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**DESIGN AND OPERATION OF A
PILOT-PLANT GETTERING SYSTEM
OF TITANIUM-METAL SPONGE FOR
REMOVAL OF NITROGEN FROM ARGON**

by

**M. L. Kyle, J. D. Arntzen,
and L. F. Coleman**

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ANL-7128

Engineering and
Equipment (TID-4500)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

CFSTI PRICES

H.C. \$ 2.00; MN. .50

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Chemical Engineering Division

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January 1966

Operated by The University of Chicago
under
Contract W-31-109-eng-38
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SUMMARY

A pilot-plant scale unit designed to demonstrate the removal of low concentrations (less than 1%) of nitrogen from large, relatively pure volumes of inert gases was constructed and operated. The system utilized titanium-metal sponge at a temperature of 900°C as the gettering agent for removal of the nitrogen impurity. Gas preheaters and regenerative heat exchangers were used to obtain better utilization of the titanium sponge and to provide heat economy.

The pilot-plant unit operated at a flow rate of 10 cfm of argon containing 100 to 1000 ppm nitrogen for a period of about 1800 hr. Operation of the system was terminated because of the deterioration of the shaft seals on the gas-circulating blower. This deterioration is believed to be the result of prolonged exposure of these seals to a low-water, low-oxygen-concentration atmosphere. No commercially available, positive-displacement blower seems capable of circulating about 10 cfm of dry gas for an extended period. However, gas circulation is not considered a serious problem since it can be accomplished by the use of diaphragm pumps or multistage centrifugal compressors.

During the 1800 hr of system operation, all equipment items except the blower performed their design functions well. The pilot-plant unit successfully demonstrated the usefulness and relative economy of titanium-metal sponge as a gettering agent for nitrogen impurity in argon. The performance of the equipment is assessed, and recommendations for design of large, inert-gas purification systems are presented.

I. INTRODUCTION

The production and maintenance of high-purity inert atmospheres present a continuing problem facing the atomic-energy industry. Inert-gas atmospheres are required when working with pyrophoric materials such as sodium, when welding refractory metals such as tantalum, when

conducting pyrochemical processes with highly reactive liquid-metal solvents, and in many other similar applications. In these cases, oxidation or nitridation resulting from contact with air would cause undesired reactions, often quite rapid, which could contaminate the desired product and render it unusable. In some cases, such as the purification and handling of sodium, the purity required of the inert atmosphere requires the virtual elimination of impurities such as oxygen, nitrogen, and water vapor.

The major contaminants in most inert-gas enclosures are oxygen, nitrogen, water vapor, and carbon dioxide resulting from air leakage into the box. For this reason, the enclosure is normally operated at a pressure slightly higher than its surroundings so that most leakage is from the enclosure to its surroundings. However, in some applications, such as the handling of radioactive materials, the enclosure must be operated at a pressure slightly less than its surroundings to prevent the escape of hazardous materials.

Both helium and argon are commonly used in these enclosures, with argon possessing the relative advantages of availability, containment (because of its higher molecular weight), and ease of pumping. Helium has the relative advantage that its lower boiling point makes cryogenic purification techniques more adaptable.

Several methods of maintaining pure atmospheres in inert-gas enclosures are commonly used. Several methods are discussed by White and Smith,¹ Walton² and Kohl and Riesenfeld.³ These methods can usually be classified into the following categories:

- (1) Continuous purging of the enclosure with a pure inert gas.
- (2) Processes in which the impurities are sorbed on activated materials such as charcoal or Molecular Sieves.* Sorption may be accomplished at cryogenic or ambient temperature.
- (3) Chemical processes in which the impurities are commonly removed by reaction with a gettering material such as calcium.
- (4) Combinations of processes such as the chemical reaction of oxygen with hydrogen to form water vapor and the subsequent sorption of the water vapor on Molecular Sieves.

Many of the chemical gas-purification processes involve a gas-solid reaction for removal of impurities. Metals are commonly used for removing oxygen and nitrogen, oxides of metals for removing hydrogen, and occasionally lower oxides for removing oxygen. These processes are generally carried out dynamically by passing the impure gas continuously through a reactor

*Trade name of the Linde Division of the Union Carbide Corporation.

containing a bed of the reactant in the form of small solid pieces. The principal controllable variables affecting such a reaction are temperature, pressure, gas flow rate, particle size and surface area of the material used, and dimensions of the bed. The operating temperature should be sufficient to provide adequate reaction kinetics but not high enough to cause problems in reactor design and operation.

The development and utilization of large inert-gas enclosures have led to interest in purification systems capable of removing impurities from large volumes of inert gas. The leak rate of the enclosure* and the required purity of the atmosphere are the major factors in determining the economics of the various purification techniques. For large-volume systems of low-impurity levels, chemical gettering methods are usually competitive. In systems of this type, water vapor is normally removed by sorption on activated sorbents such as Molecular Sieves. Oxygen is removed by reaction with copper (600°C) or by similar relatively low-temperature gettering operations. The removal of the nitrogen impurity usually presents a greater problem since it is normally present in greater concentration than oxygen or water vapor and is chemically less reactive.

Several gettering materials are available for use in the removal of nitrogen from inert gases. The most common of these are calcium, uranium, and titanium-zirconium alloys. Recently, interest has been expressed in the use of titanium as a nitrogen-gettering material. This interest has stemmed from the fact that titanium possesses several advantages over those gettering materials now commonly used. Titanium-metal sponge, a high-surface-area form suitable for gettering operations, can easily be obtained at a relatively low cost and requires no pretreatment before use as a gettering material. Both the oxide and nitride reaction products of titanium are non-pyrophoric and can easily be handled in air. The handling of titanium is also greatly facilitated because neither titanium nor its reaction products are toxic.

To investigate the possible usefulness of titanium as a gettering material for nitrogen impurities in inert gases, two sets of experimental equipment were constructed: (1) equipment for a study of the kinetics of nitrogen removal from argon on hot titanium sponge, and (2) a pilot plant for obtaining overall process-performance data and information on component reliability.

This report contains the data on the design and operation of the pilot-plant system. A report on the kinetics of the titanium-nitrogen reaction will be issued as ANL-7167.

*For a particular type of enclosure, the leak rate is normally directly proportional to the enclosure volume.

II. DESIGN CRITERIA

The pilot-plant scale unit for nitrogen removal from argon gas was designed and built to provide information on component design and reliability for large-capacity purification systems. Only the removal of nitrogen was demonstrated because a system of this type would probably use separate systems for water and oxygen removal. Concurrent oxygen and nitrogen removal is not possible with titanium sponge because oxygen inhibits the titanium-nitrogen reaction^{4,5,6} resulting in poor nitrogen removal.

In this system, metal sponge* was chosen as the form of the titanium gettering material because of its previously mentioned advantages (i.e., high surface area, no need of pretreatment, and availability at low cost) over other available forms of the metal.

A circulation rate of 10 scfm was chosen for demonstration of the purification system. This system was designed to be a prototype of larger systems, and it was felt that the design, equipment, and operational problems encountered in the 10-scfm system would be comparable to those encountered in larger systems.

