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**PRODUCTION OF PURE ZIRCONIUM
BY USE OF A RADIO FREQUENCY PLASMA**

by

Frederick Michael Gragg

**A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMICAL ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA**

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Frederick Michael Gragg entitled PRODUCTION OF PURE ZIRCONIUM BY USE OF A RADIO FREQUENCY FLASMA be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

Neil D. Cox
Dissertation Director

November 26, 1973
Date

After inspection of the final copy of the dissertation, the following members of the Final Examination Committee concur in its approval and recommend its acceptance:*

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SIGNED: F. Michael Gray

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ABSTRACT

The production of zirconium in an argon radio frequency induction plasma was investigated. The object of this research was to study the feasibility of producing zirconium in an induction plasma. This research was undertaken due to the widespread use of zirconium in the nuclear industry and the potential of expanding its usage in other industries if a less expensive method of production could be found.

The reduction of zirconium tetrachloride to zirconium was accomplished in a reactor powered by a 25 kw 4 MHz generator. The plasma was contained in a water-cooled Vycor tube. The argon used as a carrier gas was dried by a mole sieve bed before entering either the plasma reactor or the feed system. Reagent grade zirconium tetrachloride was fed by means of a sublimation feed system. This system not only further purified the zirconium tetrachloride but also fed the zirconium tetrachloride as a gas, which has transfer advantages.

The product was collected on a water-cooled cold finger probe. This system enabled the zirconium to be quenched in the hottest part of the plasma. After the zirconium was collected, care was taken not to expose the zirconium to the atmosphere at any time during analysis since finely divided zirconium is pyrophoric.

The zirconium product was positively identified by x-ray diffraction. A wet analysis was run to determine the percent conversion. The percent conversion was based on the amount collected since all the zirconium tetrachloride fed was not collected.

The feed rates were varied from 0.4404 gm/hr to 4.658 gm/hr. The probe height was varied in order to collect product at different points in the plasma ball. The generator power was kept at 5.8×10^3 Kcal/hr.

The percent conversions varied from 3.67% to 89.61%. The percent conversion increased with decreased feed rate. The percent conversion also increased as the product was collected in the hotter portion of the plasma ball.

From an energy balance over the equipment, it was determined that 36% of the power input to the generator was lost to the generator cooling water. Another 40% of this input power was lost to the reactor cooling jacket. Four percent of the total power input was lost to radiation, leaving 20% of the power input left for the plasma itself.

It was concluded that the production of zirconium from zirconium tetrachloride is technically feasible. An economic analysis, however, showed that economical production of zirconium by use of a plasma is still in doubt and future research is necessary.

CHAPTER 1

INTRODUCTION

Zirconium is a very important metal in the nuclear industry because of its use as permanent internal structure, as cladding of the fuel rods, and as additional bulk for the fuel in nuclear power plants. It has no competitor in this usage because of its low cross-section to thermal neutrons, its high melting point, its good tensile strength, its marked resistance to corrosion, and its limited formation by nuclear radiation of high activity products (13, 14, 23).

Zirconium is also widely used in the chemical industry where strength is needed at high temperatures or in highly corrosive atmospheres. Zirconium metal is relatively inert due to an oxide layer which forms on its exterior surface. This oxide layer makes zirconium superior to practically all other metals in corrosive resistance over the complete spectrum of corrosive environments (26). Because of its resistance to both alkaline and acid solutions, zirconium is also widely used to make spinnerets (14). It is replacing tantalum in surgery as a human body replacement (bone screws, suture wires, and cranial plates) because it is not corroded by body fluids and human tissue will grow to it without decay

or deterioration (22). Other uses of zirconium are as getters in vacuum tubes, as an alloy in steels, as flash bulb elements and as explosive primers (23).

Although zirconium has been found to be a very useful metal, its use is restricted by its relatively high price (13, 22, 26). It costs three times that of titanium (5). According to H.T. Reno (22), the chief problem of the zirconium industry is to reduce the production costs of zirconium. The mining, transportation and selling costs compare favorably with other metals. High temperatures are necessary to decompose the zirconium ores so no great reduction in cost in this step of the process is expected. The costs, however, of refining the zirconium appear to be excessive. Reduction of these costs, therefore, shows the greatest promise of lowering the total cost of zirconium.

Zirconium is presently being produced by the Kroll Process. The steps in this process are as follows. For nuclear applications, it is first necessary to separate the hafnium from the zirconium because of hafnium's high cross-section to thermal neutrons. For industrial applications, this separation is not necessary. This separation yields zirconium dioxide which is chlorinated to zirconium tetrachloride. The zirconium tetrachloride is then reduced by molten magnesium forming zirconium and magnesium dichloride. The magnesium and magnesium dichloride are removed from the

zirconium by vacuum distillation. The zirconium sponge is then melted into ingots.

The Kroll Process is expensive for several reasons. One of these is the large amounts of the relatively expensive magnesium used in the reduction of zirconium tetrachloride to zirconium [100 lb. magnesium to 150 lb. zirconium (14)]. The Kroll Process is also expensive because it consists of several batch steps rather than being a continuous process. The zirconium tetrachloride purification, the magnesium reduction of the zirconium tetrachloride, and the vacuum distillation are all batch steps (24). H.T. Reno (22) thus concludes that there is a need for the development of an inexpensive continuous process for the production of zirconium.

Other authors have also seen this need for a new process for the production of zirconium. As a result, there has been substantial work done in the field. Blue and Baker (2), for instance, studied the production of zirconium by electro-refining. Mauser (15) presented modifications of the Kroll Process to make it semi-continuous. K.A. Walsh (33) studied the production of zirconium in a sealed bomb, using calcium as a reducing agent. Venkataramen, Mallikarjuna, and Sandaram (29) found some success in electrolytically preparing zirconium from zirconium tetrachloride in a vacuum furnace. Grosse, Lehr, and Albert (10) were successful in

reducing zirconium oxide to zirconium with carbon, silicon, and aluminum as reactants in a high vacuum electron beam furnace. Various recent studies have also been made concerning the production of zirconium by the reduction of zirconium tetrachloride with magnesium (12, 30, 31). There has been no report in the open literature to date, however, of a successful continuous process for the production of zirconium.

Another suggestion for the production of zirconium comes from two Russian researchers. The authors Vurzel and Polak (32) have proposed that the reduction of zirconium halide by the use of a plasma might be commercially feasible.

It was proposed by this author that if a continuous process for the production of zirconium could be found using little or no reducing agent, then this might reduce the production costs of zirconium. Accordingly, the objective of this research was to determine the feasibility of the production of zirconium from zirconium tetrachloride by the use of an induction plasma. This research was conducted using a batch process, which can be easily converted to a continuous process.

CHAPTER 2

LITERATURE SURVEY OF PREVIOUS WORK WITH PLASMAS

There has been substantial work done using both arc and induction plasmas as chemical reactors. This literature survey concerns itself with selected articles dealing with solid and solid-gas reactions in a low temperature gaseous plasma (about 10,000^oK), because these conditions are similar to those under which this research was conducted.

Rains (21) successfully reduced aluminum oxide to elemental aluminum in an argon induction plasma. His conversions were as large as 46 percent. The power levels ranged from 5.03 to 6.69 kw using a 23.5 KVA 3 MHz generator. The oxide flow rates were from 0.03 to 0.6 gm/min. The argon flow rate was 52 gm/min. The product was collected by water-cooled quench probes. Rains found that additional quenching with carbon monoxide or methane doubled his yield from 23 to 46 percent, whereas quenching with hydrogen has little effect. Rains also found that the percent conversion increased with increased power levels and increased quench rate. He did not present the economics of the process but rather offered his work as a demonstration of the feasibility of reducing stable metal oxides in an induction plasma.

The reduction of molybdenum sulfide to molybdenum was accomplished by Huska and Clump (11) in an argon induction plasma. They obtained conversions as large as 70 percent, but most of the conversions ranged from 30 to 50 percent. They used a 10 kw, 4 MHz generator to produce power levels of from 2 to 5 kw. The argon flow rate was 37.3 SCFH, and the feed rate ranged from 0.67 gm/hr. to 2.5 gm/hr. They found that the conversion increased with increased power levels and decreased feed rate. They did not have a rapid quench, such as water-cooled probes, but collected the product in a water-cooled chamber. The economics of the process were not mentioned in their article; but, according to this author's copy of a personal communication from C.M. Clump to R.J. Ayen (4), the potential economics of this method of producing molybdenum were unfavorable.

Miller and Ayen (16) in their research used an argon induction plasma to reduce titanium tetrachloride to titanium trichloride. Their conversions were from 60 to 80 percent. The power levels were from 3 to 7 kw with a 60 percent coupling efficiency. The argon gas flow rate was from 9 to 23 liters per minute.

From information gained by this author when working with the same apparatus as Miller and Ayen, it is possible that the lack of further reduction of titanium tetrachloride was due to the low power availability and, therefore, a lower

energy plasma. This possibility is supported by the fact that Miller and Ayen had trouble with the torch being extinguished at high feed rates. They found that the conversion was not affected by the feed rate or power levels. This is contrary to the findings of Huska and Clump (11), Gilles and Clump (9), and Rains (21). The findings of these authors showed that the percent conversion increased as the feed rate decreased and the power input increased. Miller and Ayen (16) calculated that the utility costs for this reduction of titanium tetrachloride were about \$2.65 per pound of titanium tetrachloride.

Using a D.C. arc plasma jet, H.L. Gilles and C.W. Clump (9) were successful in reducing iron ore to elemental iron. The plasma temperature ranged from 4300°F. to 10,300°F. The feed rates were about 1 gm/min. The gas flow rates ranged from 91.5 SCFH to 158.5 SCFH. The plasma power levels were varied from 9.1 kw to 30.4 kw. Gilles and Clump (9) found that a 100 percent hydrogen plasma gave slightly better conversions than a 25 percent hydrogen and 75 percent argon plasma. Their conversions were up to 69 percent. The product was quenched and collected by a water-cooled copper surface. They found that the percent conversion of iron ore to iron increased with increased power and decreased ore size. The economics of the system were not discussed.

Audsley and Bayliss (1) studied the oxidation of silicon tetrachloride in an oxygen induction plasma. They experimented with four different torch arrangements in order to get the greatest production of silicon dioxide with greater than 99 percent conversion. There was no quench necessary because of the highly stable product. They found that the feed rate was dependent only on the stability of the plasma.

Audsley and Bayliss determined that the injection of the silicon tetrachloride into the tail flame of the plasma was the most satisfactory feed arrangement since the stability of the plasma was not affected as much as it had been when using the through-the-plasma feed configuration. It was possible to feed the silicon tetrachloride into the tail flame of the plasma and still get high yields because long residence times were not necessary due to the stability of the product.

Audsley and Bayliss used a 25 kw 5 MHz generator in conjunction with the four different torch configurations. Their most successful torch used a tangential introduction of the oxygen gas for plasma stability. With this torch they used a power level of 22.5 kw, an oxygen flow rate of 56 liters/min., and a silicon tetrachloride feed rate of 67 gm/hr. Under these conditions, they accomplished a greater than 99 percent conversion to silicon dioxide. They further

predicted that higher production rates could have been obtained. No economics were mentioned in this paper.

Dundas and Thorpe (8) proposed a process for producing titanium dioxide pigment from titanium tetrachloride using an oxygen induction plasma. They based their proposal on a 1 MW induction plasma torch with which a large quantity of oxygen could be heated to 2,000°K for about 0.56 kw-hr/lb. oxygen. This high temperature oxygen was reacted with the titanium tetrachloride to produce titanium dioxide in a separate oxidation reactor. The rate of production would be about 70 tons a day of titanium dioxide.

The advantages of the above system over present production methods of titanium dioxide are the capability of the reactor to be operated at the theoretical optimum temperature of 1,900°K and the high purity of the titanium dioxide produced (> 5 PPM contaminants). Dundas and Thorpe predicted that the cost of reduction would be \$.003 - .007 per pound of titanium dioxide. Their proposed process seemed to be based on sound economics derived from laboratory experiments.

Ionarc/TAFA is presently producing zirconium dioxide from zirconium silicate using an oxygen induction plasma (34). A 300 kw induction plasma raises the zirconium silicate to a high temperature and converts the compound to zirconium dioxide and silica. The silica is then leached out of the zirconium dioxide using sodium hydroxide. The purity

of the product depends on the number of leaching steps. The maximum flow rate of zirconium silicate is 500 lb/hr. The energy necessary for complete combustion was 0.6 kw-hr/lb. The zirconium dioxide product was very pure and of uniform spherical shape, about 0.1 to 0.2 inches in diameter. The process is non-polluting in that there are no unwanted by-products. The silica is sold at a relatively moderate price. This is one of the first American production processes using a plasma as a chemical reactor.

Newham and Watts (18) reported success in reducing zirconium tetrachloride to zirconium trichloride in an electric discharge. These authors sublimated zirconium tetrachloride in a furnace and passed the zirconium tetrachloride through a hydrogen discharge at a pressure of 3 to 4 mm Hg. No percent conversion was given.

In their article concerning the state of the art in plasma chemistry, Vurzel and Polak (32) indicated that they had had some success in reducing zirconium dioxide to zirconium in a hydrogen plasma jet. However, no further information was available concerning this research.

