A NOVEL PLASMA PROCESS FOR THE PRODUCTION OF PHOSPHOROUS ACID

MURRAY S. BRONET, B.Eng., M.Sc.A.

Under the supervision of Dr. W.H. Gauvin and Dr. M.G. Drouet

Submitted to the Faculty of Graduate Studies
and Research of McGill University in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy

Department of Chemical Engineering
McGill University
MONTREAL, Canada

May 1990

ABSTRACT

The gas-phase synthesis of phosphorous trioxide from phosphorus vapour and steam at high temperatures to produce phosphorous acid by a subsequent quench with cold water was studied. A complete experimental laboratory, containing a heavily-insulated chemical reactor, phosphorus vapour feed system and product recovery systems, was designed and constructed for this work. A plasma torch supplied the sensible heat and heat of reaction for the desired oxide formation. The effects of the steam-to-phosphorus (H_2O/P_4) ratio, temperature, plasma gas composition and flowrate, quench flowrate and position on the production rate of phosphorous acid and on its purity in the liquid effluent were examined.

A study of the concentration and temperature profiles within the reactor was first performed in order to gain a basic understanding of the mixing of two impinging jets with a plasma tailflame at the jet expansion zone and improve the design of the reactor to better achieve the production of phosphorous acid.

High-purity phosphorous acid, 90-95%, was produced at H_2O/P_4 ratios from 6 to 10, at temperatures above 1350 K. Phosphoric acid was the major impurity in the acid product. The thermodynamic equilibrium calculations showed excellent agreement with the experimental results. These calculations also predicted that this purity could be improved to 98.5% with the addition of hydrogen to the reaction system ($H_2/P_4=10$). The use of nitrogen as the plasma gas provided a relatively inexpensive gas source and did not produce phosphorus nitrides. The position, flowrate and degree of atomisation of the water quench was critical to the production rate of phosphorous acid.

RESUME

La synthése en phase gazeuse du trioxyde de phosphore, basée sur la réaction de vapeur de phosphore et de la vapeur d'eau à haute température a été étudiée dans le but de produire l'acide phosphoreux par contact subséquent avec une trempe d'eau froide. Une installation éxperimentale, consistant d'un réacteur tubulaire fortement isolé thermiquement et de systèmes d'alimentation des réactifs et de récuperation des produits, a été conçue et construite pour cette étude. Une torche à plasma a été utilisée pour fournir l'énergie nécessaire pour la réaction. Les conditions expérimentales qui ont été étudiées comprenaient la température, le rapport des réactifs (H_2O/P_4), la nature et le débit du gaz plasmagène et le débit et position de la trempe. Leurs effets sur la taux de production de l'acide phosphoreux et de son degré de pureté ont été examinés.

Une étude préliminaire des profiles de la température et de concentration des gaz dans le réacteur a été effectuée afin de comprendre le comportement du mélange des gaz en présence de la flamme de plasma dans la zone d'éxpansion de cette dernière.

Un acide phosphoreux de haute pureté allant de 90 à 95% a été produit pour des rapports de réactifs (H_2O/P_4) entre 6 et 10 et à des températures supérieurs à 1350 K. Le contaminant principal consistait d'acide phosphorique. Les calculs thermodynamiques sous conditions d'équilibre chimique étaient en excellent accord avec les résultats expérimentaux. Les calculs thermodynamiques ont permis aussi de prédire prédire que la pureté pourrait être augmentée jusqu'à 98.5% avec l'addition d'hydrogène dans les réactifs. L'emploi d'azote comme gaz plasmagène n'a pas donné

lieu à la production de nitrures de phosphore dans la zone de réaction. Il a été démontré également que la position et le débit de la trempe d'eau froide ainsi que son degré d'atomisation étaient critiques pour la production d'un acide phosphoreux de haute pureté.

ACKNOWLEDGEMENTS

I would like to thank and express my gratitude to all those "little" people who made this work possible:

Firstly, to my research supervisors who helped me gain the knowledge and maturity to undertake and successfully complete a doctoral degree; Dr. M.G. Drouet and Dr. W.H. Gauvin.

To the members of the Hydro-Québec Plasma Technology Group who supported me by both providing laboratory space and equipment and by supplying ideas and encouragement when things weren't working so well; Paul Parisi, Myu Handfield, Mike Harris, Jean Meunier, Jean-Luc Meunier, and especially Sheila Johnstone without whose help, I'd be still connecting water lines. I would also like to thank Hans Zimmermann who made me both morally and socially aware of my environment but who unfortunately passed away much before his time. I would also like to thank Jean Laflamme of Internal Markets for the procurement and financing of this project, the Mechanical Workshop and Jean-PierreKépinski of the Graphic Arts Department of IREQ. Not to be forgotten, John Godber, research chemist at Albright & Wilson for his technical, financial and moral support.

To the members of the McGill University Plasma Technology Group, who listened to my trials and tribulations without criticism and who provided helpful suggestions in furthering my research; Dr. R. Munz, Dr. D. Berk, Paul Stuart, Earle

Chin, Roberto Szente, Peter Patterson, Oliver Mersereau, Maysaa Halberith, Monica Hilborn, Mario Douyon de Azevedo, and Bogdan Dlugogorski.

Finally, I would like to thank my wife Maureen, for her understanding, patience, support, encouragement and love in my quest for my doctorat. Now we'll both be doctors!

TABLE OF CONTENTS

Page

CHAPTER I

GENERAL INTRODUCTION

CHAPTER II

LITERATURE SURVEY OF PLASMA CHEMICAL REACTIONS AND PHOSPHORUS CHEMISTRY

CHAPTER III

THERMODYNAMICS OF PHOSPHORUS/STEAM SYSTEM

CHAPTER IV

EQUIPMENT AND EXPERIMENTAL PROCEDURE

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

CHAPTER VI

GENERAL CONCLUSIONS

LIST OF FIGURES

Page

CHAPTER II

LITERATURE SURVEY

CHAPTER III

THERMODYNAMICS OF PHOSPHORUS/STEAM SYSTEM

CHAPTER IV

EQUIPMENT AND EXPERIMENTAL PROCEDURE

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

LIST OF TABLES

CHAPTER I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Over the past few years considerable interest has been shown in the industrial applications of thermal plasmas, specifically in the chemical and metallurgical industries. This interest was particularly encouraged by the availability of new plasma generating devices of industrial size which were reliable and efficient in operation.

In Quebec, where an abundance of a renewable and secure source of hydro electric energy is available at low cost, an excellent environment exists for the research and development of new industrial processes or upgrading of old conventional systems, based on plasma technology, and is demonstrated by the existence of several excellent research groups in this field.

Although plasma technology could be implemented successfully in large scale industrial applications, replacing oil or coal fired furnaces, etc., these plants tend to be fully depreciated and any attempt to penetrate this market will be met with some resistance. However, the introduction of plasma devices is entirely possible for smaller peripheral units providing additional capacity or the upgrading of certain components of a much larger system.

The development of new chemical processes employing the unique characteristics of plasma technology, whether for the high energy content of the plasma or its ability to provide reactant species as free radicals, is the area where considerable inroads have been and continue to be made.

It is in this light that the production of phosphorous acid, an important phosphorus derivative, is investigated. In the new proposed approach, phosphorous acid is synthesized by the hydrolysis of phosphorous trioxide which is formed directly from phosphorus and steam in a plasma flame. This direct route of production appears to be considerably simpler than the conventional process, which is based on the hydrolysis of phosphorus trichloride, while eliminating the toxic and explosive hazards associated with the conventional processing of phosphorus.

The advantage of this new process are:

a) its simplicity.

b) its safety [aside from using $P_{4(g)}$].

c) it replaces a two-step process with one step.

d) it does not require handling and disposing of HCl.

e) the economics are dictated by the economics of P_4/H_3PO_3 rather than Cl_2/HCl.

An extensive literature review describing the chemistry of phosphorus, and in particular, the reactions involving phosphorus to produce phosphorous acid, either by a plasma or by conventional production routes are presented in Chapter II. Also presented in this chapter are the general characteristics of a plasma along with previous work with gas-phase plasma chemical processes and reactor design. The thermodynamics of the phosphorus and steam system are presented in Chapter III, followed by the description of the experimental equipment and procedures in Chapter IV. The results and discussion of the experimental work to produce phosphorous acid are discussed in Chapter V, which includes some fundamental measurements of the gas concentration and temperature profiles of two impinging jets. Finally, a summary of the conclusions resulting from the present study as well as recommendations for future work in the development of this process are presented in Chapter VI.

Included in the Appendices are some of the physical, thermodynamic and economic data for phosphorus and its compounds (Appendix I), a comparison of the thermodynamic reaction data of the Gibbs free energy from two independent sources (Appendix II), a hazard and operability study (Appendix III), the procedures for the in-house analysis of phosphine gas and phosphorous and phosphoric acids (Appendix IV), and lastly, a complete listing of the experimental operating conditions and the resulting reaction products (Appendix V).

CHAPTER II

LITERATURE SURVEY OF PLASMA CHEMICAL REACTIONS AND PHOSPHORUS CHEMISTRY

1 INTRODUCTION

This chapter contains background information on the characteristics and generation of thermal plasmas, as well as plasma chemical reactions involving homogeneous gas-phase reactions, such as acetylene synthesis, nitrogen fixation and methanol synthesis. The review of these plasma gas phase reactions provides information on their reactor geometric configuration, feed and quench methods, product collection, etc. and could suggest where improvements and/or novel design should be used for this work.

The basic chemistry of phosphorus and its compounds, specifically its oxides and acids, are examined next with particular attention given to the thermal plasma production of phosphorus and its derivatives and compounds. Finally, the conventional production of phosphorus trioxide and phosphorous acid used in industry is investigated as a basis of comparison.

2 CHARACTERISTICS OF A PLASMA

Sometimes referred to as the fourth state of matter, the plasma state is a partially ionized gas containing free electrons, positive and negative ions and neutral atoms. The plasma overall is electrically neutral, as the positive and negative charges cancel each other, however, due to the presence of free electrons, the plasma has typically high electrical conductivity. At atmospheric pressure, the degree of ionization depends on the ionization potential of the gas and its temperature. Thus Argon (ionization potential of 15.6 eV) is only about 1.5% ionized at 10 000 K, but 100% ionized at temperatures greater than 18 000 K.

Plasmas can be basically classified into two types: thermal and cold. The thermal plasmas are characterized by temperature equality between the free electrons and the heavy particles, and are produced in ambient to high pressure systems. Thermal plasma temperatures tend to be greater than 12 000 K and emit intense radiation in the visible and ultraviolet spectra. Their enthalpy is the sum of the sensible heat of the molecules, the energy of dissociation of the latter into atoms, and the energy required to partially ionize these atoms. Thus, their enthalpy is usually quite high and rises much more rapidly with temperature for diatomic gases. Nitrogen, for example, has an enthalpy of close to 10^4 kJ/mol at 12 000 K while the enthalpy is only 200 kJ/mol for argon at the same temperature.

Cold plasmas (approx. 300 K) are generally produced at pressures less than 100 torr and are characterized by non-equilibrium temperatures between the heavy particles and the free electrons. They have found many industrial applications in the fabrication of semiconductor devices for the microelectronics industry, in the deposition and growth of dielectric films and in the synthesis of organic polymer films and membranes for the filtration of liquids or the diffusional separation of gases.

The literature on thermal plasma technology and its applications is very extensive and usually very specific. Quite complete reviews of the field have been recently published by Fauchais et al. (1980, 1983), by Drouet (1984), and by Mikhlin (1985).

The advantages of using a thermal plasma generating device for a gas-phase reaction which is thermodynamically favoured by high temperatures, are the extremely high temperatures available in the plasma gas and its equally high gas enthalpy. Considerably shorter residence times should therefore result in much smaller equipment and decreased capital cost. The option of a controlled gas environment, the ease of operation and control under continuous conditions are additional advantages.

3 GAS-PHASE PLASMA CHEMICAL PROCESSES

Chemical reactions may be broadly classified into two main groups: homogeneous (gas-phase) or heterogeneous. Heterogeneous processes are involved in the treatment of reactants in the form of relatively small particles, such as metal concentrates, and refractory materials. These are actually solid-gas reactions. Heterogeneous processes using plasma technology in both the laboratory and industry environments are too numerous to mention and are really beyond the scope of this work. However, should one of the heterogeneous reactants be phosphorus, as in the production of phosphorus from phosphate rock, the process will be reviewed.

The discussion of chemical reactions pertinent to this study involving plasma technology is limited to vapour-phase homogeneous reactions, of which the following are good examples.

3.1 Acetylene Synthesis

The first Huels plasma furnace to produce acetylene was introduced in the 1940's, in which hydrocarbons were injected into hydrogen plasmas, and then rapidly quenched to prevent decomposition of the products to C and H_2. Improvements to the process (Mueller and Peuckert, 1983) has resulted in the successful plasma process producing C_2H_2, C_2H_4, and H_2. The primary quench consisted of liquid hydrocarbons to remove the sensible heat by using it in the chemical reaction producing ethylene. A final water quench cooled the final reaction mixture from 1300 K to 500 K. Reactors operated with a long DC arc between two tubular steel electrodes and vortex introduction of the gaseous hydrocarbons between them. The labscale investigation for the synthesis of pure acetylene was first performed by Leutner and Stokes (1961), who found that by feeding methane into an argon plasma jet 80% yields could be expected. A DC plasma arc was used at 7 kW and an argon flowrate of 8.9 L/min. The quenching system consisted of a water-cooled copper chamber; soot (7%) formed on the walls.

A process developed by AVCO using a DC hydrogen plasma torch to produce acetylene from coal powder was theoretically more efficient and could compete with ethylene for the products more easily obtained from acetylene, such as vinyl acetate and acetaldehyde (Bonomi et al., 1980). However, this process was discontinued due to the additional expenditures involved in processing the coal before injection.

Another approach to producing pure acetylene was followed by Baddour and Iwasyk (1962), where a high-intensity arc reactor equipped with a consumable carbon anode was used to supply the carbon for reaction while pure hydrogen gas was employed as the plasma gas. A water-cooled gas sampling probe was used to achieve the desired quench rates of 10^7 K/s. Results demonstrated the possibility of producing 23.8% acetylene with this method.

3.2 Nitrogen Fixation

The reaction between nitrogen and oxygen was first realized with a plasma arc process in the early 1900's by Birkeland and Eyde in Norway. The process involved the passing of air through an AC electric arc to form NO. Upon cooling the air stream with air, NO_2 was formed which was subsequently absorbed in water to yield nitric and nitrous acids for the fertilizer industry. With the advent of the Haber-Bosch process for the production of ammonia, the arc process was abandoned, mainly because of its high energy requirement of 33 kWh/kg NO.

However, Bonomi et al. (1984) concluded that even with the future development of new plasma reactors, possibly capable of producing a yield of 10%, so many other detrimental economic factors are involved (price ratio between CH_4 and electrical energy, etc.), that the outlook for an industrial application of thermal plasma technology for nitric acid production is poor. A recent report by the Ontario Hydro Research Division (1986) restated this conclusion.

3.3 Methanol Synthesis

Although there are three basic types of conventional methanol synthesis processes, high, intermediate and low pressure, only the intermediate pressure process, with either the ICI or Lurgi systems, is commercially used. A preliminary economic feasibility study carried out by Gauvin and Duncan (1982) on the plasmachemical production of methanol from peat showed that the proposed process could compete favourably with the existing technology. Laboratory work by Grosdidier and Gauvin (1985) has shown that by gasifying a feed of finely-divided peat using a nitrogen plasma with injected steam resulted in a H/CO of 1.05 and a carbon conversion of 81%. Following this work, Stuart et al. (1984) used a simulated steam plasma (hydrogen plasma with oxygen injected into the tailflame) to produce a synthesis gas with a H/CO ratio of 1.8 and a carbon conversion of 89%. Reaction models predicted that the 90% conversion required for an industrial process with a H/CO ratio of 2 was possible thus making this a potentially viable commercial process.

The above process used a DC plasma torch supported on a water-cooled roof. The peat was injected at a 45° angle to intercept the plasma jet at a location 10 cm below the top of the reactor. Oxygen was injected just downstream of the torch to react with the hydrogen plasma to form steam and contribute the heat of reaction to the reaction environment.

4 GAS-PHASE PLASMA REACTORS

Conceptually, a gas-phase plasma reactor consists of the following basic components:

a) the arc where the plasma is generated.

b) a reaction zone where mixing of the reactants and the plasma occurs, leading to subsequent reaction.

c) the quenching and product recovery section, where residual heat is rapidly removed and the chemical products recovered.

The reaction kinetics at very high temperatures are known to be favourable, but good mixing of the reacting gaseous species is essential for the desired reactions to occur. The intermediate section of the reactor serves as the mixing zone necessary to maintain a uniform reaction temperature in the reaction zone and to ensure that the reaction species are fully mixed in the required concentrations. The intermediate section need not be large, but rather depends on the residence time necessary for reaction to occur. For example, mixing of the chemical reactants can occur immediately after the arc has been initiated and a plasma flame generated. As the plasma gas expands outside the confines of the torch, a low pressure region is created at the expansion point in order to conserve the overall energy of the system (Bernoulli's equation). This low pressure region causes a powerful "pumping" action whereby surrounding gas is aspirated into the plasma flow. Introduction of the gaseous reactants into this low pressure region ensures that the reactants will be drawn into the plasma flame and intimately mixed. This pumping phenomenon is described by Lewis and Gauvin (1973) and is well documented.

The last section of the reactor removes the excess heat of the reaction stream as quickly as possible, thereby freezing the reaction products in their desired forms and preventing any further reaction to undesirable products. The speed of the quench can be critical and it is generally accepted that a rate of cooling less that 10^5 K/s is less than ideal. Various quenching methods exist: jet expansion through a Laval nozzle, contact with cold walls, liquid atomization and by injection of a cold fluid, inert or not, depending on whether subsequent products are desired. Typically, contact with cold walls gives rise to a quench rate of 10^4 to 10^6 K/s while injection of a cold gas gives 10^6 to 10^8 K/s. Important as well, is the location of the quench with respect to the product temperature. A delay of $2\text{x}10^{-3}$ second in the start of the quench causes a reduction in the conversion of methane to acetylene of 15 to 10%, whereas a reduction of quench speed from 10^8 to 10^7 K/s causes a reduction in the conversion of nitrogen to NO from 9.6 to 6.4% (Polak, 1971).

A theoretical study by Amouroux and Talbot (1972) of water quenching in an argon plasma containing methane attempted to determine the optimum quench rate to a) avoid thermal decomposition of acetylene to methane and, b) eliminate the combustion of acetylene with water vapour. They showed that two key factors affected the quench rate: (1) the quantity of water contacted with the hot gas and, (2) the "exchange coefficient", defined as the ratio of the vaporization speed to the gas flow.

5 PHOSPHORUS CHEMISTRY

The preparation of compounds in which the phosphorus atom exists in the +3 oxidation state has been rendered difficult by the complex nature of the phosphorus atom. The atom can exist in compounds having oxidation states ranging from -3, as in phosphine (PH_3), to +5, as in phosphoric acid (H_3PO_4). Intermediate oxidation states for phosphorus also exist, such as phosphorus monoxide (P_2O), and phosphite salts.

The object of the present study is in a first reaction, to produce the anhydride of trivalent phosphorus, phosphorus trioxide (P_2O_3), followed by a second consecutive reaction to produce phosphorous acid (H_3PO_3).

5.1 Phosphorus

The discovery of phosphorus is generally attributed to Brandt in 1669, found while performing alchemical experiments with urine. The element was so named to denote its "light-bearing" properties (Greek *phos*, light; Greek *phoros*, bringing). Urine, boiled down to a syrupy consistency, was distilled after being admixed with sand or charcoal, producing phosphorus vapour. Another technique in the early manufacture of phosphorus involved the production of phosphoric acid from bone ash or phosphate rock by treatment with sulphuric acid. The addition of a reducing agent such as coke and the subsequent distillation produced phosphorus. All of the phosphorus commercially available at the present time comes from the reduction of phosphate rock with coke in an electric furnace:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C ==> 6\ CaSiO_3 + 10\ CO + P_4 \qquad [2.1]$$
$$\Delta H = -3060\ kJ/mol\ P_4$$

Phosphorus, P, atomic weight 30.98, is in Group VA of the Periodic Table, just below nitrogen and exists at room temperature as P_4. In the ground state, P has the electronic configuration $[Ne]3s^2 3p^3$ with 3 unpaired electrons; this, together with the availability of low-lying vacant 3d orbitals, accounts for the predominant oxidation states III and V in phosphorus chemistry. The physical as well as the thermodynamic properties of phosphorus are listed in Appendix I. Solid elemental phosphorus exists in several allotropic forms, white, red and black being the most common. White phosphorus, used in this experimental study, melts at 44.1°C (317.1 K) to a clear colourless liquid with a density of 1.82 g/cm^3. It is soluble in carbon disulphide, ether, benzene, and other organic solvents. Liquid phosphorus boils at 280.5°C (553.5 K) and has a density of 1.74 g/cm^3 and a viscosity of 1.69 cp at 50°C (323 K). At temperatures below 800°C (1073 K), phosphorus consists mainly of P_4 molecules. However, at higher temperatures, there is considerable dissociation to P_2 molecules and P atoms. The heat capacity of the P_2 vapour at 25°C (298 K) is 7.63 cal/(°C)(mole) whereas that of the P_4 vapour is 16.0 cal/(°C)(mole) at the same temperature. The variations of heat capacity and heat content of the P_2 and P_4 gas with temperature, as well as other thermodynamic data, are given by Farr (1950).

In general, white phosphorus is much more reactive than the red or black variety, and ignites spontaneously in air to form various phosphorus oxides, predominantly phosphorus pentoxide. A discussion of the reactions and chemistry of either red or black phosphorus is beyond the scope of this study, and therefore the reader is referred to an excellent reference on phosphorus by Van Wazer (1958). The rate of oxidation when P_4 comes into contact with moist air depends on the partial pressure of the oxygen and water vapour in the mixture. Other oxidizing agents, such as the halogens and sulphur produce phosphorus halides and sulphides. Carbon monoxide neither oxidizes phosphorus nor reduces its oxides, whereas carbon dioxide oxidizes phosphorus above 650°C (923 K).

White phosphorus is oxidized by aqueous solutions of metal salts, eg. silver, which have a low oxidation-reduction potential. A solution of copper sulphate, for instance, is used to neutralize persons having accidentally come into contact with phosphorus. The phosphorus would react slowly with the copper sulphate to produce a black non-toxic copper phosphide coating, thus protecting the victim from the phosphorus igniting in air.

5.2 Phosphorous Trioxide

Phosphorous trioxide is a colourless liquid with a melting point of 23.8°C (296.8 K) and a boiling point of 175.4°C (448.4 K). It is somewhat soluble in carbon disulphide and can be recrystallized from this solvent. White phosphorus is soluble in the oxide to the amount of 1.7 gram of P per 100 gram phosphorous trioxide at 25°C (298 K). Phosphorus trioxide, having an empirical formula of P_2O_3 or P_4O_6, also known as phosphorous oxide or phosphorous anhydride, was first prepared and extensively studied by Thorpe and Tutton (1891), who controlled the burning of phosphorus with air. Among their numerous results, they found that an increase in the quantity of air passed over the burning phosphorus increased the yield of the oxide, and determined that the oxide in the gaseous state corresponded to a molecular formula of P_4O_6. Crystals were obtained as aggregates, shown in Figure 2.1a, in the warmer parts of the condenser, however, once the gas was cooled, the melted oxide solidifies into thin prisms capped by pyramids, shown in Figure 2.1b, sometimes an inch long. Isolation

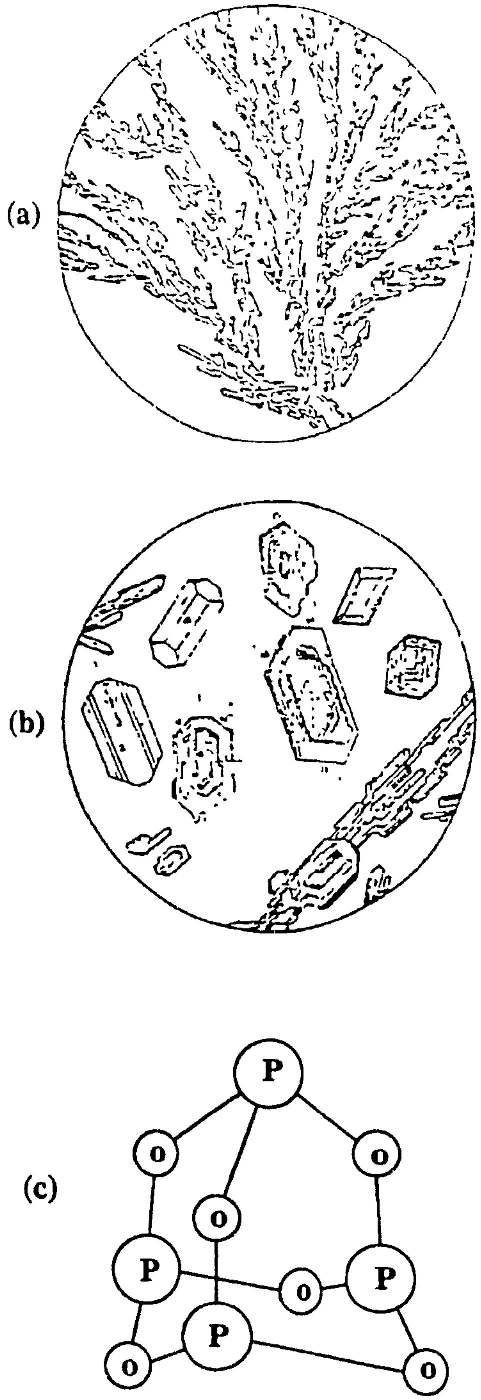


Figure 2.1 - Phosphorous trioxide
a) Warm crystals b) Cold crystals c) Molecular structure

of the individual crystals reveals prism faces and pyramidal forms, and are extremely soft and plastic. The phosphorus atoms are located at the corners of a regular tetrahedron and each of the six oxygens are located between the two phosphorus atoms in the plane of symmetry passing through the trigonal axes, shown in Figure 2.1c.

Wolf and Schmager (1929) improved the method of preparing the oxide by burning white phosphorus, kept at a temperature of 318-322 K, in a tube containing 75% total oxygen in air, at a pressure of 12 kPa with a flowrate of 30 sL/h. They thus increased the yield to 56%. Careful precautions are required to obtain reasonable yields (Heinze, 1975). Thilo and Hein (1964) patented a process for the continuous production of phosphorous oxide through the oxidation of phosphorus by nitrous oxide, N_2O, at 848 K under a reduced pressure of 9.3 kPa. Yields of 50% were reported with less than 1% impurity in the product.

Although Raman data have been interpreted to confirm Thorpe's previous work that the oxides molecular formula in all phases to be P_4O_6 (Gerding and de Decker, 1945), the air oxidation of phosphorus in a carbon tetrachloride solution performed by Blaser (1931), produced a pale yellow precipitate which was said to exhibit the empirical formula, P_2O_3. The composition of this material is questionable, however, and further study would have to be made to fully substantiate the claim.

Phosphorus trioxide decomposes slowly at 210°C and more rapidly at higher temperatures according to the following equation (Greenwood, 1984):

$$m\ P_4O_6\ <=====>\ x\ P_4O_n\ +\ y\ P(red) \qquad [2.2]$$

where n varies from 7.7 to 8.1.

Thorpe (1891) studied the reaction of phosphorous trioxide with various halogens, e.g. bromine, iodine, sulphur, and of acids, eg. HCl, H_2SO_4, as well as oxygen and water. The oxide spontaneously oxidized to phosphorus pentoxide on exposure to air or to oxygen and a glow occurred which was identical to the glow occurring during the oxidation of elemental phosphorus. This was probably due to traces of unreacted phosphorus remaining in the oxide sample since Miller (1923) removed the excess phosphorus from the phosphorous trioxide and observed no glow. When the oxide is oxidized by a mixture of oxygen and ozone, two molecules of P_4O_6 are oxidized for each mole of O_3 reaction, meaning that both oxygen and ozone take part in the oxidation. Miller concluded from this and other experiments, that P_4O_6 is always formed as an intermediate product in the oxidation of elemental phosphorus but decomposes rapidly so that the main products are phosphorus tetroxide (P_2O_4) and phosphorus pentoxide (P_2O_5).

The reaction of phosphorous trioxide with water, before the work performed by Thorpe, was reported to be violent and immediate, however in reality the oxide is somewhat inert in its attraction for water under certain conditions. Both the solid and the liquid form added slowly to still cold water are unaffected even when left standing for several days. However, if P_4O_6 is shaken rapidly with an excess of cold water, the product is exclusively phosphorous acid (Wolf et al., 1932). The oxide reaction with water is as follows:

$$P_4O_6 + 6\ H_2O <===> 4\ H_3PO_3 \qquad [2.3]$$

In hot water, the reaction is very energetic, producing large quantities of red phosphorus (Thorpe, 1891).

5.3 Phosphorous Acid

Phosphorous acid (IUPAC name: phosphonic acid) is a white deliquescent crystalline compound having a melting point of 346.6 K and a specific gravity of 1.597. It is very hygroscopic and highly soluble in water. The heat of fusion of the crystalline acid is 12.84 kJ/mol, and the heat of solution in an excess of water is -0.54 kJ/mol.

The structure of the acid is shown in Figure 2.2 in which the phosphorus atom is bonded to one hydrogen atom, one oxygen atom and two hydroxyl groups, which account for its dibasic nature (Simon, 1937). Aqueous phosphorous acid is a strong reducing agent, although it reacts slowly with oxidizing agents at room temperature. It reduces silver ion to metallic silver and reacts with hot concentrated sulphuric acid

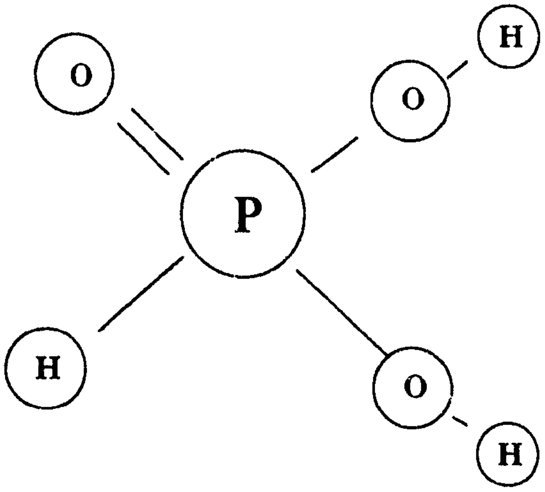


Figure 2.2 - Phosphorous acid molecular structure (IUPAC)

to form orthophosphoric acid and sulphur dioxide (Yost, 1944). It is also oxidized in aqueous solution by halogens, mercuric chloride and other oxidizing agents. Phosphorous acid was first prepared by the slow oxidation of white phosphorous in a moist atmosphere, and produced yields of 18% phosphorous acid, 75% phosphoric acid and 7% as all other oxyacids (Thorpe, 1891). Phosphorous acid can also be prepared from the direct hydration of its anhydride, P_4O_6, however the most common commercial technique involves the hydration of phosphorus trichloride as follows (Voigt et al., 1953):

$$PCl_3 + 3\,H_2O <=====> H_3PO_3 + 3\,HCl \qquad [2.4]$$

One industrial method, patented by Cremer and Martin (1972), involves the spraying of PCl_3 under nitrogen into a reactor containing an excess of steam at 458-463 K. The reaction can be violent partly because of the heat liberated in the solvation of the hydrogen chloride. The hydrolysis can be moderated by adding PCl_3 to a saturated solution of HCl. The product is then purified with the removal of the excess H_2O and HCl by boiling at 453 K. On cooling, phosphorous acid crystallizes from the melt.

Another method uses oxalic acid to produce the acid according to the following equation:

$$3\ (COOH)_2 + PCl_3 \Longleftrightarrow H_3PO_3 + 3\ CO_2 + 3\ CO + 3\ HCl \qquad [2.5]$$

The specifications for a typical technical-grade phosphorous acid are given in Appendix I. The disposal of the HCl by-product can pose problems (Kirk and Othmer, 1979) and work has been performed for the production of the acid by a non-halide route but so far, no process exists on an industrial level.

Extremely pure phosphorous acid has been made in aqueous solution by treating lead phosphite with hydrogen sulphide (Van Wazer, 1958). The lead phosphite is obtained in pure form by mixing solutions of recrystallized disodium phosphite with lead acetate. Alternatively, the recrystallized disodium phosphite can be converted directly to the acid by ion exchange.

Phosphorous acid is often the by-product of other reactions such as in the manufacture of acid chlorides from carboxylic acids and PCl_3, or in the manufacture of hypo-phosphorous acid, H_3PO_2 (IUPAC name: phosphinic acid). For example, phosphorous acid is a by-product resulting from the primary treatment of calcium salt with sulphuric acid, as follows:

$$H_2SO_4 + Ca(HPO_3) \Longleftrightarrow CaSO_4 + H_3PO_3 \qquad [2.6]$$

Phosphorous acid is recovered from the filtrate after the calcium sulphate is removed.

The thermal decomposition of phosphorous acid occurs rapidly at 523-548 K, resulting in the formation of phosphoric acid, phosphine, hydrogen, and some red phosphorus. According to Hackspill and Weiss (1932), the decomposition is as follows:

$$4\ H_3PO_3 <====> 3\ H_3PO_4 + PH_3 \qquad [2.7]$$

$$H_3PO_3 + H_2O <====> H_3PO_4 + H_2 \qquad [2.8]$$

Most of the applications of phosphorous acid are based on its salts and esters. One use is in the stabilization of polyvinyl chloride and other polymers to prevent their discolouration by heat or u.v. light. Some of the more widely used phosphites for this purpose are triphenyl phosphite, trinonylphenyl phosphite, tri-iso-octyl phosphite. The organic groups attached to the phosphorus atom, depending on their nature, improve the compatibility of the stabilizer with the polymer system (Toy, 1973).

Monsanto reacts phosphorous acid with an organic moiety, to produce aminoalkylphosphorous acids such as "Polan's" or "Roundup", a product which is a herbicide initially but decomposes to a fertilizer. Phosphorous acid is also used to form phosphonates which are used in a variety of water treatments from de-scaling to corrosion inhibitors. The textile and pulp and paper industries use phosphorous acid in the "sizing" of their products as well as making surface active additives.

5.4 Oxidation of Phosphorus with Water or Steam

The products resulting from the oxidation of phosphorus with water depend greatly on the experimental conditions, i.e. temperature, pressure, etc., and although phosphorous trioxide, the desired product in the present study, is not always produced, it is interesting to review these findings from both an analytical and historical perspective.

In 1864, Oppenheim produced minute quantities of phosphorous acid at 473 K, from the direct oxidation of phosphorus with liquid water, according to the following empirical reaction:

$$2\,P + 3\,H_2O \Longleftrightarrow H_3PO_3 + PH_3 \qquad [2.9]$$

$$\Delta H = 233.0 \text{ J/mol}$$

Hackspill (1931) repeated Oppenheim's work in the hope of completely oxidizing elemental phosphorus to its acids. As was the previous experience, the reaction proceeded very slowly (40 hours to complete reaction); however, if phosphoric acid is added and the temperature is raised slightly to 523 K, phosphorous acid is produced, according to the reaction:

$$3\,H_3PO_4 + 2\,P + 3\,H_2O \Longleftrightarrow 5\,H_3PO_3 \qquad [2.10]$$

$\Delta H = -197.5$ J/mol

Unfortunately, the phosphorous acid formed is not stable and decomposes rapidly to regenerate the phosphoric acid catalyst by two decomposition reactions:

$$4\ H_3PO_3 \ \Longleftrightarrow\ 3\ H_3PO_4 + PH_3 \qquad [2.11]$$

$$H_3PO_3 + H_2O \ \Longleftrightarrow\ H_3PO_4 + H_2 \qquad [2.12]$$

$\Delta H = -79.5$ J/mol

With the introduction of oxygen into the system a secondary reaction between phosphine and excess water results in the production of phosphoric acid, as follows:

$$4\ PH_3 + 5\ O_2 + 6\ H_2O \ \Longleftrightarrow\ 4\ H_3PO_4 + 6\ H_2 \qquad [2.13]$$

$\Delta H = -3.74$ kJ/mol

Liljenroth and Larsson (1925) patented a process for the production of phosphorus pentoxide by the direct oxidation of phosphorus with steam at temperatures of about 1275 K. The reaction was as follows:

$$P_4 + 10\ H_2O \ \Longleftrightarrow\ P_4O_{10} + 10\ H_2 \qquad [2.14]$$

At temperatures above 1275 K, any phosphine formed will decompose to pure phosphorus and hydrogen. This is important in its relevance to the present study since phosphine could pose a serious toxic gas by-product in our reaction involving steam and phosphorus.