A reaction temperature of 900°C was chosen because previous work⁷ on the titanium-nitrogen reaction indicated an appreciable increase in the rate of reaction with increasing temperature. However, as the temperature of the reaction is increased, containment of the titanium sponge becomes more difficult.

A reaction temperature of 900°C is near the highest safe operating temperature in readily available materials of construction. (Most high-temperature containment materials contain nickel, and a titanium-nickel liquid phase exists around 955°C.⁸)

Gas preheaters were used to bring the reacting gas up to 900°C before entering the reaction vessel in order to obtain better utilization of the titanium sponge (higher average conversions to the nitride). Regenerative heat exchangers provided heat economy. Both the gas preheaters and regenerative heat exchangers are not economical on systems of this size (10-scfm circulation rate), but data on their performance were desired since they might be required for larger systems.

*See Appendix A for typical analysis.

III. DESCRIPTION OF PURIFICATION SYSTEM

A. General Description

The purification system as finally constructed is shown schematically in Fig. 1 and by artist's conception in Fig. 2.* It is essentially a closed loop of circulating argon, with a nitrogen impurity introduced at a known and constant rate.

108-7166

Fig. 1. Schematic Diagram of Pilot-plant Equipment for Removal of Nitrogen from Argon

The direction of gas flow through the titanium bed was periodically reversed in order to store and subsequently recover sensible heat in the pebble-bed regenerative heat exchangers. This flow reversal should also have produced a higher average conversion of the titanium sponge to titanium nitride than could be obtained in unidirectional flow, since the average concentration gradient between the gas and the gettering agent was higher.

Fig. 2
Artist's Conception of Pilot Plant

108-7356

* A complete description of the system components is contained in Appendix B.

The flow pattern through the loop was as follows (See Figs. 1 and 2): The gas was circulated from a surge tank (11 cu ft) by means of a rotary-lobe blower, the flow rate being controlled by a butterfly valve on the blower inlet and by adjustment of blower speed. The pressure drop across a calibrated orifice plate was used to determine the flow rate. The gas passed through a four-way valve and into one of the two pebble-bed regenerative heat exchangers. These heat exchangers were made of Type 310, Schedule 80 stainless-steel pipe, 8-in. nominal OD and 48-in. length, filled with 1-in.-OD chrome-steel balls.* The heat exchangers were used alternately to cool the reacting gas and store heat on the discharge side of the titanium sponge bed and to preheat the reacting gas on the inlet side of the sponge bed.

To decrease the heat loss of the pebble-bed regenerative heat exchangers to their surroundings, so that maximum heat could be stored during the heating cycle and later recovered, insulating jackets were used on these vessels. These jackets were hollow right-circular cylinders ($8\frac{3}{4}$ -in. ID x 12-in. OD to fit over the Type 310 stainless-steel pipe containing the steel balls) fabricated of Type 304 stainless steel. The annulus of these jackets was filled with 600-mesh silicon carbide powder to provide insulation. This type of insulation was chosen because the high-temperature end of the exchanger loses most of its heat by radiation; the usefulness of silicon carbide in a similar application is described by Mark.⁹ This type insulation proved very effective and is discussed on pp. 16-17.

After leaving a pebble bed, the gas passed into one of two trickle heaters (each connected to one of the pebble-bed heat exchangers) located in a large resistance-heated furnace. The trickle heaters were 8-in.-OD by 20-in.-high pipes filled with steel rods (0.25-in. OD by 1-in. long). The trickle heaters were designed to bring the reacting gas up to reacting temperature (900°C) before the gas entered the titanium sponge bed. The titanium sponge bed was contained in a Hastelloy "X" pipe 8-in. OD by 26 in. high, lined with Type 316 stainless steel. The sponge bed consisted of approximately 30 lb of titanium sponge (screen sizes from 0.5 to 0.033 in.). Figure 3 is a photograph of the titanium-sponge-bed vessel and trickle heaters inside the furnace cavity. Figure 4 is a photograph of the other equipment items.

The gas then passed through the second trickle heater (now nonenergized) and into the second pebble-bed regenerative heat exchanger, where the gas was cooled and the heat content of the gas stored for future use. The gas then flowed through the four-way valve into a water-cooled heat exchanger, where its temperature was reduced to room temperature, and then into the surge tank for recirculation. A metered flow of nitrogen was added

*Appendix C contains the methods of calculation used to size major equipment items.

**A product of Haynes Stellite Division of the Union Carbide Corporation.

Fig. 3

Titanium Sponge Reaction Vessel and Two Trickle Heaters Located in Furnace Cavity

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108-6790A

Fig. 4. Photograph of Pilot-plant Equipment. (The titanium sponge bed and the two trickle heaters are contained in a furnace (not visible) located above the pebble-bed heat exchangers.)

to the argon stream between the gas cooler and the surge tank. Makeup argon was also added at this point.

The position of the four-way valve controlling the direction of gas flow through the purification system was normally operated on a time cycle. At a predetermined time, the valve position changed and reversed the direction of gas flow through the pebble beds, trickle heaters, and titanium-sponge vessel.

The commercial blower used to circulate the argon was designed to prevent air and oil leakage into the circulating gas stream. The blower had two ductile-iron three-lobe rotors with integral shafts. Spring-loaded carbon face seals with lapped mating rings and high-temperature O-rings were used on the rotor shafts to prevent air and oil leakage into the blower. The blower was designed to operate at inlet pressures of 0 to 2 psig and, by variation of the blower speed, at outlet pressures of 0 to 12 psig.* The system pressure drop was 1.5 psi at 10 scfm.

B. Materials of Construction

The materials of construction of the system components varied throughout the loop and were selected on the basis of several criteria, the major ones being:

1. Oxidation resistance to air at elevated temperatures.
2. Desirable physical properties at elevated temperatures.
3. Compatibility with titanium sponge at operating temperature.
4. Cost.
5. Availability.

Because of these considerations the following materials of construction were selected:

1. Conventional steel, brass, copper, etc. for those items in the system exposed to argon, nitrogen, and air at room temperature. This included those equipment items located in the gas stream from the exit of the gas cooler to the entrance of the four-way valve and included the surge tank, flow control valve, blower, and orifice assembly. Piping in this part of the system was conventional mild steel.

2. Types 304 and 316 stainless steel for those parts of the system exposed to air at temperatures between ambient and 200°C. This included the piping from the exit of the pebble-bed regenerative heat exchangers to the gas cooler, and the body material of the four-way valve.

*Appendix D contains the blower performance curves.

3. Type 310 stainless steel for most parts of the system exposed to air at temperatures between 200 and 900°C. Type 310 was chosen because of its availability and good combination of high-temperature strength and air-oxidation resistance. The regenerative heat exchangers and all system piping located in the furnace and between the furnace and the heat exchangers were Type 310 stainless steel.

4. Hastelloy "X" for applications requiring high strength at 900°C. This included the titanium-sponge reactor vessel and the two trickle heaters.

