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Publication Date
1961-08-17
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CLOSE-CAPTURE ADSORPTION SYSTEM
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ABSTRACT

Molecular sieves are used as the basic adsorber in a close-capture air recirculation system designed primarily for remote operation with master-slave equipment.

A compact evaporator-dissolver unit provides a vessel for dissolution of an aluminum slug containing the radioactive material, and provides an evaporator head under which volume reduction may be carried out within a specially prepared centrifuge cone. One movable condenser serves both operations. Platinum resistance films provide heat for the centrifuge cone and also for a jet of air impinging on the surface of the liquid being evaporated.

Moisture and acid vapors from the chemical operations are pumped from the main box and adsorbed on the molecular sieves in a separate enclosure. The dry air is then returned to the main box. Thus, by capturing vapors within a closed system and by continuously recirculating the box air through the adsorbers, a reasonably dry atmosphere is maintained at all times within the chemistry enclosure, and corrosive action is effectively reduced.
CLOSE-CAPTURE ADSORPTION SYSTEM *
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INTRODUCTION

Molecular sieves\(^1\) are synthetic zeolites which, when dehydrated, contain a network of empty pores and cavities that constitute almost 50% of the total volume of the crystals. They have the unique property of adsorbing within these cavities only those molecules that are small enough to pass through the pores of the crystals. Molecular sieves have a very strong affinity for water and other polar molecules. It is this selective property plus their stability and reasonable cost that make them of interest for the application described herein.

In designing a remotely operated facility for neutron protection during chemical operations\(^2\) we found it desirable to attempt to minimize the humidity within the enclosure and to capture any corrosive vapors at their source. Since this facility would employ master-slave type manipulators instead of "through-the-wall" shielded tongs, protection of the slave hands, as well as all other equipment within the box, from corrosive action was essential to a smooth operation.

This protection was accomplished in three ways: (a) by employing materials of construction that would be relatively free from corrosive attack, (b) by keeping reagents and solutions that contribute corrosive vapors to the atmosphere capped when not in use, and (c) by utilizing a closed system for
the dissolving and evaporating operations—wherein moisture and acid vapors would be either condensed or adsorbed, and the atmosphere of the processing enclosure maintained in a very dry condition.

Materials used in construction of apparatus were primarily glass and lucite. Type B-44-3 Tygon tubing was used for all connecting lines, and standard ball joints were used where connections might be broken for disassembly or emergency replacement of parts.

An auxiliary enclosure housed the adsorber columns. This enclosure was connected to the main box by Tygon tubing. Two columns were employed. Box air was circulated through one and returned dry to the point of origin. The second was used to scrub the effluent from dissolution and evaporations, and return dry air to the main box. The columns were packed with a mixture of soda-lime and charcoal, topped by 1/16 in. pellets of Type 13X molecular sieves. Indicating Drierite was placed on the top of each column as a warning of adsorber exhaustion.

Molecular sieves are available in several pore sizes, the sieve number being indicative of the pore diameter in Angstrom units (Å). The 13-A sieve was the largest available, and was selected because of the unknown factors relative to the radioactivity present. Under the conditions of operation, it was not known whether the sieve pores would adsorb material other than moisture and ammonia vapor. However, it is known that the long-lived radioactive gases Krypton 85, Xenon 131m, and Xenon 133 would be present in the effluent from the dissolving operation. According to measurements made by Linde\(^3\) and Oak Ridge,\(^4\) adsorption of these gases on molecular sieves is more successful at very low temperatures than at standard conditions. Likewise, it is known that radioactive particulates of 13-A diam and smaller would undoubtedly be present in the air stream from the processing...
box. Since the primary purpose of the setup is corrosion control, no attempt was made to determine what percentage, if any, of these particulates might be adsorbed by the sieve. However, since a possibility of adsorption existed, the largest pore size seemed a logical choice.

GENERAL OPERATION

Dissolver

Prior to the introduction of the radioactive capsule into the box, 50 ml of dissolver solution is placed in the dissolving vessel (Fig. 1). (The dissolver solution contains sodium hydroxide and sodium nitrate in a molar ratio of 5.4:2.6) After the capsule is dropped into the solution, the condenser is pulled forward and clamped in position to seal the system (Fig. 2.) Then the pump to the adsorption column is turned on and, by means of an air-bleed valve system described later in this paper, the pressure within the dissolver is adjusted to 5 in. Hg.