Brown (3) presented a paper concerning his work in reducing zirconium dioxide and zirconium tetrachloride to zirconium with the use of an arc plasma jet. The size and power levels were not given; neither were the flow rates of the gases and reactants. Brown's analysis was by wet

chemical methods, and his results were based simply on the increased zirconium content between the reactant and the product. This method of analysis may indicate some success but does not positively identify the presence of metallic zirconium. In attempting to reduce zirconium dioxide to zirconium using carbon, Brown found that residence time and the size of the zirconium dioxide were more important than the method of introducing the carbon. Using $10\ \mu\text{m}$ zirconium dioxide and a carbon tube to lengthen the plasma section, he found an increase in zirconium content from 38.2 percent zirconium in the feed to 58.4 percent in the product.

The results of Brown's research are not very conclusive, however. The zirconium tetrachloride could have been reduced only to zirconium dichloride to give the increase in percent zirconium in the product. If some of the zirconium tetrachloride was converted to zirconium dioxide, this would also increase the percent zirconium. Another consideration is that the small difference in zirconium content between the reactants and the products might be due to experimental error. The experimental value did not even come up to the theoretical content of zirconium in zirconium dioxide of 74 percent. In addition, Brown did not indicate how he handled the product so that the elemental zirconium would not react with atmospheric oxygen, forming zirconium dioxide, due to the pyrophoric nature of finely divided zirconium.

The above studies on plasmas as chemical reactors laid the foundation for this research.

CHAPTER 3

SPECIFIC OBJECTIVES

The overall objective of this research was to determine the feasibility of zirconium production by reduction of zirconium tetrachloride in an argon induction plasma. In order to accomplish the overall objective, the following specific objectives were carried out:

1. the development of a sublimation and purification feed system for zirconium tetrachloride;
2. the development of an induction plasma system that would reduce zirconium tetrachloride to zirconium;
3. the development of a quench probe suitable for quenching and collecting the zirconium product;
4. the development of analyzation techniques in order to determine the percent conversion from zirconium tetrachloride to zirconium;
5. the determination of the energy balances on the zirconium production apparatus; and
6. the prediction of the economics of this method of producing zirconium in order to determine the feasibility of commercial production.

CHAPTER 4

THEORETICAL CONSIDERATIONS

Thermodynamics

According to Polak (20), there are presently no well-founded mechanisms to explain most of the chemical reactions occurring in low-temperature plasmas. The difficulty in describing these types of reactions lies in the fact that they do not occur at equilibrium and thus cannot be described by means of some temperature which is characteristic of equilibrium systems. In plasmas, the electrons, atoms, and various fragments of molecules are excited differently. Each constituent of the plasma can be characterized by its own particular temperature depending on its electrical, vibrational or rotational energy level. At equilibrium, the temperature due to the electrical, vibrational or rotational energy will be equal.

Due to the complexity of determining the reaction mechanism in a plasma, the kinetic mechanism for the reduction of zirconium tetrachloride will not be presented. An indication of what might be happening in the plasma can be determined from the partial pressure versus temperature plot for the zirconium-chlorine system and the free energy

relationships of the zirconium halides as presented by Brown (3). Although it was not specifically stated in Brown's research, it is assumed that these plots were based on Dow's JANAF Tables (7) since similar plots by Brown were so referenced.

According to the zirconium-chlorine partial pressure versus temperature diagram shown in Figure 1, atomic chlorine and zirconium are the major constituents at 5,500°K of a gaseous system at 1 atm. This figure shows that if the temperature of the system is lowered slowly, the concentrations of zirconium tetrachloride, zirconium trichloride and zirconium dichloride will increase and the concentration of zirconium will decrease. If the zirconium and chlorine constituents were rapidly quenched, freezing them in their uncombined state, zirconium could be produced. Figure 1 indicates that the removal of chlorine, possibly by hydrogen, would be advantageous.

Upon examining Figure 2, it is seen that hydrogen chloride is more stable than the chlorides of zirconium at temperatures above 6,000°K. This is not strictly true, however, since hydrogen chloride is 50 percent dissociated at 3580°K. Therefore, the hydrogen would have no advantage over the zirconium in reacting with free chlorine, except due to its much higher mobility (3). Other authors (9, 21) have found hydrogen to be of little help as a reducing agent in similar reactions.

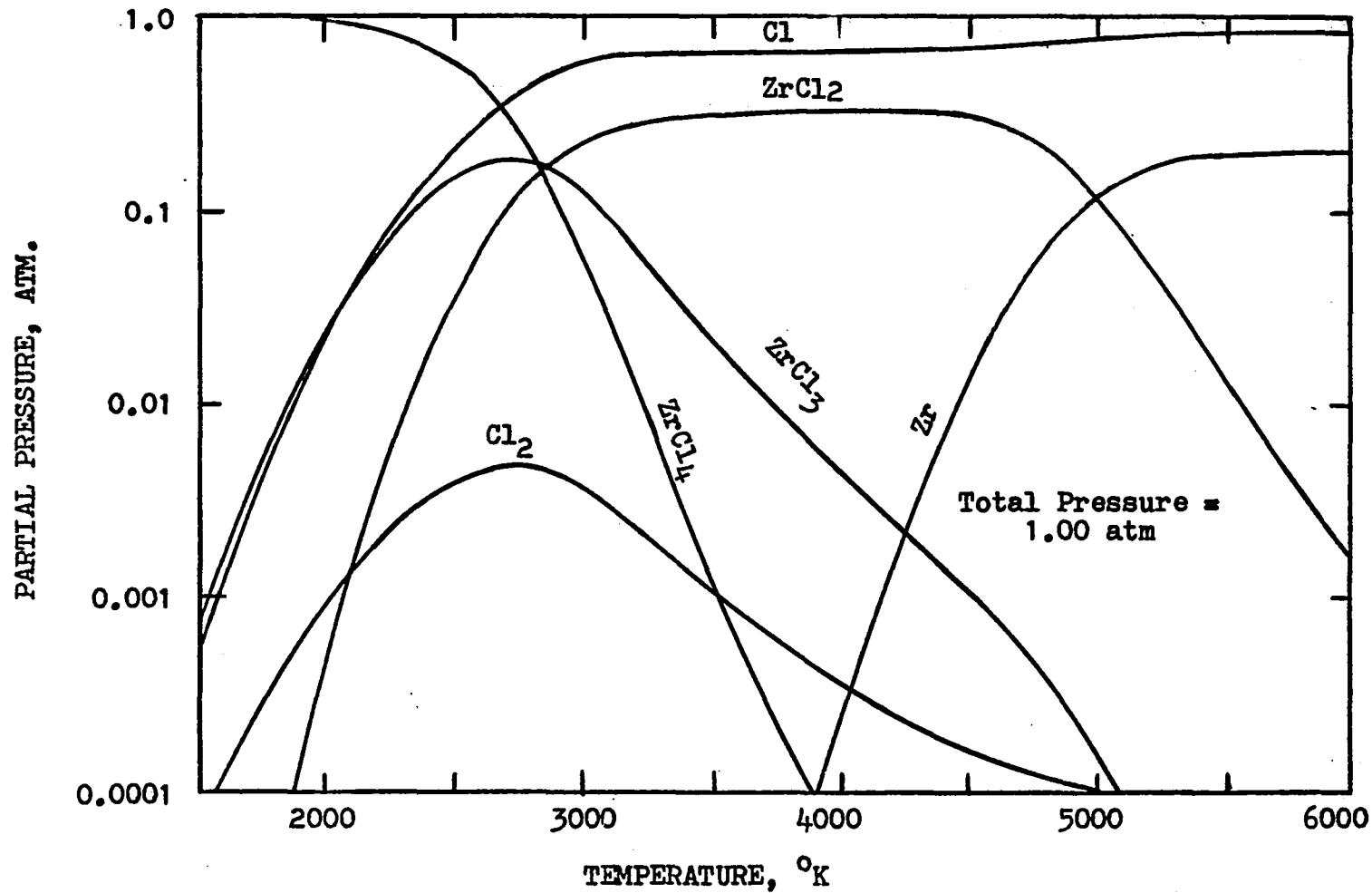


Figure 1. Partial Pressure Vs. Temperature for Zirconium Chlorides(3).

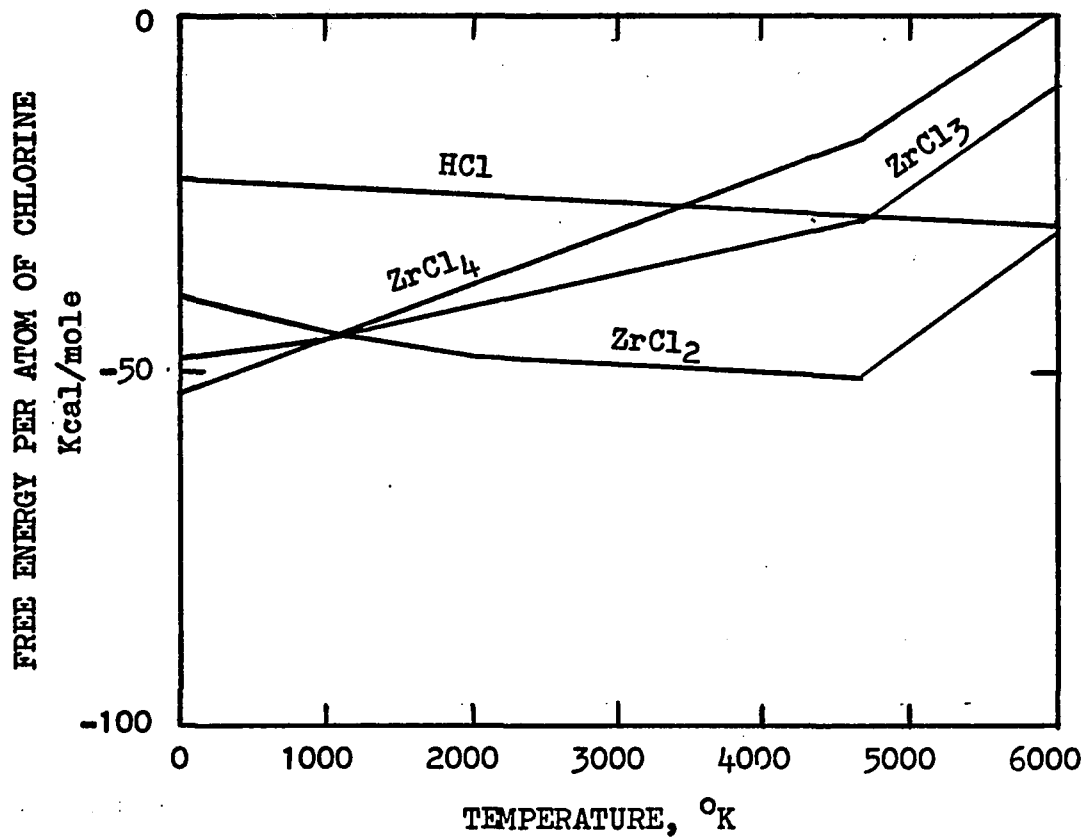
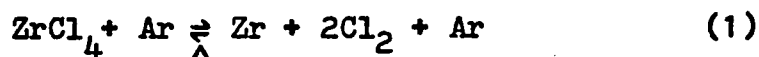


Figure 2. The Free Energy Per Atom of Chlorine Vs. the Temperature for Zirconium Chlorides(3).

The Quench Process in Product Collection

When feeding gaseous zirconium tetrachloride into a gaseous argon induction plasma with temperatures around 10,000°K, it was expected that the zirconium tetrachloride would be completely thermally dissociated with an overall reaction of:



Since this reaction is reversible, it is obvious that, by slowly cooling down the products, the zirconium would revert to zirconium dichloride, zirconium trichloride, and zirconium tetrachloride with only the interference due to the dilution effect of the argon. It is, therefore, necessary to freeze or rapidly quench the products in order to collect pure zirconium. This may be accomplished by inserting a water-cooled cylindrical probe into the hot part of the plasma flame. Under these conditions, the temperature gradient for quench could be many thousands of degrees per centimeter.

Sundstrom and DeMichiel (27) used the following equation to describe the heat transfer to a cold wall assuming no reaction:

$$N_{\text{Nu}_m} = \frac{3.66 + 0.104(x/D \cdot N_{\text{Re}} N_{\text{Pr}})^{-1}}{1 + 0.016(x/D \cdot N_{\text{Re}} N_{\text{Pr}})^{-0.8}} \quad (2)$$

Using this equation and assuming the cold wall at 100°F and the plasma temperature from 5,000 to 4,000°R around the wall, the quench rate was 0.6×10^6 °R/sec. This compares with

Vurzel's and Polak's (32) estimated quench rate in a heat exchanger of 10^6 °C/sec. Sundstrom and DeMichiel (27) compared the quench rate of the cold wall with liquid spray, fluidized bed, and gas mixing. The gas mixing was determined to have the best quench rate, with the fluidized bed next, and the cold wall the least effective. The quench rates of all the techniques were of the same magnitude.