5. Type 316 stainless steel as a lining material for the titanium sponge vessel because previous work¹⁰ had indicated a good compatibility with titanium sponge at 900°C.

C. Control System Description

The cycle time of the system (time between reversals in the direction of gas flow) was controlled by a timer adjustable over a range of 1 to 10 hr. The timer actuated the four-way valve to reverse the flow direction. The cycle time was adjusted to obtain maximum heat storage in the regenerative heat exchangers without allowing the temperature of the gas returning to the four-way valve to rise above 200°C.

The position of the four-way valve was used to activate and deactivate the trickle-heater control circuits. Switches on the shaft of the valve selectively activated the trickle-heater control circuit on the gas-inlet side of the titanium sponge vessel and deactivated the trickle heater on the gas-exit side.*

If the temperature of the gas leaving either pebble-bed heat exchanger exceeded the safe temperature (200°C) for operation of the four-way valve, the automatic timer control was dropped out of the circuit and flow reversal control was taken over by temperature controllers monitoring the temperature of the gas returning to the four-way valve.

Appropriate safety devices were employed to protect against overheating of the titanium bed, overheating of the four-way valve, rise in temperature of the gas leaving the water-cooled heat exchanger, leakage of the water-cooled heat exchanger (permitting water to enter the system), overpressure of the system, and loss of system pressure. Any one of these devices would permanently shut down all system functions and leave the system under a 2-psig argon gas blanket.

*Appendix E contains schematic diagrams of the control circuits.

IV. OPERATION OF PURIFICATION SYSTEM

A. General

The pilot-plant loop operated at 900°C for 1800 hr in increments of 1000, 650, and 150 hr. The shutdown at 1000 hr was planned for recharging of the titanium sponge bed and inspection of equipment components. The shutdowns at the end of the additional 650 and 150 hr were necessitated by failure of the system blower, resulting in oil leakage into the circulating loop. During operation of the loop, all components and instrumentation except the circulating blower performed their design functions well, and no difficulties with loop operation were noted.

B. Operational Procedures

Before operation, the entire system was degreased with Freon-13* and leak-tested with helium under both vacuum and pressure conditions by means of a mass-spectrometer leak detector. After the titanium sponge bed had been loaded and the system leak-tested, the trickle heaters and titanium bed were heated to approximately 500°C for about 16 hr with the entire system under vacuum (29 in. Hg). This provided adequate time to degas the titanium sponge and gave a final check on leak tightness. The system was pressurized to approximately 1 psig, and the blower was turned on to start gas circulation. The blower speed and butterfly valve were adjusted to obtain the desired flow rate of 10 cfm. The furnace and trickle-heater controllers were set at appropriate temperatures to insure that the temperatures of the titanium sponge bed and entering gas stream were the desired 900°C. The cycle time of the direction of gas flow was set at 30 min and slowly increased until a maximum cycle time was obtained. This slow rate of increase in cycle time also permitted the operating temperatures of the pebble-bed heat exchangers to stay roughly in balance so that one of them did not reach its operating temperature while the other one was relatively cold.

Nitrogen was introduced at a constant flow rate. The flow rate was chosen to provide the impurity level for the particular run. The system ran continuously while samples of the circulating gas stream were taken upstream of the titanium bed. These samples were "grab" gas samples of approximately 100 ml and were analyzed for nitrogen by gas chromatography. This analysis used Molecular Sieves for the nitrogen concentration media and a calibrated thermal conductivity cell as the detection instrument. The general procedures used are outlined by Jeffery and Kipping.¹¹

Gas samples were normally taken daily except when breakthrough was expected, in which case they were taken at roughly 4- to 8-hr intervals.

*Trade name of E. I. duPont de Nemours and Co., Inc.

Breakthrough was determined by an increase in the nitrogen concentration of the circulating gas. When breakthrough occurred, the nitrogen input to the system was terminated. At the conclusion of the run, the titanium bed was opened and samples of the titanium were taken at approximately six different levels in the bed.

The nitrogen concentration of each sample from the titanium sponge bed was determined by a semimicro-Kjeldahl analysis. The general method is outlined by Thompson.¹² However, complete dissolution of the highly nitrified titanium (above approximately 2 w/o nitrogen) could not be realized when the recommended procedure was used. Complete dissolution was achieved by use of the analytical procedures¹³ outlined in Appendix F.

C. Performance of Equipment

Continuous operation of the pilot-plant loop began on March 13, 1964, and continued until 1000 hr of operation had been accumulated. At that time, the unit was shut down for inspection and replacement of the titanium sponge bed. During this initial period of operation of the loop, all components and instrumentation performed their functions well.

Figure 5 is a schematic diagram of the loop as it was constructed. The numbers on the figure indicate typical temperature measurements taken throughout the loop near the completion of a flow cycle (shortly before changing the position of the four-way valve) thereby reversing the direction of flow through the hot loop.

108-7971

Fig. 5. Temperature Pattern in Pilot Plant. (Approximate temperatures prevailing throughout the system at the completion of a flow cycle are given.)

The pressure drop around the circulating loop was about 1.5 psi at a flow of 10 scfm. The temperature rise of the blower was about 30°C, well under its rated maximum of 75°C. The blower operated satisfactorily during the run. Before the start of the test, the blower shaft seals were tested for integrity with a helium-leak detector and found to be sound. At 500 hr, these seals were retested and appeared to be satisfactory. Some tendency for the flow rate to fall off during the initial 300 hr of blower operation was noted. The blower speed was intermittently adjusted to maintain the 10-scfm circulation rate. This deviation in flow rate at constant blower speed was attributed to the combined effects of sintering of the titanium bed and break-in of the blower. After this initial 300-hr period,

stant blower speed was attributed to the combined effects of sintering of the titanium bed and break-in of the blower. After this initial 300-hr period,

the circulation rate remained relatively constant at constant blower speed. During the remainder of the system operation, the blower operated at 800 rpm, slightly less than 25% of its 3500-rpm rating.

The use of Teflon* as the gasketing material in the four-way valve limited its maximum temperature to 200°C. This valve operated at temperatures up to 200°C during short-term tests, but its normal operating temperature was 70-90°C. The valve and its electric actuator, controlled by the system cycle timer, operated as desired during the system testing. Cycle times of 4, 5, and 6 hr were employed with the system. The normal cycle time of 4 hr resulted in an 85°C temperature of the four-way valve. A 5-hr time cycle increased the valve temperature to 130°C. A maximum cycle time of about 6 hr was obtainable with this system before the temperature of the four-way valve exceeded its rated 200°C maximum operating temperature.

If the exit-gas temperature from the downstream regenerative heat exchanger exceeded a certain set point before the timer was ready to change the valve position, the cycle timer was dropped out of the system and the valve position was controlled by instruments monitoring exit-gas temperatures. This feature was successfully demonstrated. The change to control of valve position by exit-gas temperatures did not materially affect operation of the loop, and it was concluded that operation by this method is acceptable.

