BNL-NUREG-50670

EVALUATION OF ISOTOPE MIGRATION - LAND BURIAL

Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites

QUARTERLY PROGRESS REPORT
OCTOBER - DECEMBER 1976

P. COLOMBO, A.J. WEISS, AND A.J. FRANCIS

Date Published - June 1977

PROCESS TECHNOLOGY DIVISION
DEPARTMENT OF APPLIED SCIENCE
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OFFICE OF NUCLEAR REGULATORY RESEARCH
UNDER CONTRACT NO. EY-76-C-02-0016

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5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $3.50; Microfiche $3.00

June 1977 200 copies

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SUMMARY

This is the third quarterly progress report of water chemistry at commercially operated low-level radioactive waste disposal sites. The program is a joint investigation undertaken by the United States Nuclear Regulatory Commission and the United States Geological Survey as part of a comprehensive plan to study the hydrogeological and geochemical behavior of existing commercially operated low-level radioactive waste disposal sites.

Procedures were developed for collecting and filtering trench water samples under anoxic conditions. These procedures prevent the formation of the undesirable brown ferric hydroxide precipitate that generally is encountered when trench water is exposed to air after removal from the ground.

I. BACKGROUND

The disposal of low-level radioactive wastes at commercially operated disposal sites began in 1962 at Beatty, Nevada. Since that time, the industry has expanded to include three private companies operating six sites. The sites are located in Maxey Flats (Morehead), Kentucky; Beatty, Nevada; Sheffield, Illinois; Barnwell, South Carolina; West Valley, New York; and Richland, Washington. The three companies operating these sites are the Nuclear Engineering Company (Illinois, Kentucky, Nevada, and Washington), Chem Nuclear Systems (South Carolina), and Nuclear Fuel Services (New York). Although these facilities are managed by private industry, they are located on Federal or State owned land. In general, the disposal sites are regulated by the state in which they are located, according to provisions of the agreements between the individual states and the United States Nuclear Regulatory Commission (NRC).[1] The one exception is the site located in Sheffield, Illinois, which is regulated by both the State of Illinois and the NRC.

The disposal sites are located in remote areas of sparse population selected for their hydrogeological environment and were considered suitable at the time of selection for the purpose of shallow land burial of low-level radioactive wastes. In addition, these locations are in proximity to centers of nuclear industry to minimize long distance transportation of wastes.

Projections have been made of the available capacity of the commercial sites and the results indicate that the current burial capacity of all six existing sites may be exceeded by 1998 when existing sites may have to be closed or enlarged or new sites will have to be established.[2]

Recently, questions have been raised regarding the adequacy of these disposal sites.[3,4] With the increasing growth of the nuclear energy industry, important considerations must be given to the selection of any new sites for disposal of radioactive wastes.

The United States Geological Survey (USGS) funded by the United States Congress and with concurrence of the individual state is conducting hydrogeological and geochemical investigations at all commercially operated low-level radioactive waste disposal sites except Richland, Washington.

The United States Nuclear Regulatory Commission (NRC) has the responsibility for establishing criteria for selection and operation of low-level radioactive waste disposal sites.

In support of USGS investigations, NRC funds Brookhaven National Laboratory (BNL) to perform analyses for USGS of natural waters and of waste leachate that have accumulated in waste trenches at the disposal sites.

II. SCOPE

The low-level radioactive waste disposal sites in use today throughout the United States are located in different hydrogeological environments. Until the various physical and geochemical processes governing transport are understood, the continued monitoring of these sites to detect movement, if any, of radionuclides from the disposal trenches is needed.

One of the goals of the USGS program is to collect hydrogeological and geochemical data at each site and to correlate these data with theoretical and laboratory results to develop a transport model for each disposal site. The ultimate goal is to establish criteria for selection, operation, and monitoring of low-level radioactive waste disposal sites.

In support of the USGS program, samples of materials from the disposal sites will be taken at selected intervals and the analysis of the chemical and radioactive species will be performed at Brookhaven National Laboratory. Methods for collecting and analyzing samples from each of the burial sites will be developed. The study will include the measurement of inorganic, organic, and radioactive constituents in water samples.

