directly from the local reservoir. In this case, the recycle flow rate (approximately 3 L/min) is controlled by a bypass valve, which diverts unused flow back to the reservoir. This technique aids in mixing the heavier recycle liquid returning from the absorption column. Also, this technique of flow control has another advantage over flow restriction in that it maintains high flow rates through the pump which prevents air accretion in the pump cavities (sometimes a problem in nonpositive-displacement types).

Figure 30 is a photo of the spray head mounted atop the absorption column approximately 6 inches (15.2 cm) above the packing media. The example spray head is basically a 1/2 inch I.D. PVC pipe cap which has been drilled with a number of small holes, so as to provide good liquid distribution at the recycle rate of 3 L/min. Figure 31 is a photo showing one possible arrangement for holding the clean-out hole cover in place. This technique needs no seals and requires only that the mating surfaces be clean before clamping. A 6 inch (15.2 cm) cover is cut from the extra 12 inch (30.5 cm) diameter PVC pipe. A small detente is cut in the center of the cover to capture the clamping bolt tip. The use of two bands distributes the force of the clamp. With the placement of the support plate in the absorption column, the collection system is ready for the addition of packing material.

The Kettering fertilizer production system construction and assembly is now complete and ready for initial testing.

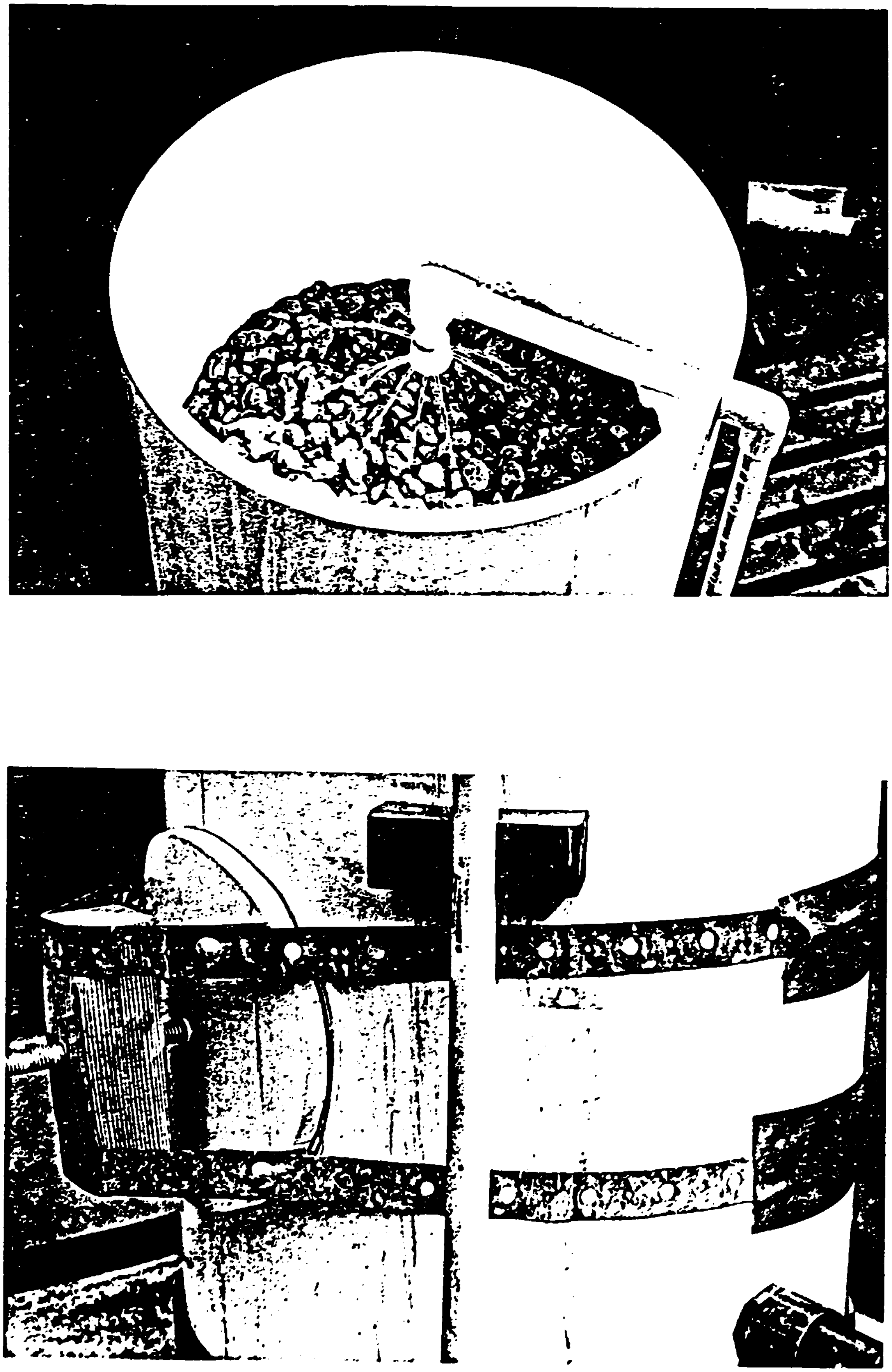


Figure 31

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