Later, Britz and Pestoff (1929) performed the same experiments but found not only the pentoxide, but lower oxides and phosphine as well. As the latter products were undesirable, efforts were directed to eliminate them by the use of low temperatures and catalysts, or by low temperatures and high pressures (Britzke, 1929 and Ipatiew, 1932).

Ipatiew and Freitag (1933) continued the previous work by extensively studying the influence of temperature, pressure and catalysts with phosphorus and water in an effort to produce hydrogen and phosphoric acid. They concluded that phosphorous acid from the primary reaction:

$$P_4 + (3+n)\,H_2O <===> P_2O_3(H_2O)_n + 2\,PH_3 \qquad [2.15]$$

is formed only when both temperatures (<523 K) and pressures are low. At higher temperatures (548 K) and pressure, the oxidation of phosphorous acid continues, forming phosphoric acid and hydrogen. Ipatiew also found that excess steam hampers the formation of both phosphorous and phosphoric acid. These results contradict the predictions of the thermodynamic study at conditions of high temperatures and excess steam on the formation of the trioxide and pentoxide, as discussed in Chapter III.

Brunauer and Shultz (1941) reacted phosphorus and steam at temperatures between 1275-1375 K, and found considerable amounts of phosphorus pentoxide, phosphorus tetroxide (P_4O_8 or P_2O_4), phosphine and hydrogen. No phosphorous trioxide was formed, however Brunauer did not use any formal quenching system for the collection of the various oxides, but rather allowed the oxides to condense in a U-tube exposed to the laboratory environment. Since it has already been shown that phosphorous acid will decompose at 523 K to phosphoric acid and phosphine, the results of Brunauer's work seem doubtful as to their validity.

Elmore (1952) patented a process to produce phosphoric acid by passing a mixture of steam and phosphorus vapour over a catalyst consisting of copper compounds supported by an aluminum orthophosphate material. When ratios of steam to phosphorus vapour were below 16:1, high percentages of phosphorous acid were produced. High percentages of phosphoric acid were produced when the steam/phosphorus ratio was between 16 and 30. Temperatures ranged between 873-1173 K.

A similar process was patented by Shultz (1952) except that the supporting material was composed of pyrophosphates of titanium and zirconium.

5.5 Plasma Production of Phosphorus and Phosphorus Compounds

A number of patents have been awarded for the conversion of phosphate rock, essentially impure fluorapatite, $Ca_5F(PO_4)_3$, to elemental phosphorus by the high temperature reduction of the ore using a thermal plasma. Goldberger and Baroch (1966) used a three electrode transferred-arc plasma system with a hydrocarbon fluidizing gas to fluidize a bed of coke and silica in order to reduce the phosphate ore to the element. Mosse et al. (1968) injected the phosphate ore into a nitrogen plasma and then rapidly quenched the system such that the ore could be leached to recover phosphorus pentoxide. An inclined rotating furnace, using two plasma jets, was tested by Foex et al. (1971) for the reduction of the phosphate rock by the addition of coke and silica. A gas-solid reaction to produce elemental phosphorus using methane as a reducing gas in a DC plasma jet reactor, by Chase et al. (1979), yielded up to 80% reduction of the phosphate rock although the power requirements were approximately three times greater than the conventional process. This was expected to decrease once the scale-up of the laboratory model was made. In all these approaches, phosphorus was recovered as a vapour, leaving the impurities in the solid phase.

Sullivan and Fonseca (1972) who studied the preparation of phosphorus nitrides in a radio frequency (RF) induction plasma, found that only small amounts could be produced (best results showed 3.2% conversion) and that conventional production techniques were much more promising.

Much work has been performed by Mosse et al. (1985) at the BSSR Academy of Sciences, in the USSR, on the thermal dissociation of phosphates in a thermal plasma to form phosphorus containing compounds. Among their work was the development of a one-stage process using an air plasma for the simultaneous production of nitrogen and phosphorus oxides from natural phosphates, thereby producing an excellent slow-release fertilizer.

A process of preparing phosphorous trioxide was described in the patent application of Mezey and Hall (1969), where a microwave plasma of carbon dioxide or nitric oxide combined with elemental phosphorus. The subsequent reaction between the electronically excited gas and phosphorus produced phosphorous trioxide.

A DC plasma jet, using argon or helium as the plasma gas, accomplished the synthesis of phosphorous trioxide by reducing an anhydride of pentavalent phosphorus, i.e. P_4O_{10}, with carbon monoxide (Reed et al., 1969). The reaction zone temperature was varied between 1500 K to about 20 000 K.

Another method for the preparation of phosphorous trioxide using a microwave plasma was described in the patent application of Mezey (1969). Electronically-excited helium provided the energy necessary to dissociate the anhydride of pentavalent phosphorus into the anhydride of trivalent phosphorus and oxygen. The phosphorous trioxide was then separated from the oxygen in a subsequent step.

Whyte et al. (1970) produced trivalent phosphorus by reacting elemental phosphorus, oxygen and at least one carbon oxide at temperatures above 1775 K, but below 5275 K. The presence of carbon monoxide (preferred ratios P_4:O_2:CO of 1:3:2 to 1:5:10) or carbon dioxide (preferred ratios P_4:O_2:CO_2 of 1:2:8 to 1:3:2) was claimed to promote the formation of the phosphorus trioxide by acting as a reducing agent for any P_4O_{10} formed, and depending on the experimental conditions, as high as 95% anhydride products were formed. An additional quenching step to decrease the product temperature from 1775 K to about 775 K in less than 3 seconds was critical to avoid disproportionation to the undesired by-products, pentavalent phosphorus oxide and red phosphorus. The quenching methods proposed in this patent included (1) the passing of the hot reaction products through a cooled tube, producing phosphorous trioxide, P_4O_6; (2) the contacting with a water spray with the formation of phosphorous acid, H_3PO_3; and (3) treating the hot reaction products with acetic acid, thereby producing ethane-1-hydroxy-1,1-diphosphonic acid, used as an intermediate for use in detergent compositions.

Krause et al. (1972) patented a process whereby a RF plasma of carbon dioxide in the range from 0.75 to 25 MegaHertz, interacts with elemental phosphorus to produce the anhydride of trivalent phosphorus, phosphorous trioxide. The product formed at temperatures between 1,500 K and 20,000 K was sent to a quenching chamber where it was cooled to below 800 K, and then onto a product recovery section composed of a series of cold traps, where the product condenses and the unreacted and inert gases were vented. Product yields of 50% phosphorous trioxide were claimed.

6 CONCLUSIONS

The production of phosphorous acid through the gas-phase reaction of steam and phosphorus vapour has never been successfully performed and thus formed the basis of the present work. The thermodynamic calculations presented in the following section, Chapter III, show that this reaction would occur at temperatures above 1500 K. The use of a plasma device to provide these high temperatures was ideal since a highly enthalpic gas providing a controlled oxidation environment could be easily supplied.

Although phosphorous acid is commercially produced via the phosphorus trichloride route, this process is complicated since it required two reaction systems; one for the production of PCl_3 and in a second, to produce the phosphorous acid. As such, high purity is difficult to obtain and the chlorine gas required along with the hydrochloric acid produced poses some corrosion, handling and disposal problems.

The oxidation of phosphorus with steam via a non-plasma route has been investigated generally for the production of phosphoric acid and not phosphorous acid. However, several authors have also inadvertently produced low concentrations of phosphorous acid while investigating methods of producing phosphoric acid. The use of plasma technology to produce phosphorous trioxide and phosphorous acid has also been studied with excellent conversion results when either oxygen or carbon oxide mixtures were used as the oxidizing reactant. However, since the purity of the phosphorous acid is extremely sensitive to small changes in the oxygen feedrate, control of this process on an industrial scale is difficult if not impossible. In general, reactions between phosphorus and carbon dioxide did not yield high conversion rates to phosphorous acid.

The experimental equipment set-up used in the gas-phase reactions described earlier using plasma technology gave some indication of the equipment configuration required for the successful gas-phase reaction of phosphorus and steam to produce phosphorous acid. For example, the introduction of a water spray as an effective quench medium (acetylene production) and the use of angled feed injection ports (synthesis gas production) are among those that were incorporated into the final equipment design.

7 REFERENCES

Amouroux, J. and Talbot, J., "Etude theorique de la trempe a l'eau d'un melange argon-acetylene", Chimie et Industrie, 205, 120 (1972)

Baddour, R.F. and J.M. Iwasyk, "Reactions between elemental carbon and hydrogen at temperatures above 2800 K", I&EC Process Design and Development, 1, 3, 169 (1962)

Blaser, B., Chem. Ber., 64B, 614 (1931)

Bonomi, A., Derouette, J.J., Gennai, V., Gold, D., Haour, G., and dePous, O., "Assessment of prospects for thermal plasma furnace technology", Battelle (1984)

Britzke and Pestoff, Trans. Sci. Inst. Fertilizers (USSR), No. 59 (1929)

Brunauer, S., and Shultz, J.F., "Oxidation of phosphorus by steam", Ind. and Eng. Chem., 33, 828-832 (1941)

Chase, J.D., Skrivan, J.F., Hyman, D., and Longfield, J.E., "Plasma jet process for making elemental phosphorus", Ind. Eng. Chem. Process Des. Dev., 18, 2, 261-266 (1979)

Cremer, J. and Martin, W., "Process for production of phosphorous acid", German Patent 2,200,653 (1972)

Drouet, M.G., "Plasma technology: Review of the state of the art and its potential in Canada", CEA No. 126 U 322 (1984)

Elmore, K.L., "Oxidation of phosphorus with steam", Patent US 2,613,134 (1952)

Farr, T.D., "Phosphorus - Properties of the element and some of its compounds", TVA Chem. Eng. Rep. No. 8 (1950)

Fauchais, P., Bourdin, J.-M., "State of the art of plasma chemical synthesis of homogeneous and heterogeneous products", Pure and Appl. Chem., 52, 1669-1705 (1980)

Fauchais, P., Bourdin, J.-M., and Coudert, J.F., "Generalities on the physical and chemical processes in a thermal plasma", Int. Chem. Eng., 23, 2 (1983)

Foex, M., Dumon, R., Bot-Langet, Y., and Verouchalim, D., Patent FR 2,079,746 (1971)

Gauvin, W.H., and Duncan, S.R., "Methanol from peat using plasma-generated superheated steam", Tech. Report, Centre de Recherche Noranda (1982)

Gerding, H. and de Decker, H.C.J., Rec. trav. chim., 64, 191 (1945)

Goldberger, W.M. and Baroch, C.J., Patent US 3,247,014 (1966)

Greenwood, N.N. and Earnshaw, A., Chemistry of the Elements, Pergamon Press (1984)

Grosdidier de Matons, P., and Gauvin, W.H., "Gasification of peat in a steam plasma reactor", Can. J. of Chem. Eng., 63, 1, 93-98 (1985)

Hackspill, L., "L'oxydation du phosphore par l'eau et la preparation de l'acide phosphorique", Chimie et Industrie, 25, 1058-1063 (1931)

Hackspill, L. and Weiss, J., Chimie & Industrie, Special No., 453 (1932)

Heinze, D., "Chemistry of phosphorus(III) oxide", Pure and Appl. Chem., 44, 141-72 (1975)

Ipatiew, W.N., "Process for production of phosphoric acid and hydrogen", Patent US 1,848,295 (1932)

Ipatiew, W.N. and Freitag, C., "The oxidation of phosphorus with water at elevated temperatures and pressures", Zeitschrift Anorgasusche und allgemeine Chemie, 215, 388-414 (1933)

Kirk, R.E. and Othmer, D.F., Encyclopedia of Chemical Technology, 17, 473, Interscience Encyclopedia, Inc., N.Y. (1979)

Krause, H.H., McNulty, J.S., and Hall, R.E., "Process for the preparation of an anhydride of trivalent phosphorus", Patent US 3,652,213 (1972)

Leutner, H.W., and Stokes, C., "Producing acetylene in a plasma jet", Ind. and Eng. Chem., 53, 5 (1961)

Lewis, J.A. and Gauvin, W.H., "The Motion of Particles Entrained in a Plasma Jet", A.I.Ch.E. J., 19, 5, pp. 982-990 (1973)

Liljenroth, F.G., CAN 247,164 (1925); US 1,594,372 (1926)

Mezey, E.J., Patent Appl. US 861,145 (1969)

Mezey, E.J., and Hall, R.E., Patent Appl. US 861,159 (1969)

Mikhlin, J.A., "Survey of the potential of plasma technology application in Canada", DSS File No. 26SQ.23440-4-9010 (1985)

Miller, C.C., J. Chem. S., 1929 (1923)

Mosse, A.L., Pechknovsky, V.V., Dzyuba, E.D., and Krasovskaya, L.I., "Preparation of condensed phosphate by plasma chemical treatment of phosphate raw material", Plasma Chem. and Plasma Proc., 5, 3, 275-282 (1985)

Mosse, A.L., Pechkovskii, V.V., Menkh, V.A., and Dvindenko, I.A., J. Eng. Phys. (USSR), 15,6 (1968)

Mueller, R., and Baronnet, J.M., Pure and Appl. Chem., 52, 1669-75 (1980)

Oppenheim, C., Bull Soc. Chem., t. 1, 163 (1864)

Polak, L., "Some principles of nonequilibrium plasma chemical reaction kinetics", Plasma Chemistry, 13, 141, Wiley Interscience, N.Y. (1971)

Shultz, J.F., "Oxidation of phosphorus with steam", Patent US 2,613,135 (1952)

Simon, A. and Feher, F., z. anorg. allgem. Chem., 230, 289-307 (1937)

Stuart, P.R., Munz, R.J., and Gauvin, W.H., "Synthesis gas production from peat using a steam plasma", Plasma Chemistry and Plasma Processing, 4, 4, 297-314 (1984)

Sullivan, J.M., and Fonseca, R.A., "Preparation of phosphorus nitrides in a thermal plasma", TVA Report No. 707 (1972)

Thilo, E. and Hein, D., Patent No. GER 1,172,241 (1964)

Thorpe, T.E. and Tutton, A.E.H., "Phosphorous oxide - Part 1", J. Chem. S., 57, 545-573 (1891)

Thorpe, T.E. and Tutton, A.E.H., "Phosphorous oxide - Part 2", J. Chem. S., 59, 1019-1029 (1891)

Toy, A.D.F., Comprehensive Inorganic Chemistry, Vol 2, 398, Pergamon Press, N.Y. (1973)

Van Wazer, J.R., Phosphorus and its compounds, Vol 1-2, Interscience Press, N.Y. (1958)

Voigt, D. and Gallais, F., Inorganic Synthesis, J.C. Bailer, Ed., McGraw Hill Book Co., N.Y., Vol 4, 55-8 (1953)

Whyte, D.D., Pflaumer, P.F., and Roberts, T.S., "Process for preparing chemical compounds containing trivalent phosphorus", Patent US 3,532,461 (1970)

Wolf, C., Jung, W., and Tschudnowsky, M., Chem. Ber., 65B, 488 (1932)

Wolf, L., and Schmager, H., "Beitrage zur kenntius des phosphortrioxyds", Chem. Ber., 62B, 771 (1929), Chem. Ber., 62B, 771 (1929)

Yost, D.M. and Russell, H., Systematic Inorganic Chemistry, 155-254, Prentice Hall, Inc., N.Y. (1944)

CHAPTER III

THERMODYNAMICS OF PHOSPHORUS/STEAM SYSTEM

1 INTRODUCTION

In this chapter, the thermodynamic equilibrium composition of the reaction between phosphorus and steam at various reactant feedrates and reaction temperatures to produce phosphorous trioxide, P_2O_3, was investigated. Phosphorous trioxide reacts readily with water to produce phosphorous acid, H_3PO_3, the desired acid product. Because the reaction between phosphorus and steam produces other phosphorus oxides, such as P_4O_5 (or P_4O_{10}), PO, and P_4O_9 among others, which produce an undesired product upon contact with water (phosphoric acid, H_3PO_4), factors influencing the selectivity of phosphorous trioxide over these other oxides were examined and are presented below. Once the factors influencing the selectivity of phosphorous trioxide were established, the experimental equipment was designed to provide the necessary operating conditions for its formation; for example, the temperature, pressure, reactant feed systems, etc. Because of the very high temperatures typically found in a plasma heated reactor, the reactant energies are so great that, in general, the reactions predicted by the thermodynamic analysis proceed rapidly as long as the residence time exceeds the reaction time required. Previous work by Whyte et al. (1970) in the preparation of the trivalent phosphorus had demonstrated that from about 1 millisecond to 1 second was required for reaction, depending on the experimental conditions. In the present work, the residence time of the reactants in the central zone of the plasma jet was calculated to be approximately 100 milliseconds, sufficient time for reaction to occur. The study of the kinetic behaviour of the reactions involved in the high temperature zone therefore was of little concern in the present study.

2 HEAT EFFECTS

The oxidation of gaseous phosphorus by steam at high temperatures results in the formation of various phosphorus oxides, principally P_2O_3, P_4O_5 (or P_4O_{10}), PO, PO_2 and P_4O_9. By rapidly cooling P_2O_3 with water, the desired phosphorous acid product, H_3PO_3, is formed. Typical thermodynamic calculations showing the heat effects at the various steps of the formation of phosphorous acid at a temperature of 1475 K are presented below. Experimental measurements obtained in this study at this temperature (Chapter V) also resulted in high conversions of phosphorus to phosphorous acid. A study of the thermodynamic equilibrium composition as a function of temperature is presented later on in this chapter. The basic reactions to form phosphorous acid were as follows:

a. Sensible heating of reactants to 1475 K

$$P_4 + 6\,H_2O \;====>\; P_4 + 6\,H_2O \qquad [3.1]$$
$$\Delta H = 330.5 \text{ kJ/mol}$$

b. Heat of reaction (endothermic) at 1475 K

$$P_4 + 6\,H_2O \overset{K_1}{\Longleftrightarrow} 2\,P_2O_3 + 6\,H_2 \qquad [3.2]$$

$$\Delta H = 179.2 \text{ kJ/mol}$$

c. Sensible heat removed in the quench (1475 to 350 K)

$$2\,P_2O_3 + 6\,H_2 \Longrightarrow 2\,P_2O_3 + 6\,H_2 \qquad [3.3]$$

$$\Delta H = -501.7 \text{ kJ/mol}$$

d. Water reaction (exothermic) at 350 K

$$P_2O_3 + 3\,H_2O \overset{K_2}{\Longleftrightarrow} 2\,H_3PO_3 \qquad [3.4]$$

$$\Delta H = -797 \text{ kJ/mol}$$

Although the various other oxide formation reactions compete for the phosphorus in the high temperature region of the reactor, experiments performed in this study have shown that the oxides other than P_2O_5 were not stable at low temperatures and were subsequently oxidized to the pentoxide state (+5) once the quench was applied. Greenwood (1984) also reports that although PO and P_2O_6 are stable under certain conditions, they readily oxidize to P_2O_5 by contact with oxygen. As for (a)+(b) above, the reaction to produce P_2O_5 at 1475 K is:

$$P_4 + 10\,H_2O \overset{K_3}{\Longleftrightarrow} 2\,P_2O_5 + 10\,H_2 \qquad [3.5]$$

$$\Delta H = 866.8 \text{ kJ/mol}$$

Thus, the formation of P_2O_3 and P_2O_5 were the two most important oxide reactions in the present study since they both produce stable products at room temperature and contact with water, H_3PO_3 and H_3PO_4, respectively.

The relative increase of K_1 and K_3 equilibrium constants as a function of temperature is plotted in Figure 3.1. Ideally, the difference in the equilibrium constants between the two competing reactions should be maximized; from the graph, this occurs at about 650 K. However, at this low temperature, kinetic considerations are important and experiments described later showed low conversion to phosphorous acid at these temperatures.

Because of the dependence of the reaction between phosphorus and steam on the reactant stoichiometry, H_2O/P_4, and the reaction temperature, the thermodynamic calculation of the Gibbs energy, $\Delta G=0$, considering as many of the conceivable reactions as possible was studied to determine under what experimental conditions the formation of P_2O_3 was favoured. These results indicate that P_2O_3 will form at temperatures less than 930 K along with P_2O_5 and other oxides. Unfortunately, these results are of limited value since they do not give the final composition of the equilibrium mixture. Nevertheless, these results are presented in Appendix II for future reference.

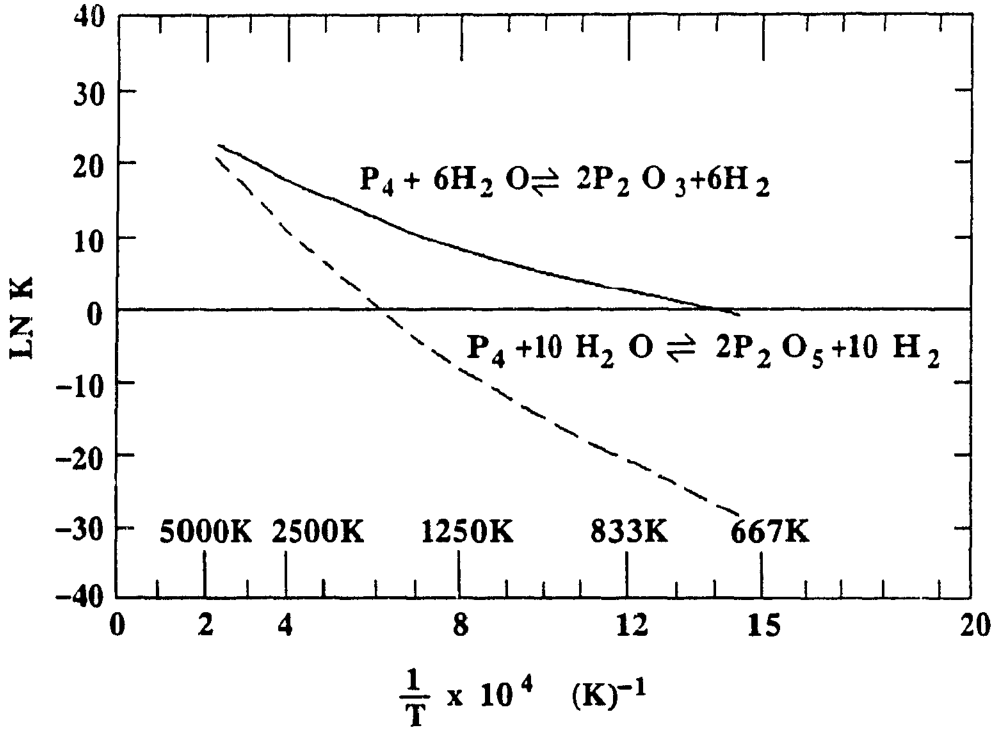


Figure 3.1 - Equilibrium constants for P_2O_3 and P_2O_5 vs temperature

3 THERMODYNAMIC EQUILIBRIUM COMPOSITION

A thermodynamic equilibrium analysis[1] for the reaction between phosphorus and steam was performed using the "Facility for the Analysis of Chemical Thermodynamics (F*A*C*T)" (Thompson et al., 1988) computer package. This algorithm determines the most stable products associated with the lowest Gibbs energy, at a specified temperature and pressure. Modifications to the main database were made to account for the unlisted phosphorus oxides (Twardowska, 1987).

3.1 Effect of Excess Steam

Thermodynamic equilibrium calculations were performed with a stoichiometric ratio of phosphorus to steam (H_2O/P_4) of 6:1 to determine whether the above analysis was adequate in describing the reaction system, the results of which are presented in Figure 3.2a. The presence of P_2O_3 was minimal at temperatures below 1000 K, however, unreacted phosphorus, P_4, and P_4O_9 were present in large quantities. As the temperature was increased, P_2O_3 formation increased sharply to a maximum at 1500 K and remained fairly constant to 2500 K, while P_4 and P_4O_9 decreased substantially. As the temperature was further increased above 3500 K, the lower oxides and compounds

---

[1] Thermodynamic calculations provided by a co-sponsor of this work (Albright & Wilson Americas) were inconsistent with the F*A*C*T analysis, but are nonetheless presented in Appendix V for comparison.

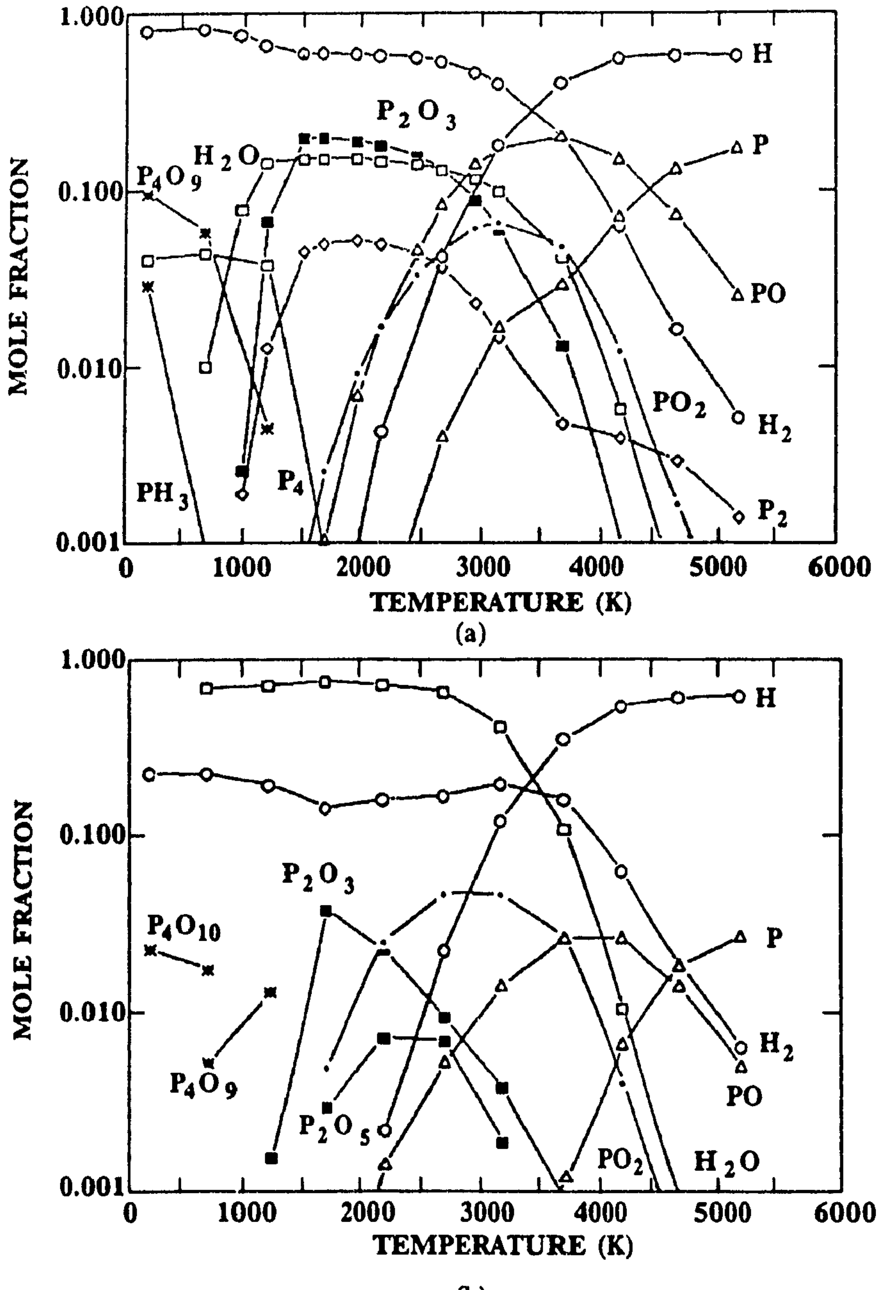


Figure 3.2 - Equilibrium composition of H_2O:P_4 at:
a) 6:1 b) 40:1

began to break up to their atomic components, P and H. Phosphine gas, PH_3, a toxic phosphorus hydride, although present in large quantities at low temperatures (<500 K), was not stable at temperatures greater than 700 K.

When the amount of steam reactant was increased seven fold over stoichiometric, i.e. $H_2O/P_4=40:1$, shown in Figure 3.2b, the formation of the P_2O_5 greatly increased. The formation of this pentoxide would have eventually increased the amount of phosphoric acid produced at the expense of phosphorous acid. Of course, the largest component of the equilibrium mixture is the excess water (steam), accounting for about 98% at temperatures lower than 2500 K.

3.2 Effect of Excess Hydrogen

A thermodynamic investigation into the effect of an excess of hydrogen on the reaction system, based on the partial pressures of the reactants and products of the two main competing reactions, [3.2] and [3.5] gave the following result:

$$P_{P_2O_3}/\,P_{P_2O_5} = (K_3/K_5)^{1/2}(P_{H_2}\,/P_{H_2O})^2 \qquad [3.6]$$

Therefore, the stress caused by the introduction of hydrogen to the equilibrium system would be relieved by a shift in equilibrium in the direction that tended to use up the added substance, i.e. to the left (Le Châtelier's Principle; Skoog and West, 1986). Since Reaction [3.5] produced more hydrogen than did Reaction [3.2], the stress caused by the addition of hydrogen to the system should favour the reverse of Reaction [3.5] over the reverse of Reaction [3.2]. Thermodynamic calculations performed at 1475 K with varying hydrogen to phosphorus (H_2/P_4) ratios and steam to phosphorus (H_2O/P_4) for the reactions between steam and phosphorus to produce phosphorous and phosphoric acid confirmed this reaction shift and are shown in Figure 3.3. Note that the H_3PO_4 concentration in the graph was multiplied by a factor of 10. Even so, without the addition of hydrogen, the concentration of H_3PO_4 varied between 6% and 4.5% of that of H_3PO_3. Increasing the hydrogen to phosphorus (H_2/P_4) ratio decreased the production of phosphoric acid in all cases. However, at $H_2O/P_4=6\text{-}12$, phosphorous acid production also decreased with increasing H_2/P_4, probably due to the shifting of the Reaction [3.2] to the left. By increasing the steam to phosphorus (H_2O/P_4) ratio from six to twelve at $H_2/P_4=10$, the production of phosphorous acid increased dramatically while the production of phosphoric acid decreased, resulting in a high degree of phosphorous acid purity, approximately 98.5%. Only at an extremely high steam feed, $H_2O/P_4=40$, did the production of phosphorous acid increase with increased H_2/P_4, however, the production of phosphoric acid was quite high. The addition of excess reacting species on the reaction products demonstrate the complex interplay of the reaction species determining the reaction shift preference.

The temperature dependency of two particular cases, $H_2O:P_4:H_2=10:1:0$ and $H_2O:P_4:H_2=10:1:10$ are shown in the thermodynamic equilibrium diagrams Figure 3.4a and Figure 3.4b, respectively. Increasing the hydrogen content of the reaction mixture not only depressed the production of P_2O_5 as desired but unfortunately forced the

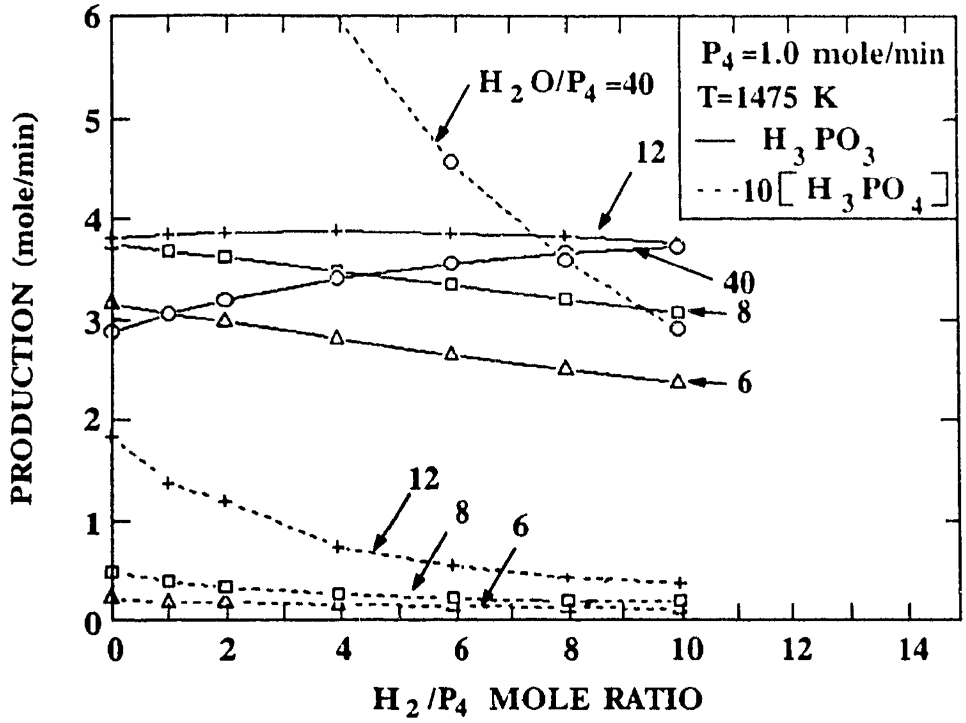


Figure 3.3 - Phosphorous and phosphoric acid thermodynamic calculations with varying H_2O/P_4 and H_2/P_4 mole ratios

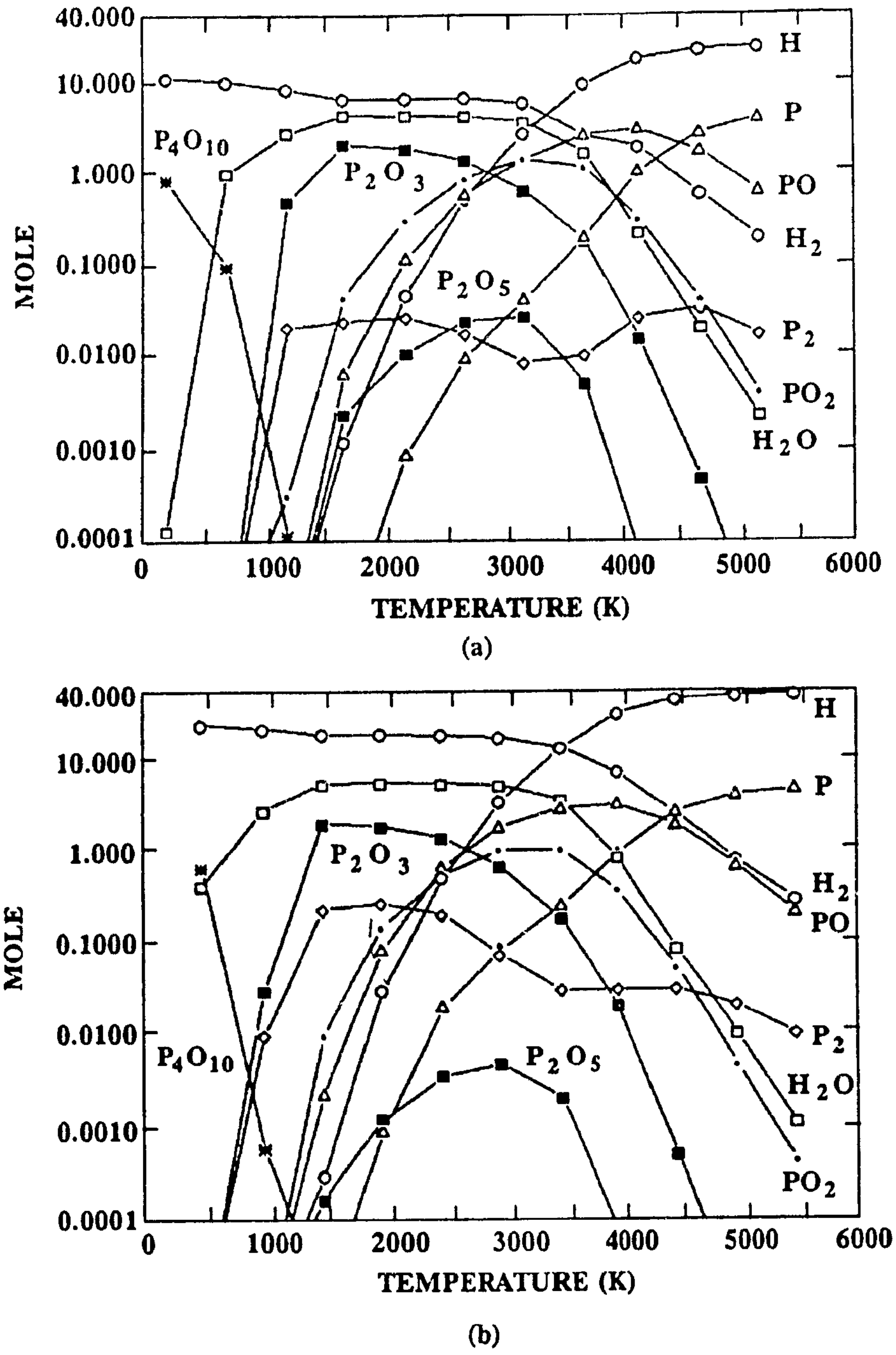


Figure 3.4 - Equilibrium composition of $H_2O:P_4:H_2$ at:
a) 10:1:0 b) 10:1:10

reaction to the left, leaving unreacted phosphorus (P, P_2) in the system. A more detailed analysis of the effect of adding hydrogen to the steam/phosphorus system is presented in Figure 3.5 at a reaction temperature of 1475 K. The addition of 10 moles of hydrogen decreased the production of P_2O_3 by 8.4%, however it also decreased the production of P_2O_5 by 97.3%, thereby substantially improving the purity of the phosphorous acid product. However, there is a 10-fold increase (from 0.0127 to 0.113 mol P_4/mol P_4 fed) in the amount of phosphorus that remains unreacted. The unreacted phosphorus, if rapidly quenched, leaves the reactor as a solid and can be recycled, however the efficiency of the process would be greatly reduced.