Soil column tests will be performed in the laboratory to simulate the hydrogeological conditions at each of the disposal sites and to measure the values of a number of factors involved in the migration rates of the various wastes.

III. INTRODUCTION

The procedures that were used to collect water samples from trenches and wells at the Maxey Flats, Kentucky, low-level radioactive waste disposal site in April 1976 were described in a previous quarterly progress report.[5] Trench water samples were obtained by lowering plastic tubing into an established riser pipe in the trench and lifting the water with a peristaltic pump. It was observed that the trench water samples changed their physical appearance after removal from the ground. Upon standing they became cloudy with the formation of a brown ferric hydroxide precipitate. The precipitate contained material that was originally dissolved in the water before its removal from the trench. It is believed that the observed precipitation is caused by a reaction of the water sample with air. Measured values of Eh and the ratio of ferrous to ferric iron of similar trench water samples from the West Valley, New York, low-level radioactive waste disposal site indicate that a reducing environment exists in the trenches which favors the ferrous state of iron.[6] Ferrous hydroxide which is more soluble than ferric hydroxide is probably oxidized to the latter when exposed to air. (K_{sp} $Fe(OH)_2$ = 8×10^{-16}, K_{sp} $Fe(OH)_3$ = 4×10^{-38}).[7] Some dissolved radionuclides could have been lost from the aqueous part of the sample by adsorption onto this precipitate. It was deemed necessary to develop a technique to collect samples under anoxic conditions.

IV. ANOXIC COLLECTION AND FILTRATION PROCEDURES

Procedures were developed to prevent the undesirable precipitation that usually occurs when collecting and filtering trench water samples. Precautions were taken to prevent air from coming in contact with the water samples during the collection and filtration operations. These procedures were used in collecting trench water samples at the Maxey Flats waste disposal site in September 1976 and are described below.

A. Sampling Bottle

A container was designed for collecting and storing trench water samples in the absence of air (Figure 1). A one gallon borosilicate glass bottle was modified by attaching stopcock valves to inlet and outlet ports. The valves are high vacuum type with teflon stems and o-rings for gas-tight sealing.

B. Collection Procedure

Figure 2 is a schematic diagram of the apparatus used to obtain the samples. The system consists of plastic tubing, peristaltic pump, inert gas cylinder with a pressure regulation valve, sample bottles, by-pass valve (V-5), air barrier coils, and waste tank. Figure 3 shows the actual components as used in collecting samples at Maxey Flats.

A few liters of trench water were initially diverted to a waste tank to purge the air trapped in the lines. The collection bottles which had previously been filled with argon were then flushed with approximately five gallons of trench water before collecting the sample. Larger quantities of sample may be obtained by connecting additional collection bottles in series as shown in Figure 4. Argon was used to displace some sample from the top of the bottle to avoid breaking the bottle as a result of an accidental temperature increase.

The air barrier coils shown in Figures 2 and 4 are obtained by coiling the waste lines several times. The water trapped in the coils after the pump is turned off acts as a barrier against air entering the system and at the same time permits the system to remain at atmospheric