Heat is applied to the inner shell of the dissolver by supplying approximately 30 amp of current to a platinum-rhodium resistance coil. As soon as the dissolving reaction reaches a vigorous stage, the heater is cut off and the dissolution allowed to proceed without assistance. However, as the capsule reaches the end of its existence, the reaction becomes less self-sustaining, and additional heat is required to complete solution.

A quench tank of cold water is connected to the outer jacket of the dissolver for quick cooling should the reaction become too vigorous.

Upon completion of the dissolution, the ball-joint clamp is released momentarily to break the vacuum and purge the line of ammonia and radioactive gases. This operation is repeated several times. Then, after a suitable cooling period, the condenser is moved to the rear of the unit and
clamped to a distillation receiver for use during subsequent evaporative operations. The total dissolving time for a 1/2-in. X 5/8-in. diam radioactive aluminum capsule is approx 1 1/2 hr.

**Evaporator**

At the completion of the dissolving operation, the O-ring joint clamp on the condenser is released and the transport system brought into play by turning the knob in front of the condenser one-quarter of a turn. This rotates an eccentric rod through a lucite fork beneath the condenser, which is raised about 1/8 in., or just enough to free the O-ring. Pressure is then applied to the stainless steel handle to move the condenser horizontally until it is in position over the evaporation receiver. A reverse turn of the knob lowers the O-ring joint onto the receiver, and a ball-joint clamp is applied to seal the system (Fig. 1). In order to ensure the presence of an O-ring in each position, one was cemented to the condenser joint with Eccosil 4520 adhesive, a flexible epoxy-silicone bonding agent.

Now the setup is ready for evaporative operations. This part of the unit was designed to control the effluent from the concentration of acid solutions during the chemical manipulations (Fig. 3). It provides a closed system so that fumes from the evaporation are either condensed into a receiver or captured on the adsorption columns.

A centrifuge cone—specially prepared with a platinum resistance film coating approx $2 \times 10^{-6}$ in. thick, and ground flat on the lip—is used as the evaporator. This cone rests within another thick-walled glass cone that acts as an emergency secondary container. Both cones are supported on the platform of a Micro Lab-Jack. The jack was modified for master-slave operation by increasing the size of the knob and securing the base to a lead brick that
could be moved along a runner made of high-density polyethylene. Thus the cone could be pulled from beneath the distilling head for addition of more liquid or ready removal from the platform.

For evaporation, the cone is pushed beneath the distilling head, then raised by the jack, until the ground surface of the cone meets the ground surface of the head. Perfect alignment of the two would result in a vacuum seal, but no attempt was made to achieve such alignment as it was found that the suction of the pump on the adsorption column was sufficient to give an inward rush of air at all times. A check of the interface with pHydron paper during box operation confirmed that acid vapor would not escape at this point as long as the pump remained in operation.

After the cone is in position, the lucite clamp holding the tantalum electrical contacts (Fig. 3) is closed about the platinum film, and the voltage adjusted by means of a powerstat to 30 v. Such a setting ensures gentle evaporation without undue boiling and spattering.

At the same time, air which had just been removed from the box and passed through the adsorption column is fed back dry through an air heater and onto the surface of the liquid being evaporated.

The air heater consisted of a platinum resistance film approx \(3 \times 10^{-6}\) in. thick fired onto the surface of a quartz rod. At 70 v, 0.97 amp of current was fed to the film. The air, passing over the heater at a rate of about 3 liters/min, reached the surface of the liquid in a full 40-ml cone at an approximate temperature of 215°C. As the liquid level dropped, the air flow was increased to a maximum of 6 liters/min, with a corresponding increase in air temperature (measured at the same point) of 30°C.

A bypass valve was used to adjust the rate at which air impinged on the liquid in the cone, in order to eliminate spattering when the cone was full.
As the level in the cone went down it was found necessary to increase the voltage on the cone heater in order to keep the evaporation rate steady. By this method 40 ml of a 6M HCl solution of radioactive salts can be reduced in volume to about 19 ml in 78 min without release of vapor to the box. However, by maintaining an even 30 v on a cone whose resistance film measures approx 35 ohms, and by adjusting the rate of air flow, 40 ml of 6M acid may be reduced to dryness in approx 3 hr. The average rate of evaporation during this period was approx 0.20 to 0.25 ml/min.