Energy Balances

An energy balance was accomplished over the experimental apparatus in order to determine the various energy losses and the energy actually used in the conversion of the zirconium tetrachloride to zirconium. As shown in Figure 3, the energy balance over the 4 MHz 25 kw generator determined the efficiency of the generator, which included the energy lost to the generator cooling water and the power input to the load coil. The energy into the generator was determined by using a calibrated voltmeter and ammeter. The energy losses to the cooling water were determined by measuring the temperature rise and flow rate of the cooling water. The energy to the load coils (E_{lc}) is described by the following equation which is simply the energy supplied to the generator (E_g) minus the energy lost to the cooling water:

$$E_{lc} = E_g - E_{gw} = \text{KVA/hr} - (\Delta T C_p W)_{gw} \quad (3)$$

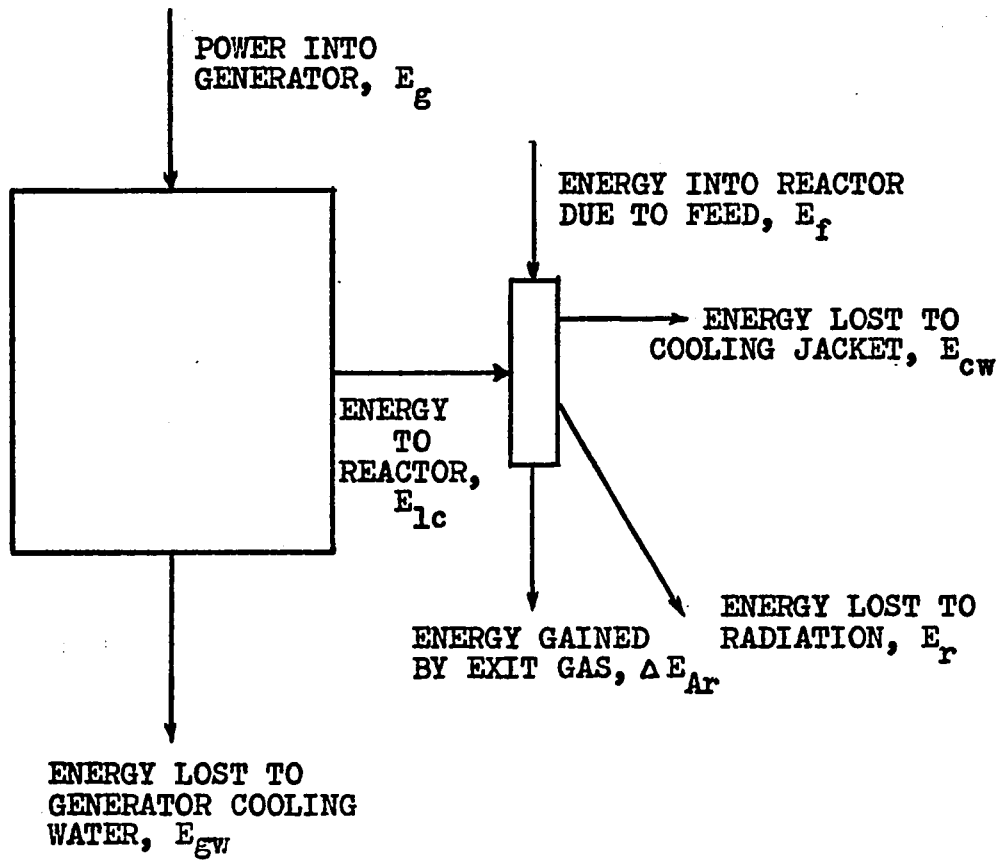


Figure 3. Energy Balance Over Apparatus.

The energy balance over the plasma reactor determined the various energy losses in that part of the experimental apparatus. The energy into the plasma reactor was taken as the energy out of the generator. The heat necessary to sublimate the zirconium tetrachloride feed was not considered in the energy balance; only the enthalpy of the gases entering the reaction chamber was considered. The enthalpy of the plasma gas was determined by a water-cooled calorimeter. The gas was cooled to approximately its entrance temperature by the calorimeter which consisted of a coil of water-cooled copper tubing. The energy gain by the calorimeter was determined by monitoring the cooling water flow rate and its increase in temperature. The enthalpy change in the gas was determined by measuring its inlet and outlet temperature and the gas flow rate.

The loss to the water-cooled jacket around the plasma reaction chamber was determined by the cooling water flow rate and temperature rise. The losses due to radiation from the plasma reactor (E_r) were determined by measuring the energy gain of the plasma reactor water-cooled jacket with and without an opaque coolant. The energy absorbed by the cooling jacket water (E_{cW}) was determined by the increase in the temperature of the water and the flow rate of the water. Carbon black dispersant was then added to the cooling water to make it opaque to radiation. The additional energy

absorbed by the opaque cooling water (E_{ow}) was the energy lost to radiation (E_r) as described by Equation 4:

$$E_r = E_{ow} - E_{cw} = (\Delta TC_p W)_{ow} - (\Delta TC_p W)_{cw} \quad (4)$$

The energy balance over the plasma reactor is shown in Figure 3 and is described by Equation 5:

$$E_{Ar} = E_{lc} - E_{ow} - \text{Losses} \quad (5)$$

The energy content of the gas (E_{Ar}) is also equal to the energy absorbed by the calorimeter (E_{cal}) plus the differential energy of the gas before the plasma and after the calorimeter (ΔE_{Ar}) as is described by Equation 6:

$$E_{Ar} = E_{cal} + \Delta E_{Ar} = (\Delta TC_p W)_{cal} + (\Delta T_{Ar} C_p W)_{Ar} \quad (6)$$

Equations 3, 4, 5 and 6 were used in determining the energy balance over the reactor system.

Determination of Feed Rate

The zirconium tetrachloride powder feed was purified and fed into the plasma reactor as a gas using a sublimation feeder. The zirconium tetrachloride was sublimated into the argon feed gas, leaving any impurities behind. Any water in the zirconium tetrachloride feed reacted with the zirconium tetrachloride to form zirconium dioxide which would be left behind in the sublimation feeder as a residual. The gaseous zirconium tetrachloride in the argon feed gas was then fed into the plasma. The argon feed gas was kept at a constant flow rate through-out each run for reasons of plasma stability.

The concentration of zirconium tetrachloride in the argon feed gas and, therefore, the feed rate of zirconium tetrachloride was determined by the energy flux to the solid zirconium tetrachloride. The more heat input, the hotter the zirconium tetrachloride and the greater the sublimation rate.

The amount of zirconium tetrachloride fed to the plasma reactor was determined by weighing the sublimation chamber before and after feeding the zirconium tetrachloride. Some water was driven off during the feed purification and was accounted for by measuring the change in weight before the zirconium sublimation was initiated.

There was a certain amount of lag in the sublimation heaters; therefore, it was necessary to monitor the temperature in the sublimation chamber and to assume that this temperature was characteristic of the feed rate. Since only the initial and final weights of the sublimation chamber could be measured, it was necessary to make a few assumptions in order to calculate the feed rate of the zirconium tetrachloride. It was assumed that the temperature in the sublimation chamber was representative of the feed rate. The initial increase in temperature at a high power input setting was linear, so it was assumed that the feed rate also increased in a linear manner. It was further assumed that the feed rate decreased in a linear manner when the power to the heaters was shut off. The temperature of the sublimation

chamber remained constant throughout the run so the feed rate was assumed to be constant also. The feed rate versus time is shown in Figure 4, where the area under the curve is the total grams of zirconium tetrachloride fed into the reaction chamber.

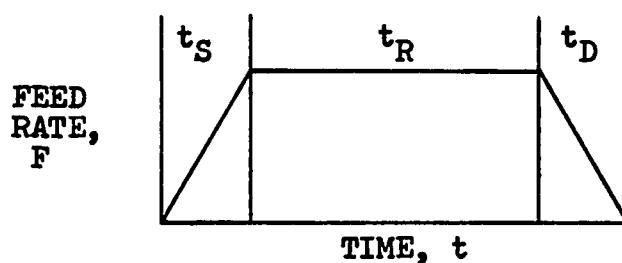


Figure 4. Feed Rate of Zirconium Tetrachloride Vs. Time

Using these assumptions, Equation 7 was derived in Appendix III for the feed rate of each run (F):

$$F = \frac{60(w_{\text{ZrCl}_4})}{0.5(t_S + t_D) + t_R} (1 - W_p) \quad (7)$$

The above equation was used in the calculation of the feed rates.

Theoretical Considerations in the Product Analysis

Zirconium metal as it comes out of a plasma is finely divided and therefore pyrophoric. Since it will spontaneously combust in the atmosphere, it is necessary to keep the zirconium product samples under an inert atmosphere during the entire analysis of the product for percent conversion of

zirconium tetrachloride to zirconium. The product sample was removed from the argon plasma in a container pressurized with argon and then placed in a nitrogen gas environmental chamber where the sample could be handled. Zirconium will not spontaneously combust in nitrogen at room temperature.

It was anticipated that the product would consist of zirconium and zirconium chlorides because great care had been taken to remove the oxygen from the experimental apparatus. This assumption was confirmed by use of x-ray diffraction. It was necessary to determine the zirconium metal content of the product as well as the total zirconium content so that the percent conversion could be calculated. All of the chlorides of zirconium are soluble in water; therefore, the chlorides of zirconium and zirconium metal could be separated by dissolving the chlorides and filtering the zirconium metal (13). The zirconium metal was dried and weighed, thus giving the total weight of the zirconium metal. The zirconium metal was positively identified and checked for impurities by x-ray diffraction (6). No contaminants were detected.

The chlorides of zirconium form a white gelatinous precipitate of zirconium hydroxide when the solution is rendered alkaline. This reaction was used to precipitate the dissolved zirconium. Since no interfering ions were present in the chloride solution, ammonium hydroxide was used

to render the dissolved zirconium chlorides solution alkaline. The precipitate was dried and ignited at 500°C, thus converting the zirconium hydroxide to zirconium dioxide. The chlorides of zirconium were weighed as zirconium dioxide and the total zirconium content of the product was calculated. The percent conversion was calculated using Equation 8, which is derived in Appendix II:

$$X_{\%} = \frac{100}{1.0 + 0.7403(w_{\text{ZrO}_2}/w_{\text{Zr}})} \quad (8)$$

The analysis procedure was checked by a prepared sample of zirconium tetrachloride and zirconium mixed in similar proportions and amount to that collected after a run.

Error Analysis

An error analysis was accomplished on the results of this research according to error analysis techniques as described by Nalimov (17).

Assuming a value (z) is calculated by multiplying a variable (x) times a variable (y) times a constant (A), then:

$$z = A x y \quad (9)$$

An approximation to the standard deviation (S) can be derived by expanding Equation 8 into a Taylor Series. By using the terms for the first order and determining the expectation of

of the second moment, Equation 10 is obtained:

$$S_z^2 = (\partial z / \partial x)^2 S_x^2 + (\partial z / \partial y)^2 S_y^2 \quad (10)$$

where:

$$\partial z / \partial x = Ay \quad (11)$$

$$\partial z / \partial y = Ax \quad (12)$$

Since there was a limited amount of data available, the standard deviations of x and y were approximated by taking the maximum expected error and dividing it by three.

The procedure for calculating the standard deviation of z would be to choose a maximum expected error for x and y and divide these values by three to approximate the standard deviation of x and y. These standard deviations plus the nominal values for x and y in conjunction with Equations 10, 11, and 12 can be used to calculate an approximate value for the standard deviation of z. The coefficient of variation (ν) of z for both the calculated standard deviation and the maximum expected deviation can be calculated by the use of Equation 13 (17):

$$\nu = 100 S_z / z \quad (13)$$

CHAPTER 5

EXPERIMENTAL APPARATUS

Overall Experimental System

The major pieces of equipment used in this research were: an argon gas purification and feed system, a 25 kw 4 MHz generator, a plasma reaction chamber, a zirconium tetrachloride sublimation feed system, a cold quench collection system, and appropriate water cooling and exhaust equipment. The general arrangement of these pieces of equipment is shown in Figure 5.

Power Generator and Cooling Equipment

The power supply used in this research was a Lepel model T-25-3-MC-FF-S, 25 kw 4 MHz generator that was modified by the Tafa Plasma Torch Company to be used specifically for plasma generation. This generator was cooled by distilled water which was supplied from a 500 gallon stainless steel tank at a pressure of 55 psi and a flow rate of 18.5 gpm. The water was returned and sprayed into the stainless steel tank in order to effect some cooling of the water. A small amount of potassium dichromate was added to the cooling water to inhibit corrosion.