Figure 1. Sample Collection Bottle

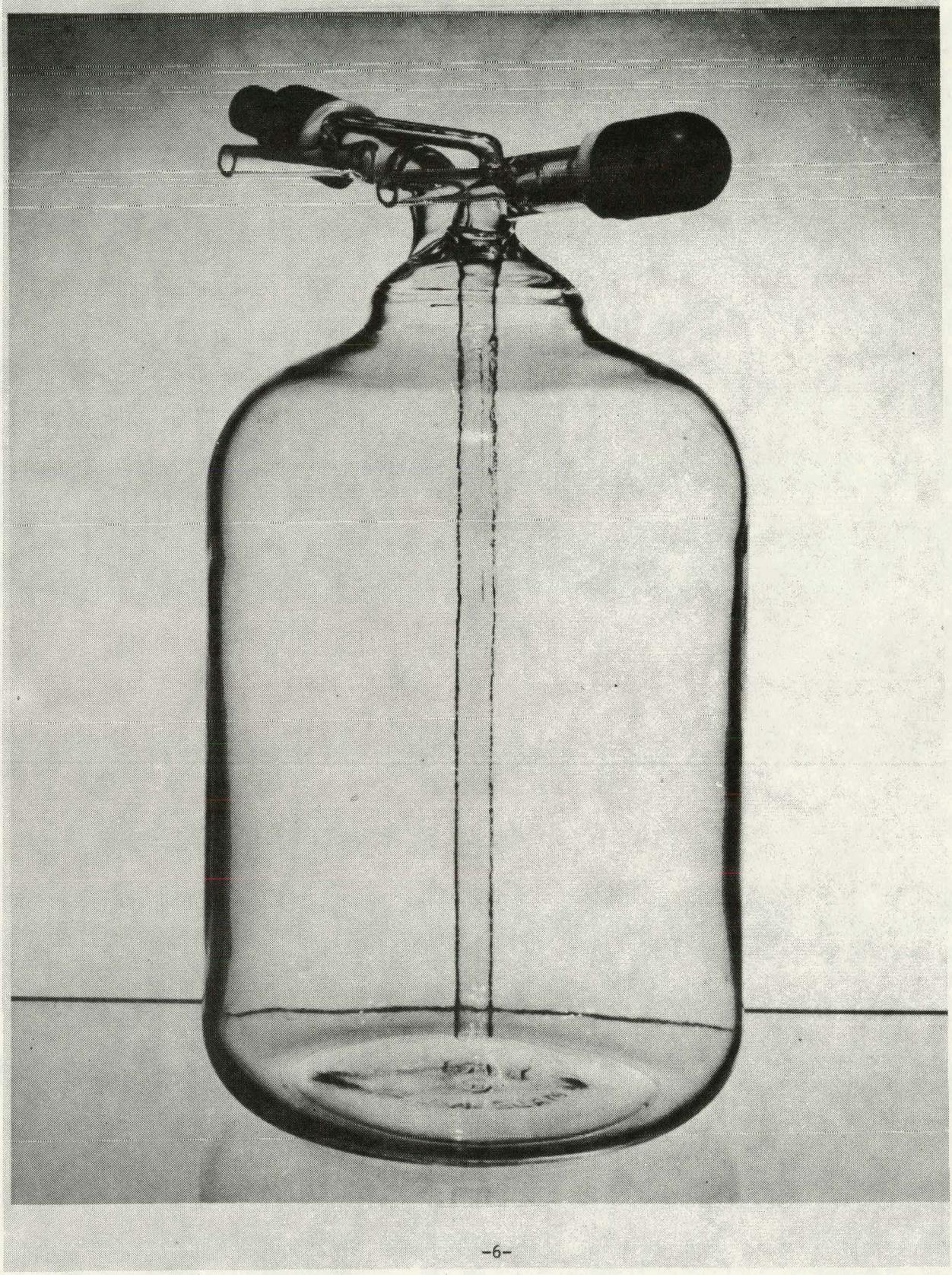