Fig. 6. Temperature-time Relationship of High-temperature End of Pebble-bed Regenerative Heat Exchanger

The pebble-bed regenerative heat exchangers were designed to preheat the gas on the entrance side of the titanium bed and cool the gas on the exit side. The heat previously stored on the discharge side of the titanium bed was utilized after reversal of the direction of flow by the four-way valve. These beds were designed to produce a 700°C axial gradient across the steel-ball packing. Gradients as high as 650°C were obtained, the normal gradient being about 500°C. Figure 6 shows typical temperature-time relationships at the high-temperature ends of the heat exchangers. These measurements were taken about 4 in. below the top of the steel-ball packing and are about 50-75°C lower than those at the top of the exchanger. These

*Product of E. I. duPont de Nemours and Co., Inc.

packing temperatures may also vary slightly from the actual gas temperature at these points. As can be seen from Fig. 6, the temperature at these points cycled between 600 and 300°C. The difference in temperature between the symmetrical beds was probably caused by the heating characteristics of the overhead furnace containing the titanium beds and trickle heaters. In this furnace, a 20-30°C temperature variation existed between the top and bottom of the furnace. This gradient was unavoidable with the furnace design, but was not considered significant to the overall operation of the loop.

The overall efficiency of the pebble-bed regenerative heat exchangers was calculated by two independent methods. The heat input to a pebble bed was calculated to be about 52,000 Btu during a 4-hr heating cycle. The estimated heat loss to the surroundings was 10,500 Btu during a 4-hr cycle, based upon the measured outside temperature of the pebble-bed insulating jacket and the assumption of an overall heat-transfer coefficient to the surrounding air of 2.1 Btu/hr ft² °F (temperature difference 100°F).¹⁴ The resultant efficiency of 77% agreed well with the 79% efficiency obtained by a graphical integration comparing the heat increase of a pebble bed during a heating cycle with the heat loss to the circulating gas stream during a cooling cycle. This heat economy of the pebble-bed regenerative heat exchangers is thought to be high and could be improved by additional insulation of the vessels.

The trickle heaters performed as designed. The wall temperature of these heaters varied between 900 and 1050°C to preheat the gas entering the titanium bed to 895-905°C.

If present, water vapor and oxygen were also removed by reaction with titanium sponge. The concentration of water vapor in the circulating gas remained at a very low level during the initial 1000 hr of operation. For the first 650 hr, the water-vapor concentration (as measured by an electrolytic water analyzer) was less than 1 ppm, after which it rose slowly to a final concentration of 13 ppm. This slow rise in water concentration occurred long after the titanium bed had lost its effectiveness for nitrogen. These results suggest that titanium sponge remains effective for water-vapor removal even after its effectiveness for nitrogen has been lost.

Inspection of the loop at the completion of 1000 hr of operation disclosed no significant component deterioration, except for the expected slight air oxidation of the external surfaces of the Hastelloy "X" and Type 310 stainless-steel vessels and pipes which were exposed to air at elevated temperatures.

After 1000 hr of operation, the cover of the titanium sponge vessel was removed and the vessel was recharged with virgin sponge. Sintering of the initial sponge charge was minor, and the sponge was easily removable. This vessel was designed to be recharged by removal of the cover by

grinding off the top weld, replacing the titanium sponge, and rewelding the top. Appendix B presents additional information on the design of this vessel.

Leak testing of the blower after 1000 hr of operation disclosed a small leak on the outboard-shaft seal. This leak was small enough that it did not warrant dismantling of the blower to rework the seal. The gas inside the blower was at a pressure of approximately 3 psig at this point; therefore any gas leakage would have been outleakage from the blower.

Inspection of the heating elements used to supply additional heat to the trickle heaters (over that supplied by enclosing furnace) disclosed several broken leads at the junction between the heating element and the supply wiring. These junctions were made in the furnace itself, and it was obvious that electrical connections in the hot zone were unsatisfactory. When the loop was constructed, the trickle heaters were deliberately made larger than the calculated requirements (see Appendix C). This compensated for end effects and oversimplifications in the assumptions made in the heat-transfer calculations. After experience had been obtained in trickle-heater operation, it was felt that the oversizing would permit operation without the heating elements. Consequently these auxiliary heaters were removed, and the pilot-plant loop was then operated without supplementary heating of the trickle heaters. The furnace temperature was adjusted to insure a reacting gas temperature of 900°C.

The loop was restarted, and nitrogen gas at a concentration of 100 ppm in argon was introduced. Shutdown of the loop after 650 hr of continuous operation was necessitated by an indicated failure of the titanium sponge bed to continue to remove nitrogen. Inspection of the loop after shutdown revealed the presence of lubricating oil in the system piping. This oil was introduced by the failure of a blower-shaft seal. The small leak, discovered after 1000 hr of operation, enlarged during this period allowing oil to enter the circulating stream.

Subsequent dismantling and inspection of the blower revealed a deterioration of the upper-shaft seals with no apparent damage to the lower seals. In an attempt to prevent these difficulties from recurring, several modifications of the blower were made. These modifications consisted primarily of (1) increasing the compression in the blower-shaft seals from 7 to 10 psi; (2) locating the blower on its side for better lubrication of the upper-lobe seals, and (3) increasing the speed of the blower for better lubrication and increased gas pressure on the face seals. It was hoped that these modifications would permit sustained operation of the blower without seal failures. The loop was restarted and operated for 152 hr under service conditions. Operation was terminated because of an additional seal failure. At this time it was decided to discontinue operation of the pilot-plant loop because of the gas circulation problem with the existing equipment.

The failure of the blower's graphite face-seals is attributed to their operation in a low water- and oxygen-concentration atmosphere. Under these conditions, graphite loses its self-lubricating properties, and the wear rate becomes appreciable. This property of graphite is discussed by Carson and Morris¹⁵ and Savage.¹⁶ These face-seals were lubricated by oil on their back side, and it was hoped that this lubrication would prevent the high wear rate. The performance of the blower indicated that this "back-side" lubrication was not effective. It is concluded that face-seals used in this blower design must be resistant to deterioration in a water-free and oxygen-free atmosphere, and standard grades of graphite are not suitable in this application.

It is believed that the gas circulation problem could be solved by using a multistage centrifugal compressor or a diaphragm pump. The performance of a 200-scfm multistage centrifugal compressor is currently being demonstrated in the purification system for the EBR-II Fuel Cycle Facility.¹⁷ Further demonstration of the ability of various compressor designs to circulate dry gas was not considered a part of this project.

The argon purification system operated about 1800 hr at 900°C and demonstrated removal of nitrogen from argon on a 10-scfm scale. During operation, all components, except the blower and the trickle-heater elements, operated without difficulty. It is believed that this system adequately demonstrated component design and operation for large-scale argon purification units. Nearly all difficulties connected with operation of the loop stemmed from the inability of the blower to circulate dry gas without the introduction of oil or air into the gas stream.

D. Removal of Nitrogen from Argon

The primary purpose in operation of the system was to obtain overall equipment-performance data and to evaluate component design and reliability. The kinetics of the titanium-nitrogen reaction were studied in a separate project.