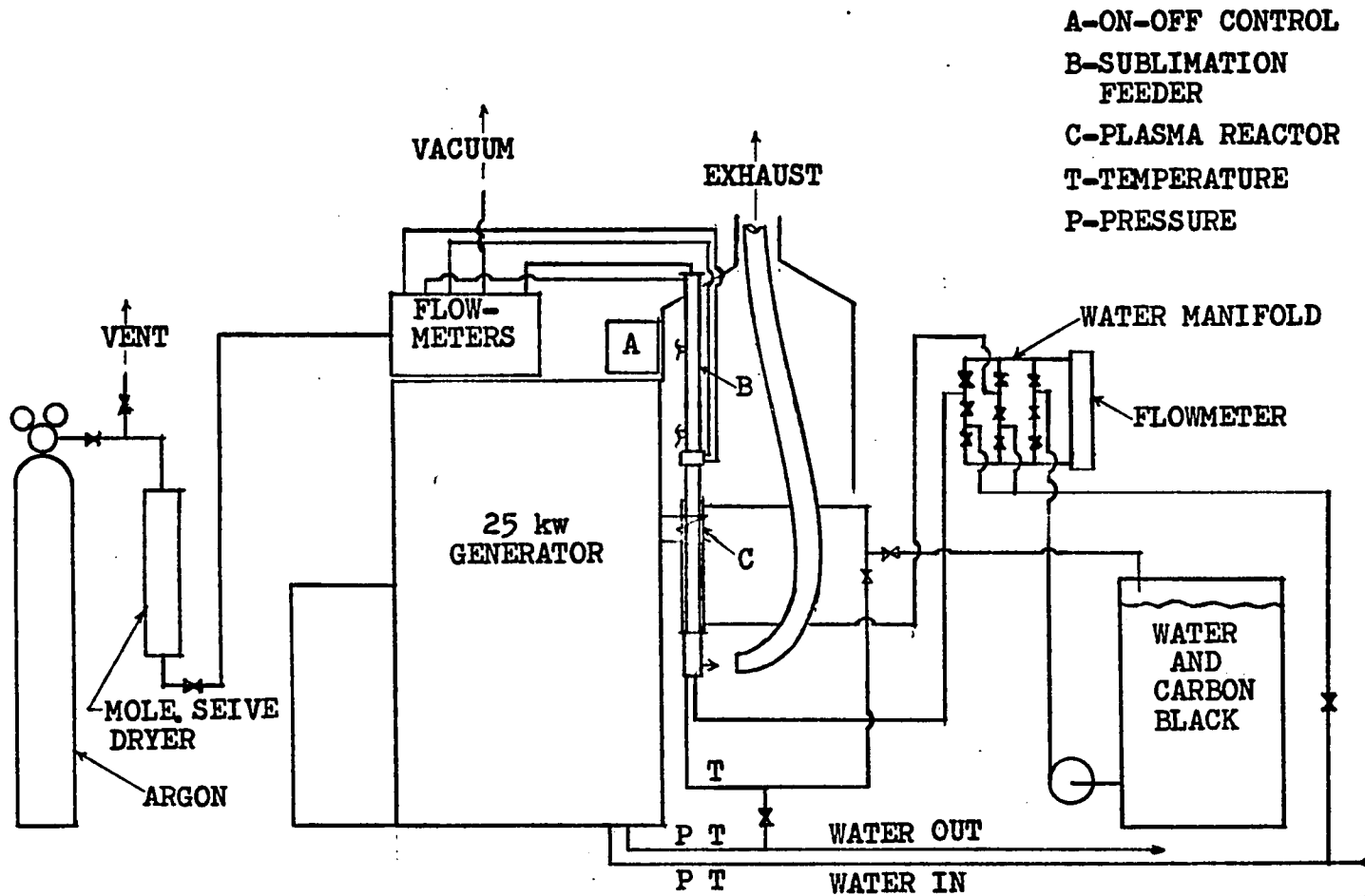


Figure 5. Experimental System

Plasma Reactor

The plasma reactor shown in Figure 6 consisted of a brass head, two concentric Vycor tubes, a water jacket and a load coil. The brass head was used as a gas distributor and a holder for the two concentric Vycor tubes. Argon gas was distributed to the annulus between the Vycor tubes at a relatively high velocity in order to help cool the outside Vycor tube (diameter = 52 mm) and stabilize the plasma in the center of the reactor. The plasma portion was greatly affected by the uniformity of the velocity of this "sheath" gas around the annulus. The small interior Vycor tube (diameter=45mm) was used simply to guide the sheath gas. A lower velocity argon gas was distributed to the interior of the small Vycor tube to provide the bulk flow for the plasma.

The load coil from the generator consisted of a six-turn coil of $\frac{1}{4}$ -inch copper tubing painted with corona dope to inhibit arcing between the coils and the plasma. The load coil was cooled by water flowing through the copper tubing.

The water-cooled jacket of the reactor was made of Pyrex and was cooled by the same water supply as the generator except that separate valves and a rotameter were used for controlling and measuring the flow rate. A separate cooling water system for the water jacket was also available. It consisted of a pump, a 55-gallon tank filled with distilled

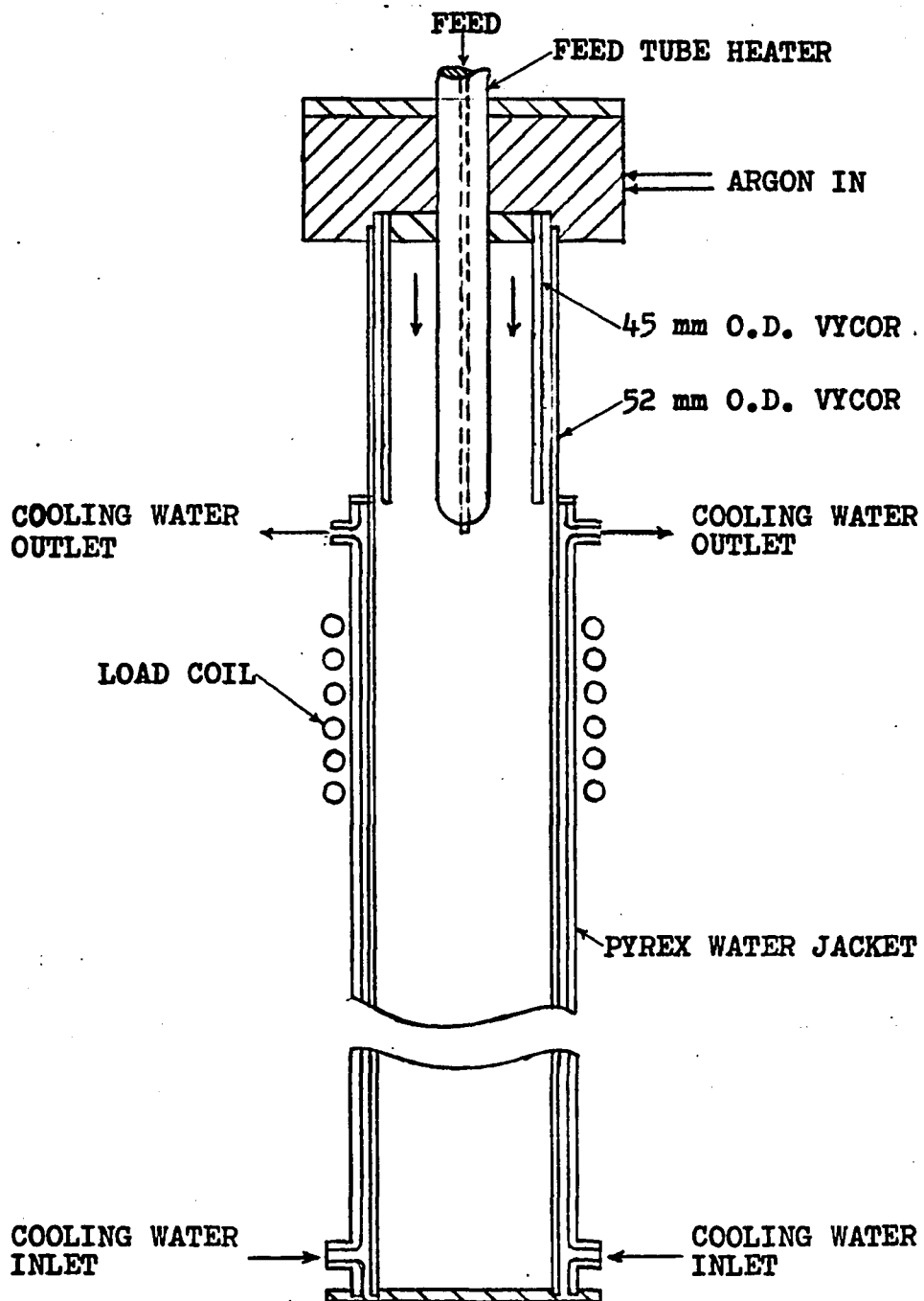


Figure 6. Plasma Reactor

water, and twice as much Pioneer Lamp Black Dispersion No. 887-9907 as was necessary to make the water opaque. This opaque solution was used to measure the amount of radiation lost through the water jacket. The cooling water for the plasma reactor jacket could be changed from opaque to clear through the use of appropriate valves.

Gas System and Sublimation Feeder

Argon gas with a purity of 99.995 percent was supplied from a 330 cubic feet tank through a regulator to the system at a regulated pressure of 15 psi. The argon was dried by a mole sieve bed containing 5 lbs. of Linde 5A mole sieve. This mole sieve bed was regenerated by heating it to 350°C under a vacuum. The dry argon gas was distributed to the sublimation feeder and the plasma reactor by four Fisher and Porter series 10A3135 rotameters. The moisture content of the gas leaving the mole sieve bed was measured by a Dupont Moisture Monitor 26-303. The entire gas system, plus the sublimation feeder and the plasma reactor, could be evacuated prior to the introduction of the dried argon gas in order to remove low vapor pressure impurities.

The sublimation feeder, shown in Figure 7, consisted of: a Vycor chamber to contain the zirconium tetrachloride, a heater for this chamber, a heater for the Vycor feed tube to the plasma, a Vycor preheat coil for the incoming gas,

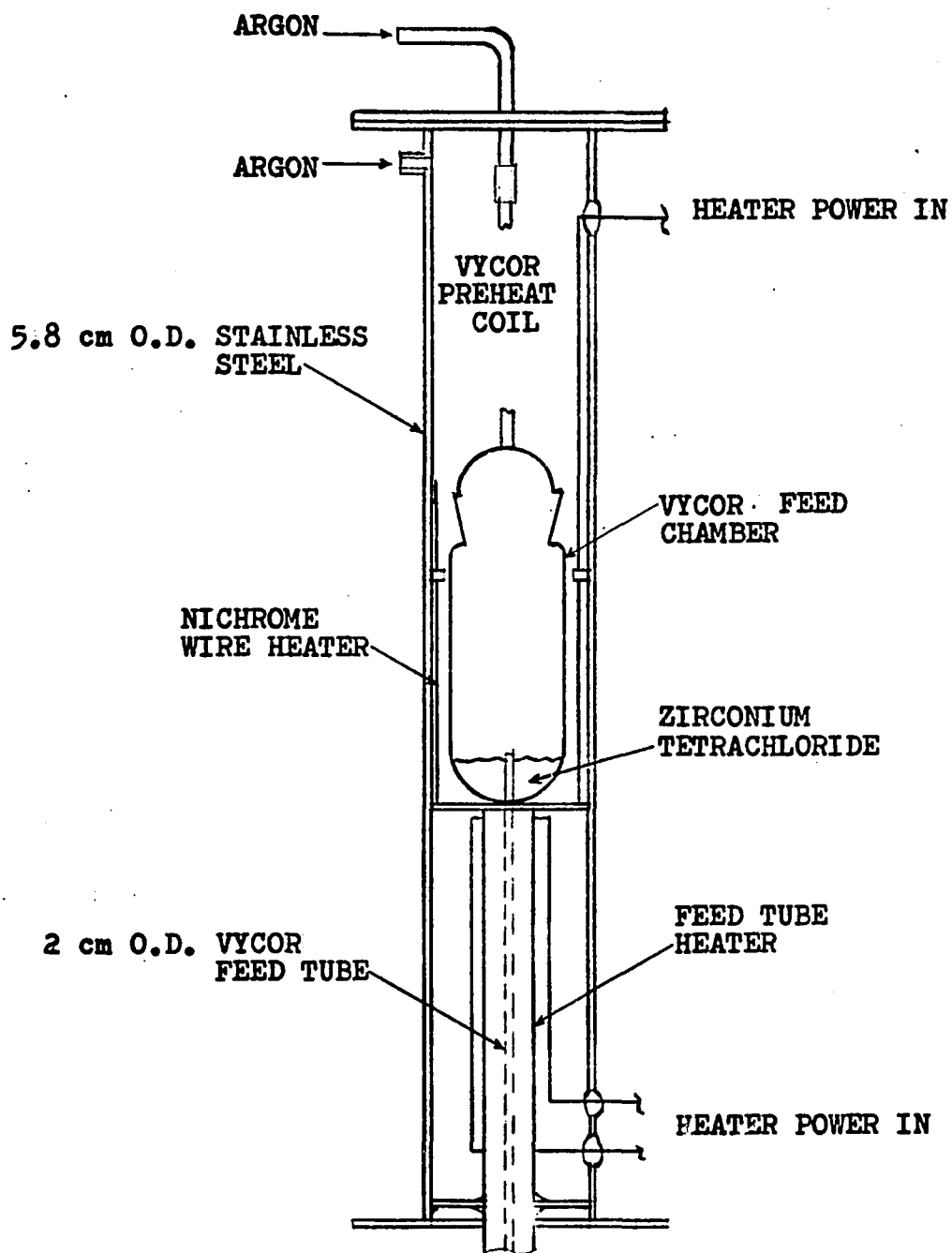


Figure 7. Sublimation Feed System.

and a stainless steel container for the sublimation chamber and its heaters. The stainless steel container was used to keep a positive pressure of argon around the Vycor sublimation chamber to eliminate contamination from atmospheric oxygen. Dry argon gas flowed into this container, past the sublimation chamber, and down between the Vycor feed tube and its heater to the plasma. The incoming feed gas was preheated by the Vycor coils at the top of the sublimation chamber. It then went into the sublimation chamber where it picked up the sublimating zirconium tetrachloride and carried it out the heated Vycor feed tube. The sublimation chamber was heated by a Nichrome wire heater which was controlled by a variable transformer. The heater for the Vycor feed tube consisted of two concentric ceramic tubes with a Nichrome wire wound between them. The tip was machined from a machinable ceramic, then fired. The ceramic tubes were used to help reduce the arcing from the plasma to the Nichrome heater during start-up. If this arcing occurred, the Nichrome wire would melt apart, and the heater would have to be re-built. The Vycor feed tube was heated to above the sublimation temperature of zirconium tetrachloride to insure that the zirconium tetrachloride would not condense but would enter the plasma reactor as a gas.

The feed rate of the gaseous zirconium tetrachloride was determined by the heat flux to the sublimation chamber. The gas flow rate through the chamber was held constant and was dictated by plasma stability. The concentration of zirconium tetrachloride in the feed gas, which was a function of the sublimation rate, determined the feed rate of the zirconium tetrachloride. The temperature of the sublimation chamber was proportional to the heat flux to the zirconium tetrachloride. This temperature was used to monitor the feed rate. The exposed surface area of the zirconium tetrachloride powder in the sublimator was increased by introducing 1/8-inch diameter glass balls into the sublimation chamber with the zirconium tetrachloride.