3.3 Effect of Excess Pressure

The effect of pressure on the phosphorus/steam system was not investigated since there was little change in the number of moles of reactants to products, i.e. from 7 to 8 for Reaction [3.2] and from 11 to 12 for Reaction [3.5]. Suffice it to say that an increase in pressure would result in a slight shift of Reaction [3.2] and Reaction [3.5] to the left that would favour the reactant species.

3.4 Selectivity of Phosphorous Trioxide

Table I summarizes the equilibrium composition of the desired product, P_2O_3 at 1500 K for the conditions tested. The mole fraction is given in the third column whereas the selectivity, calculated by dividing the moles of product produced by the

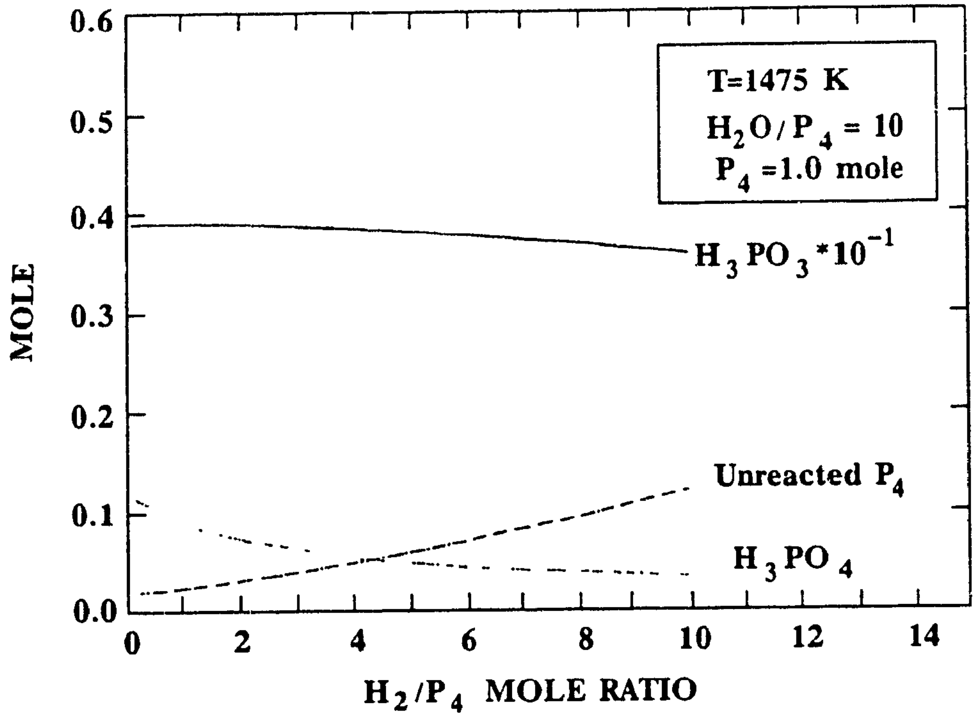


Figure 3.5 - Unreacted phosphorus, phosphorous acid and phosphoric acid calculations with varying H_2/P_4 at 1475 K and $H_2O/P_4=10$

TABLE I
SELECTIVITY OF PHOSPHOROUS TRIOXIDE AT 1500 K
% (P_2O_3/TOTAL PHOSPHORUS PRODUCTS)

$P_4 + (A)\ H_2O <==> PRODUCTS$

Case	A	Mole fraction	Selectivity (%)
1	3	0.178	43.0
2	6*	0.199	79.4
3	8	0.185	93.0
4	10	0.162	97.2
5	12	0.138	96.8
6	14	0.120	96.4
7	40	0.040	84.3

* stoichiometric amount

total number of moles of reacted and unreacted phosphorus is given in the fourth column. The selectivity gives a good idea of the conversion of the phosphorus to the trioxide predicted by the thermodynamics of the reaction system. Increasing the steam concentration, beyond the stoichiometric amount (case 2), increases the selectivity of the product, P_2O_3, to a maximum of 97%. Experiments described later show that the highest concentration (95%) of phosphorous acid was obtained at a phosphorus to steam ratio of seven.

3.5 Decomposition Reactions

The free energies for the possible trioxide decomposition reactions, listed in Table II, show that as the system cools to below 1100 K, the phosphorous trioxide decomposes to P_4O_{10} and to P_4O_7. It is only by rapid cooling, or quenching, that the decomposition is bypassed and the trioxide captured. If water is used as the quench medium, then the trioxide further reacts to form phosphorous acid, the desired product. The major factor in determining whether decomposition will occur is the kinetics of the quench process. If the quench is not rapid enough, the trioxide will decompose before undergoing the phosphorous acid product forming reaction. If the pentoxide is formed during this decomposition, the pentoxide will react with the incoming quench water to form phosphoric acid, an undesired contaminant. If phosphoric acid is found in the liquid effluent and is determined to be formed only as a result of the decomposition

TABLE II
DECOMPOSITION REACTIONS OF PHOSPHOROUS TRIOXIDE

REACTION	ΔG BECOMES NEGATIVE*
1. $10\ P_2O_3 <==> 3\ P_4O_{10} + 2\ P_4$	T < 1105 K
2. $7\ P_2O_3 <==> 3\ P_4O_7 + \frac{1}{2}\ P_4$	T < 1152 K
3. $4\ P_2O_3 <==> 3\ P_2O_4 + P_2$	always positive
4. $5\ P_2O_3 <==> 3\ P_2O_5 + 2\ P_2$	always positive
5. $2\ P_2O_3 <==> 3\ PO_2 + \frac{1}{2}\ P_2$	T > 5791 K

* = range: 200 < T < 6000 K

of P_2O_3, modifications to the quench system should be made to improve the overall yield of the desired product.

3.6 Intermediate Temperature Reactions

Two important reactions occur at temperatures in the range 575-775 K: the formation of red amorphous phosphorus (RAP), and the formation of PH_3 and H_3PO_4.

$$P_{4(yellow)} \Longleftrightarrow P_{4(RAP)} \quad \Delta H = -29 \text{ kJ/mol} \qquad [3.7]$$

$$P_4 + 11.2\, H_2O \Longleftrightarrow 1.2\, PH_3 + 2.8\, H_3PO_4 + 5.2\, H_2 \qquad [3.8]$$

The formation of RAP is a purely physical (allotropic) transformation which is induced at low temperatures and in the absence of steam. However, if steam is present at these temperatures, Reaction [3.8] occurs, producing phosphine gas and phosphoric acid contaminant in the product effluent.

4 CONCLUSIONS

Thermodynamic calculations show that the reaction temperature "window" for the formation of phosphorous trioxide, Reaction [3.2], is between 1500 K and 2500 K. A steam to phosphorus ratio of ten, slightly above the stoichiometric ratio of six, was thermodynamically determined to yield the greatest conversion to the phosphorous trioxide intermediate and should result in the highest concentration of phosphorous acid in the liquid effluent. Employing a rapid water quench will not only stabilize the phosphorous oxides formed, Reaction [3.3], but produce the desired phosphorous acid, Reaction [3.4], as well.

Thermodynamic calculations show that an excess of hydrogen should improve the phosphorous acid purity in the product. At the same time, however, the conversion of phosphorus would decrease and unreacted phosphorus would condense in the quench. Thus, considerable energy would have been expended just to heat the phosphorus from a solid at 300 K to a gas at the reaction temperature of approximately 1500 K only to then have it condense to its original state. An economic study would have to determine if the increase in the process energy requirements and the added cost for the recovery of the unreacted phosphorus would be offset by the increase in phosphorous acid purity.

5 REFERENCES

Greenwood, N.N. and Earnshaw, A., Chemistry of the Elements, Pergamon Press (1984)

Skoog, D.A. and West, D.M., Analytical Chemistry: an introduction, Saunders College Publ. (1986)

Thompson, W.T., Pelton, A.D., and Bale, C.W., Facility for the Analysis of Chemical Thermodynamics (F*A*C*T), McGill University/Ecole Polytechnique, Montréal (1988)

Twardowska, H., private communication, Albright & Wilson Americas, Toronto (1987)

Whyte, D.D., Pflaumer, P.F., and Roberts, T.S., "Process for preparing chemical compounds containing trivalent phosphorus", Patent US 3,532,461 (1970)

CHAPTER IV

EQUIPMENT AND EXPERIMENTAL PROCEDURE

1 INTRODUCTION

Since the thermodynamics of the phosphorus/steam system predicted the optimum temperature for the production of phosphorous trioxide to be in the range 1500-2200 K, a chemical reactor was designed and constructed, not only to provide the energy for the reaction but also to maintain the temperature at this level. A DC plasma torch was used for the present study since high flame temperatures were easily produced and a variety of plasma gases could be employed. A hazard and operability study (HAZOP) was carried out in an effort to identify possible problems that could occur which would interrupt operation or cause safety-related difficulties. The results of this study, found in Appendix III, included the installation of a burst plate on the reactor to relieve possible pressure build-up and the installation of an automatic argon purge should a power failure occur. Also the torch, reactor and all of the peripheral equipment was located within an exterior laboratory, shown in the photograph of Figure 4.1, specifically built for the present work because of the potential fire and explosive danger of phosphorus and of the possible evolution of toxic gases (e.g. phosphine). The equipment was controlled from a control room located on the other side of the 45-cm thick cement wall adjoining the experimental enclosure. The latter was ventilated by a strong exhaust fan to prevent toxic gas accumulation. The reaction

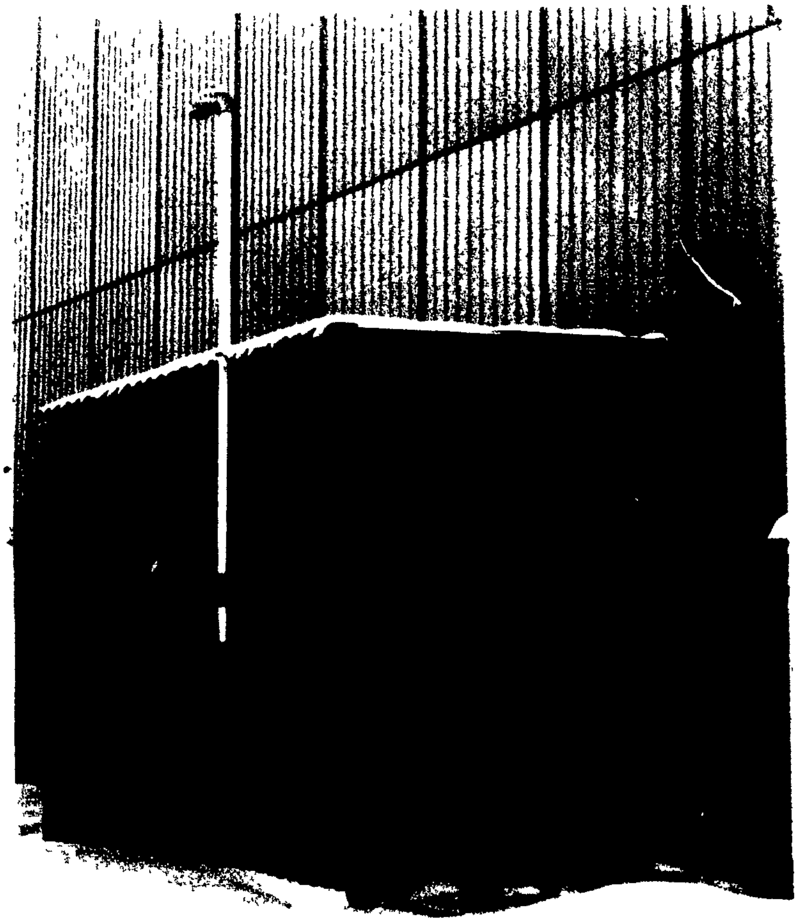


Figure 4.1 - Photograph of experimental laboratory

gaseous products were expelled from the reactor through an exhaust line to the outside of the building after being scrubbed of phosphine and residual phosphorus oxides. The ambient laboratory air was tested with Drager tubes before human entry. The placement of the reactor assembly in an exterior laboratory certainly had the advantages of increased safety and easier handling of liquid product, gaseous effluent and feed materials. With the addition of a video camera within the laboratory, visual access to the reactor environment was available. Even with the camera in place however, this arrangement posed some inconveniences such as difficulties in detecting and trouble-shooting operation upsets, sample taking, freezing of lines during winter operation and complications in the supply of the utilities. Since the safety and handling factors mentioned above far outweighed these inconveniences, this experimental arrangement was adopted. This type of experimental plan where the reactor was located in an adjoining laboratory was also used by Baddour and Iwasyk (1962) in their study of reactions between carbon and hydrogen at high temperatures.

2 EQUIPMENT

The apparatus used in the present study is shown schematically in Figure 4.2 and consists of the following equipment:

1. Power Supply
2. High-Frequency Starter

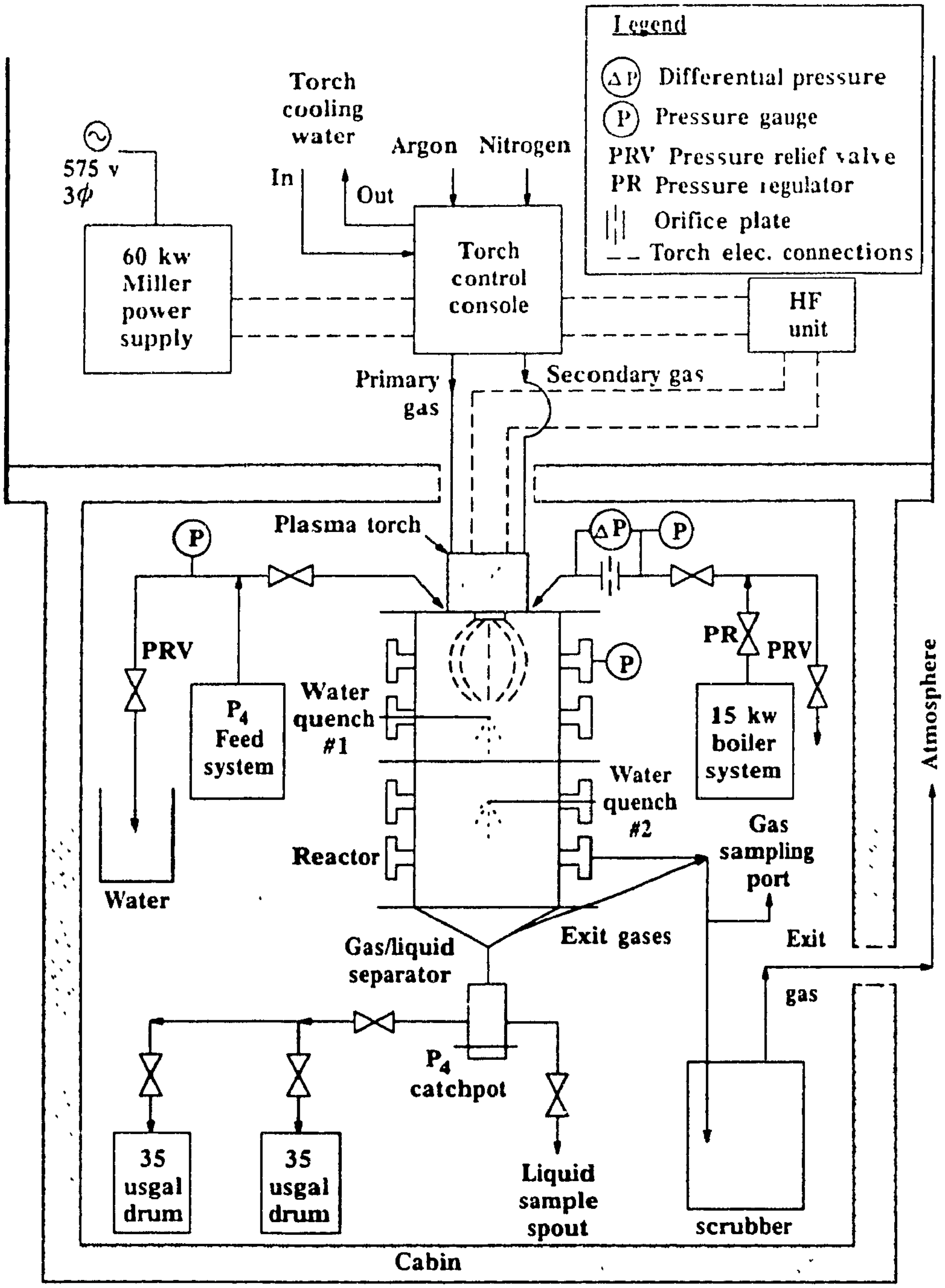


Figure 4.2 - Schematic of equipment set-up

3. Gas and Water Flow Instrumentation

4. Plasma Torch

5. Reactor

6. Gas/Liquid Separator

7. Gas Scrubber

8. Steam Supply

9. Phosphorus Feed System

The equipment chosen for this experimental work is described below. A photograph of the reactor, gas/liquid separator and scrubber is shown in Figure 4.3.

2.1 Power Supply

The power was supplied by a 60-kW rectifier (Miller Welder Model SRS-1500F7). The input voltage was 3-phase, 60 Hertz, 575-Volt while the output circuit could provide 400 volts in open circuit. The power was controlled by a current regulator contained in the plasma torch control console. The console also contained digital ampere and voltage meters. Emergency stop buttons to shut off the supply of open circuit voltage were placed on the torch control console, on the Miller rectifier, in the exterior cabin near the cabin exit, and on the platform close to the phosphorus feed system.

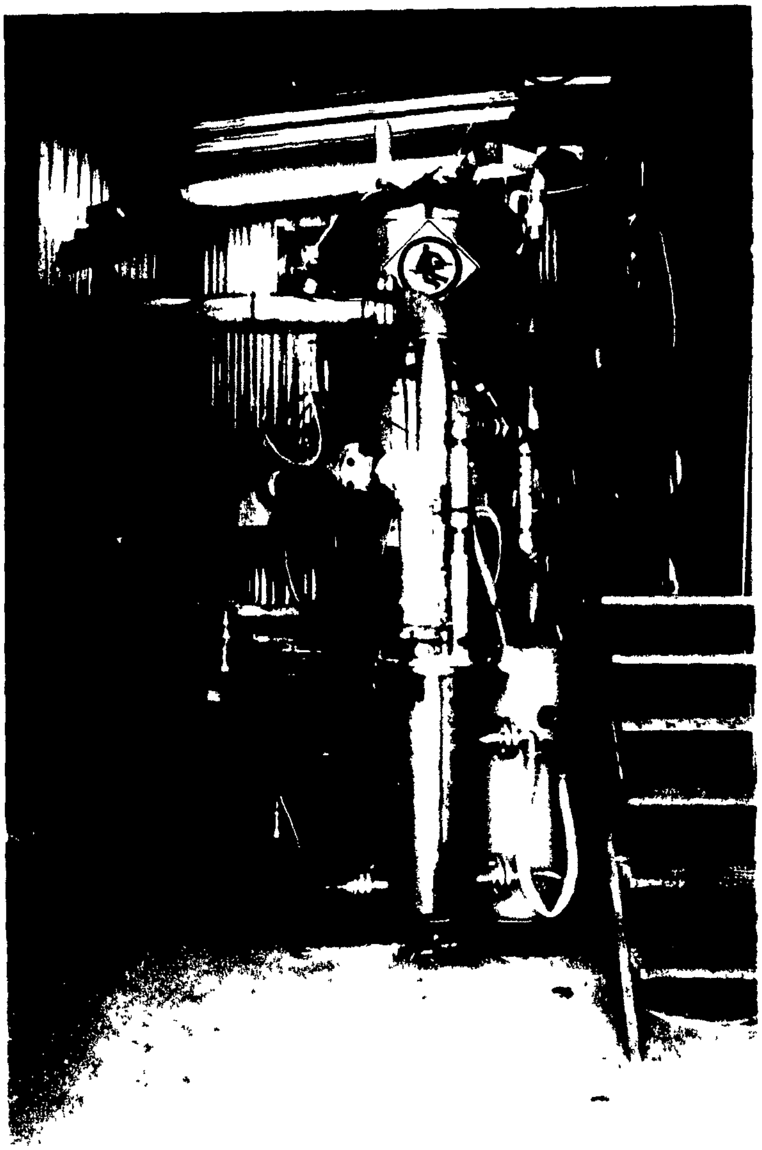


Figure 4.3 - Photograph of reactor, gas/liquid separator and scrubber

2.2 High-Frequency Starter

The high frequency starter, used to initiate the plasma arc, was a Miller Welder HF-2000. The input voltage was 115 volts and the 60% duty cycle current throughput was 2000 amperes. The unit was connected in series with the DC circuit from the rectifier to the torch. A remote switch located on the plasma torch control console was used to activate the unit.

2.3 Gas and Water Flow Instrumentation

The plasma torch various gas flowrates were measured through four Fischer and Porter calibrated rotameters incorporated into the main control console. Argon gas, with a purity of 99.996% and nitrogen gas, with a purity of 99.991% were supplied from gas cylinders and regulated by two-stage regulators. The outlet pressure was maintained at a constant value of 413.7 kPa. The control console was equipped with two adjustable pressure switches, preset at 310.3 kPa, such that if the gas line pressure fell below this pressure, an interlock system would shut the plasma arc off.

A city water distribution manifold was set up to provide cooling water for the torch and water to the quench system. The torch cooling water pressure was increased to about 689.5 kPa by means of a booster pump and measured by a Fischer and Porter calibrated rotameter installed on the main control console. A cooling water safety interlock system was installed such that should the water flowrate drop below 0.015 m^3/min, the arc would extinguish. The use of deionized water, although desirable, was not essential for normal torch operation. The quench water was regulated to a back pressure of 413.7 kPa, and was injected into the reactor as a fine spray at two locations. Both quench flows were individually measured with calibrated rotameters.

2.4 Plasma Torch

The Norton Model AA61 DC plasma torch is shown schematically in Figure 4.4a and in the photograph in Figure 4.4b and consisted of:

a) a cathode composed of tungsten alloyed with 2% thoria to improve the emission of electrons. The cathode is water-cooled to prevent excessive heating and vaporization of the tungsten tip.

b) a primary water-cooled anode made of copper and placed concentrically with the cathode.

c) an insulator section between the primary and secondary anodes.

d) a secondary water-cooled anode made of copper on which the arc attaches.

The Model AA61 was designed for operation with various gases or gas mixtures and was fitted with two gas inlets. The glass-filled teflon torch body was water-cooled and could accommodate a variety of electrode inserts for operation under different gases. The length of the thoriated tungsten cathode tip could be adjusted, depending on the gas used and the power required. This feature was novel in that the length of

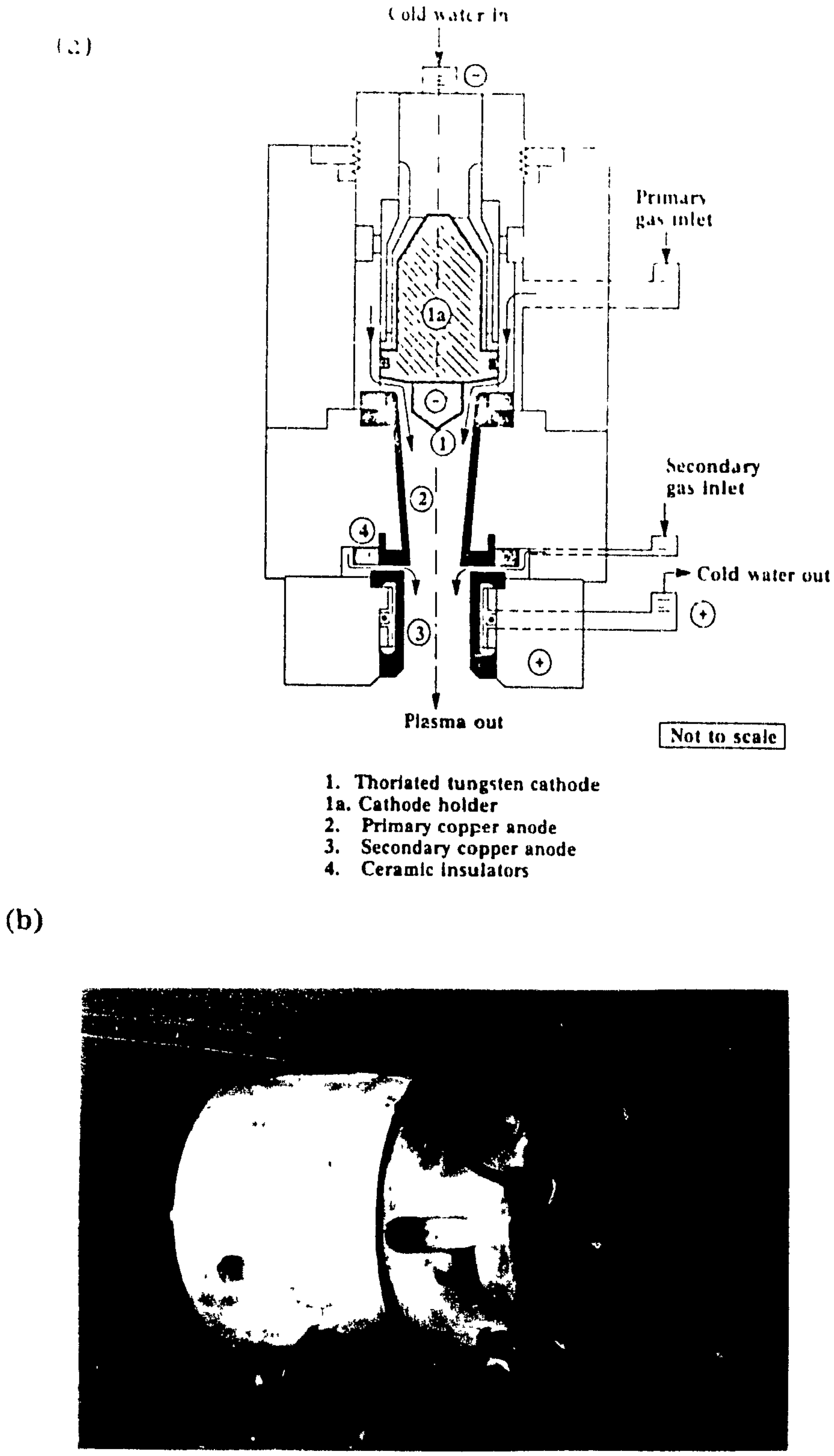


Figure 4.4 - Norton Model AA61 plasma torch
a) schematic b) photograph

the arc could be adjusted, thereby increasing the voltage drop and thus the power. Also, once the cathode tip was eroded sufficiently to require replacement, the unused portion of the tungsten rod, located inside the copper cathode body, could be removed and a new tip machined. The electrical connections to the torch were supplied through the torch cooling water circuit. The torch voltage and current characteristics for two different flowrates of Argon and Nitrogen are shown in Figure 4.5. The arc voltage depended largely on the plasma gas and to a lesser extent on the gas velocity and arc current. This is typical of DC plasma torches.

2.5 Reactor

The reactor consisted of a carbon steel cylinder with an outside diameter of 66 cm, and a height of 122 cm, made up of two 61-cm sections. The wall thickness was 1.25 cm. The inside surface of the reactor was insulated along its full length with an outer refractory layer, 5.1-cm thick Cerlite 100C castable, and an inner refractory layer, 10.2-cm thick Emerald GVM vibratable plastic. Stainless steel Y-shaped anchors, welded to the inside reactor wall held the refractory in place. The exterior surface of the reactor was insulated with 2.5 cm of Cerwool (a fibrous material) and then covered with aluminum sheeting.

The Emerald GVM is an alumina-chrome, phosphate-bonded refractory material specially recommended against phosphoric acid attack and is extremely resistant to high temperatures (max. 2144 K). However, its thermal conductivity is relatively high,

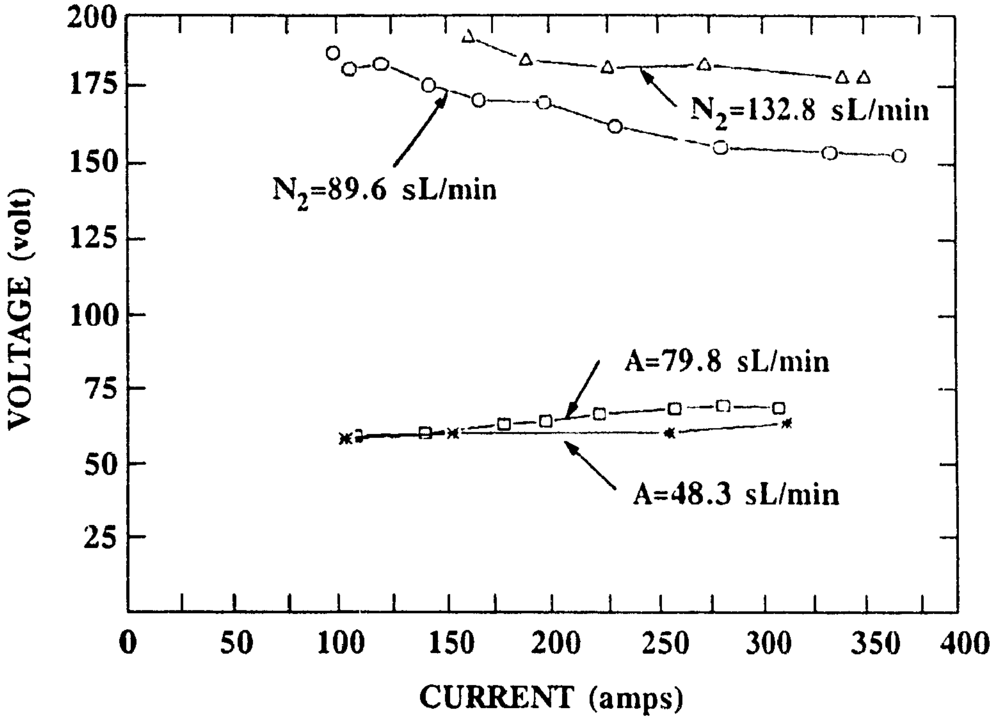


Figure 4.5 - Torch voltage and current characteristics

approximately 2.16 W/m K. To decrease the heat loss from the reactor, a second inner layer composed of Cerlite 100C, a low thermal conductivity refractory material (0.433 W/m K) and having a high (41%) silica content, was added. The inside reactor diameter of the reactor after insulation was 30.5 cm. Heat loss calculations performed by Combustion Engineering Refractories (1987) without the addition of the Cerwool outer refractory layer indicated that at 294 K ambient temperature and a hot face temperature of 2173 K, the reactor would have a cold face temperature of 603 K and a heat loss of 9.2 kW/m^2. Assuming a fairly large reaction zone of 61 cm, 11.7 kW would be lost to the surroundings at steady state This loss represented a significant amount of available power, approximately 25%, and thus heat balance calculations were repeated with the addition of an additional outer refractory material (Cerwool). These new calculations indicated that only 3.5 kW would now be lost to the surroundings and that the remaining power would be more than sufficient for the reaction system.

The roof of the reactor was made of carbon steel with a central opening (25.4 cm) covered by a copper plate installed to hold the plasma torch in place, provide heat protection from the high temperatures of the reactor and to enable the phosphorus and steam reactants to be injected through two angled feed ports. Originally, a water-cooled stainless steel plate was installed for the above tasks, however, due to the enormous heat sink provided by the plate water-cooling, temperatures in the reactor above 1000 K could not be achieved. Since the reaction temperature of the phosphorus and steam was already established to be approximately 1500 K, the water-cooled roof was replaced with a copper plate (38 cm in diameter and 1.25-cm thick), as shown schematically in Figure 4.6a and in the photograph in Figure 4.6b. This design minimized the radiation and convection heat losses to the torch support plate and enabled the reactor temperatures to rise above 1500 K. To again protect the torch from the intense heat flux rising from the reactor, the copper plate was fitted with air jets designed to impinge onto the torch body. In addition, the copper plate accommodated two injection feed ports, with an internal diameter of 0.64 cm, and angled 45° to the horizontal, through which the feedlines for phosphorus vapour and steam were connected. The reactants entered the reactor 3.2 cm from the exit of the torch, at the point where the plasma expanded into the 30-cm diameter reaction zone. This feed configuration was designed to take advantage of the "pumping" or aspiration effect of an expanding gas at which point the reactants would be drawn into the plasma tailflame where they would intimately mix.