During the initial period of operation, the qualitative performance of the titanium sponge bed as a nitrogen-gettering agent was difficult to assess because the bed was exposed to both air and water-vapor contamination during start-up operations. This contamination resulted from a small leak in the water-concentration monitoring system. Both of these contaminants decrease the reactivity of titanium with nitrogen. After discovery and repair of the leak, operation of the system was continued for 1000 hr, even though nitrogen was not effectively removed for much of this time. It was felt that the information desired on component design and reliability would not be significantly affected by the absence of the nitrogen impurity.

After discovery and repair of the small air leak, the loop was brought up to reacting temperature, and argon containing approximately 1000 ppm nitrogen was introduced into the loop. After 4 hr of operation, the nitrogen concentration was reduced to 650 ppm to permit a longer running time before breakthrough. Breakthrough in this case was defined as the time when the nitrogen concentration of the gas circulating in the loop was detectably higher than the constant input concentration. Samples to determine nitrogen concentration in the circulating gas stream were taken at 24-hr intervals and analyzed for nitrogen. For about 72 hr, the nitrogen concentration in the circulating gas stream remained essentially constant. Checks at 95 and 120 hr indicated that the nitrogen concentration was slowly increasing to 1500 ppm. Analysis of the gas stream at 144 hr showed nitrogen to be present in concentration of about 12%. At this time it was concluded that the titanium sponge was no longer useful in removing nitrogen from the argon stream, and the nitrogen input was stopped. A check at 166 hr indicated that all nitrogen present in the loop had been removed. At 168 hr, addition of nitrogen flow was resumed. The gas concentration quickly increased to 1.5%, showing that the titanium sponge was only slowly removing the nitrogen. The nitrogen input was shut off, and the run was continued to obtain information on component operation. The nitrogen input rates and measured compositions are represented graphically in Fig. 7.

Fig. 7. Removal of Nitrogen from Argon in Pilot Plant

After 1000 hr of operation, the titanium-metal sponge was removed from the loop and submitted for analytical determination of the amount of reacted nitrogen. Results are presented in Table I.

The periodic reversal of flow through the titanium bed produced the expected conversion profile, the lowest conversion occurring near the center of the bed. The average conversion was about 42%. If 50% conversion of titanium to the nitride could be obtained in plant operation, the cost of gettering material for a titanium system would be about \$10 per pound of nitrogen removed. This cost is about 60% of that for a similar calcium system and 7% of that for a uranium system, based on 50% conversions to Ca_3N_2 and UN_2 . Thus the results of this run are very encouraging.

The loop was restarted with a gas concentration of 100 ppm nitrogen in argon. Shutdown of the loop after 650 hr of continuous operation was required because of oil leakage into the circulating gas stream. The oil contamination of the gas stream resulted in poisoning of the titanium sponge,

causing the titanium bed to prematurely lose its reactivity for nitrogen. Before poisoning of the titanium, for about 600 hr, the nitrogen concentration of the circulating gas remained essentially constant, indicating that all nitrogen being added was effectively removed by the titanium sponge.

Analyses of samples from this bed are presented in Table II.

TABLE I. Conversion of Titanium to Titanium Mononitride in the Pilot Plant, 1000-hr Operation

<u>Conditions</u>	
Temperature:	900°C
Weight of titanium sponge:	25 lb
Circulation rate:	10 scfm
Length of exposure and gas composition:	150 hr to 650 ppm N ₂ in argon, 850 hr in argon
Bed Position ^a	Conversion to TiN, ^b %
Top	44.0
3-in. depth	46.9
6-in. depth	35.4
9-in. depth	35.0
12-in. depth	45.1
Bottom	46.5
Average	42.2

^aBed approximately 14 in. high.

^bComputed assuming the following reaction: $\text{Ti} + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN}$.

TABLE II. Conversion of Titanium to Titanium Mononitride in the Pilot Plant, 575-hr Operation

<u>Conditions</u>	
Temperature:	900°C
Weight of titanium sponge:	28 lb
Circulation rate:	9.8 scfm argon
Length of exposure:	575 hr
Gas composition:	100 ppm N ₂ in argon
Bed Position ^a	Conversion to TiN, ^b %
Top	34.73
3-6-in. depth	28.69
6-9-in. depth	24.57
9-12-in. depth	26.14
Bottom	40.00
Weighed average	29.81

^aBed height: 13.5 in. of titanium.

^bComputed assuming the following reaction: $\text{Ti} + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN}$.

The concentration profile in the bed was as expected. Even the average conversion of about 30% is encouraging since this value represents a cost of titanium gettering material of about \$16 per pound of nitrogen removed. It is believed that if the poisoning of the titanium by the oil had not occurred, the average conversion would have been higher and the economics even more favorable. It appears that the titanium process can compete economically in the cost of the gettering material at conversions of around 30%. Other factors such as the operating temperature, pyrophoricity, and materials of construction also affect overall economics, but at present it appears that the titanium process possesses economic and operational advantages over the gettering materials now commonly used.

V. CONCLUSIONS AND RECOMMENDATIONS

Operation of this loop has led to the following conclusions and recommendations:

a. Titanium-metal sponge possesses considerable potential as a gettering agent for the removal of nitrogen impurities in inert atmospheres.

b. The presence of oxidizing gases such as oxygen, water vapor, and carbon dioxide inhibit the titanium-nitrogen reaction, and if the gas stream to be purified of nitrogen contains such impurities, they must be removed before they get to the titanium gettering system if optimum utilization of the titanium is desired.

c. If an oxygen getter such as copper at 600°C is used, this same vessel can serve as a gas preheater for the titanium system.

d. In plant-scale operation, the cost of titanium sponge is estimated to be about \$12 per pound of nitrogen removed if 40% of the metal can be converted to the mononitride. A conversion of this magnitude is considered feasible and has been demonstrated.

e. A critical component in the purification system is the gas-circulating blower. The blower must circulate gas at a reasonable discharge pressure (around 2 psig) because of the pressure required to circulate the gas through the titanium bed. General leak-tightness of the blower or a leak-tight blower enclosure is also required to avoid air and water-vapor contamination of the circulating gas. It is recommended that the system blower be located before the water- and oxygen-removal components of a purification system so that any air contamination introduced into the circulating gas would be removed before reaction with titanium sponge.

f. Reversal of the direction of gas flow through the titanium bed produces the desired effect of permitting a higher average conversion of the sponge before nitrogen breakthrough.

g. Additional equipment items such as regenerative heat exchangers and gas preheaters are effective, but their capital cost must be compared to the projected heat and titanium savings to determine if such installations are economical.

APPENDIX A

Approximate Composition of Titanium-Metal Sponge

<u>Element*</u>	<u>Weight Percent</u>
Ti ^a	99.3 min
Fe ^b	0.05
N ₂ ^c	0.004
O ₂ ^d	0.02
Mg ^b	0.08
C ^a	0.02
Cl ^a	0.12
H ₂ ^a	0.005
Mn ^a	0.5
Si ^a	0.04
H ₂ O ^a	0.08

*All other metallic impurities below mass spectrographic level of determination.