**ADSORPTION SYSTEM**

**Enclosure**

The adsorber-column box is shown in Figs. 4 and 5. It is constructed of 3/4-in. plywood and 3/16-in. lucite, and is 1 ft wide, 1 ft deep at the bottom, 6 in. deep at the top, and 3 ft high. This entire unit is constructed for easy disposal, and every attempt has been made to keep the cost as low as possible, consistent with successful operation. It is purposely made L-shaped to accommodate the two small Dyna-pumps and to provide a shelf for the Chemical Warfare Service (CWS) filter box. Although the adsorption columns are considered reasonably tight, the possibility of radioactive leakage always exists, and the box therefore provides secondary container protection.

Room air is drawn into the box at the top of the rear panel through a filter of PF-105 fiberglas, then is exhausted at the bottom behind the pumps, after being drawn over the cold-jacketed columns and the pumps. A CWS type filter which was connected to the main building exhaust system was placed on the air outlet.
Formulation B-44-3 Tygon tubing was used throughout the system because of its greater resistance to acid attack. It was fed directly through the lucite walls of the column box and the main processing enclosure. Stationary screw clamps of lucite were used to close the Tygon lines to the adsorber columns when necessary, and ball-joint clamps covered by vinyl bags were used to effect disconnection between the boxes. The ball joints were opened within the bags, and then the vinyl sleeves were heat welded and severed through the weld.

**Adsorption Columns**

Two adsorption columns were used for each processing box with provision for switching from one column to the other, or one pump to the other, should pump failure or column exhaustion cause this to become desirable (Fig. 4).

One column was used to scrub the processing-box air clean of moisture and acid vapors. It consisted of a 4-in. o.d. lucite tube, 25 in. long, with an air inlet deflector to minimize channeling. The bottom of the column was packed with about 200 g of a mixture of 70/40 soda-lime and activated charcoal. Above this was added about 5 lb of Linde type 13X molecular-sieve pellets of 1/16-in. diam. On top of the sieve pellets sufficient 8-mesh indicating Drierite (100 g) was placed to fill the column. The top of the tube was sealed with a lucite plate containing a lucite pipe-fitting outlet.

Box air was pumped through this column continuously during the run, at a rate of 6 liters/min. These molecular sieves can adsorb approximately 25% of their weight in water before exhaustion, or in this case about 1 1/4 lb. Because this is essentially a low-leak closed system, once the box
air has been dried, the amount of pickup will be very small and confined to air introduced into the enclosure by occasional opening of the box interchange door. In normal operation the unit would have a life expectancy of about 60 days.

The second column was composed of two water-cooled glass units, each 7 1/2 in. long and about 2-in. i.d. The quantity of material in these units was sufficient to adsorb the effluent from the evaporation of approximately 400 ml of 8M HCl with suitable precondensation as provided with the evaporative unit. The following quantities of material were packed in these columns, respectively: soda-lime—charcoal, 70/40: 110 g; nonindicating Drierite, 8 mesh: 60 g; 13X molecular sieve: 158 g; and indicating Drierite, 8 mesh: 30 g.

The use of activated charcoal in combination with the soda-lime serves both as a gas adsorber and as a separator to prevent the lumps of soda-lime from fusing and plugging the column. The soda-lime is an acid neutralizer and protectant of the molecular sieves, which are readily attacked by moist acid fumes. The indicating Drierite is, of course, an obvious announcement of column exhaustion.

**Air Flow System**

Two separate pumps were used to control the flow of air for the processing box. Those selected for this task were small inexpensive diaphragm-operated Dyna-Pumps having a maximum pumping capacity of approximately 6 liters/min or about 20 in. Hg vacuum.

Air from the processing box is drawn through the large adsorption column and returned through the air heater on the evaporator via a flow-adjustment valve (Fig. 6).
During the dissolving operation, fumes from the dissolution are drawn through the reflux condenser and into the small adsorption columns. The air bleed inside the processing box is used to adjust the pressure in the dissolving vessel to 5 in. Hg. The dry air from the adsorber is then returned to the processing box through the jacket of the dissolving vessel.

Air flow for the evaporator is diagrammed in Fig. 7. When the cone is raised into position so that the ground-glass surfaces of cone lip and head meet, vapors from the cone are drawn through the condenser system by the pump before reaching the adsorption column. Most of the evaporate is condensed into the receiver, but any entrainment in the air stream is adsorbed by the soda-lime in the entrainment trap before the air leaves the processing box. This trap contains a mixture of soda-lime and charcoal in the proportion 70/40. Thus, condensation in the air lines is reduced to a minimum.