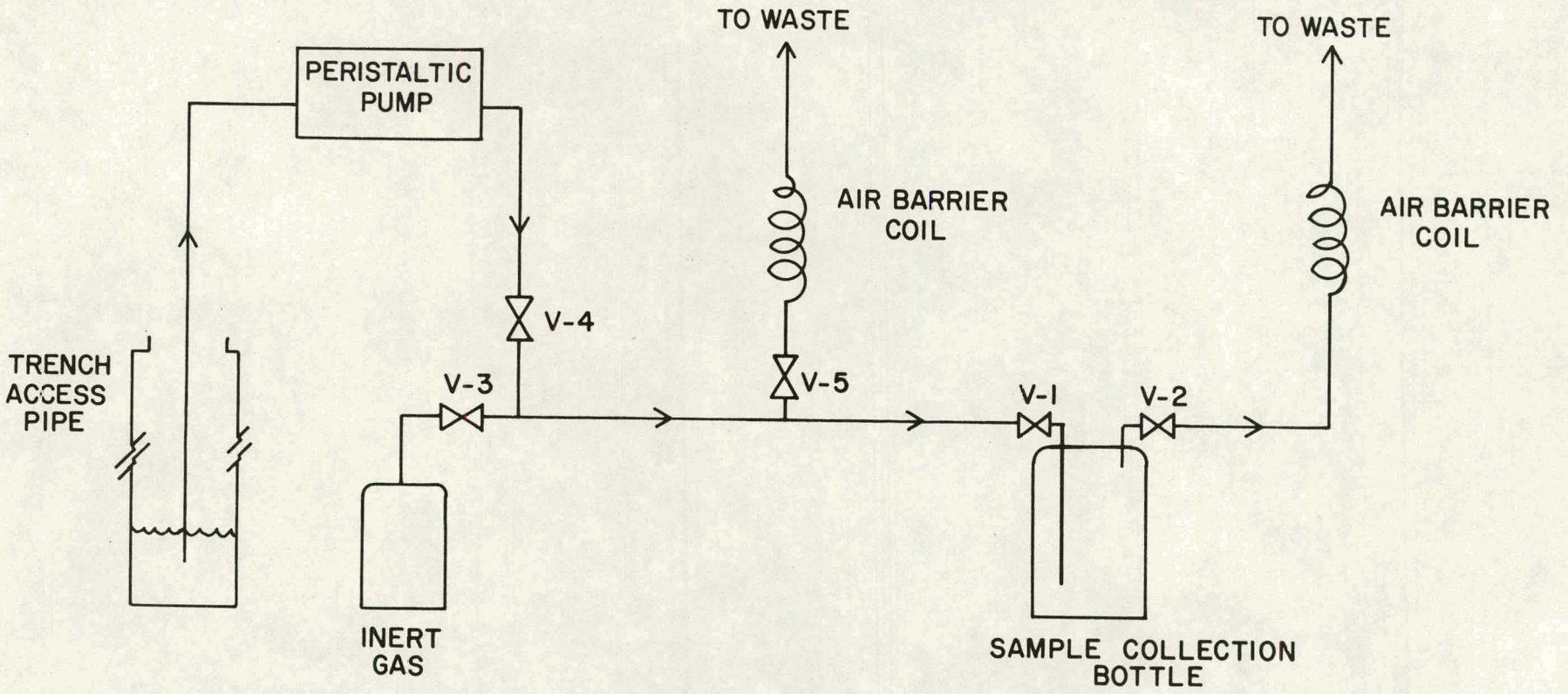