^aManufacturer's specification.

^bBy mass-spectrographic analysis.

^cBy semimicro-Kjeldahl analysis.

^dBy Vacuum-fusion analysis.

APPENDIX B

Equipment Items Used in Pilot-plant System

The equipment items used in the pilot-plant system include the commercial equipment listed in Table III and the pebble-bed regenerative heat exchanger, the trickle heater, and the titanium sponge bed (diagrams of which are shown in Figs. 8, 9, and 10, respectively):

TABLE III. Commercial Equipment Used in Pilot-plant System

Quantity	Description	Use
1	M-D three-lobe, rotary, positive-displacement blower, Model SP-51-3202.5 with 3-hp, three-phase motor, variable-speed drive, flow range 0-50 scfm at 0-2 psi differential	Gas circulation
1	Keystone butterfly valve, resilient-seated, size for 1-in. pipe	Flow control
1	Standard orifice assembly, orifice size 0.67 in.	Flow measurement
1	Dwyer Magnahelic Pressure gauge, 0-8-in. water pressure, differential	Measurement of pressure drop across orifice
2	Taylor Pulsation Damper Model 58S104	Damping pressure fluctuations in lines across flow-measuring orifice
1	Tuflin, Type 316 stainless steel, four-way plug valve, Model 47, flow reversal with 90° rotation, Teflon-seated; electric actuator, Tuflin Model 4210	Flow reversal
1	Resistance furnace, 40 kW, 440 V, three-phase, capable of maintaining equipment inside at 1200°C. Heating chamber 30 in. square x 36 in. high	Titanium bed and trickle heater furnace
1	Graham "Panaflo" heat exchanger, water-cooled, size 4810; approximately 4 ft ² of heat-transfer surface area	Cooling gas leaving pebble bed
1	Brooks Sho-rate rotameter, 150-mm scale, tube R-2-15-AAA, glass float, factory-calibrated, flow range 0-53 cc/min N ₂	Nitrogen addition

TABLE III (Contd.)

Quantity	Description	Use
1	Sears glass-lined, 82-gal water tank, Model W42H3179N	Surge tank
1	1B26 Cuno-Klean filter for 1-in. pipe, 5-micron pore size	Protecting blower against dirt particles
1	Model W Electrolytic Water analyzer, Type VAC, duPont Type P ₂ O ₅ cell; Manufacturers Engineering and Equipment Corp.; range 0-1000 ppm water	Gas-stream monitoring for system leakage and protection against heat-exchanger failure
1	Flexopulse repeat cycle timer, Model H. G. 98A6, Eagle Signal Co.; max repeat cycle time, 10 hr	Cycle time control
5	Honeywell Versatronik indicating and controlling potentiometer, Type R7161A, 0-1100°C Type K thermocouple, thermocouple-burnout protection and adjustable proportioning band	Furnace control, trickle-heater control, and cycle control by temperature
1	Honeywell 24-point strip-chart recorder, 0-1200°C, Type K thermocouple	Measuring and recording system temperatures
4	Simply Trol Meter Relay, 0-1200°C, Type K, Assembly Products Inc.	Overtemperature safeties
100 lb	Titanium-metal sponge, Grade A-1, particle size 0.5 to 0.033 in., bulk density, 60-90 lb/ft ³ analysis as listed in Appendix A	Gettering agent

Note: The complete engineering drawings of the components of this system are contained in Argonne National Laboratory drawing No. CE-5043 (Argon Purification System).

Fig. 8. Pebble-bed Regenerative Heat Exchanger

Fig. 9. Trickle Heater

Fig. 10. Titanium Sponge Bed

APPENDIX C

Determination of Size of Pebble-bed Regenerative Heat
Exchangers and Trickle Heaters

1. Pebble-bed Size and Temperature Profile

a. Determination of Size of Pebble-bed Regenerative Heat
Exchangers

The size of the two identical pebble-bed regenerative heat exchangers was determined by a trial-and-error calculation. An initial diameter and height of the packed bed were selected, and the cycle time (i.e., length of time of unidirectional gas flow through the exchanger) of the system was computed. This computation requires the selection of several design criteria, which are outlined below. The calculation presented shows the approximate cycle time that could be obtained in the heat exchanger used in this study (8-in. ID x 48-in. length).

(1) Design Criteria

- (a) Inlet-gas temperature during a bed-heating cycle = 900°C
- (b) Outlet-gas temperature during a bed-heating cycle = 200°C
- (c) Gas flow = 10 scfm of argon
- (d) Heat-exchanger size = 8-in. ID x 48-in. length
- (e) Heat-exchanger packing = 1-in.-OD chrome-steel balls

(2) Values Used in Computation

- Specific surface area of 1-in. steel balls, $a_v = 65 \text{ ft}^2/\text{ft}^3$ (Ref. 20)
- Void volume of randomly packed spheres, $f = 0.38$ (Ref. 21)
- Heat capacity of argon at 600°C, $C_p = 0.125 \text{ Btu/lb-}^\circ\text{F}$ (Ref. 22, p. 198)
- Heat capacity of steel at 600°C, $C_p = 0.16 \text{ Btu/lb-}^\circ\text{F}$ (Ref. 22, p. 77)
- Viscosity of argon at 600°C, $\mu = 0.118 \text{ lb/hr-ft}$ (Ref. 22, p. 200)
- Thermal conductivity of argon at 600°C, $k = 0.0226 \text{ Btu/hr-ft-}^\circ\text{F}$ (Ref. 22, p. 197)

Prandtl number of argon at 600°C, $\frac{\mu C_p}{k} = N_{Pr} = 0.66$
(Ref. 22, p. 201)

Diameter of steel ball = 1 in.

Height of bed, $x = 4$ ft

Diameter of bed, $D = 0.667$ ft

Flow rate of argon, $w = 10$ scfm = 62.1 lb/hr

Density of chrome steel, $\mu = 490$ lb/ft³

- (3) Calculation of Superficial Mass Velocity of Fluid, G_0 ,
lb/hr-ft²

$$\begin{aligned} G_0 &= \frac{w}{A} \\ &= \frac{62.1 \text{ lb}}{\text{hr}} \times \frac{4}{\pi(0.667)^2 \text{ ft}^2} \\ &= 178 \text{ lb/hr-ft}^2. \end{aligned}$$

- (4) Estimation of Overall Coefficient of Heat Transfer, h ,
Btu/hr-ft²-°F

$$\begin{aligned} h &= C_p G_0 \times 1.06 \left[\frac{D_p G_0}{\mu} \right]^{-0.41} [N_{Pr}]^{-2/3} \text{ (Ref. 19, p. 295)} \\ &= \frac{0.13 \text{ Btu}}{\text{lb } ^\circ\text{F}} \times \frac{178 \text{ lb}}{\text{hr ft}^2} \cdot 1.06 \left[\frac{(1/12)(178)}{0.118} \right]^{-0.41} (0.66)^{-2/3} \\ &= 4.3 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F} \end{aligned}$$

- (5) Calculation of Volumetric Heat Transfer, h_v

$$\begin{aligned} h_v &= h a_v \\ &= \frac{4.3 \text{ Btu}}{\text{hr-ft}^2\text{-}^\circ\text{F}} \times \frac{65 \text{ ft}^2}{\text{ft}^3} = 280 \text{ Btu/hr-}^\circ\text{F-ft}^3 \end{aligned}$$

- (6) Calculation of Volumetric Heat Capacity of Steel, C_{vs}

$$\begin{aligned} C_{vs} &= C_p \rho = \frac{0.16 \text{ Btu}}{\text{lb-}^\circ\text{F}} \times \frac{490 \text{ lb}}{\text{ft}^3} \\ &= 78.4 \text{ Btu/ft}^3\text{-}^\circ\text{F} \end{aligned}$$

(7) Estimation of Cycle Time, t .