Quench System and Sample Transfer Cup

The collection system used in this research was a cold finger probe which is shown in Figure 8. The cold finger probe was constructed of stainless steel and was 12.5 mm in diameter, 102 mm long, and has a 5 mm diameter hole down the center. It was designed so that the water flowed by way of a stainless steel tube into the cold finger probe where a baffle would force it to the tip of the probe, thus keeping the tip cool. This was necessary since the tip of the probe was in the hottest part of the plasma. The water would then flow over the baffle and out the other stainless steel

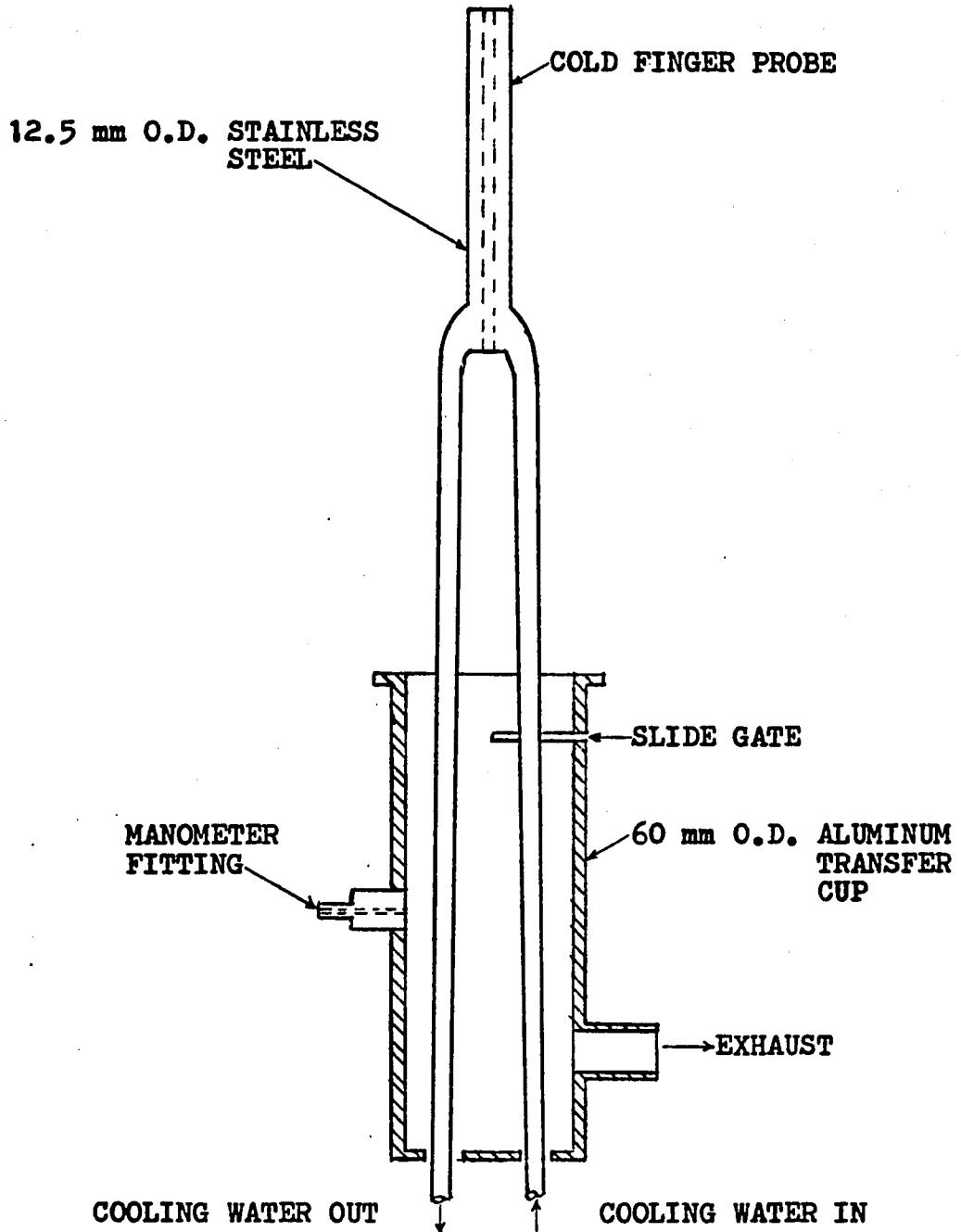


Figure 8. Product Collection System

tube. The cold finger probe was originally designed so that gas could flow through the center of the cold finger where any precipitating product would collect in a sleeve insert. This insert could easily be removed and the product collected. However, the majority of the product was collected on the outside top edge of the cold finger and not in the sleeve insert, due to the characteristics of the plasma.

Finely divided zirconium is pyrophoric in the air. It was, therefore, necessary to move the zirconium product collected on the probe from the argon atmosphere of the reaction chamber to a nitrogen gas chamber so that an analysis of the product could be made. This was accomplished by the use of the aluminum transfer cup shown in Figure 8. During a run, the transfer cup was attached to the bottom of the reaction chamber and was used to create a slightly positive pressure in the reaction chamber, thus eliminating contamination by atmospheric oxygen.

The tube fitting shown in Figure 8 was used to connect a manometer to the reaction chamber in order to measure the pressure of the reaction chamber during a run. The gases exited the reaction chamber through the exhaust fitting to the exhaust duct. After a run, with the argon flowing through the reaction chamber, the cold finger probe was pulled down into the transfer cup. A slide gate was inserted in the slot to seal off the top of the cup. To eliminate atmospheric

contamination, a tube supplying dry argon was attached to the manometer fitting to keep the cup under positive argon pressure. The transfer cup and the cold finger probe with the product could then be safely moved to the nitrogen gas chamber.

Calorimeter

A calorimeter was used to measure the heat content of the plasma. The calorimeter consisted of a coiled piece of $\frac{1}{4}$ -inch copper tubing. The cooling water flow rate through the calorimeter and the inlet and outlet temperatures of this cooling water were measured. The calorimeter was installed in place of the cold finger probe. The calorimeter cooled the gas to approximately the inlet temperature of the gas. By knowing the total heat removed from the gas by the calorimeter, and by knowing the enthalpy change in the gas, the energy balance over the plasma reactor, and, therefore, the whole system, was closed.

Analytical Equipment

Standard techniques and glassware were used in the gravimetric analysis. The materials were weighed on a Mettler H10T within 0.1 mg. In the x-ray analysis for positive identification of the crystalline materials, a Phillips type 52056/0 Debye-Scherrer powder camera was used. The x-ray source was a Phillips Electronic Inc. type 12045/3 x-ray

generator with a copper x-ray tube rated at 2.3 KVA. A nickel filter was used, and the power levels were at 40 KV at 20 ma. The film used was Kodak Blue Brand Medical x-ray film BB-54. The samples were inserted into 0.3 mm glass capillary tubes in a nitrogen atmosphere. The tubes were sealed with silicon grease. Standard powder diffraction techniques were used.

Equipment Design Considerations

Type of Plasma

There are two basic methods of plasma generation, the arc plasma and the induction plasma. The arc plasma is produced by striking an arc between two electrodes and passing a gas between these electrodes. The gas is heated by collisions in the arc. The velocities of an arc plasma must be relatively high in order to keep the electrodes cool, to distribute the arc around the electrode, and to reduce degradation of the electrodes. The degradation of the electrodes by the arc causes contamination of the gas stream.

The induction plasma, on the other hand, creates a plasma using a fluctuating magnetic field which adds energy to the ionized particles in the gas by forcing the ions first in one direction, then the other. The gas velocities can be relatively low giving longer residence time for reactants in the plasma. Furthermore, the gas stream is uncontaminated

by electrode degradation, since there are no electrodes. These are the main considerations in the choice of an induction plasma.

Reaction Chamber

The plasma torch supplied by Tafa had two drawbacks. first, it was prone to cooling water leakage into the reaction chamber. This water would react with the zirconium to produce zirconium dioxide. The second drawback was that it was impossible to feed gaseous zirconium tetrachloride into the top of the plasma. The feed port through the top of the plasma torch could not be heated so that the zirconium tetrachloride would condense in the feed tube.

The previously described torch was, therefore, redesigned. The head of the torch was designed so that a heated feed tube could be inserted into it. The Vycor reaction chamber was water-cooled so higher energy plasmas could be generated without breaking the Vycor plasma containing tube.

Sublimation Feed System

In designing a feeder for the zirconium tetrachloride, several things had to be considered. First, the zirconium tetrachloride is hygroscopic and, therefore, picks up atmospheric moisture. The feed thus had to be purified before it was fed into the reactor or the water would react with the zirconium tetrachloride, giving zirconium dioxide in the

product. The feed and reactor system was designed so it could be evacuated. After the feed was placed in the sublimation chamber, it was heated and evacuated, driving off any free water. There would still be some combined water left. It was, therefore, decided to design the feeder as a sublimation feeder since zirconium tetrachloride sublimates at 1 atmosphere and 331°C . The sublimation of the zirconium tetrachloride had two advantages: first, the combined water would react with some zirconium tetrachloride and form zirconium dioxide which would be left behind during the sublimation; second, the zirconium tetrachloride would enter the plasma as a gas and would eliminate the necessity of vaporizing solid feed and also the rate of heat transfer to the gaseous zirconium tetrachloride from the plasma would be greater than to solid zirconium tetrachloride.

Since it was desirable to have the zirconium tetrachloride enter the plasma as a gas, it was necessary to heat the feed tube all the way to the plasma in order to keep the zirconium tetrachloride from condensing. Resistance wire was chosen as the only feasible way to accomplish the required heating. This presented a problem, however, because the plasma during the start-up was very likely to arc to any metal object close at hand even though it was insulated from ground. The wire would then be melted and rendered useless. A coating of refractory cement did not reduce the arcing. In

the final configuration, the arcing was not eliminated but was significantly reduced.

The feed tube heater used consisted of two concentric mullite tubes with the heating wire coiled in the annulus. The tip of this heater, which was not susceptible to arcing, was machined from refractory lava. This refractory tip was fired and became very hard. The resultant feed tube heater was satisfactory.

CHAPTER 6

EXPERIMENTAL PROCEDURE

This section describes the procedures used in the operation of the previously described equipment. This includes the operation of the plasma reactor, the collection of the product, and the analysis of the product.

Preparation For a Run

The sublimation chamber was cleaned and dried. The 1/8-inch glass balls were added, and the sublimation chamber was weighed. The zirconium tetrachloride was added to the chamber, and the chamber was again weighed in order to determine the initial weight of the feed. The feed chamber was then placed into the stainless steel container. The stainless steel container was evacuated and heated to about 200°C with the feed tube heated to about 400°C. This heating and evacuation purified the feed of any uncombined water and eliminated any vaporous contaminants in the reactor system. The reactor system, which consisted of the reactor, feeder and connecting tubing, had been previously tested for leaks by a helium leak detector, so no atmospheric water or oxygen could come into the system during evacuation. After four hours, the feed was ready for sublimation.

During the purification of the zirconium tetrachloride in the sublimation chamber, some weight was lost. This was accounted for in the calculation of the total zirconium fed to the reactor.

The mole sieve bed was regenerated by heating it to 350°C under a vacuum. The bed was then allowed to cool to room temperature.

After preparing the sublimation feed chamber and the mole sieve bed, the reactor start-up was initiated.

Reactor Start-Up

Before the plasma reactor could be operated, it was necessary to turn on and adjust to the proper flow rate the cooling water to the generator, to the reactor jacket, and to the cold finger probe. The radio frequency generator was then turned on and allowed to warm up for ten minutes. There was a safety interlock which would shut the generator off if the exit cooling water temperature rose above a certain point.

The reactor system, including the reactor, the sublimation feed chamber, and connecting tubing, was pressurized to 2 psi with dry argon. This was to insure no oxygen contamination when the sealed bottom of the reactor was opened to install the collection probe and transfer cup. The sealing plate was loosened and the pressure was raised to 15 psi,

and the argon flow rates were adjusted to the proper values in order to keep the atmospheric oxygen out of the reactor. The collection probe and transfer cup were then mounted in place, and the argon was allowed to flow for thirty minutes to purge the system.

A protective shield was placed around the plasma reactor. This shield had two viewing areas made of number 9 welder's glass at a 90° angle from one another. This shield made it unnecessary to wear welder's helmets or goggles when viewing the plasma. Since this shield was grounded, it also reduced the amount of extraneous radio waves emitted from the equipment.

A Tesla coil was permanently placed approximately 3 inches below the generator load coil. The Tesla coil was used to initiate the plasma by striking an arc to the cold finger through the water jacket. After the shield was in place, a chain was placed across the entry to the reactor area as a precaution against anyone coming into contact with the reactor or load coil while the system was in operation.

The sublimation heaters were turned off to reduce the chance of the plasma arcing to the heaters during start-up.

Next, the generator plate was turned on, and the power control was adjusted to zero. The power and the Tesla coil were then turned on. The power was increased until the plasma initiated. The power was then set to the desired

value. The sublimation heaters were again turned on. The feed gas flow rate was adjusted, and the sublimation heater was turned to a high value in order to reach the desired feed rate rapidly. When the desired feed rate was reached, the sublimation heater was turned back to a value that would maintain the proper feed rate of gaseous zirconium tetrachloride.

Each run was terminated after 60 minutes of steady feed rate. After 30 minutes of a steady feed rate, all pertinent data were taken: gas flow rates, water flow rates, water temperatures, and power levels.