Figure 2

SCHEMATIC WATER SAMPLE COLLECTION SYSTEM



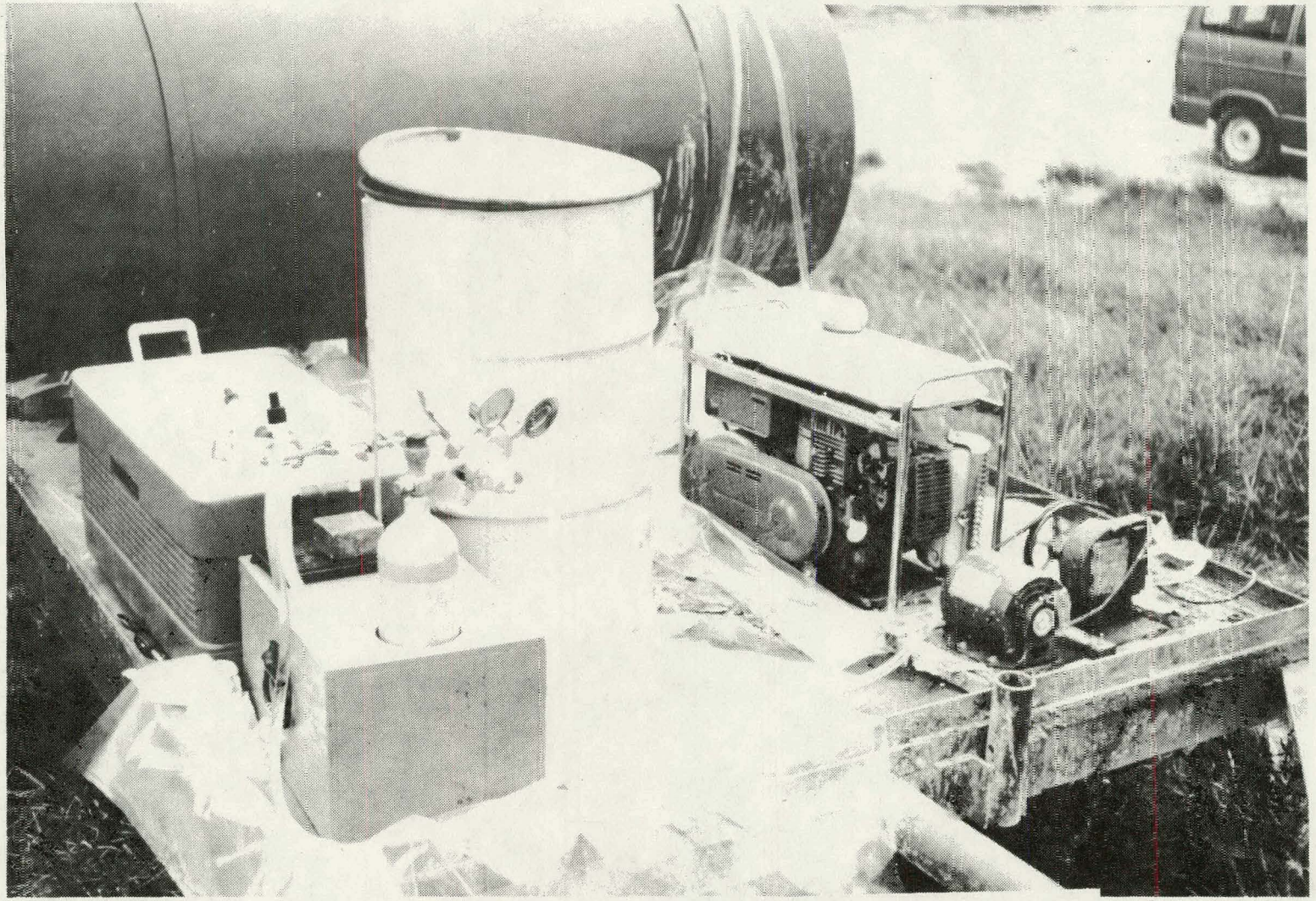


Figure 3. Portable Unit Used for Pumping Water from Trenches at Maxey Flats.