Four flanged ports of 8.9-cm i.d. were installed in each of the reactor sections: two ports on each side of the reactor and offset vertically 10.2 cm from each other. These ports were used to insert thermocouples and quench nozzles at various axial locations along the reactor, and a hole through the copper plate allowed the vertical movement of an additional quench nozzle. Only two quench nozzles were used at any given time; the remaining six ports were plugged with refractory insulation until needed. The quench medium was untreated tap water. The quench nozzles were positioned at

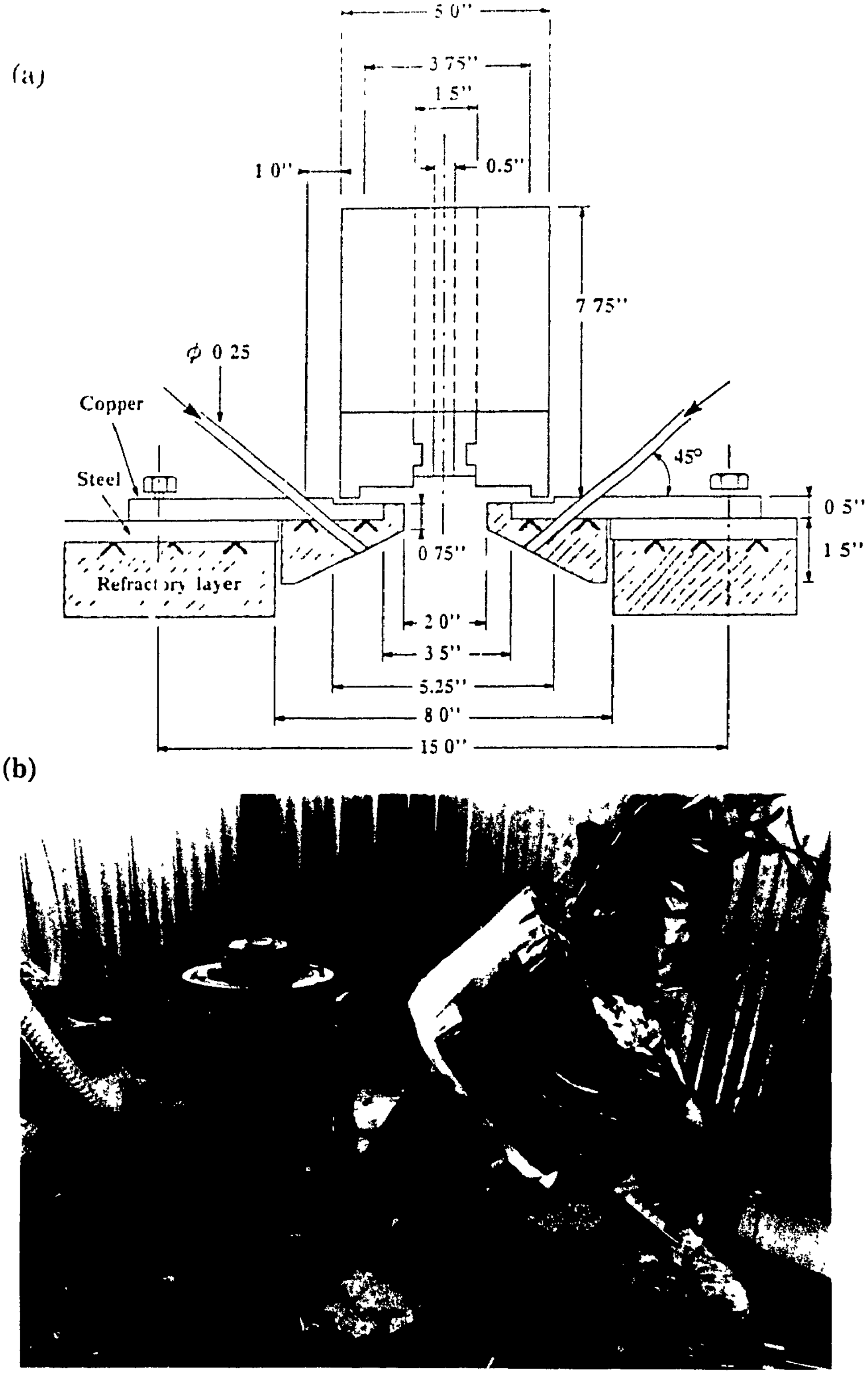


Figure 4.6 - Copper roof with plasma torch
a) schematic b) photograph

the centerline of the reactor, pointing in the direction of flow; the primary quench being the first encountered by the hot reaction gases. The secondary quench was located downstream of the primary quench.

Additional ports, 1.9-cm i.d., positioned along the reactor height, were used for the insertion of thermocouples and gas sampling ports as shown in the photograph in Figure 4.7.

2.6 Gas/Liquid Separator

The carbon steel gas/liquid separation unit consisted of a conical section, 30.5 cm in height, attached to the reactor bottom to collect the liquid product and a 5.1-cm diameter side exhaust port for the gas. The inside surface was coated with Sauereisen primer #47 and acid-proof sealer #44 to protect the steel from the corrosive chemical attack of the phosphorous and phosphoric acids. The conical shape was chosen so that no unreacted phosphorus or other solid material, such as refractory material, would collect in any dead space. This geometry also had the advantage of minimizing the amount of liquid required to produce the pressure head for the liquid product to flow. This reduced volume was important so that when liquid samples were taken, a minimum lag time to purge the separator was required. The separator also had a 38.1-cm diameter screen, consisting of 0.64 cm holes, so that if large pieces of refractory broke from the reactor walls, the liquid exit line, 2.5-cm i.d., would not block.

Figure 4.7 - Photograph of auxiliary thermocouple ports spaced 7.6 cm apart

At the bottom of the gas/liquid separator, a liquid seal, 10.2 cm i.d. and 25.4 cm in height, with a liquid sampling port located within the downspout, enabled samples to be withdrawn. A catch pot attached to the bottom of the liquid seal collected any solid material or unreacted phosphorus. The catch pot was easily removed by first draining the seal container and then disabling a series of four clamps.

The phosphorus acids flowed by gravity from the separator through the water seal and then was collected in a series of drums (35-US Gallon). Once full, these drums were replaced with empty ones during the course of the experiment without interruption of the test.

2.7 Gas Scrubber

The gas scrubber consisted of a stainless steel cylinder, 25.4 cm o.d. and 76.2 cm in height, and was fitted with a sight glass along the length of the scrubber to indicate the level of the scrubbing solution at all times, as shown in Figure 4.8. A fill spout, 1.3 cm i.d., on the scrubber roof enabled the scrubber solution to be added. The reactor gases, consisting of hydrogen, nitrogen, argon and small amounts of phosphine and helium, exit the gas/liquid separator through both the 5.1-cm and the 10.2-cm diameter exhaust ports and enter the scrubber through two down-pipes, into a liquid

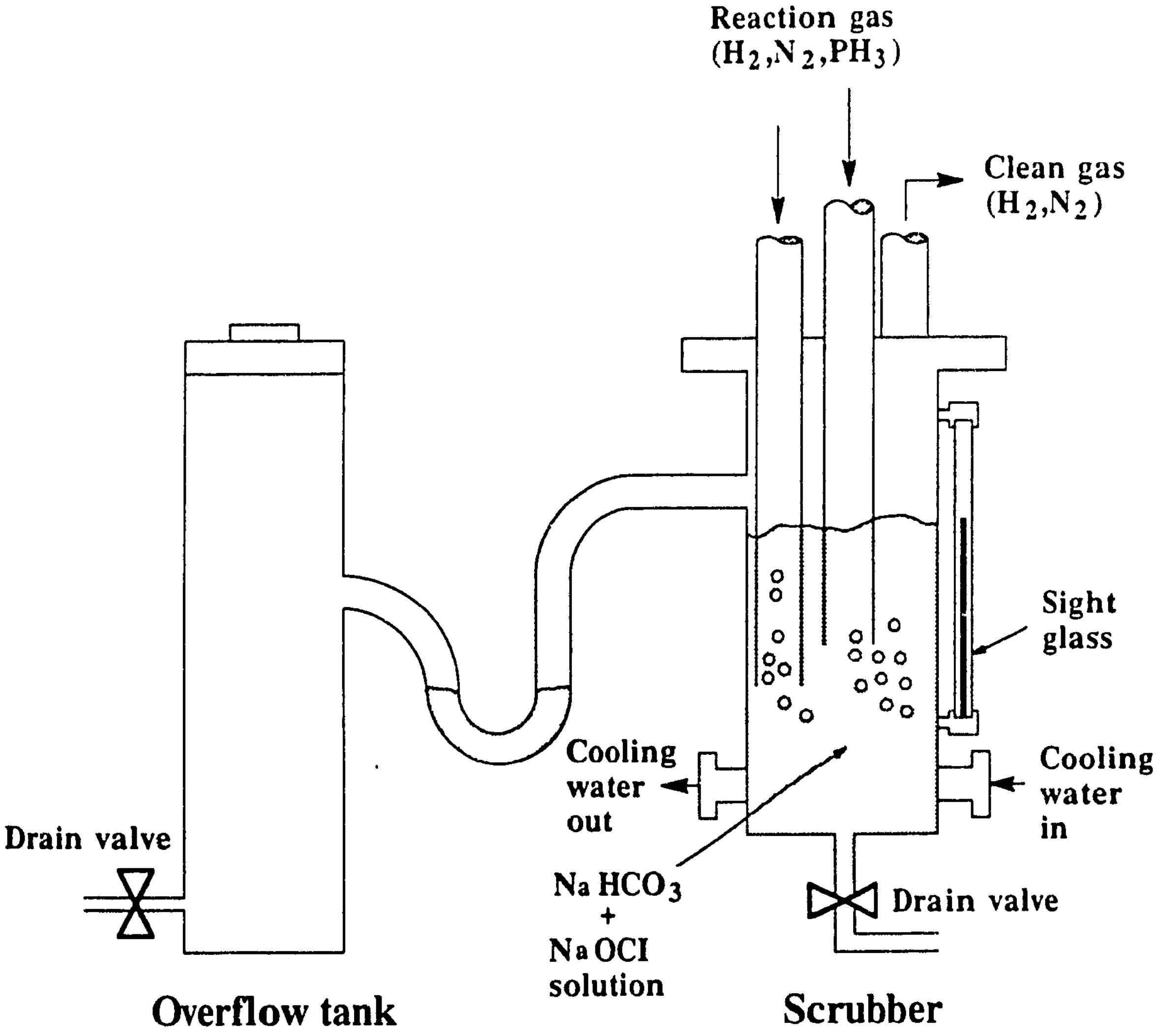


Figure 4.8 - Gas scrubber

solution of sodium bicarbonate, $NaHCO_3$ and sodium hypochlorite, NaOCl. Sodium hypochlorite reacts with phosphine according to the following equation:

$$PH_3 + 2\ NaOCl <====> H_3PO_2 + 2\ NaCl \qquad [3.1]$$

Sodium bicarbonate was added to reduce the acidity of the scrubber solution caused by the formation of hypophosphorous acid. A strongly acidic solution would cause the decomposition of sodium hypochlorite and result in the evolution of chlorine gas. The clean gas was exhausted to the atmosphere immediately after the scrubbing stage. The scrubber was water-cooled and acted as a auxiliary condenser for the condensable exit gases.

2.8 Steam Supply

The steam was supplied by a 15 kW Volcano boiler, capable of delivering 23.5 kg/h of steam at 373 K and 101.4 kPa. The steam was slightly superheated as it was transported to the reactor. The steam flow passed through an orifice plate having an orifice diameter of 0.752 cm and was connected to a Viatran Model 504 differential pressure transmitter and a Viatran Model 500 static pressure transmitter. The differential and static pressures were used to determine the steam flowrate. The steam flow was controlled by a metering valve downstream of the orifice plate before being directed to the reactor. A pressure relief valve set to release at 1.14 MPa and a steam trap was installed in the steam line. All of the lines were insulated and heat traced.

2.9 Phosphorus Feed System

The phosphorus was supplied by the feed system shown schematically in Figure 4.9a and in the photograph in Figure 4.9b. Before the water supply line to the phosphorus egg was attached, all the air within the lines and egg had to be expelled in order to prevent the reaction between phosphorus and oxygen. The phosphorus egg, initially containing solid phosphorus under a water cover, was melted in a hot water bath controlled by two immersion heaters. Water from a small metering pump was pumped from a beaker, placed on a digital scale to measure the water flowrate, through a 0.3175 cm i.d. line into the phosphorus egg. The water, heated slightly as it passed through the hot water bath before entering the egg, displaced the liquid phosphorus and forced it to enter the evaporator. To prevent the accidental addition of water to the evaporator should the phosphorus egg empty, a timer was connected to shut off the metering pump at a preset time. A pressure gauge just downstream of the pump indicated the water line pressure. A pressure relief valve placed on the water line was set to release at approximately 70 kPa in case of a pressure build-up. The inside wall temperature of the evaporator was maintained at 725 K with a temperature controller. The liquid phosphorus was flash-evaporated and the vapours injected into the reactor using nitrogen as the carrier gas. All of the phosphorus

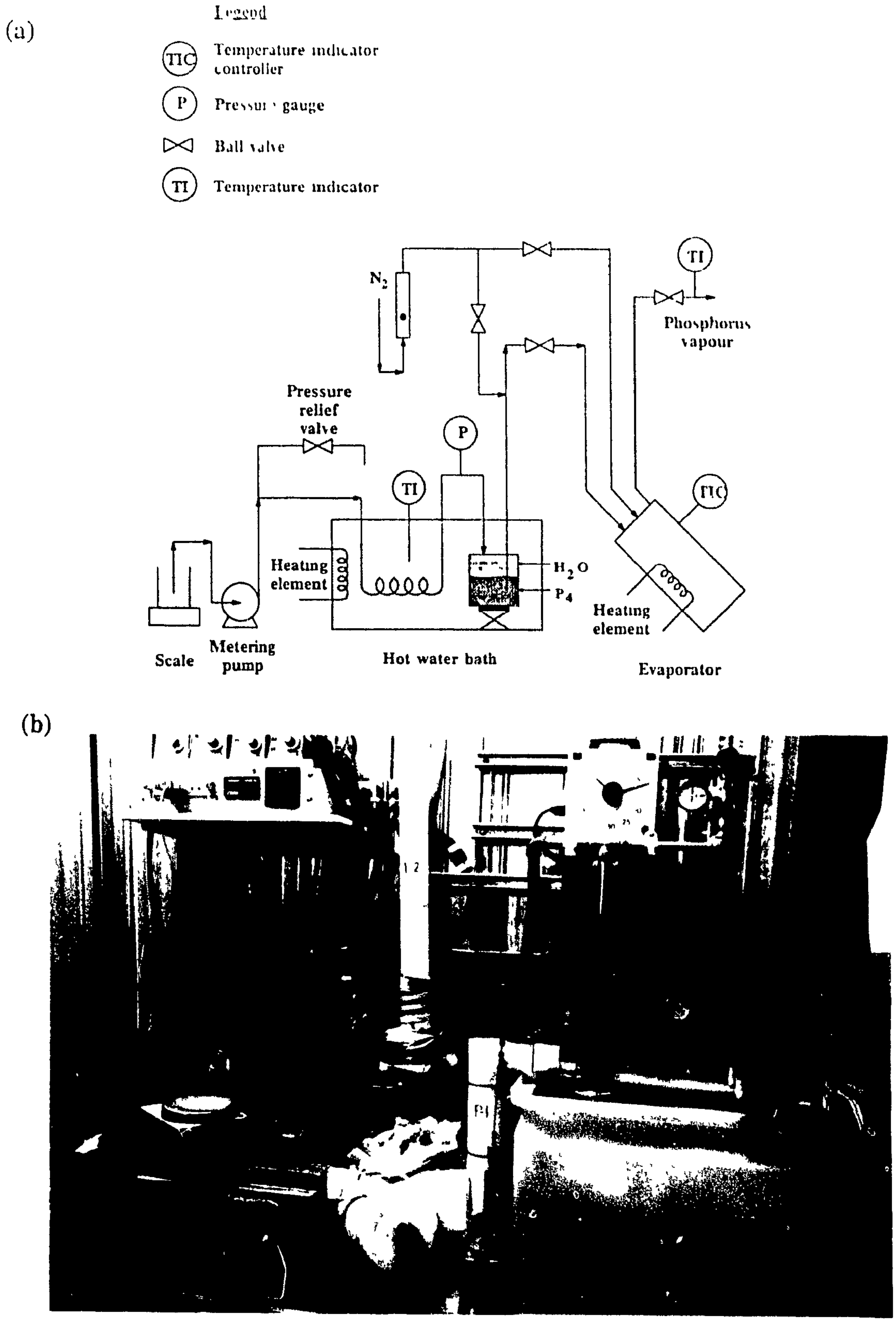


Figure 4.9 - Phosphorus feed system
a) schematic b) photograph

vapour lines were insulated and heat traced to achieve a line temperature of at least 575 K. The system was designed to deliver 62 g/min of phosphorus at atmospheric pressure, but could deliver up to 100 g/min.

3 MEASUREMENT TECHNIQUES

3.1 Power

The total power supplied to the torch was measured by two LFE Model 40 digital voltage and current meters mounted on the main control console. An Omega 3-pen strip chart recorder recorded the voltage and current fluctuations during operation. The power was controlled by a variable resistance Power Control dial mounted on the main control console. An arc-time meter, which operated whenever the DC power supply was delivering an open circuit voltage, was installed on the main control console.

3.2 Calorimetric Measurements

Temperature measurements were taken within the reactor refractory, along the outside surfaces, and within the reactor itself. All of the temperature measurements reported in this work relied on thermocouple probes. Grounded K-type (3.125 mm o.d.) thermocouples with a maximum temperature limit of 1375 K were mostly used, however, one high-temperature (maximum temperature: 1755 K) R-type thermocouple was used near the plasma tailflame. In general, thermocouples were shielded by stainless steel tubes surrounding the thermocouple junction while allowing gas to be drawn past the hot junction. This arrangement was used by Mullikin (1939) to reduce the radiation errors involved with thermocouples in high temperature environments. Because of the very large temperature "window" , 1500 to 2500 K, to produce P_2O_3 from the reaction between phosphorus and steam, accurate measurement and control of the reaction temperature environment, although desirable, was not critical. For example, an unshielded thermocouple in error of 100-200 K due to radiation losses to the cold walls was still useful in indicating whether reaction would proceed as long as the displayed temperature was at least 1400 K.

Temperatures were displayed and recorded through a Chino Hybrid Model AA 30-channel data logger with printer and digital display. Data acquisition was performed through a RS-232 serial port which connected the data logger to an IBM-AT personal computer.

The fraction of the input arc power transferred to the plasma was determined by calculating the supplied power, $P=V*I$, and subtracting the heat lost to the torch cooling water. The amount of torch cooling was determined by measuring the water coolant flow rate and its temperature rise. An Omega Model 383 digital temperature display with a precision of ±0.1°C was connected to the coolant lines, and was installed on the main control console for this purpose.

3.3 Barometric Measurements

A Bourdon type pressure gauge indicated the pressure within the reactor and was checked frequently throughout the experimental trials to ensure that there was no pressure buildup. The reactor pressure during the course of a typical experimental trial was slightly above atmospheric.

3.4 Gas Analysis

The gas exiting the reactor, excluding phosphine, was analyzed by a Varian Vista 6000 gas chromatograph (GC) equipped with a 2.74 m x 0.3175 cm ss Spherocarb 80/100 column, designed to separate hydrogen, helium and nitrogen. The GC was fitted with a pneumatic valve including a constant volume sample loop for on-line sampling. To determine the exit gas concentrations, an accurately measured tracer gas, helium, was added to the reaction gas mixture.

The gas samples, taken from the exit line just preceding the scrubber, were drawn through a condenser, acid scrubber, phosphine scrubber, desiccant, gas rotameter and into the GC using a vacuum pump as shown in Figure 4.10. The condensable portion of the gas sample was collected as the sample passed through the water-cooled condenser before being passed through the phosphoric acid bath where phosphorous and phosphoric acids were collected. The gas then passed through the mercuric chloride bath which removed the phosphine, after which the gas was dried with a desiccant before being sent through the rotameter to the GC's sample loop. The gas samples were withdrawn at 1.5 sL/min to ensure that the gas sample line, approximately 15 meters in length and with an i.d. of 0.64 cm (0.0005 m^3), was purged of "stale" or unrepresentative gas within about 20 seconds. The gas component of particular interest

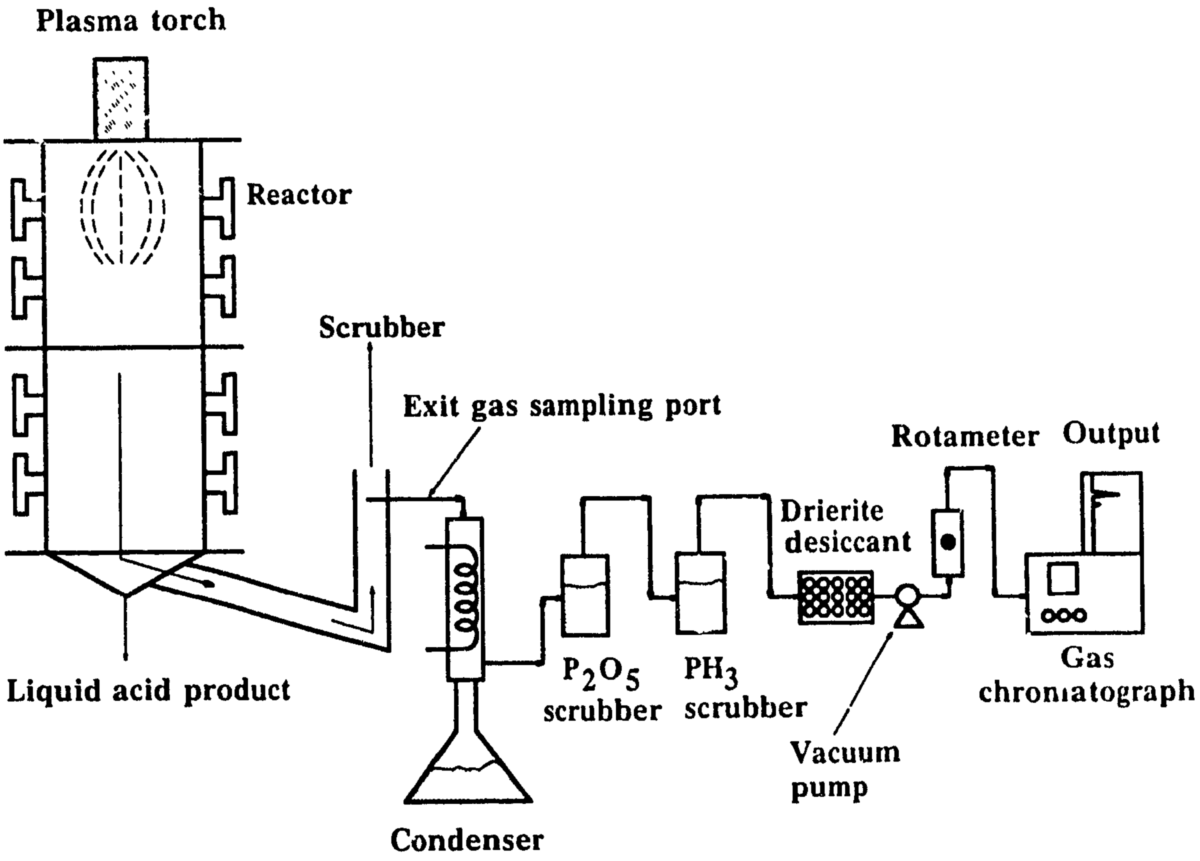


Figure 4.10 - Gas sampling train

was hydrogen. Not only did the concentration of hydrogen in the gas sample reveal the extent of the oxidation reactions taking place, but it also served as an indication of whether steady state conditions had occurred. Steady state was assumed to have been achieved once the hydrogen content of the gas sample did not vary appreciably during the experimental trial. Phosphine gas was analyzed using the technique outlined in Appendix IV.

3.5 Liquid Analysis

Liquid samples containing phosphorous and phosphoric acids were analyzed using a Dionex Model 2010I ion chromatograph (IC) equipped with AG5 and AS5 columns and conductivity detection. Calibration samples were analyzed with respect to time, agitation and initial concentration. No change in the acid concentrations were found.

Liquid samples were withdrawn from the drop tube of the water seal apparatus located directly under the Gas/Liquid Separator. The location of the liquid sample point was chosen so that the least amount of liquid hold-up was present, and also so that the sample taken would be representative of the reactions taking place. Liquid samples were drawn periodically under constant experimental conditions, and analyzed to verify steady or quasi-steady state operation.

Estimates of the phosphorous acid content of the sample were performed on-site using the titration technique described in Appendix IV. This technique yielded results comparable to the IC. A colorimetric technique, also described in Appendix IV, was occasionally employed to determine the phosphoric acid content of the sample, however, this determination was inaccurate and only gave gross estimates of the phosphoric acid concentration.

4 EXPERIMENTAL PROCEDURE

Although much care and attention had been given to the remote control operation of the plasma reactor, some entry into the exterior laboratory was necessary; e.g. to adjust the radial location of the thermocouples, to collect product samples, and to troubleshoot operation upsets. As such, the operation of the plasma process involved at least four persons; someone knowledgeable in the operation of the torch, reactant feed control and data acquisition, a second person to take product samples and monitor the reactor and feed systems, a third person conducting liquid and gas analysis, and a fourth to conduct ambient air sampling for toxic gas accumulation, provide general assistance and be present to dispense emergency care.

In order to minimize the expense (i.e. plasma gas, electricity, and electrode replacement) of preheating the reactor to near operating temperatures, a Globar silicon carbide heating element, providing up to 8 kW, was inserted through the top reactor flange for a period of approximately 24 hours. To avoid thermal shock and possible damage to the element, the applied voltage to the element was slowly increased through the use of a voltage regulator to about 200 volts. Once this initial pre-heating was complete, the power to the resistance element was stopped and the element was allowed to cool for about 15 minutes while remaining within the reactor. The element was then removed manually with asbestos lined gloves, and laid aside carefully because of its brittleness. The plasma torch, with its water cooling circuit in operation, was then positioned on the copper plate and secured into place. The plasma was then started on argon gas and slowly switched over to nitrogen.

During the final stages of the reactor preheat, the solid "frozen" phosphorus container was heated in the hot water bath in order to liquefy the phosphorus. The water pump line was purged of residual air and then connected to the phosphorus egg. At the same time, the evaporator and the heat tracing of the phosphorus feed system were energized. The boiler providing the steam for reaction was energized during the heating of the phosphorus egg. The steam lines were drained of the steam condensate, and the heat tracing was turned on to prevent further condensation.

Once the reactor achieved the desired temperature, steam addition was initiated. The power had to be further increased to compensate for the cooling effect of the steam. Once the desired temperature was again acheived, phosphorus vapour was injected into the reactor.

Access to the reactor laboratory was limited to persons clothed in an asbestos-lined suit for protection against accidental phosphorus fire. A second person positioned just outside the laboratory stood by for safety reason. He was also responsible for testing the laboratory air for the accumulation of phosphine (PH_3), which is an extremely poisonous, highly reactive, colourless gas which has a faint garlic odour at concentrations above 2 ppm by volume. Procedures were set up in case of fire or other emergency requiring additional assistance.

Gas samples were taken at three-minute intervals throughout the experiment whereas liquid samples were taken periodically, generally at five minute intervals. The progress of the reaction was followed by measuring the amount of hydrogen produced with the GC. Once the hydrogen content of the off-gas remained constant, the reaction was considered to be at steady state and final samples were taken. Experimental conditions were then either changed, or the experiment halted. Operation of the equipment was semi-continuous, due to the limited capacity of the phosphorus egg, and the need to recuperate all of the phosphorus acids within the 35-US Gallon drums Visual inspection of the off-gas, either by colour or density, usually gave some indication of the reactions occurring within the reactor. For example, at times, red or brown smoke, signifying red amorphous phosphorus formation, or flames, signifying unreacted yellow phosphorus, exited the smokestack.

5 CONCLUSIONS

The various techniques to determine the gas and liquid flowrates, temperatures, and gas and liquid concentrations were found to be suitable for the present study. Rough on-the-spot analysis of the liquid samples gave quick qualitative results that were used to plan the subsequent tests. More accurate liquid analysis techniques were used to quantitatively determine the final product composition. The experimental procedures used ensured the safety of the persons involved in the tests and the smooth operation of the equipment.

The chemical reactants, phosphorus and steam, used in the present study were generated in sufficient quantity by a phosphorus-vapour feed system and a steam boiler, respectively, and were introduced into the reactor through the torch support plate's two angled injection ports. The reactants were aspirated into the plasma tailflame and reacted to form various phosphorus oxides, of which phosphorous trioxide was the desired product. The DC plasma torch used supplied enough energy to heat the reactants to the reaction temperature of about 1500 K, supply the necessary heat of reaction and overcome the heat losses through the reactor. The reaction gases as well as the plasma gas were cooled abruptly with quench water sprays, and at the same time, the oxides were hydrolyzed to phosphorous and phosphoric acid. These acids flowed into the acid collection barrels where they were stored until they were recuperated and subsequently treated. The non-condensable gases exited the reactor and were passed through a gas scrubber where phosphine gas was eliminated. The cleaned gases, consisting of hydrogen, nitrogen, and some helium were then exhausted to the atmosphere at a height of about seven meters from the ground. The reactor was heavily insulated which resulted in a rather large experimental installation. In spite of its size and complexity, the experimental apparatus was ideal for the overall evaluation of the process and the study of important operating variables, as will be discussed in the proceeding chapter, Chapter V.

6 REFERENCES

Baddour, R.F. and J.M. Iwasyk, "Reactions between elemental carbon and hydrogen at temperatures above 2800 K", I&EC Process Design and Development, 1, 3, 169 (1962)

Mullikin, H.F., Temperature: Its measurement and control in science and industry, papers entitled "Gas-temperature measurement and the high-velocity thermocouple", p. 775-804, and "Accuracy tests of the high-velocity thermocouple", p. 805-829, Reinhold Publ. Corp. (1939)

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

1 INTRODUCTION

In this chapter, the experimental results of the reaction between phosphorous vapour and steam are presented. However, in order to gain some fundamental understanding of the mixing behaviour between the injected gases and the plasma tailflame, temperature and gas concentration measurements were first performed with the injection of nitrogen and hydrogen (i.e. without phosphorus vapour) through the injection ports under various operating conditions. These gases were used instead of phosphorus vapour and steam in order to facilitate the injection, operation and analysis of the resulting gaseous mixture. The results of this study are presented in the first section of this chapter.

As a result of this work, a basic understanding of the transport processes of gases injected at the jet expansion zone was achieved from which the expected interaction of phosphorus vapour and steam with the plasma tailflame was ascertained. This knowledge led to some equipment modifications and changes in operating conditions in order to ensure that phosphorus vapour and steam mixed intimately and simultaneously attained the thermodynamically-predicted reaction temperature of 1500 K. The results of the reaction between phosphorus vapour and steam are presented following the gas mixing work.

2 PLASMA JET AND INJECTION GAS INTERACTION

In the present study, nitrogen and hydrogen were injected into the reactor through the reactant feed ports in order to understand the interaction of these gases with an argon plasma tailflame. Tests were performed at both ambient conditions and in the presence of an argon plasma jet at various power levels. The net power transferred to the plasma was varied between 6 and 12 kW, while the impinging jet flows were varied between 30 and 80 sL/min. Measurements of the temperature and of the gas mixture composition as a function of position in the reactor were taken.

A previous study of the turbulent mixing of a primary argon plasma jet with a cool secondary stream (helium) was performed by Grey and Jacobs (1964). Their measurements of the velocity, temperature and gas concentration profiles demonstrated the effect of the entrainment of the surrounding gas where, for example, at 5.1 cm from the jet exit, 60% of the injected helium gas was found at the centerline of the jet, increasing to 90% just 7.6 cm from the exit. The presence of helium in high concentrations close to the jet exit was in part due to its extremely high diffusivity

Grey et al. (1966) studied laminar arc jet mixing where the argon jet discharged either into a square duct (45.7x45.7x45.7 cm), or into a 7.6-cm diameter and 45.7-cm long duct with their downstream ends open. They found that up to three jet diameters (30 mm), there seemed to be no difference between a free and a confined jet behaviour and that mixing was minimal; however, once turbulence was initiated, complete mixing of the jet was accomplished in less than three jet diameters from the nozzle exit.

O'Conner et al. (1966) extended the work of Grey and his co-workers by studying the turbulent jet mixing of a high-enthalpy gas at high subsonic Mach numbers, using a nitrogen plasma issuing into ambient air. They found that with increasing axial distance, the centerline nitrogen concentration decreased the most rapidly, followed by the centerline enthalpy and finally the centerline velocity. Lewis and Gauvin (1973) showed that the free expansion of an argon plasma jet issuing from a plasma torch exerts such a powerful entraining effect on the surrounding gas that the temperature, velocity and gas concentration of the jet fell to 10% of their initial values just eight centimeters from the torch exit. This is a very important effect, which must always be kept in mind when interpreting the interaction between an expanding jet and the surrounding gas.

A turbulent K-epsilon model, used in conjunction with a forward marching procedure, was used by Pfender and Lee (1985) to determine the temperature and velocity fields of a confined plasma jet. Their results showed laminar flow with high thermal and velocity gradients near the water-cooled walls. Three-dimensional temperature measurements were performed by Gravelle et al. (1983), who found that when a cold side jet was introduced normal to a plasma jet, the latter distorted from near-concentric circular isotherms to elliptical isotherms. It is interesting to note that perfectly symmetrical temperature profiles were never attained. This is similar to the results obtained in the present work.

Lana and Kassabji (1987) performed measurements as well as numerical calculations on the mixing of an air plasma jet, positioned 45° to the horizontal, with a confined horizontal cold air flow. Their results showed strong recirculation patterns from the wall into the jet region, confirming the entrainment of the surrounding gas found by Lewis and Gauvin.

2.1 EXPERIMENTAL RESULTS

The equipment differed from that described earlier in that the plasma torch was held in place by a water-cooled roof, 38.1 cm in diameter and 2.54-cm thick, shown in Figure 5.1. A ceramic insert with an internal diameter of 6.35 cm and a length of 3.2 cm was placed into the 7.6 cm roof opening to reduce the radiative heat transfer from the plasma to the water-cooled walls. The distance between the exit of the torch and the point at which the injection gases intercept the torch centerline was 9.5 cm. The gas sampling probe was approximately 8.9 cm from the torch exit. The injection gases (Q_1 and Q_2) were introduced through the roof's two 45° angled ports, having 1.2-cm internal diameter. Gas sampling probes, 10 in all (only one of which is shown), traversed the reactor in both axial and radial directions, at 0°, 45°, and 90° normal to the axis of injection. Measurements were taken radially, starting at the reactor inside wall and moving inwards 2.5 cm at a time, as long as the sample composition remained constant. The radial movement of the probe was reduced to 0.5 cm as the axis of the torch was approached. The sampling probe consisted of a stainless steel tube with an internal diameter of 0.64 cm and samples were drawn at a rate of 1.5 sL/min.

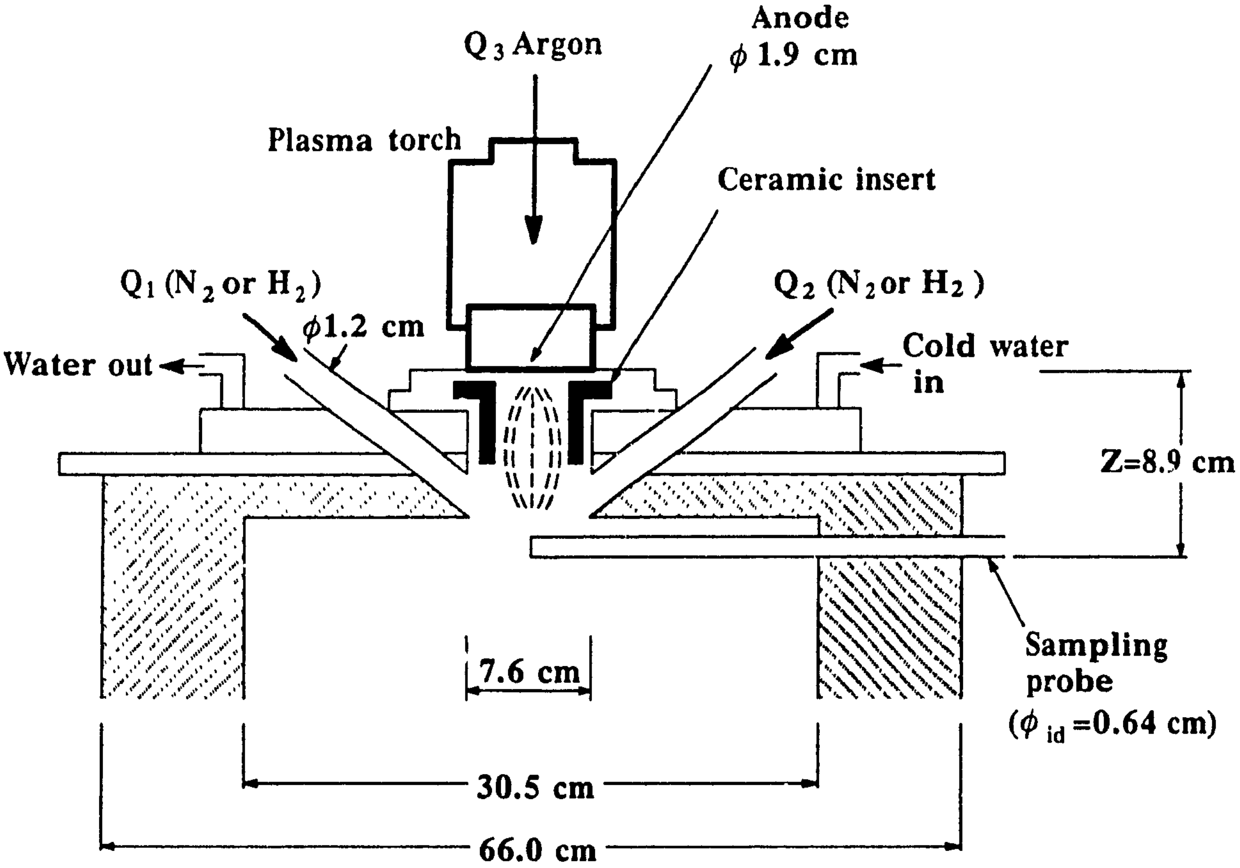


Figure 5.1 - Water-cooled torch support roof

In most cases, the argon plasma gas flowrate (Q_3) and plasma power (P_{net}) were kept constant at 87 sL/min and 6 kW, respectively. Before each experimental trial, a gas sample was taken at the exit of the reactor, where the gas mixture was confirmed to be well-mixed, i.e. the concentrations of the various gas components equalled that of the injected amounts.