After the processing-box air passes through the large adsorption column, it is returned to the box and passes through a flow-control valve arrangement that can be set to regulate the rate at which the air is admitted to the evaporation cone (Fig. 1). Immediately following the valve is an airflow meter graduated in percent of total flow or, by dividing by 10, in liters/min. The control valves are 1/8-in. Vee seat stainless steel Hoke valves. Valve A is a line bleed to the box and should be wide open at the start of the operation whereas valve B may be open or closed. When the cone is in position it is opened, and a glance at the flow meter will indicate at once whether a vacuum seal has been obtained. If it has, the meter will indicate maximum flow or about 6 liters/min. The flow may then be reduced by closing valve B until the desired rate is obtained. For a full 40-ml cone this should be about 1 to 2 liters/min. As the liquid level drops the rate should be increased gradually to 6 liters/min.
If, when the cone is in position, the flow meter indicates about 2 liters/min when valve B is opened, a vacuum seal has not been obtained. In this case, valve A should be used to regulate the air flow and B left wide open. Either method of operation is satisfactory and will give exactly the same results.

After the air passes through the flow meter it is channeled through the air heater and onto the surface of the liquid to be evaporated. The air stream should only slightly ripple the surface of the liquid. Hence, a low flow is desirable for a full cone and a higher rate as the liquid level recedes.

**EVAPORATOR-DISSOLVER UNIT**

**Dissolver**

The dissolver vessel is essentially a jacketed centrifuge bottle with a built-in heating unit (Fig. 8). The inner container is a 250-ml heavy-wall pyrex centrifuge bottle which has been fitted with a standard No. 20 O-ring joint. The pyrex jacket serves as a container for cooling water that may be required to quench the dissolving reaction. In addition, 13 in. of a 40-mil platinum-rhodium heating wire is inserted through the jacket directly below the reaction chamber.

Beneath the vessel is a 4-way stopcock that controls the admission of air from the adsorption column pump. The dry air assists in dispersing the heat from the resistance coil upwards around the sides of the bottle, and thus reduces the possibility of a hot spot developing that might crack the container. The stopcock handle should be horizontal for air intake to the jacket.
Should quenching of the reaction appear to be necessary, the heater is turned off and the 4-way stopcock rotated one quarter of a turn to channel the air stream downward through the drain tube. Water is admitted through the intake tube on the upper jacket from a cooled dropping funnel.

When the reaction has subsided, the stopcock is rotated momentarily one-quarter of a turn to drain the side arm, and then another quarter of a turn to drain the jacket. On this last turn the air stream is channeled upward through the side arm and the water downward to a waste container.

**Evaporator**

**Condenser**

The condenser is a specially constructed water jacketed Vigreaux tube 14 1/4 in. long with a maximum number of indentations in the tube to provide as much restriction to carry-over of entrainment as possible. More than 80% of the evaporate is returned to the receiver by a condenser of this type of construction. The over-all length of condenser is critical in order to facilitate packaging and removal as waste if desired.

**Evaporator cone**

A standard pyrex 40-ml centrifuge cone is used as the evaporating vessel. To prepare the cone, an area is masked with tape to provide a clear strip 7/8 in. wide from the top lip down one side of the cone and back up the opposite side (Fig. 9). The unmasked area skirts the graduations on the cone and covers the bottom tip so that the graduations are easily readable. The unmasked half is first etched with Al₂O₃ abrasive powder No. 2 (such as that produced by the S. S. White Industrial Abrasive Unit) used in a nitrogen jet. When etching is complete, the surface is cleaned well, first with a detergent
such as "Liqui-Det" or equivalent, and then with ethyl alcohol, without removing the tape. When the surface is dry, a thin even coat of Hanovia Chemical Co.'s Liquid Bright Platinum 05 is applied to the etched area. After a 30-min drying period the masking tape is gently stripped from the surface, and the cone is placed in a muffle furnace or kiln. The temperature of the furnace is raised slowly over a period of 30 to 45 min to a temperature of $800^\circ F$. A current of air circulating through the furnace assists in removing the oxidation products of combustion until the temperature of $800^\circ F$ has been reached. Then the air flow is cut off, the door closed, and the temperature raised to $1220^\circ F$. This temperature is held for 3 min., and then the furnace is allowed to return slowly to room temperature. The platinum film thus produced has a thickness of about $1 \times 10^{-6}$ in.