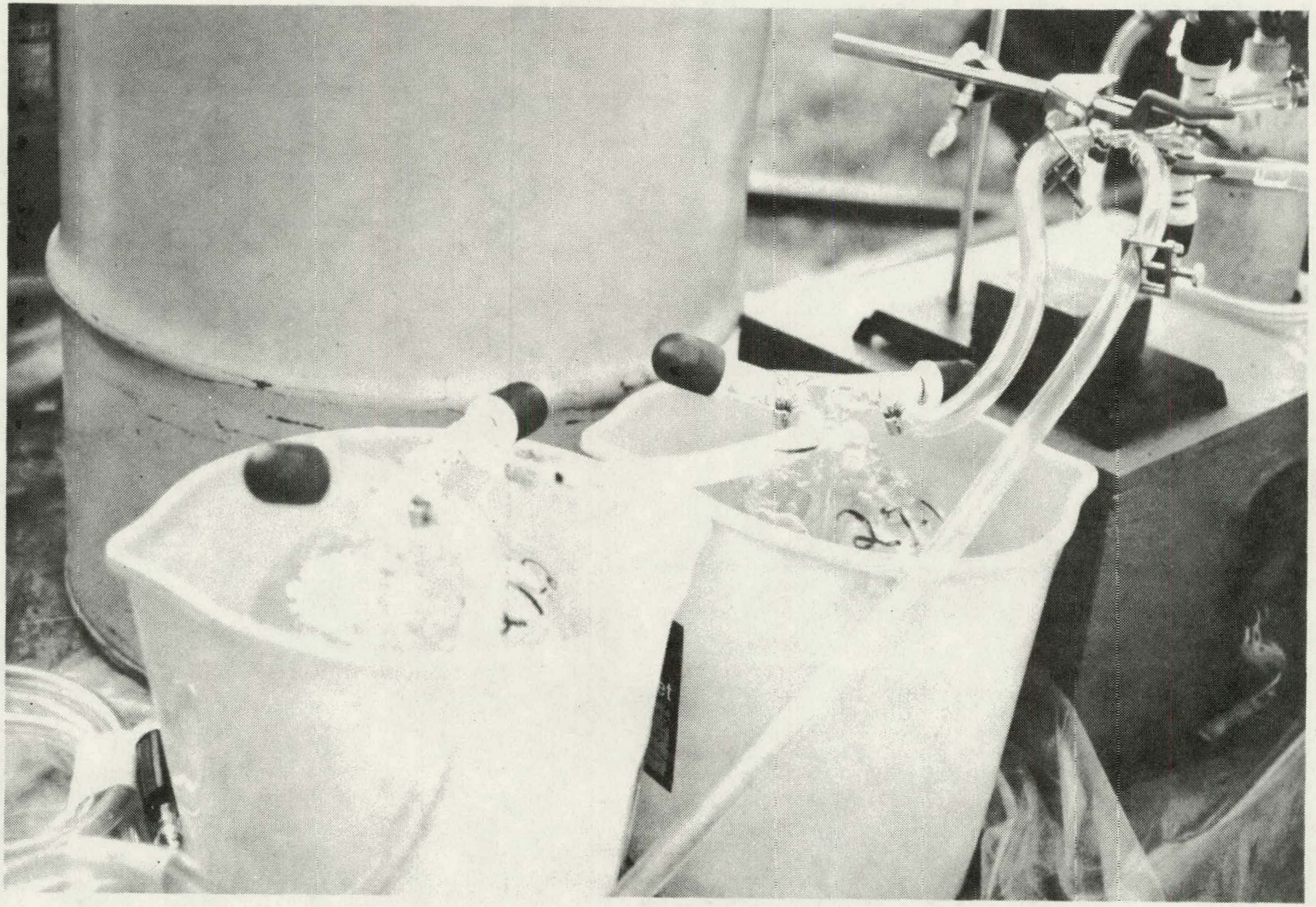


Figure 4. Collection Bottles Connected in Series for Sampling Trench Water.

pressure.