2.1.1 Effect of Gas Injection on the Temperature Profile

Radial temperature profiles were plotted in Figure 5.2 at an axial position of Z=8.9 cm from the torch exit, with and without gas injection for the different conditions studied. Temperature measurements of the central zone of the reactor without nitrogen side injection exceeded 1400 K, the maximum allowable limit of the thermocouple used, and thus were not obtained. The addition of nitrogen in the two angled injections lowered the temperature by approximately 200 K and thus centerline measurements could be performed. Radial temperature measurements taken normal to the torch outlet were bell-shaped with a maximum temperature of 1300 K at the centerline of the reactor (R=0 cm), and 650 K near the reactor wall (R=15.2 cm). At -3.8>R>3.8 cm, the thermocouple was positioned under the refractory layer and encountered a stream of colder gas being aspirated by the expanding plasma jet which accounts for the sudden drop in temperatures. The addition of nitrogen in the two angled injections did not change appreciably the temperature distribution as long as their total flowrate remained constant. The unbalanced nature of the two flows did

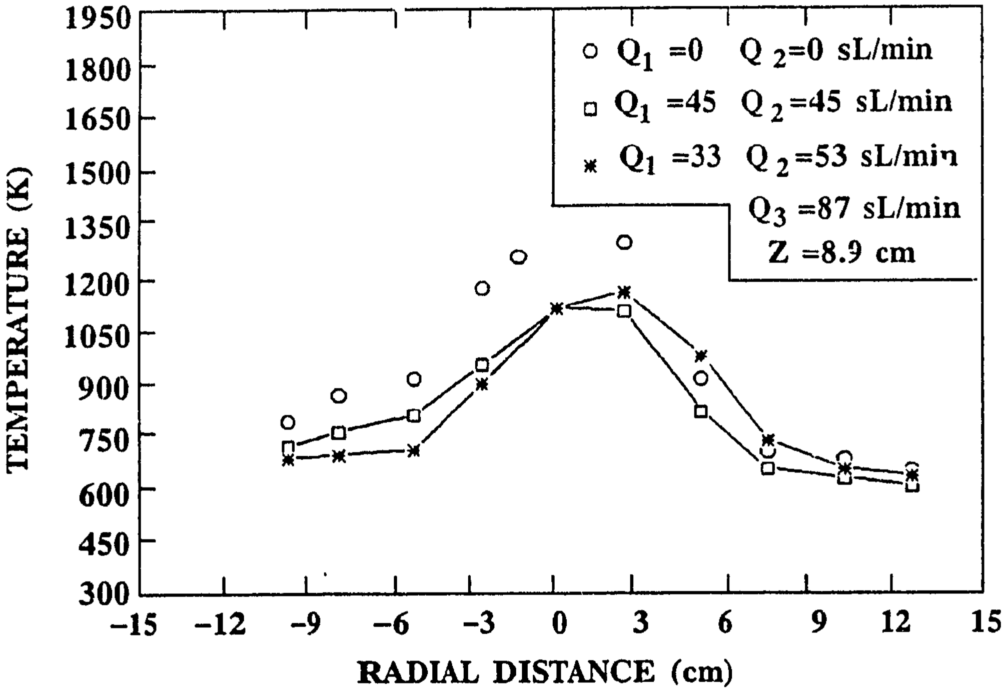


Figure 5.2 - Radial temperature profiles with and without gas injection

have the effect of displacing the gas temperature profile by about 2.5 cm so that when the injection flows were equal, the maximum temperature appeared at R=0, but when the flows were uneven, the maximum temperature appeared at R=2.5 cm.

2.1.2 Effect of Equal Gas Injection on Concentration Profile

Measurements were taken of the nitrogen concentration in the gas sample and these results normalized by the injected nitrogen amounts in the following manner:

$$N/N_{CAL} = \frac{\{ [N_2]/([N_2]+[Ar]) \}_{MEASURED}}{\{ [N_2]/([N_2]+[Ar]) \}_{INJECTED}} \qquad [5.1]$$

The concentration profiles, N/N_{CAL}, along with the temperature profiles for the case of equal injection, are shown in Figure 5.3. Far from the torch centerline, R=-12.7 and R=7.6 cm, the concentration ratio was close to one, indicating excellent mixing behaviour. As the axis of the torch was approached, from either direction, at R=-2.5 cm or R=2.5 cm, nitrogen levels increased due to the presence of the angled jets, although the concentration of argon was quite substantial. At the centerline of the argon plasma jet, where one would expect to find little nitrogen, the concentration ratio fell to just 0.9, indicating an appreciable nitrogen content in a region expected to contain mostly argon. It is important to note that there appear equal-sized nitrogen peaks on both sides of the centerline with this injection configuration. In general, these results show that under these conditions and with this type of injection, excellent entrainment of the injected gases into the core of the plasma flame occurred.

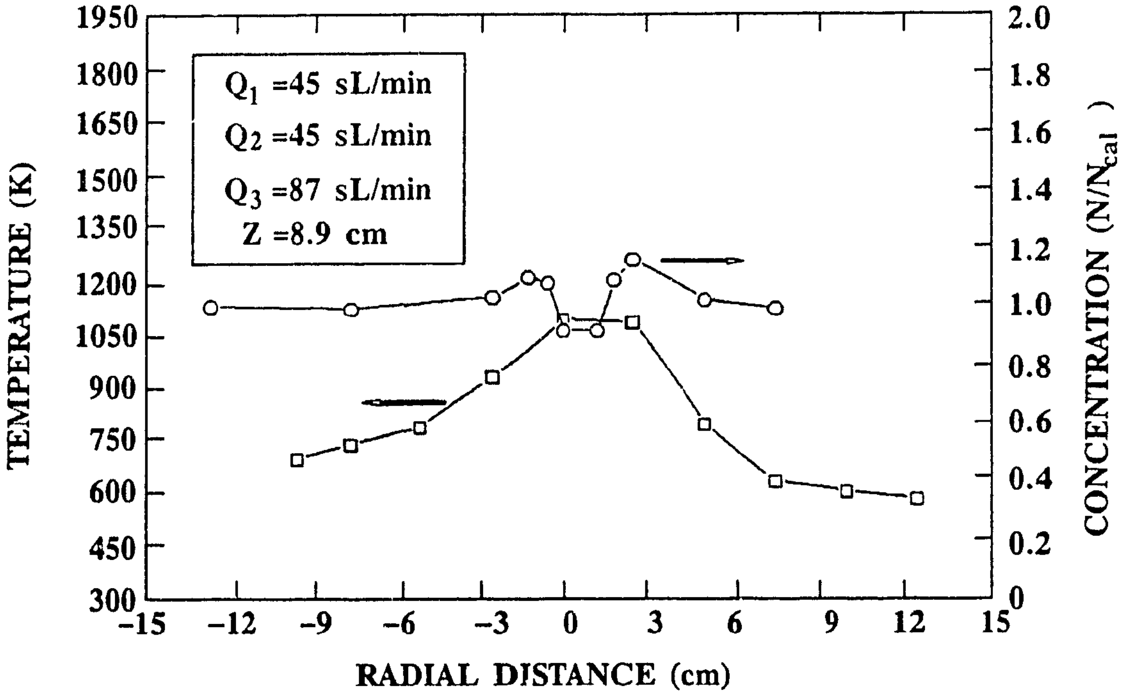


Figure 5.3 - Gas concentration and temperature profiles with equal gas injection

2.1.3 Effect of Unequal Gas Injection on Concentration Profile

When the angled injection of gas was unequal, as shown in Figure 5.4, non-uniform mixing occurred near the center of the plasma flame, such that at R=3.8 cm, for example, a pocket of high nitrogen concentration appeared. Even with this unbalanced flow arrangement, considerable nitrogen nonetheless entered the center region, R=0 cm, where the concentration ratio was maintained at about 0.9.

Gas concentration isocontour maps were also drawn to illustrate the degree of mixing attained under unbalanced injection conditions. These are shown in Figure 5.5a with cold argon and in Figure 5.5b with argon plasma operation. A mixture of 53.9% nitrogen and 46.1% argon represented perfectly mixed proportions. Under cold conditions, Figure 5.5a demonstrates how the impinging jets of nitrogen completely displaced the jet of argon entering through the torch. With the plasma torch operating however, much less displacement occurred and pockets of unmixed gas found under cold conditions were greatly reduced in both size and number. The plasma jet, being more viscous at high temperatures and with a much higher velocity, resisted displacement by the two cold jets while the expansion of the jet improved the entrainment of the gases into the hot zone. In addition, the few remaining gas pockets in the hot zone were virtually eliminated with increased axial distance. At the centerline, for example, nitrogen concentrations of 66.3%, 54.5%, and 54.7% were measured at Z=7.6, 14.0, and 17.5 cm, respectively, with 53.9% being ideal. In fact,

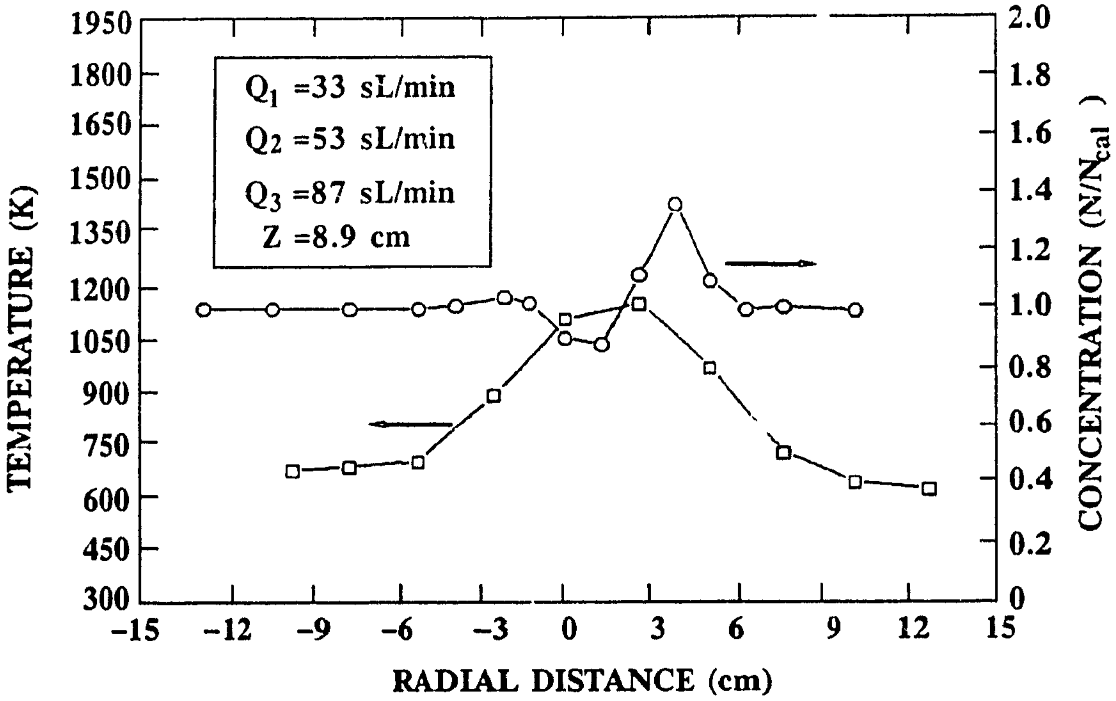


Figure 5.4 - Gas concentration profiles with unequal gas injection

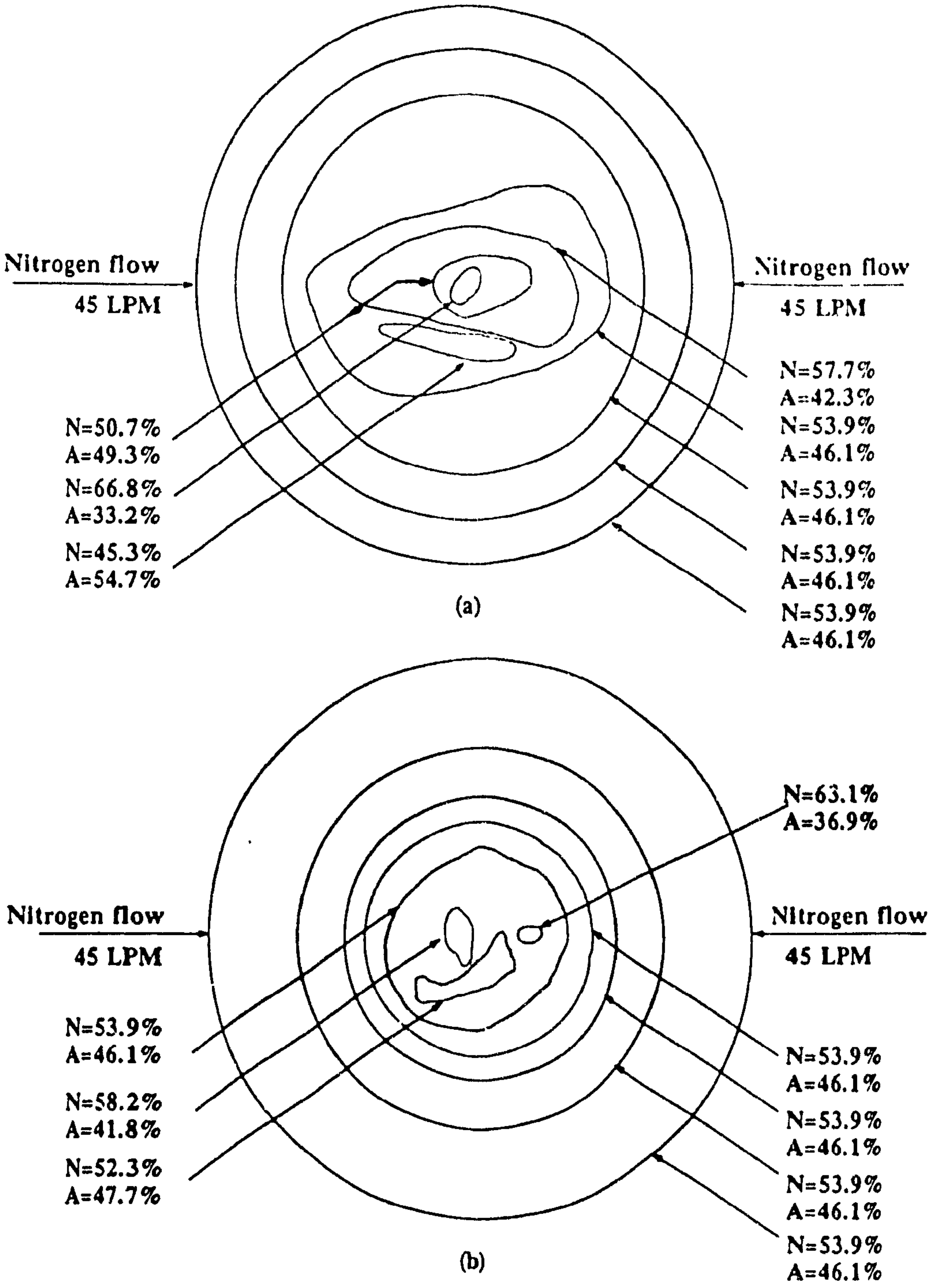


Figure 5.5 - Gas concentration isocontours with equal gas injection at:
a) ambient conditions b) plasma conditions

in all the experimental trials, increasing the axial distance, by as little as 7.6 cm, increased the gas composition uniformity substantially.

Experiments were also conducted with hydrogen as one of the injected gases. The results showed the entrainment of both hydrogen and nitrogen into the central region of the plasma flame in proportions similar to those injected, again demonstrating excellent mixing behaviour.

Increasing the power to the plasma from $P_{NET}=6$ to 12 kW had little effect on the measured gas compositions. However, more work at plasma powers greater than 30 kW would be necessary to extrapolate this result.

3 PRODUCTION OF PHOSPHOROUS ACID

The measurements made in the mixing study demonstrated that with the roof injection of two angled impinging jets directed at the plasma jet expansion zone, the phosphorus and steam injected into the reactor would be entrained into the plasma tailflame and be intimately mixed. Although net plasma powers of only 6-12 kW were used in the mixing study, temperatures above 1500 K at the torch centerline were achieved. Therefore, it was assumed that at higher power levels, the thermodynamically-predicted temperatures of between 1500 and 2200 K in the reacting zone, necessary for the reaction between phosphorus and steam to produce phosphorous trioxide (P_2O_3) and subsequently phosphorous acid (H_3PO_3), would have been easily attained with the existing equipment. However, at net power levels of over

40 kW, and with steam injection, temperatures never exceeded 1000 K. A detailed analysis of the experimental equipment determined that the torch support roof had to be modified, and additional reactor insulation installed. Another important change was the use of a nitrogen plasma as a more energetic source of heat, replacing the argon plasma previously used. Subsequent experiments with steam injection had reactor temperatures exceeding 1600 K.

The mixing study also demonstrated that although balanced injection flows were desirable, it was not critical to the intimate mixing of the reactants in the hot zone of the reactor. Unbalanced injection flows left unmixed gas pockets close to the torch exit but these pockets quickly disappeared as the axial distance was increased.

Following the mixing study using nitrogen, argon and hydrogen, phosphorus and steam were injected into the reactor in order to produce phosphorous trioxide (P_2O_3) and phosphorous acid (H_3PO_3). The independent variables that were varied in order to both understand and optimize the production of phosphorous acid were as follows:

1. Temperature dependency of the reaction mixture
2. H_2O/P_4 feed ratio
3. Quench location and flowrate within the reactor
4. Plasma gas flowrate

Each of these factors will be discussed as to their effect on the resulting phosphorous acid product quality. Overall material and energy balances are included in this section as well as a discussion of the experimental error and experimental lag time.

3.1 THERMODYNAMIC EQUILIBRIUM COMPOSITION

The thermodynamic calculations discussed in Chapter III determined the concentrations of the chemical species when phosphorus and steam reacted and attained a state of chemical equilibrium. These species not only included phosphorous trioxide and phosphorus pentoxide, but generally other higher and lower oxide species as well as some unreacted phosphorus. These other oxides were considered to form phosphoric acid since they are extremely unstable and oxidize readily to the pentoxide state at the low temperatures of the quench zone. The thermodynamically-predicted unreacted phosphorus was also considered to produce phosphoric acid according to Reaction [3.5] since substantial quantities of unreacted phosphorus were never observed in the product effluent. When the new equilibrium product mixture was then compared to the actual liquid and gaseous products, extremely close agreement was observed. For example, the measured hydrogen concentration compared excellently, as shown in Figure 5.6, with the theoretically-predicted hydrogen concentration when all the phosphorus and phosphorus oxides were considered to form phosphorous and phosphoric acids. Therefore, throughout the theoretical analysis, the unreacted

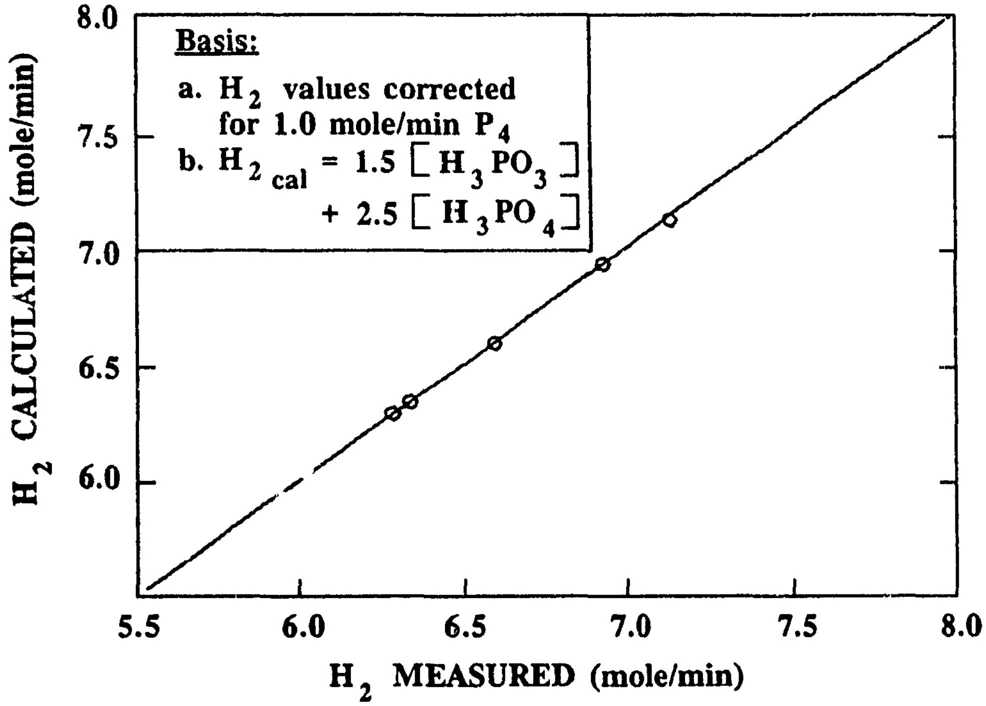


Figure 5.6 - Predicted vs measured H_2 production

phosphorus and phosphorus oxides other than P_2O_3, were assumed to form phosphoric acid in the product liquid. In general, only phosphorous and phosphoric acids, and hydrogen were the reaction products. Hypophosphorous acid, H_3PO_2, unreacted phosphorus and phosphine gas, PH_3, were present in very small quantities.

3.2 EXPERIMENTAL RESULTS

A complete listing of the experimental operating conditions and the resulting measurement of hypo-phosphorous, phosphorous, and phosphoric acid, as well as phosphine and hydrogen can be found in Appendix IV.

A typical example of centerline gas temperature measurements at R=0 and Z=15.2 cm and refractory temperature measurements at R=17.1 cm and Z=14.6 cm is shown in Figure 5.7 for a complete experimental trial. The gas temperature was extremely sensitive to changes in both plasma power level and reactant feedrates. As soon as the steam was introduced into the reactor, the temperature dropped 100 K. The temperature rose once the power was further increased. During the experimental test with phosphorus vapour and steam addition, the fluctuations in the temperature was due to the necessity of adjusting operating conditions to maintain an average measured gas temperature for this trial of approximately 1375 K (at R=0 and Z=15.2 cm). Once the two reactant feeds were stopped, the temperature quickly rose to approximately 1700 K before the plasma was extinguished. Thermocouples

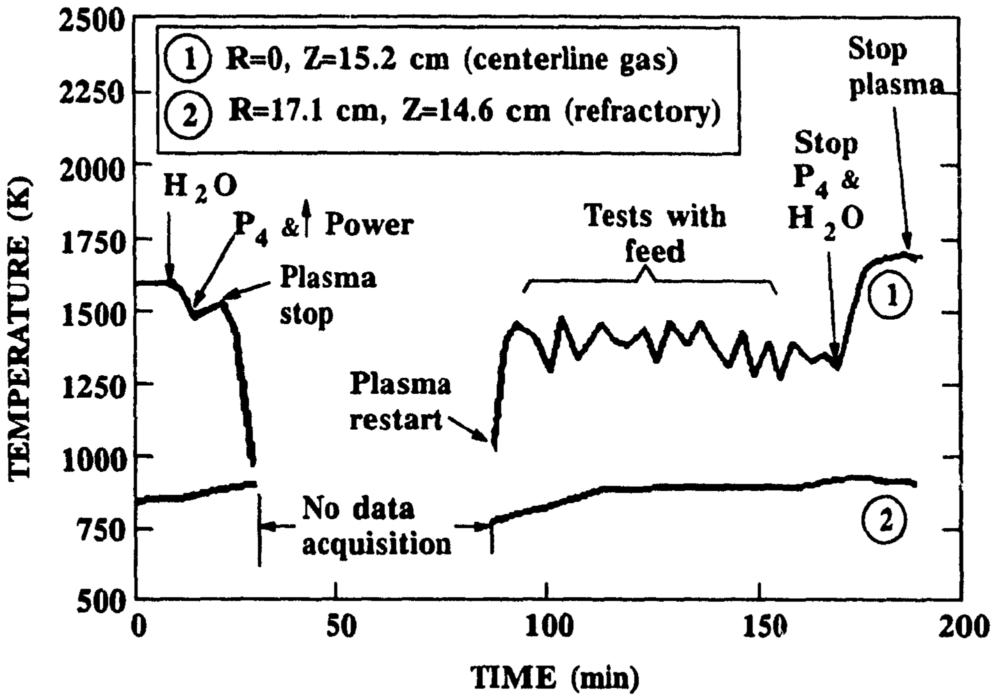


Figure 5.7 - Centerline gas and refractory temperature measurements

imbedded into the refractory were much less sensitive to the system changes and continuously increased during the course of the trial to a maximum of 900 K.

3.2.1 Effect of Reaction Temperature

The thermodynamic analysis of the reaction between phosphorus and steam (H_2O/P_4=6-10) previously presented predicted that the mole fraction of phosphorous trioxide, P_2O_3, increased sharply from 0.26% to a maximum of 20% as the reaction temperature was raised from 1000 to 1500 K (see Figure 3.2). The proportion of phosphorous trioxide in the equilibrium mixture remained fairly constant from 1500 to 2500 K. Hydrogen gas produced from the oxidation of phosphorus was the single largest component in the mixture, almost 60%.

Temperature measurements, at the centerline of the reactor, R=0, and at an axial distance of Z=15.2 cm, were taken simultaneously with liquid product samples, to determine the effect of reaction zone temperature on the final liquid composition and purity is shown in Figure 5.8. The various reactor temperatures of 625, 925 and 1200 K were obtained by increasing the power to the plasma torch. At a temperature of 625 K, over 50% of the phosphorus fed converted to red amorphous phosphorus (RAP), resulting in low phosphorous acid (H_3PO_3) as well as phosphoric acid (H_3PO_4) production. As the temperature was increased to 925 K, only 25% of the phosphorus transformed to RAP and the production of H_3PO_3 and H_3PO_4 increased dramatically.

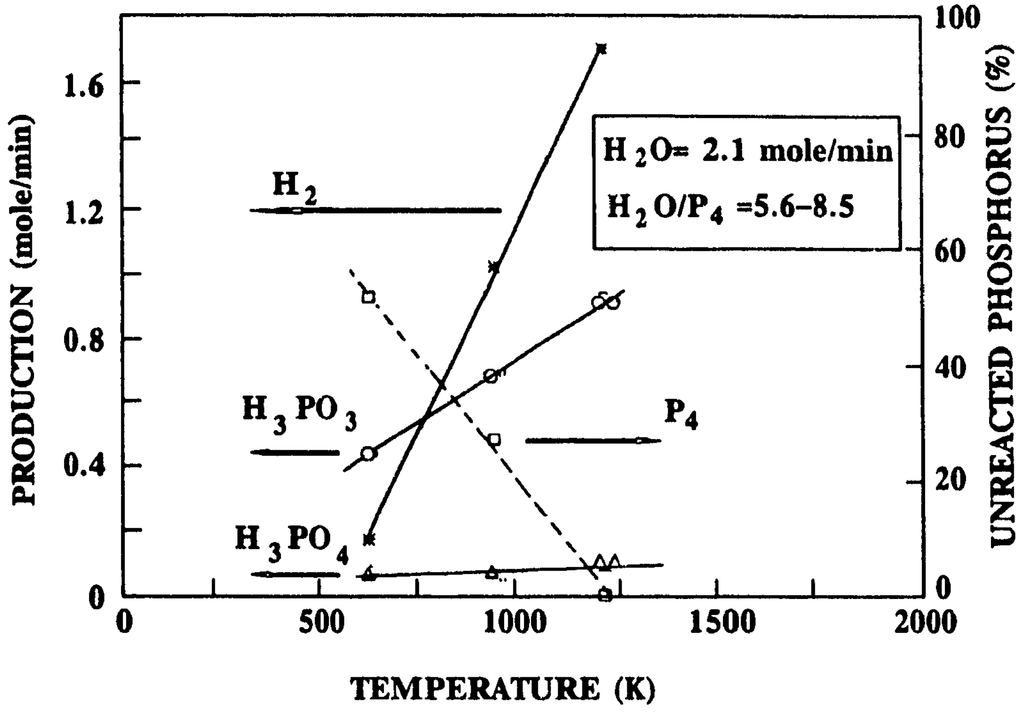


Figure 5.8 - Reaction products vs temperature

Complete oxidation of phosphorus occurred at measured temperatures at R=0 and Z=15.2 cm of 1200 K and higher.

Thermodynamic calculations predicted that at a reaction temperature of 625 K, phosphorous trioxide was not stable, and thus phosphorous acid would not form. However, phosphorous acid was found in the liquid effluent, indicating that phosphorus and steam did in fact react to form phosphorous trioxide. Of course, even at this low temperature measured at R=0 and Z=15.2 cm, some of the phosphorus and steam were nonetheless aspirated above 15.2 cm where the temperature exceeds 625 K and into the central core of the plasma jet and reacted at the high temperature prevailing at that point to form the various oxides. These oxides eventually formed phosphorous and phosphoric acid product when contacted with the quench water. The amount of reactant aspirated into the plasma flame seemed to be directly proportional to the nitrogen volumetric gas flowrate. As the temperature of the plasma increased, resulting in a greater volumetric flowrate, increasingly greater amounts of the reactants became aspirated and reacted to form the various oxides. At reactor temperatures of 1200 K, all of the phosphorus reacted to produce the oxides either in the plasma flame region or within the hot zone of the reactor.

3.2.2 Effect of Steam to Phosphorus Ratio

Steam and phosphorus were fed to the reactor with the molar ratio, H_2O/P_4, between 6 and 40. Thermodynamic calculations at these various ratios and a reactor temperature of 1475 K are shown along with the experimental data in Figure 5.9. Stoichiometrically, phosphorous acid is produced at a reactant ratio of $H_2O/P_4=6$, and using an excess of steam ($H_2O/P_4=40$) was thought to drive the reaction to completion (Law of Mass Action). However, experimental results indicated that the highest phosphorous acid concentration was produced at about $H_2O/P_4=7$ whereas the thermodynamic calculations predicted the maximum at about $H_2O/P_4=10$. Both the experimental and theoretical results show that increasing the steam-to-phosphorus ratio above $H_2O/P_4=10$ caused the amount of phosphorous acid, H_3PO_3, to decrease and the amount of phosphoric acid, H_3PO_4, to increase. Thus the purity of the phosphorous acid product decreased with excess steam. In fact, the application of the Law of Mass Action did not account for a second competing oxidation reaction, Reaction [3.5], namely the production of phosphorus pentoxide, P_2O_5. Not only did this second unwanted reaction remove phosphorus from producing phosphorous acid, but the pentoxide reacted with the quench water to produce phosphoric acid which contaminated the final product.

The temperature measured at R=0 and Z=15.2 cm in the reactor in most of the experiments was about 1475 K, however this temperature was difficult to control and thus varied between tests. A sensitivity analysis on the effect of the reaction temperature on the thermodynamic calculations of the phosphorous acid (H_3PO_3) production, shown in Figure 5.10, demonstrated that the actual reaction temperature could have been over 700 degrees higher than that measured and still compare

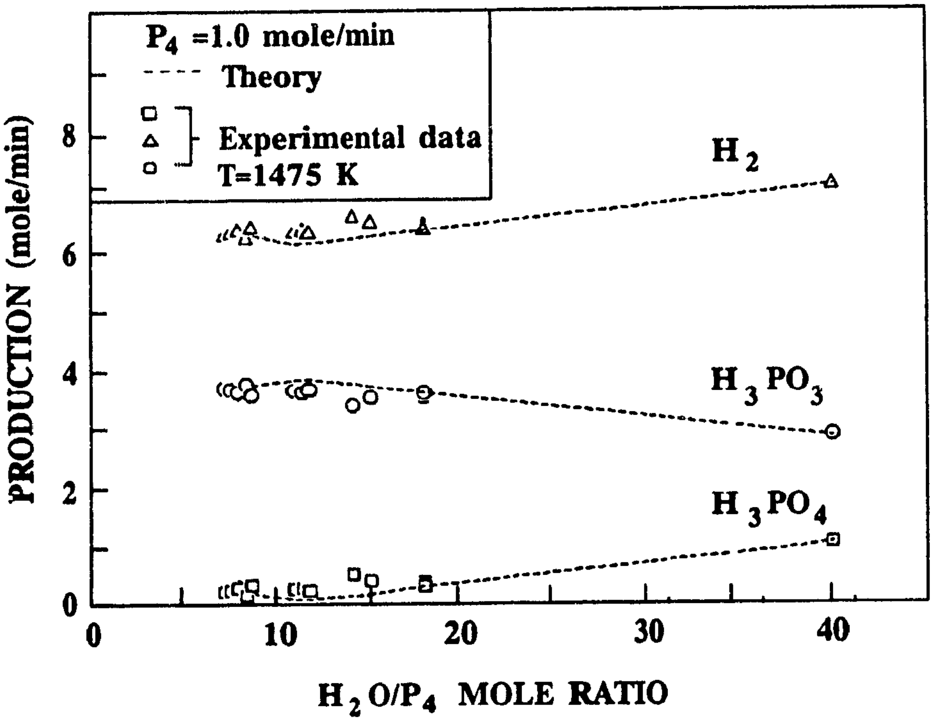


Figure 5.9 - Reaction products vs. H_2O/P_4 ratio

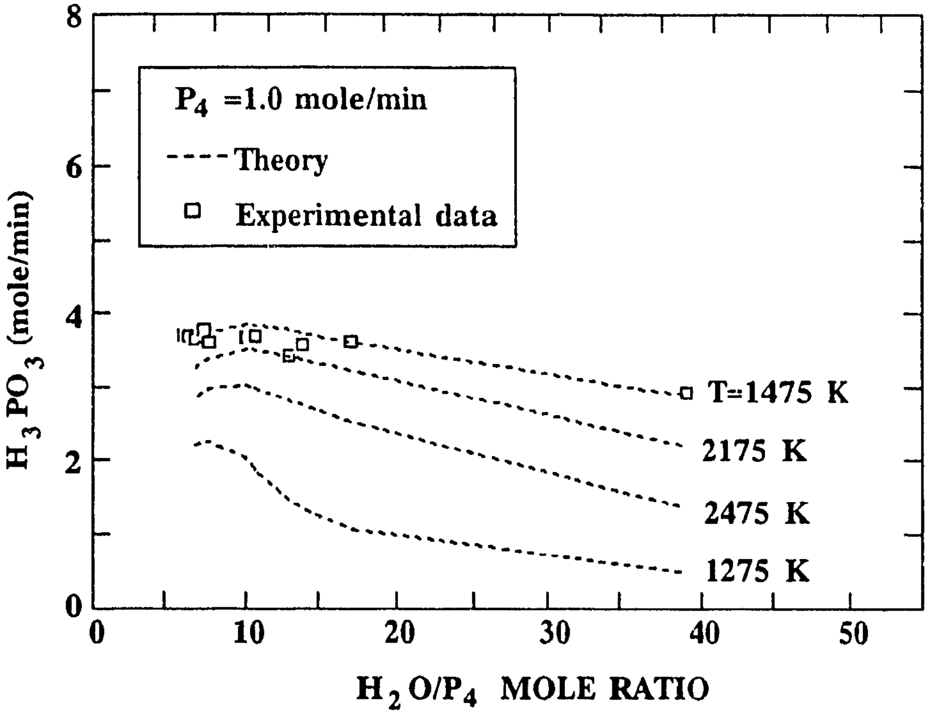


Figure 5.10 - Sensitivity analysis of H_3PO_3 production vs temperature and H_2O/P_4 mole ratio

favourably with the experimental results. According to these calculations, as long as the measured temperature is between 1475 K and 2175 K, the resultant product composition would not appreciably change. There is little agreement between the thermodynamic calculations and the experimental results outside this "window" of operation.