Reactor Shut-Down

At the end of 60 minutes of steady state operation, the reactor was shut down. The sublimation heaters were turned off, and the feed was allowed to cease. After the zirconium tetrachloride was no longer feeding to the reactor, the power to the plasma was turned off. The cooling water and the argon gas, however, continued to flow for 30 minutes in order for the entire apparatus to cool down.

Product Collection

At the end of the cooling period, the cold finger was loosened from its support and pulled down into the transfer cup (Figure 8). A line with flowing argon was attached to the transfer cup, and the cup was closed by a sliding

plate, and, therefore, put under positive argon pressure. The cup and the water-cooled probe were removed and placed in a nitrogen gas chamber where the product could be analyzed. This procedure was necessary to keep the zirconium metal from reacting spontaneously with atmospheric oxygen.

Operating Conditions

According to the findings of authors Huska and Clump (11), Gilles and Clump (9), and Rains (21), the yield of pure zirconium should be greater with a higher energy plasma. The plasma was, therefore, operated at the maximum power that the water-cooling jacket could possible handle. When the water in the cooling jacket started to boil, this was considered the maximum power level.

The gas flow rates, including the feed gas flow rate, were adjusted for maximum plasma stability and held constant throughout all runs. The range of zirconium tetrachloride feed rates was also determined by plasma stability. The cooling water flow rates were held at maximum levels except in the case of the water-cooled jacket where the back pressure had to be kept below a certain value in order to prevent breakage.

Product Identification

The zirconium metal product was positively identified by standard Debye-Sherrer x-ray techniques (6). A

sample of the product was placed in a 0.3 mm diameter glass tube inside the nitrogen gas chamber. The end of the tube was sealed with silicon grease. The pattern of the sample from the Debye-Sherrer powder camera was then compared with the pattern of pure zirconium. The pattern of pure zirconium was obtained by exposing a sample of pure zirconium in the Debye-Sherrer powder camera. This pattern was also compared to the pattern found in the Powder Diffraction Index (25).

Product Analysis

After the sample of the product was collected in the weighing bottle, the bottle was sealed and the initial weight of the sample was determined to the nearest 0.1 mg. The sample was then returned to the inert gas chamber which was again filled and emptied three times. Distilled water was added to the sample in order to dissolve all of the soluble zirconium chlorides. The sample was then filtered to separate the zirconium metal from the soluble chlorides. The zirconium metal was washed with water and dried by washing with acetone and then placing it under a vacuum. After drying, the sample was sealed in the filter chamber and weighed to the nearest 0.1 mg. This procedure determined the amount of zirconium metal in the sample. The zirconium metal was checked for purity by x-ray diffraction. The solution of

zirconium chlorides was rendered alkaline by the addition of a few drops of ammonium hydroxide. The precipitate dried overnight and then was ignited at 500°C. After cooling, the amount of zirconium dioxide was determined to the nearest 0.1 mg. From this process, the combined zirconium in the product could be determined and, therefore, with the weight of free zirconium, the percent zirconium tetrachloride which had been converted was determined.

Energy Balance

Data for the energy balance were taken under the same conditions as the runs except that a calorimeter, consisting of coiled $\frac{1}{4}$ -inch copper tubing, was mounted in place of the cold finger probe and that an opaque coolant was used in the water-cooled jacket for the plasma reactor. The apparatus was prepared and started up as previously described. A small variance in the feed rate of the zirconium tetrachloride was determined not to be significant in the energy balance.

When the apparatus had reached steady state, all data were taken. These data included: the temperature differential and flow rates of all cooling waters, the power input by the generator, and the temperature differential and flow rate of the gas. With these data, the energy into the system and the energy out of the system, except for radiation losses,

could be determined. In order to determine the radiation losses from the plasma, an opaque coolant was used to replace the clear coolant in the reactor cooling jacket. This coolant absorbed the radiation from the plasma and by measuring the additional energy rise of the opaque coolant over the clear coolant, the losses by radiation were determined. The opaque coolant was contained in a separate reservoir and was switched into the system by a series of valves.

After the necessary data were taken, the apparatus was shut down in the normal manner.

CHAPTER 7

EXPERIMENTAL RESULTS

This section contains the results of this research. This includes the effect of the feed rate of the zirconium tetrachloride on the conversion of the zirconium tetrachloride to zirconium, the effect of the cold finger probe position on the conversion of the zirconium tetrachloride to zirconium, the results of the energy balance over the experimental apparatus, the results of the product analysis, a correlation of the feed rate versus conversion data, the economic analysis, and the error analysis.

Analysis of Product

The product was analyzed as was outlined in the procedure section. The analytical procedure was checked by preparing a sample of reagent grade zirconium and zirconium tetrachloride in similar proportions and amounts as were encountered in the actual product. These known samples were analyzed in the exact manner as the product. These checks were performed both prior to and during the experimental runs. The error for the weight of free zirconium was always

within 0.6 percent of the true value. The weight of the combined zirconium was always within 1.5% of the true value. This accuracy was considered satisfactory for the purposes of this research.

Reagent grade chemicals were used so no significant error due to impurities was expected. The uncombined zirconium in the product was positively identified by x-ray diffraction. This product was assumed to be pure since all lines in the x-ray diffraction pattern were accounted for and attributed to zirconium. This was checked in two ways. First, the lines were measured and compared with the angles on file in the Powder Diffraction Index (25). Second, pure zirconium was exposed in the very same powder diffraction camera used in the product analysis, and this pattern of lines was compared to the pattern of the zirconium product. All of the expected impurities such as zirconium dioxide are crystalline and would show up in the x-ray diffraction pattern if they were present.

Feed Rate and Probe Position Versus Conversion

The results pertaining to the feed rate of the zirconium tetrachloride and the cold finger probe position on the conversion of zirconium tetrachloride to zirconium are shown in Table I. The feed rate and the conversion were

calculated in the manner described in the theory section, according to Equations 7 and 8 respectively. Runs 1 through 6 show the results of varying the feed rate at a constant probe height. These runs demonstrate that the percent conversion drops sharply as the feed rate is increased.

Runs 7 through 10, in conjunction with runs 1 and 6, show the result of keeping the feed rate relatively constant and varying the probe position. As the probe is placed further into the plasma, the residence time of the feed in the plasma is reduced. As the cold finger probe goes more towards the center of the plasma ball, the temperature surrounding the probe increases. This has two effects. First, the probe is moved into a region where a higher dissociation of zirconium tetrachloride is expected. Second, the temperature difference between the cold finger probe and the surrounding plasma is increased and, therefore, the quench rate of the dissociated zirconium tetrachloride is increased. The result of these two effects is to increase the percent conversion of zirconium tetrachloride to zirconium.

A Students t-test was accomplished on the data for the three different probe heights at the low rate of feed. This analysis is given in Appendix III. At the 97.5% confidence level, the results of this analysis show that there is a significant difference in the conversion of the three probe heights.

TABLE I

RESULTS OF FEED RATE OF $ZrCl_4$ VS. CONVERSION TO Zr

Run	Feed Rate of $ZrCl_4$	Percent Conversion of $ZrCl_4$ to Zr	Percent of Feed Collected	Probe Height from bottom of Plasma Tube
no.	gm/hr	%	%	cm
1	0.4404	78.81	19.88	30
2	4.658	3.674	2.84	30
3	1.8165	25.61	5.214	30
4	1.321	34.36	14.17	30
5	4.566	19.37	1.90	30
6	0.7870	66.27	20.26	30
7	0.5385	61.77	21.04	27
8	0.5808	89.61	39.06	33
9	0.6217	61.18	16.06	27
10	0.6552	89.33	47.43	33

In addition to the feed rate and the percent conversion of zirconium tetrachloride to zirconium, Table I also shows the percent collected and the percent zirconium. The percent of the feed collected is the percent of the total zirconium tetrachloride that was collected as product based on zirconium.

Due to the characteristics of the apparatus, the weight loss of the weight of the feed during purification could not be measured for each run. Therefore, several readings were taken and an average value was used (0.03 gm) in the calculation of the feed rate.

Energy Balance

An energy balance was accomplished over the experimental apparatus in order to determine the efficiency of power usage in the reduction of zirconium under the experimental conditions. The energy balance results were obtained under four separate conditions: clear and opaque cooling water in the plasma cooling jacket, and with and without feed. The energy lost by radiation was determined by comparing the energy absorbed by the opaque cooling water to the energy absorbed by the clear cooling water. The values were also compared with and without the zirconium tetrachloride feed in order to determine the effect of the feed on the energy balance.

The feed rate used in the energy balance runs was approximately 0.480 gm/hr. This feed rate was chosen because the best conversion of zirconium tetrachloride to zirconium was observed at this rate. The results of the energy balance are shown in Table II.

By examining runs 1 and 2, it can be seen that the loss due to radiation with zirconium tetrachloride being fed was 0.224 Kcal/hr or 3.9% of the power input. The radiation loss without the zirconium tetrachloride being fed was slightly lower, about 3.0%. This decrease can be explained by the loss of the radiation from the excited particles of the zirconium tetrachloride feed.

The value of the power to the generator increased when zirconium tetrachloride was fed to the plasma. It is possible that this was due to the zirconium tetrachloride increase in the conductivity of the plasma and the effect of the load of the generator.

The generator cooling water removed 36% of the total power input to the generator. About 40% of the total power input went to the reactor jacket cooling water. This means that only about 24% of the power into the generator went to the plasma itself. It would be difficult to determine how much of the power went into the reduction of zirconium

TABLE II

ENERGY BALANCE SUMMARY

RUN	E_g	E_{gw}	E_{rw}	E_{Ar}	E_{cal}	Discrepancy in Energy Balance	Percent Discrepancy of Nominal Input Power	Conditions Reactor Feed Cooling Water
no.	$\times 10^3$ <u>Kcal</u> hr	$\times 10^3$ <u>Kcal</u> hr	$\times 10^3$ <u>Kcal</u> hr	$\times 10^3$ <u>Kcal</u> hr	$\times 10^3$ <u>Kcal</u> hr	$\times 10^3$ <u>Kcal</u> hr	%	
1	5.815	2.190	2.361	0.057	1.373	-0.166	-2.9	clear with
2	5.815	1.972	2.585	0.057	1.173	+0.028	+0.5	opaque with
3	5.538	1.972	2.042	0.045	1.253	+0.226	+4.1	clear with- out
4	5.538	1.972	2.148	0.032	1.267	+0.084	+1.6	opaque with- out
5	5.538	2.410	1.936	0.067	1.307	-0.182	-3.3	clear with- out
6	5.538	2.190	2.101	0.077	1.240	-0.070	-1.3	opaque with- out

tetrachloride to zirconium due to the increase in power input as a result of the change in load on the generator.

The standard deviation of the percent discrepancy of each energy balance was calculated in Appendix IV as 2.84. The average discrepancy was assumed to equal zero, and the "t" test was used to determine the significance of this hypothesis. As a result, "t" was calculated to be 0.188. This value of "t" is not significantly different from zero. Therefore, the discrepancy in the energy balance can be considered due to random error.

Correlation of Results

The energy input to the plasma was approximately the same for each run. The plasma had an energy content of approximately 1.3×10^3 Kcal/hr as is shown in Table II. The energy of formation of zirconium tetrachloride (230 Kcal/gm at 25°C) was used as a first approximation of the dissociation energy of zirconium tetrachloride to zirconium and chlorine. It, therefore, can be shown that the energy necessary to completely dissociate zirconium tetrachloride at a feed rate of 2 gm/hr is approximately 35% of the total energy available. We may thus conclude that the feed rate had a large effect on the plasma energy. This effect is even greater because all the zirconium tetrachloride was fed

into the center portion of the plasma. Assuming that the sensible heat requirements are negligible compared with the dissociation requirements, we may postulate that the above effect will decrease the percent conversion linearly with increased feed rate, or

$$dX/dF = b \quad (14)$$

Upon integration, we get:

$$X = bF + C \quad (15)$$

Assuming that where $F = 0$, $X = 1$, we get:

$$X = bF + 1.0 \quad (16)$$

Using the data in Table I and Equation 10, which is the least squares model, we find:

for 27 cm probe height -

$$\bar{F} = 0.580 \quad \bar{X} = 0.615 \quad b = -0.661$$

for 30 cm probe height -

$$\bar{F} = 1.091 \quad \bar{X} = 0.520 \quad b = -0.440$$

for 33 cm probe height -

$$\bar{F} = 0.618 \quad \bar{X} = 0.895 \quad b = -0.170$$

At the high feed rates (runs 2 and 5), the data become scattered. This is probably due to several factors. At feed rates around 4.6 gm/hr, the energy required for

complete dissociation is approximately 82% of the total energy in the plasma. The center portion of the plasma would, therefore, be greatly affected by these high feed rates. The collection at these feed rates was also a problem because the collected product would build up and flake off the quench probe causing an uneven collection. For these reasons, the high feed rate data were not included in the above analysis.

Equation 16 is plotted in Figure 9 for the three probe positions presented above. It is shown in Figure 9 that as the probe moved closer to the center of the plasma, the fractional conversion for a given feed rate increased. A plot of the slope of Equation 16 versus probe height, shown in Figure 10, suggests that in the range of conditions under consideration there is a linear relationship between the slope of the fractional conversion versus feed rate and the probe position.