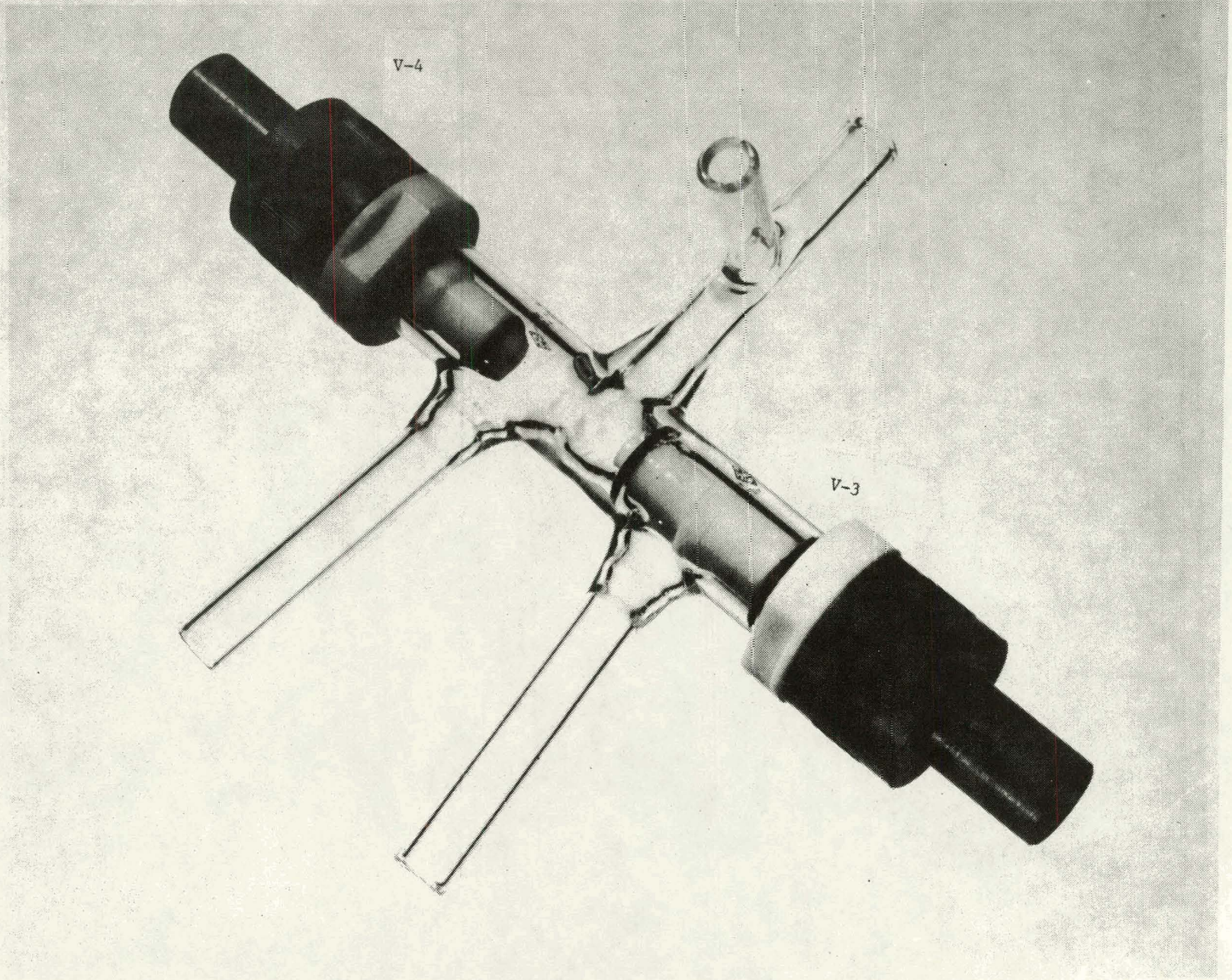
The combination valve in Figure 5 combines the functions of V-3, V-4, and V-5 as shown in Figure 2. This valve uses two high vacuum stopcocks of the type used on the collection bottle. The stopcock on the left shown in the open position illustrates the non-restrictive flow design which is necessary to allow the passage of particulate material while purging the system. The stopcock on the right shown in the closed position, illustrates the sealing action of the o-rings against the glass. Valve V-5 is controlled by a hose clamp on tubing connected to the glass tee of the combination valve.

The detailed procedure for collecting water samples is described as follows:

1. Valves V-1, V-2, and V-3 are closed
2. Valves V-4 and V-5 are open
3. Turn on pump
4. When the lines are purged open V-2
5. Open V-1
6. Close V-5
7. When sufficient water is purged through the collection bottle open V-5
8. Close V-1
9. Turn off pump
10. Close V-5
11. Open V-1
12. Open V-3 to introduce argon into the top of the sample bottle
13. Close V-3
14. Close V-1
15. Close V-2

Immediately after collecting a sample, the bottle is sealed in a plastic bag, placed in an insulated cooler, and maintained at $\sim 4^{\circ}C$ with ice until the sample is filtered.

Figure 5. Combination Valve for Purging and Collecting Trench Water Samples.



C. Filtration Procedure

The procedure for filtering trench water samples described in a previous report[5] was modified to exclude air from the system during the filtration. Figure 6 is a schematic diagram of the apparatus used in the filtration procedure. The system consists of the sample bottle, a filtration vessel containing a 0.45 micron filter, a by-pass valve (V-3), two nitrogen cylinders with pressure regulation valves, an air barrier vent, and laboratory grade plastic tubing which connects all system components. It has been shown that laboratory grade tygon tubing, R3603 is one of the least contaminating flexible tubing available.[8] The contamination of concern is organic material, e.g., plasticizers, that may be released by the tubing.