3.2.3 Effect of Quench Flowrate and Position

As previously mentionned, there was a primary quench water nozzle that could be axially adjusted and a secondary quench water nozzle fixed at Z=87.5 cm, both positioned at the centerline of the reactor and pointing in the direction of flow. The results showing the effect of varying the primary quench position, Z_1, and flowrate are presented in Table III. When the primary quench water nozzle was positioned close to the plasma torch, Z=39.5 cm, some of the finely divided droplets in the water spray were aspirated into the hot zone of the plasma, effectively increasing the H_2O/P_4 ratio and decreasing the temperature of the reaction zone. As previously stated, at $H_2O/P_4>>10$ the formation of P_2O_5 is favoured which subsequently increases the production of phosphoric acid. This is also seen as extremely low values of the acid mole ratio, $[H_3PO_3]/[H_3PO_4]=1\text{-}2.7$, in cases 1 to 3. This effect cooled the reactor to measured temperatures of 600 K or lower, and was responsible for red amorphous phosphorus (RAP) and PH_3 formation. These products effectively removed phosphorus from the reaction system and reduced the conversion efficiency. Higher quench

TABLE III

EFFECT OF QUENCH FLOWRATE AND POSITION ON ACID CONVERSION

Case	H_2O/P_4*	Quench L/min	Z_1 cm	$[H_3PO_3]/[H_3PO_4]$
1	36.2	2.5	39.5	1.52
2	39.0	2.5	49.5	2.68
3	39.0	3.5	49.5	1.26
4	17.2	3.5	80.0	7.60
5	17.2	6.0	80.0	9.35
NEW QUENCH NOZZLES				
6	7.6	5.0	55.9	8.90
7	7.7	5.0	81.3	8.30

* = based on amounts fed

flowrates of 3.5 L/min (case 3) also upset the stoichiometry because smaller droplets were produced and were easily aspirated into the reaction zone, even though the quench was 49.5 cm from the plasma. By placing the quench at a distance where the spray does not interfere with the stoichiometry of the reaction, one can significantly increase the production of phosphorous acid. Thus, by placing the quench at Z=80 cm, the water spray did not get drawn up into the upper zone of the reactor. To determine the effect of the quench flowrate on the phosphorous acid production, the quench flowrate was increased from 3.5 to 6.0 L/min. The phosphorous acid ratio increased by almost 20%, from 7.6 to 9.35 (case 4&5). By cooling the reaction products quickly and efficiently the breakdown of P_2O_3 to P_2O_5 and PH_3 was prevented. Therefore, the quench had to be positioned low enough in the reactor to prevent it from interfering with the hot zone as well as be high enough to prevent the breakdown of P_2O_3 to P_2O_5.

The original quench spray nozzles were replaced with nozzles producing a finer spray in order to increase the capture of the gaseous species and cool the reaction gases more efficiently. These new nozzles (cases 6&7) sprayed water droplets co-current with the gaseous reaction mixture, and also had a narrower spray angle to inhibit the spray from being aspirated upstream into the plasma flame. It was determined that a minimum distance of 56 cm was required between the quench location and the torch exit to ensure that no droplets would be aspirated into the upper zone of the reactor. The position of the nozzle was varied from Z=55.9 to 81.3 cm and no effect on the resultant purity of the product was observed. The secondary quench spray was positioned so far downstream of the plasma (Z=87.5 cm) that it was not aspirated into the reaction zone.

3.2.4 Effect of Plasma Gas Type and Flowrate

Preliminary experiments were performed with argon/nitrogen mixtures; argon was required to stabilize the plasma jet. Although the formation of phosphorus nitrides was expected from the reaction between the phosphorus vapour and the nitrogen plasma gas, no such compounds were found in the liquid product. Operation on pure nitrogen, made possible by the change in the anode configuration, also did not produce phosphorus nitride compounds.

The nitrogen plasma gas flowrate was varied between 137-191 sL/min at the same experimental conditions and had no significant effect on the production of phosphorous acid. The resulting phosphorous acid purity ranged from 88.6-89.7% and did not follow any specific trend.

3.2.5 Acid Purity and Production

The purity of the phosphorous acid was determined by the ratio of the phosphorous acid formed to the total acid formed. The purity of the acid did not take into account any solid contamination, such as copper oxides, phosphides or pieces of refractory brick that may have entered the liquid product. In general, this contamination was minimal.

The purity of the liquid effluent varied between 42-95%; most operating conditions yielded purities between 90-95%. Phosphorus feedrates of 100 g/min yielded 92% conversion to phosphorous acid which corresponds to an annual production rate of 100 metric tons of pure phosphorous acid (based on 7200 hours) with the experimental unit as is. It was calculated that this experimental unit operating with a net plasma torch power of 36 kW and a theoretical energy requirement of 0.24 kWh/mole P_4, could produce 335 tonnes per year of phosphorous acid, along with 20 tonnes per year of phosphoric acid. Of course this production rate would demand that the phosphorus feedrate be increased, and therefore would require some equipment modifications. It is uncertain at the time of writing whether the degree of phosphorous acid purity produced with this unit is commercially viable.

3.2.6 Unsteady State Results

Analysis of the liquid and gaseous products from the reaction between phosphorus and steam indicated an 8-10 minute delay before steady state operation was achieved. The cause of this delay was due to the time required by the phosphorus feed system to achieve steady flow operation. By back calculating the amount of phosphorus that must have been consumed in order to form the phosphoric and phosphorous acid found in the liquid product before steady state was achieved, new stoichiometric feed ratios (H_2O/P_4) were determined. For example, a very high ratio of $H_2O/P_4=425$ was calculated due to the extremely low phosphorus feedrates found either during start-up or shutdown of the phosphorus system. The results presented in Figure 5.11 demonstrate the excellent agreement between the predicted and experimental results for hydrogen gas and phosphorous acid at the calculated H_2O/P_4 ratios. Chemical equilibrium for the reaction was achieved even though the phosphorus feed system was not at steady state. All of the thermodynamic calculations were performed assuming that the reaction temperature was 1475 K.

3.2.7 Experimental Lag Time

Experiments were performed to determine the time required for the gas sample to arrive at the GC for analysis, as well as the hold-up time of the liquid product, at typical experimental conditions. There were five distinct gas "lag" times, θ, inherent in the reaction system:

θ_1: the time from when the phosphorus pump was turned on and water displaced the liquid phosphorus in the egg;

θ_2: the time it took for the liquid phosphorus to arrive at the evaporator;

θ_3: the time it took to vaporize the liquid phosphorus;

θ_4: the time it took for the gaseous phosphorus to go from the evaporator to the reactor;

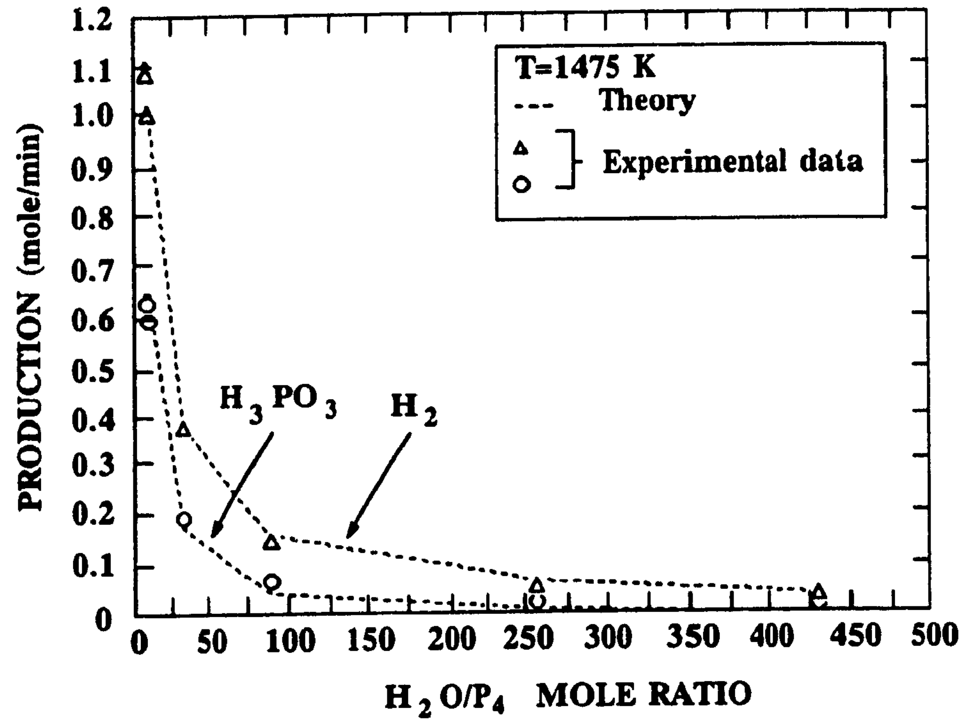


Figure 5.11 - Reaction products vs H_2O/P_4 at unsteady state conditions

θ_5: the time it took for the gaseous products to move through the reactor to the exit line, and through the sampling line to the gas chromatograph.

Measurements showed that once the water pump was started, the water began to flow immediately into the phosphorus egg, $\theta_1=0$, which forced the liquid phosphorus into the line to the evaporator. The time required for the liquid phosphorus to flow from the egg to the evaporator was measured as $\theta_2=45$ sec, at the flow conditions studied. It was assumed that the liquid phosphorus flashes as soon as it entered the evaporator, $\theta_3=0$, and that the residence time of the phosphorus vapour in the line from the evaporator to the reactor equaled the residence time of the carrier gas, $\theta_4=0.41$ seconds. The residence time of the reaction gases in the reactor and gas sampling line was measured as $\theta_5=180$ seconds. The total time was therefore $\theta_t=225$ seconds (3.75 min). The liquid hold-up time in the reactor is low, since most of the quench water dropped directly into the gas/liquid separator. However, some of the quench water did splash onto the reactor walls and slowly ran down the walls into the separator.

In two lag-time experiments phosphorus was fed to the reactor for a period of ten minutes, then stopped for ten minutes, and then repeated, and in a third experiment, phosphorus was added for fifty minutes, then stopped. Gas and liquid samples were taken every two minutes over the 90 minute test as shown in

Figure 5.12, where at the two-minute mark in each of the three tests, neither hydrogen nor acid was detected. This was consistent with the lag time experiments previously done, since it took almost four minutes for the reaction gases to arrive at the gas chromatograph. The production of both the hydrogen from the oxide formation reactions, and the production of phosphorous and phosphoric acids, were detected after four minutes of operation. In the third experiment, the concentrations increased continuously until the eight-minute mark at which time the concentrations leveled off, indicating that steady-state had been achieved. After the phosphorus feed was stopped, seen clearly in the first two experiments, the production of both the hydrogen and the acids decreased rapidly for about ten minutes, after which negligible amounts were found.

3.2.8 Experimental Error

The sources of error included the errors in the analytical equipment for the gas and liquid analysis, the error in temperature measurement due either to radiation losses from the thermocouple or due to the instability of the plasma and power, the errors in the reactant feed systems, and the fluctuations in the quench water flowrates to the reactor. Calibrated rotameters were used to measure the plasma gas flows having an estimated precision of ±7-10 sL/min. The precision of the torch cooling water rotameter was estimated at ±2.0 L/min. The precision of the quench water rotameters was ±0.1 L/min.

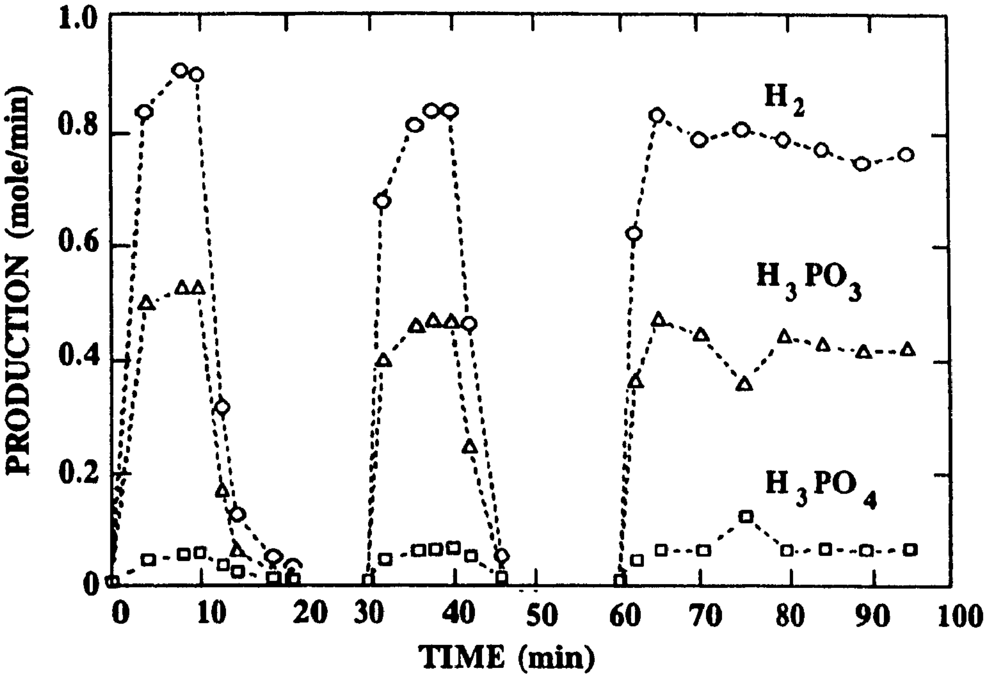


Figure 5.12 - Lag time tests: H_2, H_3PO_3 & H_3PO_4 vs time

The phosphorus feed system was verified to have a constant flow during a 15-minute test before installation of the unit. However, during the final experimental trials it was discovered that the phosphorus flow decreased by approximately 5% of its initial value after about 1.5 hour of continuous operation at P_4=21.6 g/min. Assuming that the decrease in phosphorus flowrate was caused by an increase in back pressure downstream of the phosphorus feed pump, flow measurements were carried out against a 30-cm water head, representing a differential pressure increase of 10 kPa. This resulted in a 5% decrease in the flowrate from the phosphorus feed pump. In a thirty-minute experimental trial with steam and phosphorus at constant operating conditions, hydrogen production decreased slowly with time, indicating that a 2.5% drop in the phosphorus flowrate had occurred. Since the phosphorus level within the phosphorus egg dropped only 0.6 cm in this test, there should only have been a 0.1% decrease (5%*0.6/30=0.1%) instead of the 2.5% decrease in the phosphorus flowrate. Since the change in the phosphorus level did not retard the phosphorus flow sufficiently to account for the decrease in the hydrogen production with time, some other change within the equipment during an experimental trial may have occurred, thus causing an increasing back pressure with time. Neither the reactor pressure nor other auxilliary equipment pressure was continuously monitored or recorded during the experimental tests so that this hypothesis cannot be confirmed.

With an experimental equipment as large as that used, it is difficult, if not impossible, to eliminate all the sources of error. Replicate experiments were performed to determine the reproducibility of the experimental results and are shown in Figure 5.13. The analyses between two identical experiments showed no significant deviation when calculated at a 95% confidence interval for phosphorous acid. Liquid product sample analysis at steady state conditions, showed less than 2% deviation in phosphorous acid concentration. Replicate experiments made for the gas measurements showed less than 1% deviation from the injected standard.

3.2.9 Overall Material Balance

A complete material balance on the reactor for a typical experiment is presented in Figure 5.14. The species balances described below refer to general observations and do not correspond exactly to the overall material balance presented in Figure 5.14. Helium was used as a tracer gas for the gas chromatographic analysis.

a. Hydrogen Balance

In general, there occurred a serious discrepancy between the amount of hydrogen actually measured and the amount of hydrogen expected based on the acid liquid analysis, as shown in Figure 5.15. The amount of hydrogen that should have been generated based on the actual acid analysis was calculated to be $H_{ACID}=0.4$ mole/min. However, the hydrogen measured by the gas chromatograph was more than double that anticipated with $H_{GC}=0.92$ mole/min. Since hydrogen comes from the reduction of steam during the phosphorus oxide formation, this result

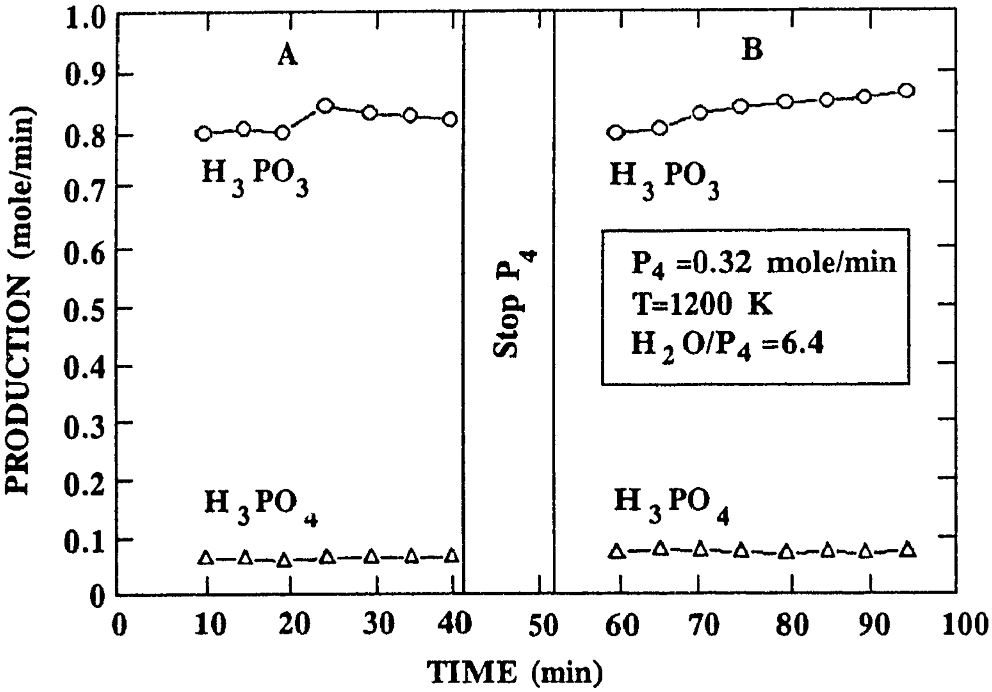


Figure 5.13 - Repeat experiments of H_3PO_3 production vs time

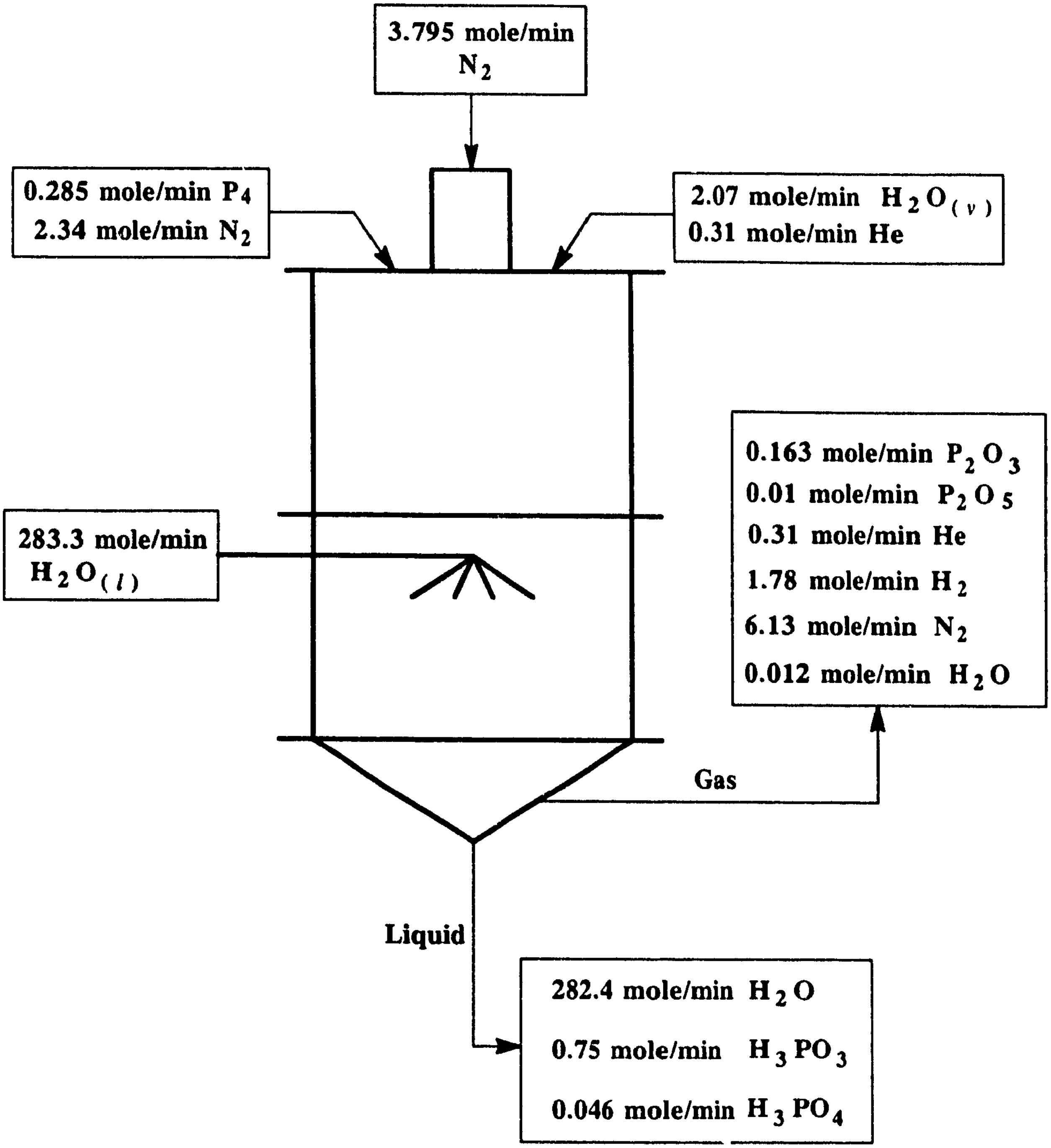


Figure 5.14 - Overall material balance

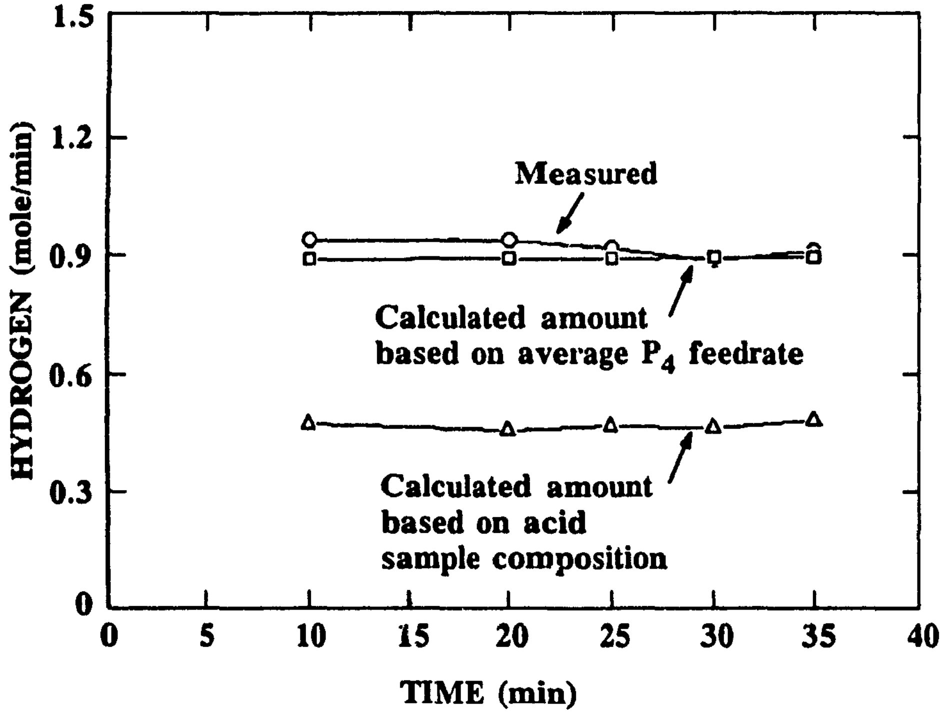


Figure 5.15 - Predicted H_2 production vs measured quantities

suggested that not all of the phosphoric and phosphorous oxides produced were accounted for in the liquid product. This was confirmed when samples taken from the gas exit line in subsequent experiments contained phosphorous and phosphoric acid in the same proportions as the liquid product. Since unreacted phosphorus was not found during the above mentioned test, if one assumed that all of the phosphorus fed reacted in the proportions found in the liquid product to form phosphorous and phosphoric acid, hydrogen would have been produced at H_{THEORY}=0.89 mole/min, about 3% difference from that actually measured.

To improve the collection efficiency of the phosphorus oxides, the quench spray nozzles were changed to provide a finer mist, and the quench flow was increased to improve the condensation of the hot gas and the reaction of the oxides to form the acids. Experiments showed that the collection efficiency, based on H_{ACID}/H_{THEORY}, increased from 41% to 73%.

b. Water Balance

Approximately 4% of the quench water added to the system was recovered as condensate in the water-cooled scrubber while the balance flowed into the acid collection system.

c. Phosphorus Balance

In general, the phosphorus reacted completely to form phosphorous and phosphoric acid and no phosphorus was recovered in the catchpot. At extreme operating conditions, however, such as at low temperatures or low H_2O/P_4 ratios, all of the phosphorus did not react. Some of the unreacted phosphorus was recovered in the catchpot, although, the vast majority of the unreacted phosphorus was either entrained in the exit gas stream and burned in the atmosphere or else flowed into the collection barrels. The amount of phosphorus that formed phosphine gas, PH_3, was always small ($\sim 2\text{x}10^{-5}$ mole/min) and was never considered in any of the mass balance calculations.

3.2.10 Overall Energy Balance

The complete energy balance on the reactor for a typical experiment is presented in Figure 5.16. The heat lost to the walls was calculated as the difference between the energy from the reactants and plasma gas and the energy from the product gas and liquid. For this case, approximately 60% of the total energy was lost either to the torch cooling (40%) or through the reactor walls. The theoretical energy requirement of the process to produce a mixture of 95% phosphorous acid and 5% phosphoric acid was calculated as 0.24 kWh/mol P_4. This amount takes into account

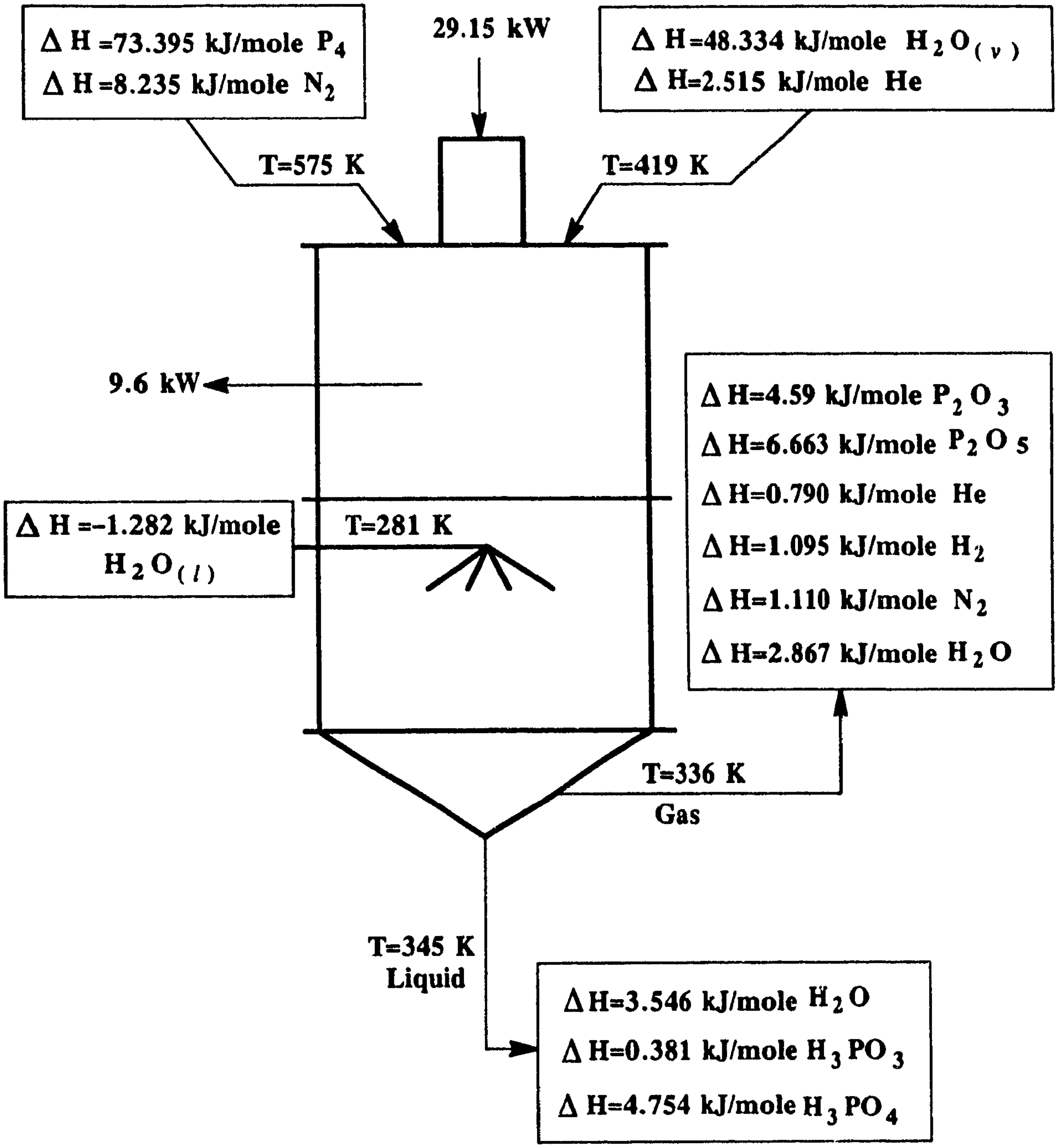


Figure 5.16 - Overall energy balance for material balance data shown in Fig. 5.14

the energy required to heat the plasma gas and reactants to 1475 K, the heat of reaction to produce the both the phosphorous and phosphoric oxides and the energy required to heat a slight excess of steam ($H_2O/P_4=10$).

To quantify the difference in the overall energy balance with and without the phosphorus addition and subsequent reaction, temperature measurements of the gas and liquid products exiting the reactor were taken for the two cases. When the phosphorus was introduced into the reactor, the temperature in the "hot" zone decreased by approximately 200 K, whereas the temperature in the gas and liquid products increased by 11 and 7 K, respectively. Expressed in power units, a balance showed that approximately 1.7 kW and 0.035 kW were transferred to the liquid and gas products, respectively. As expected, the increase in the heat content of the gas was small in comparison to that of the liquid products. Using the heats of reaction from thermodynamic data for the production of phosphorous acid from elemental phosphorus and steam, the net heat of reaction at the same experimental conditions was 2.3 kW. The difference between the measured and calculated increase in heat content was less than 25%. This "ballpark" calculation was based on 100% conversion of the phosphorus to phosphorous acid, a reaction temperature of 1475 K, heat losses to the walls of the reactor being constant with or without reaction, and the liquid products being essentially water. The heat transfer to the walls in fact increased since the exit gas was hotter with phosphorus than without phosphorus addition.

3.2.11 Anodic Corrosion by Phosphorus Attack

As mentioned previously, the expanding plasma flame exiting the torch created a strong aspiration action, thereby drawing the reactants into the high temperature plasma tailflame where reaction occurred. However, this aspiration also drew the phosphorus vapour into contact with the copper anode surface, whereby the phosphorus reacted with the copper to form a copper phosphide that was found in the liquid samples. This reaction resulted in severe corrosion, and usually within a short time (20 minutes) anode failure occurred. The corrosion always developed at the same position on the anode, as shown in Figure 5.17. The plasma gas exited the torch with a tangential component, imparted to it within the torch for flame stabilization and as the phosphorus vapour entered the reactor, the plasma gas swept around the perimeter of the anode and aspirates the vapour into contact with the anode whereupon the phosphorus attacked the copper anode. A thermodynamic analysis indicated that the reaction between phosphorus and copper, seen below, occurs at temperatures of 500 K:

$$P_4 + Cu <===> 2\,P + CuP_2 \qquad [5.2]$$

To prevent the contact between the copper anode and the phosphorus vapour, a low carbon steel ring was soldered onto the anode surface, with the intention of reacting the iron with the phosphorus to provide an in situ chemical barrier of Fe_xP_y.

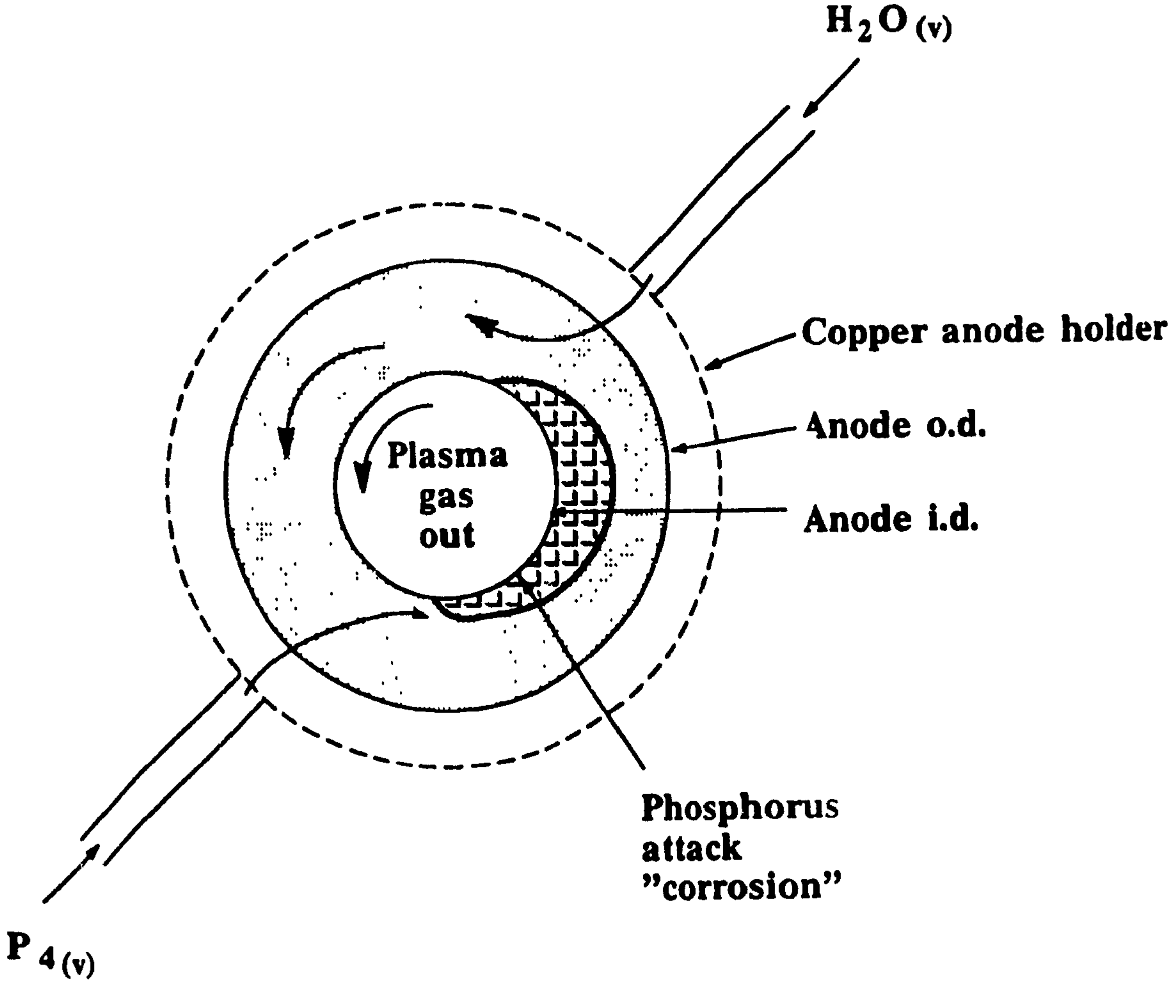


Figure 5.17 - Position of phosphorus attack on anode

These trials were unsuccessful in preventing the chemical attack, however, it did extend the life of the anode due to its increased mass.