Without additional masking, a second coat is applied over the first and the firing procedure is repeated. When this is completed, a thin even coat of Hanovia Liquid Bright Gold is applied to the top of the platinum film for a distance of 1 in. from the lip of the cone. The gold film is then fired to a final temperature of $1300^\circ F$, and the application is repeated a second time. Thus a conductive coating is applied to the area that will be in contact with the tantalum electrodes. The platinum film produced by this procedure will have a resistance of approximately 35 ohms.

Thin films for heating purposes have been prepared by other experimenters but their prime objective has been transparency. Also, the use of such films in a corrosive atmosphere was not anticipated. For the purposes of our operation, transparency is not a consideration. In fact, more than one coat is desirable, in order to reduce the incidence of pinholes and obtain a more uniform film. Resistance to corrosive action is a factor, however, and this is provided by the noble metals. The Liquid Platinum 05 used for
coating has a composition that, after firing, yields a film containing 95% platinum, gold, and rhodium metals plus 5% tin and bismuth oxides. Under the corrosive conditions present in the processing box, the bismuth and tin, which provide adhesive quality to the noble metal film, may be slightly attacked. To offset this effect and obtain greater film adherence, etching of the glass surface (as described above) is desirable before coating.

Air heater

The platinum resistance-film air heater (Fig. 10) is prepared in a manner similar to that for the centrifuge cone. However, in this case both the air-heater rod and the attached ball joint are both made of quartz glass. This is desirable inasmuch as the temperatures at the surface of the film are considerably higher than at the surface of the centrifuge cone.

The glass rod should be suitably masked with tape to allow a 3/8-in. wide path from the bottom of the glass joint down one side of the rod, across the tip, and up the opposite side. The etching, coating, and firing procedures are exactly the same as previously described for the cone. However, in this case it was found desirable to place three coats of platinum on the heater rod. The electrical resistance of a 3/8-in. wide, 3-coat film is approximately 50 to 60 ohms; of a 2-coat film, 70 to 80 ohms.

Two coats of Liquid Bright Gold were fired to the top of the platinum film and 0.060-in. tantalum-wire electrical leads were cemented to the gold-coated area with Eccobond 58C solder. This is a conductive epoxide-based adhesive with an electrical resistivity below 0.1 ohm-cm. As shown in Fig. 10 the tantalum leads project through the top of the ball joint. These leads are sealed into the joint with Eccosil 4520 adhesive.

For the 70- to 80-ohm heater operating at 70 v, about 50 w, and with an air flow of 6 liters/min, the exit-air temperature is about 180°F at a
distance of approximately 3 in. from the tip of the heater. On the other hand, the 50- to 60-ohm heater operating at 70 v, 68 w, and 6 liters/min of air will yield an exit-air temperature of approximately 245°C. It is possible to operate this type of heater at voltages as high as 88, but for optimum life the 70-v operating range is desirable.

Temperature measurement

During operation of the evaporator we desired to know the approximate temperature of the liquid being evaporated, in order that spattering might be reduced and the temperature of the liquid kept just slightly below the boiling point. In order to accomplish this, an iron-constantan thermocouple wire, size No. 30, was soldered to a piece of Be-Cu spring with Eccobond 58C solder. The thermocouple was then placed between the centrifuge cone and the secondary cone at the 2-ml level. Advance calibration was then carried out by inserting a thermocouple within the cone during evaporation, and comparing the temperature inside with that shown by the outside thermocouple. We noted that this temperature differential remained reasonably constant at approximately 23°C until the liquid level in the cone approached the point of contact of the outside thermocouple. As the level dropped, the difference between the two thermocouples narrowed until both were reading the same temperature.

No attempt was made to measure the temperature of the air reaching the surface of the liquid in the cone because the heater was precalibrated.
ACKNOWLEDGMENTS

The authors wish to express their appreciation to Peter Cadra and Harry Powell for their invaluable assistance in the design and construction of many items used in this system.
FOOTNOTES AND REFERENCES

*Work done under the auspices of the U.S. Atomic Energy Commission.


FIGURE CAPTIONS

Fig. 1. Evaporator-dissolver unit, front view.

Fig. 2. Evaporator-dissolver unit, side view.

Fig. 3. Cone evaporator assembly.

Fig. 4. Adsorber-column box, front view.

Fig. 5. Adsorber-column box, side view.

Fig. 6. Dissolver air-flow system.

Fig. 7. Evaporator air-flow system.

Fig. 8. Dissolver vessel.

Fig. 9. Evaporator cone.

Fig. 10. Air heater.
Fig. 1
Fig. 3
Fig. 5
Fig. 6
Fig. 7
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