The basic method of computation used is outlined in Ref. 18 and involves the calculation of the three dimensionless parameters outlined below. Curves relating these parameters are contained in Ref. 18.

(a) Calculation of T_g/T_0

T_0 = initial uniform temperature of fluid, °C

T_g = temperature of fluid at any point at any time, °C

For entrance-gas temperature of 900°C and exit-gas temperature of 200°C,

$$\frac{T_g}{T_0} = \frac{200}{900} = 0.22.$$

(b) Calculation of Dimensionless "Y" Parameter

$$\begin{aligned} Y &= \frac{h_v x}{C_p G_0} \\ &= \frac{280 \text{ Btu}}{\text{hr-}^\circ\text{F-ft}^3} \times 4 \text{ ft} \times \frac{\text{lb-}^\circ\text{F}}{0.125 \text{ Btu}} \times \frac{\text{hr-ft}^2}{178 \text{ lb}} \\ &= 50. \end{aligned}$$

(c) Estimation of "Z" Parameter

From Fig. 6, p. 155, of Ref. 18:

At $T_g/T_0 = 0.22$ and $Y = 50$,

$Z = 43$.

Assuming x/G_0 is negligible compared to time t ,

$$Z = \frac{h_v t}{C_{vs}(1-f)}$$

(d) Estimation of Cycle Time, t

$$\begin{aligned} t &= \frac{Z C_{vs}(1-f)}{h_v} \\ &= \frac{(43)(78.4)(0.62)}{280} = 7.5 \text{ hr} \end{aligned}$$

Note: In actual operation, a cycle time of approximately 6 hr was obtained before the exit-gas exceeded 200°C.

b. Calculation of Pebble-bed Temperature Profile

This same method of calculation can be used to estimate the gas or solid temperature profile for any given time cycle. These calculations have been made for the estimated maximum cycle time of 7.5 hr and the 4-hr time cycle used during most of this project. These temperature profiles are shown in Fig. 11.

Fig. 11

Calculated Gas-temperature Profile in Pebble-bed Regenerative Heat Exchanger

2. Trickle-heater Size and Heating Requirement

The trickle heaters were designed to utilize external resistor-type electrical heating elements. The temperature limitations of such elements and the temperature limitation of the heater shell required that the trickle heater operate with high heat-transfer rates. This condition could not be readily met by using beds packed with regularly shaped objects such as spheres or right cylinders since such packed beds exhibit very poor wall-to-bed heat-transfer rates. Previous experiments²³ at this Laboratory with 1/8-in.-diam, 1-in.-length stainless-steel rods in 4-in.- and 6-in.-diam steel cylinders had shown that such beds had high wall-to-bed heat-transfer rates. Accordingly, rod packing was chosen for the trickle heaters, utilizing 1/4-in.-diam, 1-in.-length steel rods.

The previous experiments had shown that the heat transfer for the midaxial portion of a bed of randomly distributed rods could be predicted by

$$Q = 0.174 \times 10^{-8} A_w \epsilon_w (T_w^4 - T_r^4) \text{ Btu/hr,}$$

where

A_w = area of inner wall, ft^2 ,

ϵ_w = emissivity of inner wall,

T_w = temperature of inner wall, $^{\circ}\text{R}$,

and

T_r = temperature of rods, $^{\circ}\text{R}$.

Each trickle heater had to heat 10 scfm of argon from 1570 to 2110 $^{\circ}\text{R}$, at peak load. The heater shell was assumed to be an 8-in.-ID cylinder with

the length L (ft) to be determined. The heat-transfer situation was considered equivalent to transferring heat from the cylinder wall at 2000°R to rods at T_r , and transferring heat from the rods at T_r to argon at 1840°R .

For the radiative heat transfer, assuming $\epsilon_w = 0.4$,

$$Q = 0.174 \times 10^{-8} \left(\frac{8\pi L}{12} \right) (0.4)(2000^4 - T_r^4)$$

$$\approx 0.146 \times 10^{-8} (L)(4 \times 2000^3)(2000 - T_r)$$

$$\approx 46.7L(2000 - T_r).$$

For the convective heat transfer from the rods to the argon,

$$Q = hA(T_r - 1840).$$

The heat-transfer coefficient h at 1840°R was determined to be $6.7 \text{ Btu/hr-ft-}^\circ\text{F}$ from²⁴

$$\frac{h}{C_p G_0} (N_{Pr})^{0.67} = 1.82 \left(\frac{D_p G_0}{\mu} \right)^{-0.51}$$

The convective surface area A_r was determined from the rod dimensions and the previously determined 240-lb/ft^3 bed density as follows:

$$\text{Area/rod} = \frac{2\pi(0.125)^2 + \pi(0.25)(1)}{144} = 0.00613 \text{ ft}^2/\text{rod};$$

$$\text{Weight/rod} = \frac{\pi(0.125)^2(1)(490)}{1728} = 0.0139 \text{ lb/rod};$$

$$A_r = \left(\frac{16\pi L}{144} \right) (240) \left(\frac{0.00613}{0.0139} \right) = 37L \text{ ft}^2.$$

Therefore convective heat transfer is

$$Q = 6.7(37L)(T_r - 1840)$$

$$= 248L(T_r - 1840).$$

Equating radiative and convective heat transfer, we obtain

$$46.7L(2000 - T_r) = 248L(T_r - 1840)$$

or

$$T_r = 1870^\circ\text{R}.$$

Each heater must supply

$$(10)(60)(0.104)(0.125)(2110 - 1570) = 4920 \text{ Btu/hr.}$$

The necessary length, based on the assumptions, is

$$L = \frac{(4920)}{248(1870 - 1840)} = 0.66 \text{ ft.}$$

A 16-in. packed length of 8-in. pipe was selected for each trickle heater to compensate for end effects and oversimplifications in the heat-transfer calculations. This oversizing proved desirable when it became necessary to operate without the heating elements on the trickle heaters.

APPENDIX D

Circulating-gas-blower Performance Curves

The blower performance curves are shown in Fig. 12.

Fig. 12. Circulating-gas-blower Performance Curves

APPENDIX E

Schematic Diagrams of Control Circuits

The schematic diagrams of the control circuits are shown in Figs. 13 and 14.