An investigation of the plasma arc behaviour showed that at the experimental conditions tested, the plasma arc attached itself onto the exterior surface of the anode as shown in Figure 5.18a. This explains why the 500 K temperature required for Reaction [5.2] to occur was acheived. Decreasing the anode internal diameter and modifying the secondary gas distribution head to increase the swirl component of the plasma gas along with a reduction in gas flowrate caused the arc to rotate within the anode, Figure 5.18b. Since a thermodynamic analysis revealed that boron nitride as well as some ceramic materials resist the chemical attack of phosphorus, torch anodes with smaller diameters were assembled, complete with boron nitride, stainless steel and ceramic barriers. Experimental trials were extremely successful and no visible corrosion was observed. The ceramic barriers were then removed from the smaller anode diameter and tests repeated. No anodic corrosion was observed. Experiments were then done with the original anode configuration and anode arc foot outside that precipitated this work to see if corrosion would indeed occur. Severe corrosion re-occurred.

4 CONCLUSIONS

In the initial phase of this study, the gas composition measurements showed evidence of strong aspiration of the cold jets into the central flame region, essential for

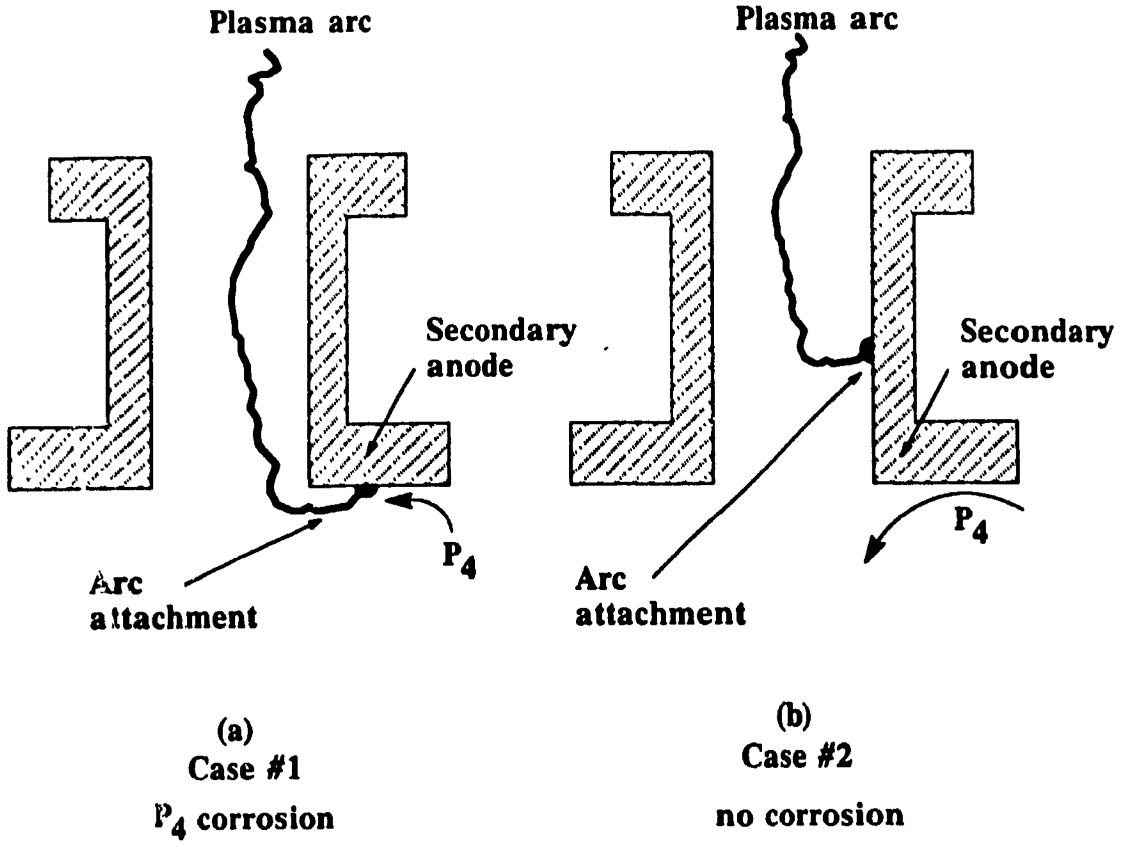


Figure 5.18 - Plasma arc attachment at:
a) anode exterior surface b) anode interior surface

good mixing. The plasma flame was easily displaced by the impinging jets, and when the injection flows were unequal, pockets of unmixed gas and non-uniform temperature distributions were produced. This asymmetry lead to imperfect mixing conditions, with large thermal gradients and minimal contact of the injected gases when measured at a short axial distance from the torch exit. However, the results demonstrated that with a slight increase in axial distance, even unbalanced flow conditions would equilibrate and good mixing would result.

The purpose of using a high temperature source, such as a nitrogen plasma, was based on the thermodynamic predictions that temperatures in the order of 1500 K were required for phosphorous acid production. Experimental results showed that the phosphorous acid purity decreased while unreacted phosphorus increased dramatically with decreasing reactor temperatures from 1200 K to 625 K at $R=0$ and $Z=15.2$ cm. However, phosphorous acid formed in low concentrations even at low temperatures (625 K) when thermodynamic calculations predicted that no acid formation should occur. It is believed that although the temperature was low 15.2 cm away from the torch, a portion of the phosphorus and steam was nonetheless aspirated into the central plasma flame region and reacted to form phosphorous trioxide. This oxide eventually formed phosphorous acid when quenched. The amount of the reactants aspirated into the central flame region depended on the plasma volumetric flowrate and hence on its temperature, therefore it was critical to the acid production process that high temperatures be maintained not only to produce the oxide and hence the phosphorous acid but also to ensure complete entrainment of the reactants into the hot plasma flame.

One of the most important parameters affecting product quality and yield was the feed ratio of steam to phosphorus, H_2O/P_4. When this ratio was $H_2O/P_4=6\text{-}10$, phosphorus conversion was excellent and phosphorous acid purity of 95% was achieved. As the feed ratio was increased, the production of phosphorous acid decreased and a corresponding increase in phosphoric acid was observed.

By positioning the quench so that it did not interfere with the hot zone reaction and yet effectively cooled the hot oxide species, high-purity (95%) phosphorous acid was obtained. One of the minor difficulties encountered in the experimental trials was the inability to trap all the phosphorus oxides into the liquid phase. The capture efficiency improved with increased quench water. A further improvement would be to contact the hot exhaust gas containing uncollected oxides with phosphorous acid, a method employed in the conventional production of phosphoric acid to capture all the oxides. Certainly, a demister on the gas exhaust line would also increase the capture efficiency.

A sensitivity analysis based on thermodynamic calculations revealed that the actual reaction temperature could have been over 700 degrees higher than that measured at $R=0$ and $Z=15.2$ cm, i.e. between 1475 K and 2175 K, and still compare favourably with the experimental results. There was very little agreement between the thermodynamic calculations and the experimental results outside this "window" of operation.

The increase of energy in the product acid and gas streams was approximately equal to that released from the net reaction to form phosphorous acid.

Although it was feared that a nitrogen plasma would form phosphorus nitrides once the phosphorus vapour was injected into the reactor, no such compounds were produced.

5 REFERENCES

Gravelle, D., Beaulieu, M., Carlone, C., Iacocca, D., and Boulos, M.I., "Three-dimensional temperature field measurements in an asymmetric DC plasma jet", A-4-3, ISPC-6, Montreal (1983)

Grey, J. and Jacobs, P.F., "Experiments on turbulent mixing in a partially ionized gas", AIAA J, 2, pp. 433-438 (1964)

Grey, J., Sherman, M.P., Williams, P.M., and Fradkin, D.B., "Laminar arcjet mixing and heat transfer: theory and experiments", AIAA J, 4, pp. 986-993 (1966)

Lana, F. and Kassabji, F., "The mixing of a plasma jet in a cold flow: comparison between numerical and experimental results in a three-dimensional (3-D) configuration", P-013, ISPC-8, Tokyo (1987)

Lewis, J.A. and Gauvin, W.H., "The motion of particles entrained in a plasma jet", AIChE J, 19, 5, pp. 982-990 (1973)

O'Connor, T.J., Comfort, E.H., and Cass, L.A., "Turbulent mixing of an axisymmetric jet of partially dissociated nitrogen with ambient air", AIAA J, 4, pp. 2026-2032 (1966)

Pfender, E., and Lee, Y.C., "Particle dynamics and particle heat and mass transfer in thermal plasmas. Part I. The motion of a single particle without thermal effects", Plasma Chem. Plasma Process., Vol. 5, No. 3, pp. 211-237 (1985)

Sundstom, D.W. and DeMichiell, R.L.. "Quenching processes for high temperature chemical reactions", Ind. Eng. Chem. Process Des. Develop., Vol. 10, No. 1, pp. 114-122 (1971)

CHAPTER VI

GENERAL CONCLUSIONS

1 CONCLUSIONS

The work presented in this thesis proved that it was technically feasible to produce high-purity phosphorous acid by reacting phosphorus and steam at high temperatures. The reaction was carried out in a single reaction vessel to produce the desired synthesis. In the initial phase of this work, the gas composition measurements showed evidence of the strong aspiration of the nitrogen that was injected through the angled ports into the central argon flame region. Since these ports were to be used for the injection of phosphorus vapour and steam into the reactor, excellent mixing of the reactants and heating to high temperatures within the hot zone were anticipated. This would be essential for the desired reaction to occur. Although the plasma flame was easily displaced by the impinging jets and pockets of unmixed gas was produced, the results demonstrated that with a slight increase in axial distance, good mixing would result.

The purity of the phosphorous acid product was generally higher than 90% and some experimental trials produced acid purities of 95%. Phosphorus conversion was normally 100%, giving products of mainly phosphorous and phosphoric acid, some phosphine and very small amounts (<50 ppm) of hypophosphorous acid. It was critical to maintain high operating temperatures, not only to produce the desired phosphorous trioxide, but also to ensure the complete entrainment of the reactants into the hot plasma flame. One of the most important parameters affecting the acid product purity and yield was the steam to phosphorus ratio, H_2O/P_4. The best results (95% purity) were obtained at H_2O/P_4=6-10. Also important was the position of the quench water spray with respect to the torch exit and the degree of atomisation of the spray. Although small droplets rapidly cooled the reaction gases, they were easily aspirated into the hot zone of the reactor, thereby increasing the steam reactant feedrate and simultaneously cooling the hot zone. This resulted in poor product purity and low yield. Positioning the quench spray too far from the torch exit resulted in the decomposition of the phosphorous trioxide to phosphorus pentoxide, an undesired precursor to the formation of phosphoric acid.

A sensitivity analysis based on thermodynamic calculations revealed that the actual reaction temperature could have been over 700 degrees higher than the measured temperature of 1475 K at R=0 and Z=15.2 cm, i.e. between 1475 K and 2175 K, and still compare favourably with the experimental results. There was very little agreement between the thermodynamic calculations and the experimental results outside this "window" of operation.

Under certain operating conditions, red amorphous phosphorus (RAP) was produced with particle sizes controlled by the operating conditions.

The general simplicity in the operation of the plasma torch along with the minimal maintenance required are distinct advantages of this process. Of course, the process could only be considered for commercialization once the anodic corrosion by phosphorus that was so prevalent in the initial experimental trials was eliminated. This was accomplished by modifying the anode configuration, plasma gas flowrate, and secondary gas distribution annulus. It was calculated that the experimental unit could provide 100 metric tonnes of pure phosphorous acid per year based on actual acid production trials. The production rate of phosphorous acid could be increased to 335 tonnes per year together with 20 tonnes per year of phosphoric acid, with the present experimental configuration (P_{NET}=36 kW), based on a theoretical energy requirement of 0.24 kWh/mole P_4. However, the impurity of phosphoric acid (~5%) in the present process is serious if pure phosphorous acid is require as the separation of the two acids is difficult. The possibility of using hydrogen as the plasma gas (~200 sL/min) to increase the purity of the product has been demonstrated theoretically and this might tip the economic balance for commercialization. This semi-pilot plant had the added advantage of demonstrating a possible industrial application on a reasonable scale.

2 CONTRIBUTION TO KNOWLEDGE

1. The thermodynamic calculations performed demonstrated the theoretical feasibility of oxidizing phosphorus with steam at high temperatures.

2. The process yielded phosphorous and phosphoric acid from the gas-phase reaction of phosphorus and steam at high temperatures to produce P_2O_3 and P_2O_5 and their subsequent quench with water. The effects of various operating parameters on the phosphorus conversion to the desired phosphorous acid product were studied. Some optimization of the process was effected.

3. The work was supported by thermodynamic analyses of the system which generally agreed with the experimental results and were very useful in predicting their trends. In particular they predicted the theoretical feasibility of producing high-purity phosphorous acid (>98.5%) by introducing large quantities of hydrogen gas (200 sL/min) into the reaction mixture.

4. Prolongation of the electrode life of the plasma torch anode was achieved by modifying the anode geometric configuration and gas-distribution annulus and by adjusting plasma gas flowrates. These steps lead to the prevention of phosphorus attack on the anode.

5. Procedures for the analysis of the reaction gas and liquid samples were developed for the special situation prevailing in this study. A gas sampling train was designed to scrub the gas sample of phosphine, phosphorus oxides and water. Iodine and a sodium phosphate buffer were added to liquid samples before being titrated with

a sodium thiosulphate solution to determine the phosphorous acid content. Ammonium vanadate, ammonium molybdate and nitric acid were combined before being added to the phosphoric acid sample and analyzed in a one wavelength colorimeter.

6. The production of red amorphous phosphorus (RAP), a potential marketable product, was shown to be possible by controlling the reactant feedrates and the reactor temperature.

7. The proper design of the reactant feed entry system was shown to be instrumental to take advantage of the aspiration effect due to the expanding plasma gas.

8. The mixing behaviour of argon, nitrogen and hydrogen at the plasma tailflame at various operating conditions was determined.

3 RECOMMENDATIONS FOR FUTURE WORK

In the light of the experimental and theoretical information provide by the present work, future work is required for the development of a continuous industrial process yielding pure phosphorous acid. Some of the areas that need attention are:

Short term

1. Use of a hydrogen plasma to increase the purity of the phosphorous acid product obtained in this study. Theoretical calculations have shown that by using 200 sL/min of hydrogen, 98.5% phosphorous acid can be attained.

2. Feeding of phosphorus liquid instead of phosphorus vapour. On an industrial scale, the feeding of phosphorus vapour is expensive since evaporators are costly and thermally inefficient. Liquid phosphorus can be atomised and sprayed with little equipment modification into the existing reactor experimental set-up.

3. Recycling of the dilute acid product into the quench system. This recycling would not only concentrate the acid but would avoid the cost of other methods of concentration. This recycling would also help in hydrating the phosphorus oxides since it has been previously shown that phosphorus acid solutions are more efficient in their capture of oxides than water. This recycle would have to be cooled before entering the quench system.

Medium term

4. Perform optimization experiments to determine whether an industrial process for the production of red amorphous phosphorus (RAP) can be developed.

5. Determine temperature and concentration profiles of reactant and product gases in the hot zone of the reactor to optimize the design of the reacting zone.

6. Use of a non-aqueous quench method to recover pure phosphorous trioxide as a solid (m.p.:296 K). The use of nitrogen as a quench gas might be a possibility.

7. Install a venturi-type restriction within the reactor equipped with a quench water spray nozzle. This arrangement would force the gaseous reaction products to pass through the restriction and contact the quench spray at high velocity and prevent the backflow of spray into the hot zone of the reactor. This venturi could be made vertically adjustable to optimize the final position of the quench.

Long term

8. Recycling of the hydrogen gas produced from the oxidation reaction of phosphorus with steam into the plasma torch to serve as the plasma gas. Of course, the reaction gases would have to cleaned to remove phosphine and other impurities before hydrogen gas could be used.

9. Recycling of the phosphine gas into the reaction zone to serve as a source of phosphorus and a source of hydrogen, and also to avoid the necessity of using a phosphine scrubbing system.

10. Use of a steam plasma torch as a source of reactant steam and plasma gas as soon as a commercial steam torch becomes available.

11. Scaling up of the experimental equipment from semi-pilot plant to pilot plant operation.

APPENDIX I

A) THERMODYNAMIC PROPERTIES

B) PHYSICAL PROPERTIES

C) PRODUCT SPECIFICATIONS

D) ECONOMIC DATA

E) REFERENCES

TABLE I

THERMODYNAMIC DATA ON PHOSPHORUS COMPOUNDS

$$C_p = a + bT + cT^{-2} + dT^2 \text{ [cal/deg mol]}$$

Subs.	H_{298} kcal/ mole	S_{298} cal/ K mole	a	bx10^3	cx10^{-5}	dx10^6	Range °C	Ref.
P_2O_3	-163.6	74.7	34.4	-2.11	-4.81	.26	<3000	1
PO	-6.68	53.2	11.4	-.57	-.40	.077	<3000	1
PO_2	-75.17	60.6	10.5	3.2	-1.4	.000	<800	4
	-74.9	61.3	13.7	.060	-6.14	.000	800-3000	
P_4O_{10}	-694.1	96.5	98.8	-4.9	-38.0	.604	<3000	1
P_2O_4	-223.2	74.7	41.7	-2.5	-9.3	.302	<3000	1
P_2O_5	-268.7	87.6	50.1	-3.03	-7.3	.368	<3000	1
P_4O_7	-474.3	90.8	75.3	-4.5	-27.0	.742	<3000	1
P_4O_8	-550.2	94.34	88.8	-6.8	-25.8	.111	<3000	1
P_3O_6	-376.6	86.1	60.9	-2.1	-26.0	.263	<3000	1
P_4O_9	-624.7	96.1	88.4	-3.8	-36.5	.463	<3000	1
P_4O_6	-383.8	85.2	58.1	-.71	-31.4	.094	<3000	1
P_{wht}	0.0000	9.8	4.57	3.78	****	****	<317	2
P_{wht}	****	****	6.29	****	****	****	317-553	
P_{wht}	75.64	38.9	****	****	****	****	553-2000	
P_{red}	-4.15	5.45	4.05	3.56	****	****	870	2
P_2	34.4	52.1	8.68	.19	-.995	****	2000	2
P_4	14.1	66.9	19.6	0.16	-3.21	****	553-2000	
PH_3	1.3	50.2	9.11	2.86	-1.71	****	<2000	3

TABLE II

PHYSICAL DATA ON PHOSPHORUS COMPOUNDS

Subs.	m.pt. K	b.pt. K	s.g.	range K	sol.w/H_2O	V.P. mmHg	M.W.
P_4	317.1	553.5	1.83	317-553	0.3 g/100g	0.28@50°C	124
			1.74	>553.5			124
PH_3	140	185.3	1.19			360ppm@25°C	34
P_4O_6	296.8	448.4	2.135			10@53°C	110
P_4O_{10}-H	subl. at 633		2.38		infinite		142
H_3PO_3	346.6	473	----		309g/100ml		82
H_3PO_4@75%	255.5	408	1.574		infinite	5@25°C	98
H_3PO_2	299.5						66

TABLE III

SPECIFICATIONS FOR TECHNICAL-GRADE PHOSPHOROUS ACID[5]

Requirements	Technical-Grade	Laboratory
assay,%	69-71	97
arsenic(as As), max ppm	1	
insoluble matter,%		0.005
sulphates,%		0.002
heavy metals, max ppm	300	0.002%
iron(as Fe), max ppm	250	
chloride(as HCl),%	<0.01	0.003
colour, APHA	<40	

TABLE IV

ECONOMIC ASPECTS

Item	$CDN/kg.	Year
Phosphorus, 99% pure	30.00 (lab)[8]	1987
Phosphorus, yellow	3.00[9]	1987
Phosphorus pentoxide, 99% pure	99.30 (lab)[7]	1987
	2.53(bulk)[9]	1987
Anhydrous flake	2.80 (tech.,bulk)[5]	1980
(phosphorous acid)		
	105.20 (lab)[7]	1987
Phosphoric acid	0.71(com'l)[9]	1987
	4.35/ton (agr'l)[9]	1987

Note: $US = 1.4 $CDN

V REFERENCES

1. Glushko, V.P and L.V. Gurvich, Thermodynamic Properties of Individual Substances, V. 1-2, Nauka, Moscow (1978)

2. JANAF Thermochemical Tables (1965-68)

3. K.K. Kelley, Critical evaluation of high temperature heat capacities of inorganic compounds, US Bureau of Mines, Bulletin No. 476,1949

4. Barin, I., Knacke, O. and O. Kubaschewski, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin (1977)

5. Kirk, R.E. and D.F. Othmer, Ed., Encyclopedia of Chemical Technology, V. 17, Interscience Encyclopedia, N.Y. (1985)

6. J.R. Van Wazer, Phosphorus and its Compounds, V. 1, Interscience Publ. Inc., N.Y. (1958)

7. Fischer Scientific, 87/RS

8. Aesar, 1987

9. Chemical Marketing Reporter, August 24 (1987)

APPENDIX II

A) OXIDE FORMATION REACTIONS

B) RECOMBINATION REACTIONS

TABLE I
POSSIBLE REACTIONS OF OXIDE FORMATION IN P_4-H_2O-H_2 SYSTEM

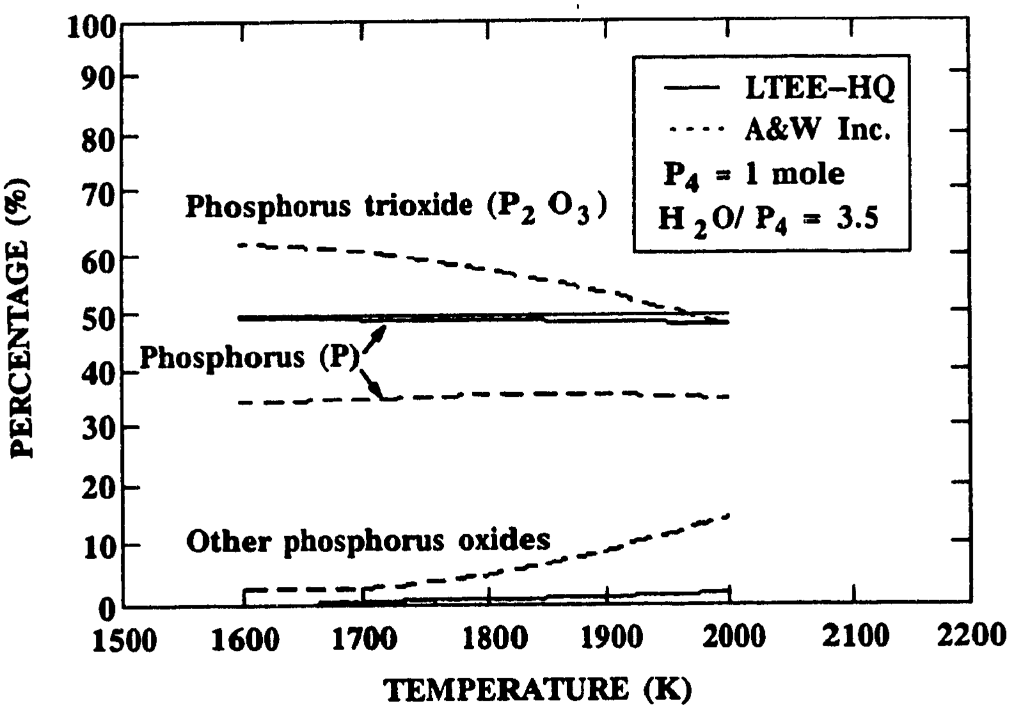
	REACTION	ΔG BECOMES NEGATIVE	
		HQ-LTEE*	A&W
1.	$P_4 + 6\,H_2O \Longleftrightarrow 2\,P_2O_3 + 6\,H_2$	T > 720 K	T > 950 K
2.	$P_2 + 3\,H_2O \Longleftrightarrow P_2O_3 + 3\,H_2$	always negative	T < 2450 K
3.	$P_4 + 10\,H_2O \Longleftrightarrow P_4O_{10} + 10\,H_2$	T < 1436 K	T < 1475 K
4.	$P_4 + 7\,H_2O \Longleftrightarrow P_4O_7 + 7\,H_2$	T < 1945 K	T < 1450 K
5.	$P_4 + 8\,H_2O \Longleftrightarrow P_4O_8 + 8\,H_2$	T < 4566 K	T < 1570 K
6.	$P_4 + 9\,H_2O \Longleftrightarrow P_4O_9 + 9\,H_2$	T < 2054 K	T < 1550 K
7.	$\frac{1}{2}\,P_2 + H_2O \Longleftrightarrow PO + H_2$	always negative	T > 2180 K
8.	$\frac{1}{2}\,P_2 + 2\,H_2O \Longleftrightarrow PO_2 + 2\,H_2$	T > 2138 K	T > 2670 K
9.	$P_2 + 4\,H_2O \Longleftrightarrow P_2O_4 + 4\,H_2$	always negative	T < 930 K
10.	$2\,P_2 + 6\,H_2O \Longleftrightarrow P_4O_6 + 6\,H_2$	T < 1237 K	T < 1160 K
11.	$2\,P_2 + 10\,H_2O \Longleftrightarrow P_4O_{10} + 10\,H_2$	T < 1467 K	T < 1485 K
12.	$P_2 + 5\,H_2O \Longleftrightarrow P_2O_5 + 5\,H_2$	433 > T > 1806 K	always (+)
13.	$2\,P_2 + 7\,H_2O \Longleftrightarrow P_4O_7 + 7\,H_2$	T < 1677 K	T < 1470 K
14.	$2\,P_2 + 8\,H_2O \Longleftrightarrow P_4O_8 + 8\,H_2$	T < 2031 K	T < 1550 K
15.	$P_4 + 6\,H_2O \Longleftrightarrow P_4O_6 + 6\,H_2$	T < 930 K	T < 890 K
16.	$3/2\,P_2 + 6\,H_2O \Longleftrightarrow P_3O_6 + 6\,H_2$	T < 1448 K	T < 1330 K
17.	$2\,P_2 + 9\,H_2O \Longleftrightarrow P_4O_9 + 9\,H_2$	T < 1766 K	T < 1560 K

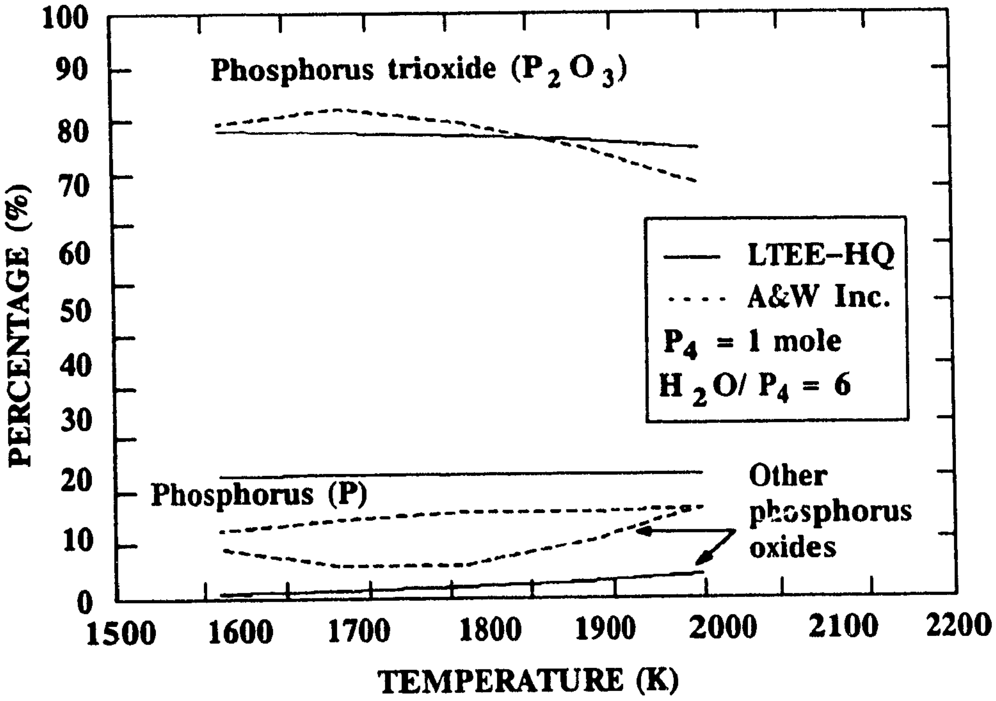
* = range: 200 < T < 6000 K

TABLE II
PRODUCT RECOMBINATION REACTIONS
IN P_4-H_2O-H_2 SYSTEM

REACTION	ΔG BECOMES NEGATIVE	
	HQ-LTEE*	A&W
1. $P_4O_{10} + 4\ H_2 <==> 2\ P_2O_3 + 4\ H_2O$	$T > 1185$ K	$T > 1350$ K
2. $P_4O_{10} + 2\ H_2 <==> 2\ P_2O_4 + 2\ H_2O$	$T > 1431$ K	$T > 1790$ K
3. $P_4O_{10} + 2\ H_2 <==> 4\ PO_2 + 2\ H_2O$	$T > 1699$ K	$T > 1915$ K
4. $3\ P_4O_{10} + 6\ H_2 <==> 4\ P_3O_6 + 6\ H_2O$	$T > 1484$ K	$T > 1720$ K
5. $P_4O_7 + H_2 <==> 2\ P_2O_3 + H_2O$	$T > 1188$ K	$T > 1300$ K
6. $P_2O_3 + 2\ H_2O <==> P_2O_5 + 2\ H_2$	always positive	always (+)
7. $P_2O_3 + H_2O <==> 2\ PO_2 + H_2$	$T > 3835$ K	$T > 2660$ K
8. $3\ P_2O_3 + 3\ H_2O <==> 2\ P_3O_6 + 3\ H_2$	$T < 920$ K	$T < 1050$ K
9. $P_4O_8 + 2\ H_2 <==> 2\ P_2O_3 + 2\ H_2O$	$T > 1389$ K	$T > 1390$ K
10. $P_4O_9 + 3\ H_2 <==> 2\ P_2O_3 + 3\ H_2O$	$T > 1325$ K	$T > 1430$ K

* = range: $200 < T < 6000$ K


LTEE-HQ
A&W Inc.
P_4 = 1 mole
H_2O/P_4 = 3.5
Phosphorus trioxide (P_2O_3)
Phosphorus (P)
Other phosphorus oxides
PERCENTAGE (%)
100
90
80
70
60
50
40
30
20
10
0
1500
1600
1700
1800
1900
2000
2100
2200
TEMPERATURE (K)


100
90
80
70
60
50
40
30
20
10
0
PERCENTAGE (%)
Phosphorus trioxide (P_2O_3)
LTEE-HQ
A&W Inc.
P_4 = 1 mole
H_2O/P_4 = 6
Phosphorus (P)
Other phosphorus oxides
1500
1600
1700
1800
1900
2000
2100
2200
TEMPERATURE (K)

APPENDIX III

HAZARD AND OPERABILITY STUDY
(HAZOP)

Guide word	Deviations
NONE	No forward flow when there should be, i.e. no flow or reverse flow
MORE OF	More of any relevant physical property than there should be, e.g., higher flow, higher temperature, higher pressure, etc.
LESS OF	Less of any relevant physical property than there should be, e.g., lower flow, lower pressure, etc.
PART OF	Composition of system different from what it should be, e.g., change in ratio of components, component missing, etc.
MORE THAN	More components present in the system that there should be, e.g., extra phase present, impurities, etc.
OTHER THAN	What else can happen apart from normal operation, e.g., startup, shutdown, failure of plant services, maintenance, etc.