Error Analysis

An error analysis was accomplished on representative runs according to Nalimov (17). The error analysis indicated the areas where the contributions to the uncertainty were large. Energy balance run #4 and percent conversion run #10 were selected as representative runs. This was possible because the nominal value for each variable

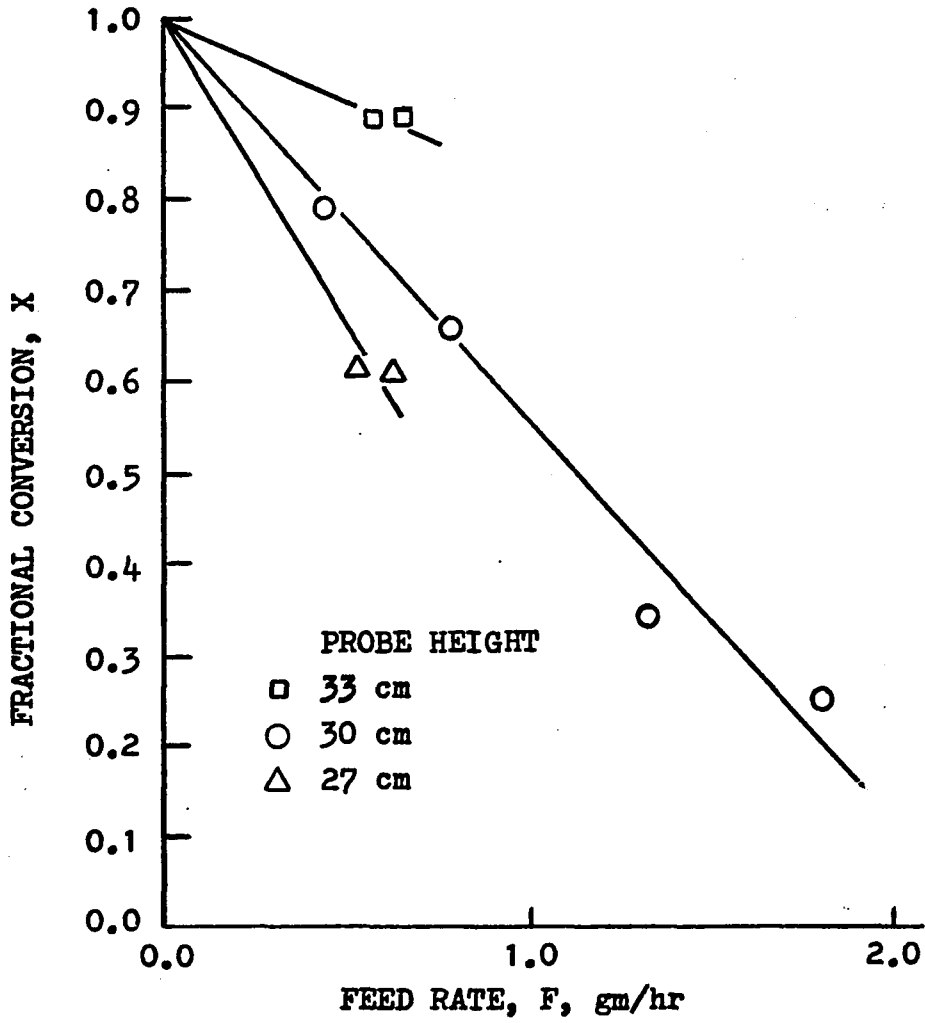


Figure 9. Fractional Conversion Vs. Feed Rate.

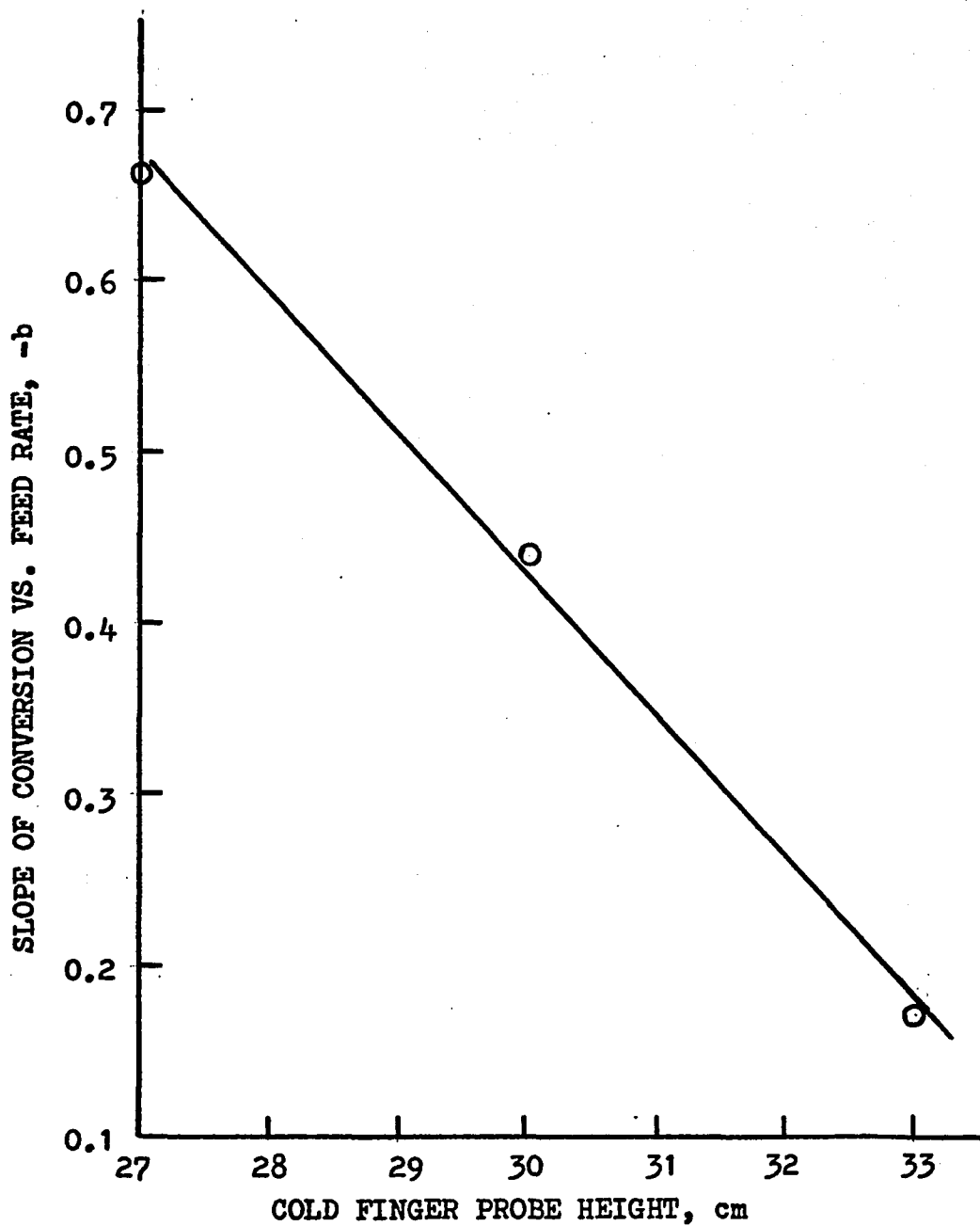


Figure 10. Slope of Conversion Vs. Feed Rate,
Vs. Cold Finger Probe Height.

was the same for all energy balance runs. An error analysis on selected data, therefore, was deemed sufficient for the purposes of this research.

Because of the limited amount of data, it was assumed that the standard deviation of the measured variables would be approximately one-third of the maximum expected error. The standard deviation for all raw data was calculated in this manner. The standard deviation of the refined values was calculated according to the methods presented in the Theory Section. The results of this error analysis are shown in Table III.

As can be seen in Table III, the major contributor to uncertainty is the power to the cooling water. This results in the rather large uncertainty in the power to the plasma. The power to the gas has a relatively large standard deviation, but because of its relatively small nominal value adds little to the overall uncertainty of the energy balance.

Economics

An energy balance and material balance were accomplished in order to determine the economic feasibility of zirconium production using a plasma. The data necessary for the calculation of the economic feasibility of zirconium production were taken from the results of production run 10

TABLE III

SUMMARY OF ERROR ANALYSIS

Run	i	Nominal	Standard Deviation	Max. Error	% of Nominal		Variance
no.			Si	3 Si	Std. Dev.	Max. Error	Si ²
4	E _g	5.53 x 10 ⁶ cal/hr	7.65 x 10 ⁴	2.295 x 10 ⁵	1.32	3.95	5.85 x 10 ⁹
4	E _{gw}	2.0 x 10 ⁶ cal/hr	1.02 x 10 ⁵	3.1 x 10 ⁵	5.17	15.5	10.40 x 10 ⁹
4	E _{ow}	2.18 x 10 ⁶ cal/hr	1.7 x 10 ⁴	5.1 x 10 ⁴	0.78	2.33	2.89 x 10 ⁸
4	E _{cal}	1.27 x 10 ⁶ cal/hr	8.94 x 10 ³	2.68 x 10 ⁴	0.70	2.1	0.8 x 10 ⁸
4	E _{Ar}	3.15 x 10 ⁸ cal/hr	3.3 x 10 ³	9.93 x 10 ³	10.5	31.5	0.11 x 10 ⁸
10	X	0.893	6.67 x 10 ⁻³	2.0 x 10 ⁻²	0.75	2.24	4.40 x 10 ⁻⁵
10	F	0.655 gm/hr	2.05 x 10 ⁻³	6.14 x 10 ⁻³	0.31	0.94	4.2 x 10 ⁻⁶
10	Zr in ZrCl ₄	0.584	4.9 x 10 ⁻³	0.0148	0.85	2.5	2.4 x 10 ⁻⁵

and calorimetry run 4. These runs were considered representative of normal operating conditions. Using the total power input of 6.76 kw, a feed rate of 0.655 gm/hr and a yield of 89.3 percent, we obtain:

$$\begin{aligned} \text{Power/lb. Zr} &= (\text{Power Input})/(\text{lb. Zr Produced}) \\ &= \frac{(6.76 \text{ kw})(454 \text{ gm/lb})}{(0.655 \text{ gm/hr ZrCl}_4)(0.893)(0.392)} \\ &= 13.4 \times 10^3 \text{ kw-hr/lb Zr} \end{aligned}$$

Using a utility cost of 0.006 dollars/kw-hr, we obtain:

$$\$/\text{lb Zr} = \$80.40 / \text{lb Zr}$$

This is a high cost and does not include capital costs, maintenance, and other costs.

One problem with the experimental apparatus is its inefficient use of input energy. Of the 6.76 kw-hr input, only 1.43 kw-hr goes into the plasma itself. The rest is lost to the cooling water of the generator and the plasma jacket. This gives an efficiency of 21.2 percent. Larger installations of plasma torches have increased this efficiency to 85 percent (19). Using this figure, the utility costs were:

$$\begin{aligned} \$/\text{lb Zr} &= \frac{(1.43 \text{ kw})(454 \text{ gm/lb})(0.006 \text{ \$/kw-hr})}{(0.85)(0.655 \text{ gm/hr ZrCl}_4)(0.893)(0.392)} \\ &= \$20.00 / \text{lb Zr} \end{aligned}$$

This cost is still high. If we investigate further, we find out that even assuming an 85 percent efficiency, the energy per pound zirconium product was 3,330 kw-hr/lb zirconium. According to Thorpe (28), it takes about 1 kw-hr/lb of material for this type of separation in a 1,000 kw plasma torch. Using this figure of \$23.35/1000 kw-hr given by Dundas and Thorpe (8) for a 1,000 kw induction plasma gives a production cost of about \$0.023/lb. This would appear to be an attractive production cost for zirconium. Further research is necessary to determine the validity of these figures.

CHAPTER 8

DISCUSSION OF RESULTS

Effect of Feed Rate on Conversion

The feed rate of any given run could not be duplicated exactly since the feed rate was not monitored continuously during a run but was determined after the run was completed. The feed rate could be approximated, however, by setting the sublimation heaters at the same power levels. The sublimation rate and, therefore, the feed rate depended somewhat on the variance in the exposed surface area of the zirconium tetrachloride.

At the higher feed rates (runs 2 and 5), the variation in conversion is probably due to the large buildup of material on the cold finger probe. The buildup was so heavy that the collected material would flake off the cold finger probe and cause a very uneven coating. It was further noted that conversion reduces sharply as the feed rate increases. Two factors probably contributed to this result. First, as more feed was introduced into the plasma, the more energy was taken from the plasma to dissociate the zirconium

tetrachloride and thus cool the plasma. This effect is significant even at the small amount of zirconium tetrachloride fed.

The significance of the affect of the feed rate of the zirconium tetrachloride on the plasma can be shown as follows. The energy necessary for heating the zirconium tetrachloride up to its dissociation temperature was calculated to be insignificant (approximately 0.1% of power input). As a first approximation, the energy of formation of zirconium tetrachloride was taken as the dissociation energy of zirconium tetrachloride to zirconium and two chlorides (230 Kcal/gm at 25°C). Using the high feed rate of 4.6 gm zirconium tetrachloride per hour, the energy for 100% dissociation is approximately 1.060×10^3 Kcal/hr. This is the same order of magnitude for the energy in the plasma as determined by the calorimeter (approximately 1.3×10^3 Kcal/hr). Taking a lower feed rate of 0.44 gm zirconium tetrachloride per hour, it can be shown that for 100% conversion this would take only about 0.101×10^3 Kcal/hr or about 8% of the plasma power. It, thus, can be concluded that the higher feed rate could cause a lower conversion simply due to the large power demand.

According to the results in the least square analysis, shown in Figure 9, the percent conversion of zirconium

tetrachloride to zirconium becomes less sensitive to the feed rate as the probe is placed further into the plasma. This is shown by the decrease in the slope of Equation 16 with increased probe height. Thus, we can conclude that the production of zirconium can be increased by collecting the product in the hottest part of the plasma without increasing the power input.