Fig. 13

Valve-position Control Circuit

Fig. 14
Electrical-power
Control Circuit

APPENDIX F

Analytical Procedures

Nitrogen is determined in samples of titanium sponge by first digesting the sponge in sulfuric acid, which converts the nitrogen to ammonium sulfate. The nitrogen is then determined by a modified semimicro-Kjeldahl method. The liberated ammonia is trapped in a dilute boric acid solution and titrated with standard sulfuric acid.

1. Dissolution of Titanium Nitride

<u>Procedure</u>	<u>Note</u>
a. Weigh sample (~3 g),* and transfer to a 500-ml quartz Erlenmeyer flask. Add 80-100 ml ~6N H_2SO_4 and 10-20 ml 50% HBF_4 .	a. The amount of HBF_4 depends on nitrogen conversion. For samples less than 5% N, 10-15 ml HBF_4 is sufficient; for more than 5% N, use 15-20 ml HBF_4 .
b. Place the quartz flask near the bottom of the sand on a hot plate. When fine bubbles start to appear from sample, raise the flask closer to the surface of the sand.	b. Reaction requires an initial high temperature, but will continue at a lower temperature once started.
c. Dilute with H_2O as necessary to keep H_2SO_4 concentration at 6N.	
d. When the remaining nuggets or residue cease to react with the H_2SO_4 - HBF_4 solution, cool and then transfer the sample to a 100-ml centrifuge tube and centrifuge for ~10 min. Decant and save supernatant. Transfer residue to a 110-ml platinum crucible. Add 3-5 ml conc. HF, and heat. When solution is hot, add 20-30 mg solid KMnO_4 slowly. Continue heating, and keep crucible covered with platinum cover.	If too much KMnO_4 is added, the sample may overflow.

*Samples are not usually homogeneous. The entire sample should be taken unless otherwise instructed.

Procedure

- e. Add KMnO_4 , and continue heating until MnO_4 color persists on boiling of solution. Cool, and add 30% H_2O_2 , dropwise until solution clears. If no residue remains, add this solution to H_2SO_4 - HBF_4 solution, and make up to volume. Store samples in polyethylene bottles.

If part of sample still remains, decant supernatant into H_2SO_4 - HBF_4 solution and try to grind remaining sample. Add more HF and KMnO_4 , and heat until sample is completely dissolved.

Combine solution with the H_2SO_4 - HBF_4 solution, and make up to volume.

Note

- e. Solution should be heated to expel excess H_2O_2 when entire sample is dissolved.

NOTE: Solutions of TiN samples may be brown, green, orange, purple, or colorless depending on amount of HF, H_2O_2 , HBF_4 , or H_2SO_4 used.

2. Semimicro-Kjeldahl Procedure

Prior to the determination of nitrogen, the apparatus (see Fig. 15) should be thoroughly cleaned by running steam through it for about one-half hour. Any glassware and equipment used should be free from ammonium chloride.

a. Apparatus

- (1) Distillation apparatus, Parnas and Wagner type with 200-ml distillation flask.
- (2) Buret, semimicro, 10 ml in 0.05-ml divisions.

b. Reagents

- (1) Ammonium chloride. Dissolve 0.3820 ± 0.0002 g dry C. P. reagent in deionized water and dilute to one liter. One ml of this solution is equivalent to 1.00×10^{-4} g of nitrogen.
- (2) Sulfuric acid, conc..

- (3) Sodium hydroxide, 9M. Dissolve 365 g of NaOH in one liter of H_2O , add 1.0 g of DeVarda's alloy, boil gently for 0.5 hr, cool, and dilute to one liter. Store in a tightly stoppered bottle.
- (4) Boric acid, 0.17%, 0.850 g/500 ml H_2O .
- (5) Mixed indicator. Dissolve 0.0167 g of methyl red and 0.0833 g of brom cresol green in 100 ml of ethyl alcohol.

c. Preparation and Standardization of Sulfuric Acid

Pipet 2.0 ml of conc. sulfuric acid into a one-liter volumetric flask containing about 500 ml of deionized water. Make up to one liter. Dilute 100 ml of this solution to one liter in a second flask, and mix. This diluted sulfuric acid solution is approximately 0.007N, and 1.0 ml is equivalent to about 0.001 g of nitrogen.

Standardize as follows: Pipet 10.0 ml of the ammonium chloride solution into the distillation flask, and add 20 ml of deionized water and 5.0 ml of conc. H_2SO_4 . Cool and attach to the distillation apparatus, add 30 ml of the 9M sodium hydroxide solution, and distill. Collect 25 ml of distillate under 10.0 ml of 0.17% boric acid solution as detailed below. Add eight drops of mixed indicator, and titrate with the ~0.007M solution.

Determine a reagent blank as above by distilling 5.0 ml of conc. sulfuric acid and 30 ml of distilled water.

<u>Procedure</u>	<u>Note</u>
(1) Fill steam-generating flask with deionized water. Steam out apparatus with deionized water in the sample flask, for approximately one-half hour.	
(2) Pipet suitable aliquot into 200- or 250-ml round-bottom distillation flask containing 5 ml of conc. H_2SO_4 and 20 ml of deionized H_2O .	(2) Aliquot should contain 0.1-1.0 mg of nitrogen. Flask should have previously been rinsed out with deionized H_2O .
(3) Pipet 10.0 ml of 0.17% H_3BO_3 solution into 125-ml Erlenmeyer flask, and place in position under delivery tube with the tip of the condenser in the solution.	

Procedure

- (4) Add 30 ml 9M NaOH to reservoir.
- (5) Put sample flask in position, and allow NaOH to flow in slowly.
- (6) After formation of violet Ti_2O_3 is noted, let remainder of NaOH in quickly as this will cause no further reaction. (At this time, the sample flask heating mantle should be raised into position.)
- (7) Collect 25 ml of distillate, lower receiving flask so that condenser tip is out of the solution, and continue distillation for 2 min. Rinse tip, and remove.
- (8) Add eight drops of mixed indicator, and titrate to end point with standard sulfuric acid.

Note

- (5) Do this slowly so as not to cause a violent neutralization reaction and possible contamination of the system due to bumping.
- (6) Take care to leave enough NaOH in the reservoir to act as a trap to prevent the atmosphere from contaminating the system.
- (7) Complete distillation takes about 30 min.
- (8) End point is absence of blue color (dirty-grey solution).

Calculation

$$\% N = \frac{(\underline{NH_2SO_4})(\text{Equiv Wt N})(\text{Vol Fac})(10^2)(\text{Vol of Sample})(\text{Titer})}{(\text{Wt of Sample})}$$

Fig. 15

Semimicro-Kjeldahl
Apparatus

ACKNOWLEDGMENTS

The authors wish to express their appreciation to L. Burris, Jr., R. D. Pierce, and R. C. Vogel for their interest in, and support of, this project. R. J. Meyer and L. E. Ross were responsible for developing the analytical procedures used in the nitrogen determinations. N. P. Quattropani and W. A. Pehl aided in the construction and operation of the experimental equipment.

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