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
NONE	No steam flow	boiler not on	a. no P_4 and steam reaction so no acid produced b. P_4 entering reactor and then condensing as flammable P_4, thereby causing health and safety hazard c. heating tape around steam pipe possibly overheating, creating fire hazard	1. turn boiler on
		main steam supply valve closed	d. see above	2. open valve
		inlet water valve to boiler closed; boiler dry	e. see above	3. check boiler and city water supply

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
	no P_4 flow	no power to P_4 equipment	f. only steam enters reactor;no acid produced	4. check electrical connections; fuses; shut-off timer; power switches
		no P_4 in egg	g. see above	5. fill
		P_4 line blocked	h. see above; possible over pressure in P_4 in evaporator	6. INSTALL pressure relief valve on feed system and pressure gauge
	no oxygen flow	main oxygen supply valve closed	h1. no P_4 and O_2 reaction, so no P_2O_3 formed h2. see b.	6a. INSTALL pressure switch on O_2 line to ensure reserve

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
		oxygen supply tank empty	h3. see above	6b. replace tank and purge reactor of residual phosphorus
	no cooling water flow	pump failure	i. arc goes out from low flow interlock; see section on NO ARC.	7. repair or replace pump
		no city water	j. see above	8. check main supply valve on water manifold
		power failure	k. see above	9. check electrical connections
	no quench water	no city water	l. no acid formed	10. STOP experiment
			m. hot products exiting reactor and cooling slowly, leading to decomposition products, PH_3, etc.	10a. GAS SEAL POT (GSP) to contain solution of mercuric chloride ($HgCl_2$) to absorb PH_3

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
		quench valve not open	n. see above	11. open valve
	no dc arc	low primary gas line pressure	o. P_4 and steam enter reactor and depending on reactor temperature, form products; if unreacted, then P_4 will condense (flammable) on walls and in sump p. argon or nitrogen floods reactor	12. INSTALL pressure switch to warn of argon or nitrogen low pressure; INSTALL automatic argon purge of reactor
		low secondary gas line pressure	q. see above	13. see above
		low cooling water flow	r. see above	14. see NO COOLING WATER

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
		torch water leak	s. see above t. water leak may cause thermal shock to refractory causing breakage	15. STOP experiment
		no dc potential	u. see NO ARC o. above	16. check power supply
		power failure	v. see NO ARC o. above	17. see NO ARC
	reverse flow of reactor products into P_4 line, including O_2 reactant	high reactor pressure	w. if O_2 exists in reactor products, then danger of EXPLOSION or FIRE x. if N_2, then possible nitride formation	18. INSTALL burst plate to relieve reactor over pressure

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
	reverse flow of reactants or reactor products into O_2 line	high reactor pressure	x1. danger of EXPLOSION or FIRE if P_4 enters O_2 line	18a. INSTALL one way valve on O_2 line; see above 18
MORE OF	more steam than required	boiler flow not adjusted	y. more steam to ultimately quench y1. possibly different reaction products	19. adjustment of steam flow
	more P_4	feed system not adjusted	z. unreacted P_4 exits system, possibly condensing on walls of reactor; FIRE hazard on contact with air or oxygen	20. always purge system with some air to combust all residual P_4, have water hose available
	more power		aa. product temperature rises possibly causing decomposition reactions, TOXIC products	21. monitor reactor temperature

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
	more reactor pressure	reactor outlet blocked	bb. possible reverse flow cc. liquid level in reactor rises to gas outlet line	22. INSTALL burst plate to relieve over pressure and pressure guage 22a. ENSURE that GSP liquid level is adequate to provide pressure relief as well as gas seal
	more reactor temperature	no reaction so no sensible or reaction heat required	dd. possibility of destroying burst plate seals thus possible leakage of gas dd1. unreacted reactants; P_4 condensing and possibility of FIRE	23. check reactant addition 24. monitor temperature distribution in reactor 25. PURGE with air before opening reactor

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
		too much power supplied	ee. see above	26. reduce power
LESS OF	less reactants	feed systems not adjusted	ff. see MORE OF	26. see MORE OF
	low primary or secondary gas pressure	no argon	gg. no arc	27. see NO DC ARC
	low steam pressure	pressure loss in lines or boiler not working	hh. possible reverse flow from reactor to boiler	28. MONITOR steam flowrate
	low power	power supply not configured properly	ii. unreacted species in reactor; possible side reactions and/or condensation in reactor	29. check electrical configuration

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
	low steam line temperature	heating tape or boiler not functionning	jj. condensing in lines possibly producing partial vacuum and drawing reactants into steam line kk. less steam for reaction thus unreacted P_4 in system	30. MONITOR steam temperature
MORE THAN	air in system	pressure in reactor less than atmospheric	ll. possible formation of nitrides mm. possible EXPLOSIVE mixture of H_2 and O_2	31. INSTALL low pressure gauge and MONITOR during test

GUIDE WORDS	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
OTHER THAN	torch spits copper	no secondary gas	oo. destruction of secondary anode and eventual production of water leak	32. INSTALL secondary gas flow low pressure alarm and MONITOR rotameter float

REFERENCES

1. Kletz, Trevor, "Eliminating potential process hazards", Chemical Engineering, 92, 7, pp. 48-68 (1985)

2. Lawley, H.G., "Operability studies and hazard analysis", Chemical Engineering Progress", 70, 4, pp. 45-56 (1974)

APPENDIX IV

GAS/LIQUID ANALYSIS PROCEDURES
(ON-SITE)

LIQUID ANALYSIS

PHOSPHORIC ACID

DATE: ____________

EXPERIMENT #: ______________SAMPLE #: _____________

COLORIMETER SETTINGS

___ Wavelength = 420 nM

___ Reading settig = 0 - 1 A

SAMPLE PREPARATION

___ Add _____ ml of the acid sample to a 100 ml flask.

___ Add 20 ml of the vanado-molybdate-nitric acid solution to the flask.

___ Dilute to 100 ml with distilled water.

___ Let stand for 10 minutes. START _________ END ________

ANALYSIS

Reading ________ Å

Using the calibration curve: mg P_2O_5 = ________ * 2.89 = ________ mg/ml H_3PO_4

LIQUID ANALYSIS

PHOSPHOROUS ACID

DATE: ____________

EXPERIMENT #: ______________ SAMPLE #: _____________

IODINE ANALYSIS

Oxidation reaction: $H_3PO_3 + H_2O + I_2 = H_3PO_4 + 2\,H^+ + 2\,I^-$

Titration reaction: $2\,S_2O_3^{2-} + I_2 = 2\,I^- + S_4O_6^{2-}$

SAMPLE PREPARATION

___ Add 25 ml phosphate buffer solution to a 250 ml iodine flask.

___ Add 25 ml of the acid sample to the flask.

___ Add 25 or 50 ml (depending on the amount of H_3PO_3 expected) of approximately 0.1 N standard iodine solution.

______ml

______N (actual normality of the iodine solution)

___ Leave for 1 hour in the dark.

_____TIME IN

_____TIME OUT

___ Add 5 ml of 6 N acetic acid to the flask.

___ Add thyodene (starch indicator) to the flask.

___ Titrate immediately with 0.1 N standard thiosulfate solution.

_____START ml

_____STOP ml

ANALYSIS

A. Moles/liter iodine solution = actual normality (N) ________/2 = _______ moles/liter solution

B. Iodine added = ml iodine sol'n ________ * A / 1000 = _______ moles

C. ml thiosulfate sol'n used _______ * 10^{-4} = ________ moles

D. Unreacted iodine = C / 2 = ________ moles

E. B - D = _______ moles of phosphorous acid oxidized to phosphoric acid by iodine.

F. e * 82 g/gmole = ________ g H_3PO_3 * 1000 mg/g = _______ mg

G. F / ________ ml sample added = __________ mg/ml H_3PO_3

GAS ANALYSIS

PHOSPHINE (PH_3)

DATE: ____________

EXPERIMENT #: ______________SAMPLE #: _____________

IODINE ANALYSIS

Oxidation reaction: $P(HgCl)_3 + 4\ I_2 + 4\ H_2O = H_3PO_4 + 3\ HgI_2 + 2\ HI + 3\ HCl$

Titration reaction: $2\ S_2O_3^{2-} + I_2 = 2\ I^- + S_4O_6^{2-}$

SAMPLE PREPARATION

___ Add 25 ml phosphate buffer solution to a 250 ml iodine flask.

___ Add the $P(HgCl)_3$ solid to the flask.

___ Add 25 or 50 ml (depending on the amount of $P(HgCl)_3$) of approximately 0.1 N standard iodine solution.

______ml

______N (actual normality of the iodine solution)

___ Leave for 1 hour in the dark.

_____TIME IN

_____TIME OUT

___ Add 5 ml of 6 N acetic acid to the flask.

___ Titrate immediately with 0.1 N standard thiosulfate solution. Add the thyodene indicator when the solution has turned pale yellow in colour.

_____START ml

_____STOP ml

ANALYSIS

A. Moles/liter iodine solution = actual normality (N) ________/2 = _______ moles/liter solution

B. Iodine added = ml iodine sol'n ________ * A / 1000 = _______ moles

C. ml thiosulfate sol'n used _______ * 10^{-4} = ________ moles

D. Unreacted iodine = C / 2 = ________ moles

E. B - D = ________ moles of $P(HgCl)_3$

F. 1 mole $P(HgCl)_3$ = 1 mole phosphine (PH_3)

REAGENT PREPARATION

DATE: ___________

1) VANADO-MOLYBDATE-NITRIC ACID SOLUTION

A - Dissolve 20.0 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}*4\text{-}H_2O]$ in 250 ml of distilled water.

B - Dissolve 1 g ammonium vanadate (NH_4VO_3) in 200 ml of distilled water.

C - Acidify B by adding 40 ml of concentrated nitric acid.

D - Mix C into A in a 1 L flask, add 100 ml of concentrated nitric acid and dilute to 1 L with distilled water.

2) CALIBRATING PHOSPHATE SOLUTION (1 mg of P_2O_5 / ml solution)

___ Dissolve 1.917 grams of dried KH_2PO_4 in 1 L of distilled water.

3) IODINE SOLUTION PREPARATION AND STANDARDIZATION

___ Weigh 40 g of KI into a 100 ml beaker.

___ Add 13 g of iodine

___ Add 10 ml of water

___ Stir for several minutes

___ Carefully decant or filter the bulk of the liquid into a storage bottle containing 1 L of water. Avoid transferring any of the undissolved iodine.

___ Standardize the solution by titrating it with 0.1 N thiosulfate solution using thyodene powder as the starch indicator.

    ___ Titrate the iodine solution until the strong red colour is reduced to pale yellow.

    ___ Add the thyodene indicator and the solution will turn blue.

    ___ Continue titrating until the blue colour is gone.

4) 6 N ACETIC ACID PREPARATION

___ Add 360 grams (343.2 ml) glacial acetic acid to 1 L of distilled water.

5) SODIUM PHOSPHATE BUFFER SOLUTION (pH = 7.3)

A - Dissolve 60 g (0.5 mole) NaH_2PO_4 in 100 ml distilled water.

B - Dissolve 11 g (0.275 mole) NaOH in 100 ml distilled water.

C - Slowly add B to A

D - Dilute to 1 L with distilled water.

APPENDIX V

EXPERIMENTAL DATA

N.B. Results based on actual recovery of product and not based on 100% coversion of phosphorus to acid.

CASE	TIME min	H_2O/P_4 mole ratio	P_4 molepm	QUENCH$_1$ lpm	QUENCH$_2$ lpm	Z_1 cm	Z_2 cm	Q_A slpm	Q_{N2} slpm	R_T cm	Z_T cm	TEMPERATURE K	CONVERSION %	H_3PO_2 molepm	H_3PO_3 molepm	H_3PO_4 molepm	PH_3^* molepm	H_2 molepm	P_4 n/c	ANODE cm	CORROSION of anode
1	21	9.0	0.242	0.4	1.2	49.5	80.0	47	136	0	15.2	1156	100		0.067	0.012			NO	1.9	YES
2	4	8.6	0.150	1.0	2.0	49.5	80.0	74	132	0	23.5	1405	72	0.004	0.028	0.022	3.7E-6		YES	1.9	YES
	12	8.6	0.150	1.0	2.0	49.5	80.0	74	132	0	23.5	1398	72	0.003	0.044	0.028	3.7E-6		YES	1.9	YES
2a	34	8.6	0.150	1.5	2.0	49.5	80.0	74	132	0	23.5	1356	72		0.078	0.066	3.7E-6		YES	1.9	YES
	41	8.6	0.150	1.5	2.0	49.5	80.0	74	132	0	23.5	1417	72		0.084	0.066	3.7E-6		YES	1.9	YES
3	5	13.0	0.166	0.5	2.0	49.5	80.0	48	160	0	23.5	1336	100				1.4E-5	0.00	NO	1.9	YES
	10	13.0	0.166	0.5	2.0	49.5	80.0	48	160	0	30.8	1342	100	0.002	0.037	0.014	1.4E-5	0.04	NO	1.9	YES
	15	13.0	0.166	0.5	2.0	49.5	80.0	48	160	0	30.8	1349	100	0.001	0.109	0.030	1.4E-5	0.09	NO	1.9	YES
	20	13.0	0.166	0.5	2.0	49.5	80.0	48	160	0	30.8	1299	100	0.002	0.296	0.051	1.4E-5	0.19	NO	1.9	YES
	25	13.0	0.166	0.5	2.0	49.5	80.0	48	160	0	23.5	1295	100	0.002	0.368	0.123	1.4E-5	0.22	NO	1.9	YES
	30	13.0	0.166	0.5	2.0	49.5	80.0	48	160	0	23.5	1164	100	0.002	0.284	0.151	1.4E-5	0.21	NO	1.9	YES
	35	13.0	0.166	0.5	2.0	49.5	80.0	48	160	0	23.5	1075	100	0.002	0.232	0.146	1.4E-5	0.20	NO	1.9	YES
	40	13.0	0.166	0.5	2.0	49.5	80.0	48	160	0	23.5	1042	100	0.002	0.243	0.142	1.4E-5	0.18	NO	1.9	YES
3a	10	40.0	0.054	0.5	2.0	49.5	80.0	48	160	0	23.5	820	100	0.001	0.042	0.057	1.4E-5	0.07	NO	1.9	YES
4	10	39.0	0.059	0.5	2.0	49.5	80.0	48	122	0	23.5	1485	100		0.022	0.013	2.2E-5	0.38	NO	1.9	YES
	15	39.0	0.059	0.5	2.0	49.5	80.0	48	122	0	23.5	1495	100		0.046	0.022	2.2E-5	0.42	NO	1.9	YES
	20	39.0	0.059	0.5	2.0	49.5	80.0	48	122	0	23.5	1481	100		0.059	0.024	2.2E-5	0.46	NO	1.9	YES
	25	39.0	0.059	0.5	2.0	49.5	80.0	48	122	0	23.5	1481	100		0.074	0.028	2.2E-5	0.45	NO	1.9	YES
	30	39.0	0.059	0.5	2.0	49.5	80.0	48	122	0	23.5	1475	100	0.005	0.084	0.032	2.2E-5	0.48	NO	1.9	YES
4a	5	39.0	0.059	1.5	2.0	49.5	80.0	48	122	0	23.5	1601	100		0.074	0.069	2.8E-5	0.55	NO	1.9	YES
	10	39.0	0.059	1.5	2.0	49.5	80.0	48	122	0	23.5	1489	100	0.002	0.068	0.054	2.8E-5	0.57	NO	1.9	YES
4b	5	17.8	0.130	0.5	2.0	49.5	80.0	48	122	0	23.5	1569	100	0.005	0.216	0.046	4.5E-5	1.19	NO	1.9	YES
	10	17.8	0.130	0.5	2.0	49.5	80.0	48	122	0	30.8	1331	100	0.005	0.209	0.085	4.5E-5	1.06	NO	1.9	YES
	15	17.8	0.130	0.5	2.0	49.5	80.0	48	122	0	30.8	1292	100	0.003	0.230	0.099	4.5E-5	1.17	NO	1.9	YES
	20	17.8	0.130	0.5	2.0	49.5	80.0	48	122	0	30.8	1273	100		0.200	0.108	4.5E-5	1.17	NO	1.9	YES
5	10	36.2	0.058	0.5	3.0	39.4	49.5	48	100	0	23.5	1173	100		0.018	0.022	0.000	0.27	NO	1.9	YES
	15	36.2	0.058	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.046	0.035	0.000	0.34	NO	1.9	YES
	20	36.2	0.058	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.054	0.039	0.000	0.38	NO	1.9	YES
	25	36.2	0.058	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.064	0.042	0.000	0.38	NO	1.9	YES
	30	36.2	0.058	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.053	0.036	0.000	0.35	NO	1.9	YES
5a	1	19.2	0.110	0.5	3.0	39.4	49.5	48	100	0	23.5		100	0.002	0.042	0.032	1.1E-5	0.45	NO	1.9	YES
	5	19.2	0.110	0.5	3.0	39.4	49.5	48	100	0	23.5		100	0.002	0.100	0.057	1.1E-5	0.45	NO	1.9	YES
	10	19.2	0.110	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.112	0.063	1.1E-5	0.62	NO	1.9	YES
	11	19.2	0.110	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.114	0.074	1.1E-5	0.63	NO	1.9	YES
5b	3	12.1	0.174	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.135	0.039	7.3E-6	0.39	NO	1.9	YES
	5	12.1	0.174	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.206	0.049	7.3E-6	0.92	NO	1.9	YES
	10	12.1	0.174	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.307	0.061	7.3E-6	1.06	NO	1.9	YES
	15	12.1	0.174	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.308	0.066	7.3E-6	1.03	NO	1.9	YES
5c	2	8.3	0.254	0.5	3.0	39.4	49.5	48	100	0	23.5		100		0.383	0.111	1.6E-5	1.01	NO	1.9	YES
	5	8.3	0.254	0.5	3.0	39.4	49.5	48	100	0	23.5		100	0.002	0.526	0.129	1.6E-5	1.54	NO	1.9	YES
	10	8.3	0.254	0.5	3.0	39.4	49.5	48	100	0	23.5		100	0.002	0.536	0.125	1.6E-5	1.59	NO	1.9	YES
	12	8.3	0.254	0.5	3.0	39.4	49.5	48	100	0	23.5		100	0.002	0.558	0.167	1.6E-5	1.58	NO	1.9	YES
6	2	10.3	0.174	3.0	0.5	80.0	87.6	48	115	0	23.5	1384	100	0.000	0.143	0.011	1.9E-5	0.11	NO	1.9	NO
	4	10.3	0.174	3.0	0.5	80.0	87.6	48	115	0	23.5	1350	100	0.000	0.222	0.017	1.9E-5	1.09	NO	1.9	NO
	6	10.3	0.174	3.0	0.5	80.0	87.6	48	115	0	23.5	1345	100	0.001	0.219	0.020	1.9E-5	1.09	NO	1.9	NO
	8	10.3	0.174	3.0	0.5	80.0	87.6	48	115	0	23.5	1341	100	0.000	0.272	0.026	1.9E-5	1.08	NO	1.9	NO
	10	0.0	0.0	3.0	0.5	80.0	87.6	48	115	0	23.5	1357	100	0.001	0.263	0.024	1.9E-5	1.06	NO	1.9	NO
	13	0.0	0.0	3.0	0.5	80.0	87.6	48	115	0	23.5	1316	100		0.092	0.016	1.9E-5	0.37	NO	1.9	NO
	15	0.0	0.0	3.0	0.5	80.0	87.6	48	115	0	23.5	1304	100		0.036	0.011	1.9E-5	0.14	NO	1.9	NO
	17	0.0	0.0	3.0	0.5	80.0	87.6	48	115	0	23.5	1285	100		0.023	0.009	1.9E-5	0.05	NO	1.9	NO
	19	0.0	0.0	3.0	0.5	80.0	87.6	48	115	0	23.5	1300	100		0.016	0.007	1.9E-5	0.03	NO	1.9	NO
	21	0.0	0.0	3.0	0.5	80.0	87.6	48	115	0	23.5	1275	100		0.012	0.006	1.9E-5	0.03	NO	1.9	NO

* Moles of phosphine measured averaged over the total time of the experiment to give moles per minute

CASE	TIME min	H_2O/P_4 mole ratio	P_4 molepm	QUENCH$_1$ lpm	QUENCH$_2$ lpm	Z_1 cm	Z_2 cm	Q_A slpm	Q_{N2} slpm	R_T cm	Z_T cm	TEMPERATURE K	CONVERSION %	H_3PO_2 molepm	H_3PO_3 molepm	H_3PO_4 molepm	PH_3* molepm	H_2 molepm	P_4 n/c	ANODE cm	CORROSION of anode
6a	2	13.6	0.174	3.0	0.5	80.0	87.6	48	115	-	38.7	1345	100	0.001	0.173	0.016	1.9E-5	0.81	NO	1.9	NO
	4	13.6	0.174	3.0	0.5	80.0	87.6	48	115		38.7	1355	100	0.001	0.231	0.025	1.9E-5	0.97	NO	1.9	NO
	6	13.6	0.174	3.0	0.5	80.0	87.6	48	115		38.7	1308	100	0.001	0.248	0.029	1.9E-5	0.97	NO	1.9	NO
	8	13.6	0.174	3.0	0.5	80.0	87.6	48	115		38.7	1333	100	0.000	0.268	0.033	1.9E-5	1.00	NO	1.9	NO
	10	0.0	0.0	3.0	0.5	80.0	87.6	48	115		38.7	1396	100	0.001	0.263	0.033	1.9E-5	1.00	NO	1.9	NO
	12	0.0	0.0	3.0	0.5	80.0	87.6	48	115		38.7	1394	100	0.001	0.134	0.023	1.9E-5	0.55	NO	1.9	NO
	14	0.0	0.0	3.0	0.5	80.0	87.6	48	115		38.7	1457	100	0.001	0.042	0.015	1.9E-5	0.05	NO	1.9	NO
	16	0.0	0.0	3.0	0.5	80.0	87.6	48	115		38.7	1379	100		0.024	0.010	1.9E-5		NO	1.9	NO
	18	0.0	0.0	3.0	0.5	80.0	87.6	48	115		38.7	1318	100		0.016	0.007	1.9E-5		NO	1.9	NO
	20	0.0	0.0	3.0	0.5	80.0	87.6	48	115		38.7	1304	100		0.012	0.005	9E-5		NO	1.9	NO
	22	0.0	0.0	3.0	0.5	80.0	87.6	48	115		38.7	1306	100	0.001	0.009	0.004	1.9E-5		NO	1.9	NO
6b	2	17.2	0.138	3.0	0.5	80.0	87.6	48	115	0	23.5	1277	100	0.001	0.127	0.013	1.9E-5	0.74	NO	1.9	NO
	5	17.2	0.138	3.0	0.5	80.0	87.6	48	115	0	23.5	1287	100	0.000	0.214	0.024	1.9E-5	0.99	NO	1.9	NO
	10	17.2	0.138	3.0	0.5	80.0	87.6	48	115		15.2	1311	100	0.000	0.263	0.031	1.9E-5	0.94	NO	1.9	NO
	15	17.2	0.138	3.0	0.5	80.0	87.6	48	115		15.2	1311	100	0.000	0.257	0.083	1.9E-5	0.96	NO	1.9	NO
	20	17.2	0.138	3.0	0.5	80.0	87.6	48	115		15.2	1339	100	0.000	0.253	0.031	1.9E-5	0.94	NO	1.9	NO
	25	17.2	0.138	3.0	0.5	80.0	87.6	48	115		15.2	1361	100	0.000	0.257	0.033	1.9E-5	0.92	NO	1.9	NO
	30	17.2	0.138	3.0	0.5	80.0	87.6	48	115		15.2	1352	100	0.001	0.255	0.033	1.9E-5	0.89	NO	1.9	NO
	35	17.2	0.138	3.0	0.5	80.0	87.6	48	115		15.2	1351	100	0.000	0.262	0.036	1.9E-5	0.91	NO	1.9	NO
	40	17.2	0.138	3.0	3.0	80.0	87.6	48	115		15.2	1361	100		0.325	0.036	1.9E-5	0.70	NO	1.9	NO
	45	17.2	0.138	3.0	3.0	80.0	87.6	48	115	0	23.5	1344	100		0.252	0.027	1.9E-5	0.82	NO	1.9	NO
	50	17.2	0.138	3.0	3.0	80.0	87.6	48	115	0	23.5	1314	100		0.260	0.027	1.9E-5	0.79	NO	1.9	NO
	55	0.0	0.0	3.0	3.0	80.0	87.6	48	115	0	23.5	1355	100		0.032	0.011	1.9E-5	0.09	NO	1.9	NO
	60	0.0	0.0	3.0	3.0	80.0	87.6	48	115	0	23.5	1078	100		0.015	0.006	1.9E-5	0.02	NO	1.9	NO
7	5	6.2	0.330	2.5	2.5	80.0	87.6	0	92		38.7	1199	100	0.003	0.722	0.058		1.84	NO	1.3	NO
	10	6.2	0.330	2.5	2.5	80.0	87.6	0	92		38.7	1191	100	0.003	0.794	0.067		1.95	NO	1.3	NO
	15	6.2	0.330	2.5	2.5	80.0	87.6	0	92		38.7	1203	100	0.003	0.800	0.067		1.93	NO	1.3	NO
	20	6.2	0.330	2.5	2.5	80.0	87.6	0	92		38.7	1220	100	0.003	0.794	0.063		1.90	NO	1.3	NO
	25	6.2	0.330	2.5	2.5	80.0	87.6	0	92		38.7	1199	100	0.003	0.836	0.068		1.87	NO	1.3	NO
	30	6.2	0.330	2.5	2.5	80.0	87.6	0	92		38.7	1220	100	0.003	0.825	0.067			NO	1.3	NO
	35	6.2	0.330	2.5	2.5	80.0	87.6	0	92		38.7	1213	100	0.003	0.821	0.068			NO	1.3	NO
	40	6.2	0.330	2.5	2.5	80.0	87.6	0	92		38.7	1206	100	0.003	0.813	0.066			NO	1.3	NO
7a	5	6.6	0.315	2.5	2.5	80.0	87.6	0	92		38.7	1189	100	0.002	0.734	0.065			NO	1.3	NO
	10	6.6	0.315	2.5	2.5	80.0	87.6	0	92		38.7	1104	100	0.002	0.787	0.074			NO	1.3	NO
	15	6.6	0.315	2.5	2.5	80.0	87.6	0	92		38.7	1123	100	0.002	0.796	0.077			NO	1.3	NO
	20	6.6	0.315	2.5	2.5	80.0	87.6	0	92		38.7	1118	100	0.002	0.819	0.076			NO	1.3	NO
	25	6.6	0.315	2.5	2.5	80.0	87.6	0	92		38.7	1109	100	0.002	0.828	0.073			NO	1.3	NO
	30	6.6	0.315	2.5	2.5	80.0	87.6	0	92	1	15.2	1287	100	0.002	0.837	0.072		1.87	NO	1.3	NO
	35	6.6	0.315	2.5	2.5	80.0	87.6	0	92	1	15.2	1287	100	0.002	0.839	0.074		1.84	NO	1.3	NO
	40	6.6	0.315	2.5	2.5	80.0	87.6	0	92	1	15.2	1288	100	0.002	0.843	0.072		1.87	NO	1.3	NO
	45	6.6	0.315	2.5	2.5	80.0	87.6	0	92	1	15.2	1259	100	0.002	0.853	0.073		1.86	NO	1.3	NO
8	5	4.5	0.345	2.5	2.5	80.0	87.6	0	90	0	46.4	1140	100	0.001	0.678	0.057	6.8E-6	1.36	NO	1.3	NO
	10	4.5	0.345	2.5	2.5	80.0	87.6	0	90	0	46.4	1154	100	0.002	0.737	0.048	6.8E-6	1.81	NO	1.3	NO
	15	4.5	0.345	2.5	2.5	80.0	87.6	0	90	0	46.4	1168	100	0.002	0.723	0.056	6.8E-6	1.50	NO	1.3	NO
	20	4.5	0.345	2.5	2.5	80.0	87.6	0	90	0	46.4	1153	100	0.002	0.732	0.061	6.8E-6	1.72	NO	1.3	NO
	25	4.5	0.345	2.5	2.5	80.0	87.6	0	90	0	46.4	1135	100	0.002	0.725	0.064	6.8E-6	1.79	NO	1.3	NO
	30	4.5	0.345	2.5	2.5	80.0	87.6	0	90	0	46.4	1162	100	0.001	0.804	0.069	6.9E-6	1.83	NO	1.3	NO
	35	7.0	0.220	2.5	2.5	80.0	87.6	0	90	0	46.4	1146	100	0.001	0.679	0.067	6.8E-6	1.52	NO	1.3	NO
	40	7.0	0.220	2.5	2.5	80.0	87.6	0	90	0	46.4	1103	100	0.001	0.635	0.062	6.8E-6	1.27	NO	1.3	NO
9	6	7.5	0.275	2.5	2.5	80.0	87.6	0	92	0	15.2	1361	100		0.500	0.035	8.8E-6		NO	1.3	NO
	10	7.5	0.275	2.5	2.5	80.0	87.6	0	92	0	15.2	1345	100	0.002	0.710	0.039	8.8E-6	0.95	NO	1.3	NO
	15	7.5	0.275	2.5	2.5	80.0	87.6	0	92	0	15.2	1340	100	0.002	0.67	0.038	8.8E-6	1.69	NO	1.3	NO
	20	7.5	0.275	2.5	2.5	80.0	87.6	0	92	0	15.2	1338	100	0.003	0.75	0.046	8.8E-6	1.86	NO	1.3	NO
	25	7.5	0.275	2.5	2.5	80.0	87.6	0	92	0	15.2	1352	100	0.003	0.73	0.044	8.8E-6	1.85	NO	1.3	NO
10	5	5.6	0.375	2.5	2.5	80.0	87.6	57	0	0	15.2	653	49	0.004	0.035	0.009	8.4E-6	0.15	YES	1.3	NO
	10	5.6	0.375	2.5	2.5	80.0	87.6	57	0	0	15.2	613	49	0.001	0.039	0.006	8.4E-6	0.17	YES	1.3	NO
	15	5.6	0.375	2.5	2.5	80.0	87.6	57	0	0	15.2	609	49	0.001	0.034	0.005	8.4E-6	0.16	YES	1.3	NO

* Total moles of phosphine measured averaged over the total time of the experiment to give moles per minute

CASE	TIME min	H_2O/P_4 mole ratio	P_4 molepm	QUENCH$_1$ lpm	QUENCH$_2$ lpm	Z_1 cm	Z_2 cm	Q_A slpm	Q_{N2} slpm	R_T cm	Z_T cm	TEMPERATURE K	CONVERSION %	H_3PO_2 molepm	H_3PO_3 molepm	H_3PO_4 molepm	PH_3^* molepm	H_2 molepm	P_4 n/c	ANODE cm	CORROSION of anode
10a	3	7.7	0.275	2.5	2.5	80.0	87.6	39	58	0	15.2	928	74	0.003	0.22	0.064	8.4E-6		YES	1.3	NO
	5	7.7	0.275	2.5	2.5	80.0	87.6	39	58	0	15.2	919	74	0.003	0.26	0.021	8.4E-6		YES	1.3	NO
	10	7.7	0.275	2.5	2.5	80.0	87.6	39	58	0	15.2	927	74	0.003	0.25	0.021	8.4E-6		YES	1.3	NO
	15	7.7	0.275	2.5	2.5	80.0	87.6	39	58	0	15.2	914	74	0.003	0.28	0.024	8.4E-6		YES	1.3	NO
	20	7.7	0.275	2.5	2.5	80.0	87.6	39	58	0	15.2	911	74	0.003	0.28	0.025	8.4E-6	0.70	YES	1.3	NO
	25	7.7	0.275	2.5	2.5	80.0	87.6	39	58	0	15.2	909	74	0.003	0.25	0.025	8.4E-6	0.87	YES	1.3	NO
10b	5	8.5	0.250	2.5	2.5	80.0	87.6	0	91	0	15.2	1182	100	0.003	0.42	0.041	8.4E-6	0.61	NO	1.3	NO
	10	8.5	0.250	2.5	2.5	80.0	87.6	0	91	0	15.2	1198	100	0.003	0.48	0.049	8.4E-6	1.38	NO	1.3	NO
	15	8.5	0.250	2.5	2.5	80.0	87.6	0	91	0	15.2	1182	100	0.003	0.49	0.049	8.4E-6	1.62	NO	1.3	NO
	20	8.5	0.250	2.5	2.5	80.0	87.6	0	91	0	15.2	1179	100	0.003	0.52	0.058	8.4E-6	1.66	NO	1.3	NO
	25	8.5	0.250	2.5	2.5	80.0	87.6	0	91	0	15.2	1191	100	0.003	0.51	0.057	8.4E-6	1.67	NO	1.3	NO
	30	8.5	0.250	2.5	2.5	80.0	87.6	0	91	0	15.2	1185	100	0.003	0.50	0.057	8.4E-6	1.67	NO	1.3	NO
	35	8.5	0.250	2.5	2.5	80.0	87.6	0	91	0	15.2	1167	100	0.003	0.53	0.061	8.4E-6	1.66	NO	1.3	NO
11	5	10.8	0.305	2.5	2.5	80.0	87.6	47	100	0	15.2	1450	100	0.008	0.48	0.051	1.4E-4	1.60	NO	1.9	YES
	10	10.8	0.305	2.5	2.5	80.0	87.6	47	100	0	15.2	1467	100	0.009	0.58	0.050	1.4E-4	1.74	NO	1.9	YES
	15	10.8	0.305	2.5	2.5	80.0	87.6	47	100	0	15.2	1450	100	0.008	0.61	0.054	1.4E-4	1.74	NO	1.9	YES
11a	3	6.5	0.775	2.5	2.5	80.0	87.6	0	92	0	15.2	1312	100	0.010	1.23	0.115	1.4E-4	4.65	NO	1.3	NO
	5	10.4	0.487	2.5	2.5	80.0	87.6	0	92	0	15.2	1314	100	0.010	1.36	0.133	1.4E-4	3.79	NO	1.3	NO
	8	10.4	0.487	2.5	2.5	80.0	87.6	0	92	0	15.2	1334	100	0.011	1.23	0.132	1.4E-4	3.48	NO	1.3	NO
	10	10.4	0.487	2.5	2.5	80.0	87.6	0	92	0	15.2	1281	100	0.009	1.21	0.150	1.4E-4	3.43	NO	1.3	NO
	13	10.4	0.487	2.5	2.5	80.0	87.6	0	92	0	15.2	1385	100	0.008	1.09	0.108	1.4E-4	3.27	NO	1.3	NO
12	3	9.7	0.216	2.5	2.5	55.9	87.6	0	85	0	15.2	1115	93	0.002	0.326	0.033	1.8E-5	1.29	YES	1.3	NO
	6	9.7	0.216	2.5	2.5	55.9	87.6	0	85	0	15.2	1036	93	0.002	0.415	0.047	1.8E-5	1.67	YES	1.3	NO
	9	9.7	0.216	2.5	2.5	55.9	87.6	0	85	0	15.2	1054	93	0.002	0.446	0.052	1.8E-5	1.72	YES	1.3	NO
	12	8.0	0.264	2.5	2.5	55.9	87.6	0	85	0	15.2	1055	93	0.002	0.45	0.053	1.8E-5	1.77	YES	1.3	NO
	16	8.0	0.264	2.5	2.5	68.6	87.6	0	85	0	15.2	1149	100	0.001	0.45	0.049	1.8E-5	1.72	NO	1.3	NO
	18	8.0	0.264	2.5	2.5	68.6	87.6	0	85	0	15.2	1116	100	0.001	0.452	0.047	1.8E-5	1.75	NO	1.3	NO
	21	8.1	0.258	2.5	2.5	68.6	87.6	0	85	0	15.2	1120	100	0.001	0.390	0.041	1.8E-5	1.78	NO	1.3	NO
	24	8.3	0.252	2.5	2.5	68.6	87.6	0	85	0	15.2	1121	100	0.001	0.466	0.048	1.8E-5	1.76	NO	1.3	NO
	27	9.1	0.258	2.5	2.5	68.6	87.6	0	112	0	15.2	1127	100	0.001	0.461	0.055	1.8E-5	1.73	NO	1.3	NO
	30	7.8	0.269	2.5	2.5	68.6	87.6	0	112	0	15.2	1225	100	0.001	0.508	0.059	1.8E-5	1.90	NO	1.3	NO
	33	7.4	0.283	2.5	2.5	68.6	87.6	0	112	0	15.2	1246	100	0.001	0.521	0.060	1.8E-5	1.88	NO	1.3	NO
	36	7.4	0.283	2.5	2.5	68.6	87.6	0	112	0	15.2	1249	100	0.001	0.514	0.062	1.8E-5	1.86	NO	1.3	NO
	39	7.6	0.276	2.5	2.5	68.6	87.6	0	112	0	15.2	1220	100	0.001	0.454	0.056	1.8E-5	1.87	NO	1.3	NO
	42	7.6	0.276	2.5	2.5	68.6	87.6	0	139	0	15.2	1294	100	0.001	0.523	0.066	1.8E-5	1.96	NO	1.3	NO
	45	7.7	0.274	2.5	2.5	68.6	87.6	0	139	0	15.2	1276	100	0.001	0.514	0.067	1.8E-5	1.92	NO	1.3	NO
	48	7.7	0.274	2.5	2.5	68.6	87.6	0	139	0	15.2	1333	100	0.001	0.539	0.072	1.8E-5	1.95	NO	1.3	NO
	51	7.6	0.276	2.5	2.5	68.6	87.6	0	139	0	15.2	1342	100	0.001	0.535	0.074	1.8E-5	1.90	NO	1.3	NO
	54	7.6	0.276	2.5	2.5	68.6	87.6	0	85	0	15.2	1349	100		0.445	0.064	1.8E-5	1.92	NO	1.3	NO
	57	7.6	0.276	2.5	2.5	68.6	87.6	0	85	0	15.2	1089	100	0.001	0.532	0.066	1.8E-5	1.96	NO	1.3	NO
	60	7.6	0.276	2.5	2.5	81.3	87.6	0	85	0	15.2	1148	100	0.001	0.512	0.058	1.8E-5	1.83	NO	1.3	NO
	63	7.7	0.272	2.5	2.5	81.3	87.6	0	85	0	15.2	1157	100	0.001	0.492	0.052	1.8E-5	1.76	NO	1.3	NO
	66	7.7	0.272	2.5	2.5	81.3	87.6	0	85	0	15.2	1160	100	0.001	0.507	0.052	1.8E-5	1.80	NO	1.3	NO
	69	7.0	0.302	2.5	2.5	81.3	87.6	0	85	0	15.2	1142	100	0.001	0.510	0.054	1.8E-5	1.84	NO	1.3	NO

* [illegible] of phosphine measured averaged over the total time of the experiment to give moles per minute

NOMENCLATURE

R = Radial distance, cm

Z = Axial distance, cm

V = Voltage, volts

I = Current, amps

T = Temperature, K

K = Equilibrium constant

ΔG = Gibbs free energy

GC = Gas chromatograph

IC = Ion chromatograph

k = Thermal conductivity, W/m K

θ = Residence time, seconds