The second factor affecting the reduction in conversion was the buildup on the cold finger quench probe. As the coating on the probe became thicker, the quenching of the product would become less efficient. The outside layer of the collected product would be at a higher temperature than the cold finger probe due to the insulating effect of the collected products. Rains (21) also found that as the buildup on the collection surface increased, the percent conversion decreased.

Discussion of Energy Balance

In comparing runs 2 and 3, as shown in Table II, it was found that the power into the generator increased slightly with the addition of feed even though the power setting remained the same. This phenomena was probably due to the creation of a more conductive plasma by the presence of zirconium and chlorine ions, so that a greater load was placed on the generator.

It is found from Table II that only 20% of the power input to the generator was determined to be in the plasma as measured by the calorimeter. The generation of a radio frequency plasma on the scale used in this research is, therefore, not a very efficient use of energy from a process standpoint.

Discussion of Economics

This research has successfully demonstrated that zirconium can be produced from zirconium tetrachloride in an induction plasma. It also uncovered some of the problems that might be encountered in commercial production.

The present apparatus was not designed to be an economical production unit for zirconium but rather a tool for investigating its production. The \$80.40/lb zirconium cost of production using the experimental apparatus was expected.

A first approximation of the process economics may be developed using Thorpe's (28) estimate of 1 kw-hr/lb of material separated, using a commercial-sized plasma. Using this figure, the production cost of zirconium would be 2.4¢/lb zirconium. This figure would seem to be competitive with the present process for the production of zirconium.

Verification of Thorpe's production cost estimate will require a pilot plant operation with suitable scale-up properties.

Discussion of Error Analysis

The error analysis shown in Table III indicates that the error in measuring the percent conversion is well within acceptable limits, and thus the data can be relied on.

The error analysis on the energy balance shows that the major sources of error were the power input and the energy lost to the generator cooling water. The high uncertainty in the energy to the gas (after the calorimeter) was due to the fluctuations in the gas exit temperature. This result does not, however, affect the overall analysis significantly because of the rather small nominal value of this energy.

The power into the generator and the energy lost to the generator cooling water were subject to rather large uncertainty. The error in determining the power into the generator, which was 35% of total variance, was due to the inaccuracy of the input voltmeter and ammeter. These meters were calibrated, but there was still a relatively large uncertainty in reading them. The large error in determining the energy lost to the generator cooling water, which was 62.5% of the total variance, was due to the large flow rate of the cooling water (approximately 18 gpm) and the relatively small temperature rise (1.5°F). With the large flow rate of the cooling water, a change in temperature of 0.1°F would cause a 5% change in the energy lost.

The power input and the energy losses were used to calculate the discrepancy in energy balance. The sum of the variances shown in Table III was the variance of the discrepancy in the energy balance and was calculated to be $166.4 \times 10^8 \text{ cal}^2/\text{hr}^2$. The standard deviation of this value is $\sqrt{\text{Var}}$ or $0.129 \times 10^3 \text{ Kcal/hr}$. This standard deviation of the discrepancy of the energy balance is approximately 2.5% of the nominal value of the power input. All the percent discrepancy values shown in Table II are within two standard deviations.

Considerations Associated with Plasma Production of Zr

There are a number of important considerations associated with the plasma production of zirconium. The major problem is that finely divided zirconium is pyrophoric in the air. This high reactivity meant that an inert gas such as argon had to be used. The entire reactor system had to be purified of all moisture and oxygen. To accomplish this, the system was first made completely gas tight. This was checked with a helium mass spectrometer leak detector. The system was then evacuated through a liquid nitrogen trap to remove most of the gaseous impurities in the system. A mole sieve bed was used to remove trace amounts of moisture from the argon gas. The system was then purged by the dry argon. This removed most of the contaminants from the reactor system.

The zirconium tetrachloride used as feed was hygroscopic and would, therefore, pick up moisture from the surrounding air. This moisture at higher temperatures would react with the zirconium tetrachloride to form zirconium dioxide and hydrogen chloride. The feed, therefore, had to be purified of all absorbed moisture. This was accomplished by heating the zirconium tetrachloride to approximately 200°C under a vacuum. This procedure drove off most of the moisture. The rest of the moisture reacted with the zirconium tetrachloride when the zirconium tetrachloride was sublimated. This gave a pure zirconium tetrachloride feed which did not have the heat transfer problems of solid feed.

With solid feed, heat must be transferred through a boundary layer surrounding each particle. The particle must be melted and then vaporized from the outside towards the center in order for a gaseous compound to be obtained. The gaseous material can then be raised to the dissociation temperature. This mechanism necessitates longer residence times in the plasma.

Another consideration in the plasma production of zirconium is the cold quench of the product. It is necessary that the zirconium be condensed rapidly or it will recombine with the available chlorine. In the present research, a water-cooled probe was used because it was a convenient

means of quenching and collecting the zirconium product. On a commercial scale, it would be more efficient to quench with cold gases so the zirconium product could be collected in a cyclone separator. The zirconium product would be finely divided and would need to be washed of any residual zirconium tetrachloride, then dried, and melted into ingots, all under an inert atmosphere. After the ingot is formed, it can be removed from the inert atmosphere as it forms a film of zirconium dioxide on its exterior and becomes relatively inert. In the present investigation, it was found that after the zirconium was cooled down to room temperature in the argon gas, it could be transferred to a nitrogen atmosphere without fear of combustion. At higher temperatures, the zirconium could react with the nitrogen to form zirconium nitride. The analysis for percent conversion was, therefore, carried out in a nitrogen atmosphere after the zirconium had cooled to room temperature.

CHAPTER 9

CONCLUSIONS

The following are the main conclusions of this research:

1. Zirconium can be produced in an argon induction plasma from zirconium tetrachloride.

2. Production of zirconium is not economical on the scale of this research.

3. Further research using much larger plasmas is necessary to determine the economic feasibility of plasma production of zirconium.

4. Sublimation feeding of zirconium tetrachloride into an induction plasma is a satisfactory means of introducing zirconium tetrachloride into the plasma for reaction.

5. The production rate of zirconium tetrachloride can be increased to some maximum value, without increasing the power demand, by the quenching of the product in the hottest part of the plasma.

APPENDIX I

DERIVATION OF FEED RATE FORMULA

The sublimation rate, and, therefore, the feed rate of the gaseous zirconium tetrachloride were assumed to be responsive to the temperature in the sublimation chamber. The feed rate of the zirconium tetrachloride (F) could not be measured during the run so the sublimation chamber was weighed before and after a run to determine the total zirconium tetrachloride fed (w) to the plasma reactor. The small weight loss due to water evaporation prior to a run during the feed purification was accounted for. The temperature of the sublimation chamber during a run would increase linearly to operating temperature over a finite time (t_S), then remain at the temperature until the end of the run (t_R) when the temperature would decrease linearly over a finite time (t_D). This is shown in Figure 11.

The area under the curve in Figure 11 is the total zirconium tetrachloride fed to the plasma reactor and is represented by:

$$w = \frac{[\frac{1}{2}(t_S)(F) + (t_R)(F) + \frac{1}{2}(t_D)(F)]}{[1/60 \text{ min/hr}]} \quad (a)$$

Therefore, the feed rate can be found:

$$F = 60 \frac{w(1-w_p)}{0.5(t_S + t_D) + t_R} \quad (b)$$

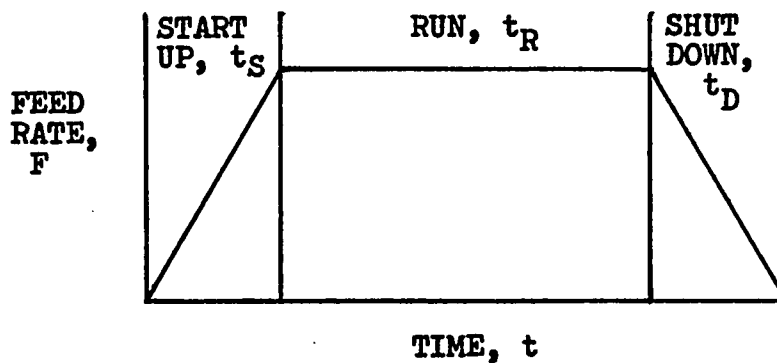


Figure 11. Feed Rate of Zirconium Tetrachloride Vs. Time.

APPENDIX II

DERIVATION OF EQUATION FOR THE CALCULATION OF THE PERCENT CONVERSION OF Zr TO ZrCl₄

The percent conversion of zirconium tetrachloride to zirconium was defined as the total amount of zirconium metal collected, divided by the total zirconium collected both combined and uncombined, times 100. The combined zirconium is calculated from the weight of zirconium dioxide derived from the zirconium chlorides as follows:

$$\text{Zr in ZrO}_2 = 0.7403 (w_{\text{ZrO}_2}) \quad (\text{c})$$

The percent conversion is therefore:

$$X\% = \frac{100 w_{\text{Zr}}}{0.7403 w_{\text{ZrO}_2} + w_{\text{Zr}}} \quad (\text{d})$$

Simplifying, this equation reduces to:

$$X\% = \frac{100}{1 + 0.7403(w_{\text{ZrO}_2}/w_{\text{Zr}})} \quad (\text{e})$$

Equation (e) was used to calculate the percent conversion of zirconium tetrachloride to zirconium in this investigation.

APPENDIX III

STATISTICAL SIGNIFICANCE OF THE PERCENT CONVERSION VS. PROBE HEIGHT

The statistical significance of the change in percent conversion with the change in probe height for the lowest feed rates will be tested by use of the Student's t-test.

The average percent conversions for the three probe heights were calculated from Table I and are shown below. The standard deviation could have been calculated for this data by using Equation f:

$$S = \sqrt{\Sigma(x_i - \bar{x})^2 / (n-1)} \quad (f)$$

This equation assumes that all conversion data were taken at the same feed rate. However, since one feed rate for the 30 cm height is almost double that of the other feed rate, it was not felt that this assumption would be valid in this case. Use of equation f would give an erroneously high standard deviation for this data. The standard deviation of 0.75% of the nominal value of the percent conversion, as determined in Table III, was, therefore, used. Thus we

obtain the following figures:

Height of Probe -	27cm	30cm	33cm
Average Percent Conversion -	61.47	72.54	89.47
Standard Deviation -	0.485	0.544	0.671

We will first consider the statistical significance of the difference between the 27 cm probe height and the 30 cm probe height. The hypothesis is that the means of the percent conversion at each probe height are the same, and we assume that $\sigma_1 = \sigma_2$. In order to use the Student's t-test, we must first calculate the pooled variance estimate using Equation g:

$$S^2 = \frac{(n_1-1)S_1^2 + (n_2-1)S_2^2}{n_1+n_2-2} \quad (g)$$

With $n_1 = n_2 = 2$, we get that $S = 2.154$. We can now calculate "t" by using Equation h:

$$t = \frac{\bar{x}_2 - \bar{x}_1}{S\sqrt{(1/n_1) + (1/n_2)}} \quad (h)$$

We find that $t = 30.852$. This value of "t" indicates that there is a significant difference in conversion at a greater than 97.5% confidence level which refutes the original hypothesis.

We will now test the statistical significance of the difference between the 30 cm probe height and the 33 cm probe height. Using the same hypothesis and assumption as above, we calculate that $s^2 = 0.36906$ using Equation g. Using Equation h, we calculate that $t = 91.747$. This value of "t" indicates that there is a significant difference in the conversion at a greater than 99.5% confidence level.

APPENDIX IV

THE STATISTICAL SIGNIFICANCE OF THE DISCREPANCIES IN THE ENERGY BALANCES BY THE STUDENT'S T-TEST

An estimate of the standard deviation of the discrepancies in the energy balances 1 through 6 can be determined by Equation i:

$$S_D = \sqrt{\Sigma(x-\bar{x})^2 / n-1} \quad (i)$$

Using the discrepancies in the energy balances found in Table II and Equation i, we get:

$$S_D = 2.84$$

Using the t-test to test the hypothesis that the average of the discrepancies is not significantly different from zero, it was found that the average of the discrepancies found in Table II was -0.217. Using this average and the standard deviation and the equation for "t", we get the following:

$$t = (-0.217-0)/(2.84/\sqrt{6}) \quad (j)$$

$$t = -0.188$$

From the t-distribution, it may be determined that a value as large as or larger than the above value of "t" can occur

through chance variation about 80% of the time. Thus, we may assume that the discrepancies are due to random error.

NOMENCLATURE

Symbol

A = constant

b = slope

C = constant

C_p = heat capacity at constant pressure, cal/gm °C

D = diameter of cold wall tube

E = energy, Kcal/hr

F = feed rate of zirconium tetrachloride, gm/hr

N_{Pr} = Prandtl Number

N_{Re} = Reynolds Number

N_{Num} = Nusselt Number

n = number of data points

S = standard deviation

T = temperature, °C

t = time, min.

"t" = Student's t-test

ν = coefficient of variation

V = linear velocity, ft/sec

W_p = fraction of weight loss during purification

W = mass flow rate, gm/hr

w = weight, gm

Symbol

X = fractional conversion

X% = percent conversion, %

x = distance from entrance

x = variable

y = variable

z = variable

μ = viscosity, centipoise

Subscripts

Ar = argon

cal = calorimeter

cw = clear reactor cooling water

D = shut down

f = feed

g = generator

gw = generator cooling water

lc = load coil

o = initial

ow = opaque reactor cooling water

R = run

r = radiation

rw = reactor cooling water

S = start up

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