After purging the air from the filtration system with nitrogen, trench water sample is transferred from the sample bottle to the filtration vessel with nitrogen at 3 psi. The sample is filtered by applying pressure up to 30 psi.

The detailed procedure for filtering the water samples is described below. Figure 7 shows the actual filtration equipment with labels corresponding to the components in the schematic diagram of Figure 6.

A. Initial Conditions

1. Valves V-3, V-5, V-7 are open
2. Valves V-1, V-2, V-4, V-6, V-8 are closed
3. Filtration vessel is filled with distilled water; top of vessel disconnected
4. Outlet stem of filtration vessel is plugged

B. Purging of lines

5. Open V-4 at nitrogen tank, N_2 pressure at 3 psi
6. Close V-5
7. Open V-6 slowly, N_2 pressure at 30 psi
8. Open V-8
9. Attach top of filtration vessel
10. Remove plug from outlet stem of filtration vessel

Figure 6

SCHEMATIC FILTRATION SYSTEM

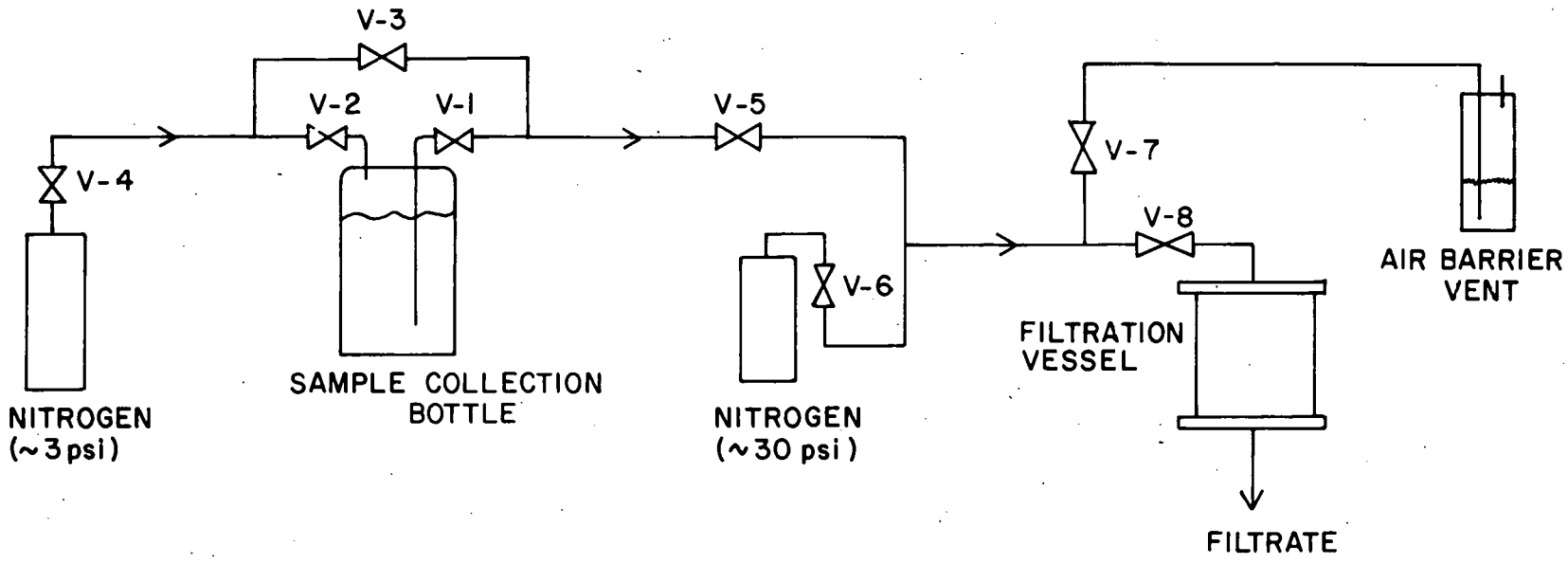
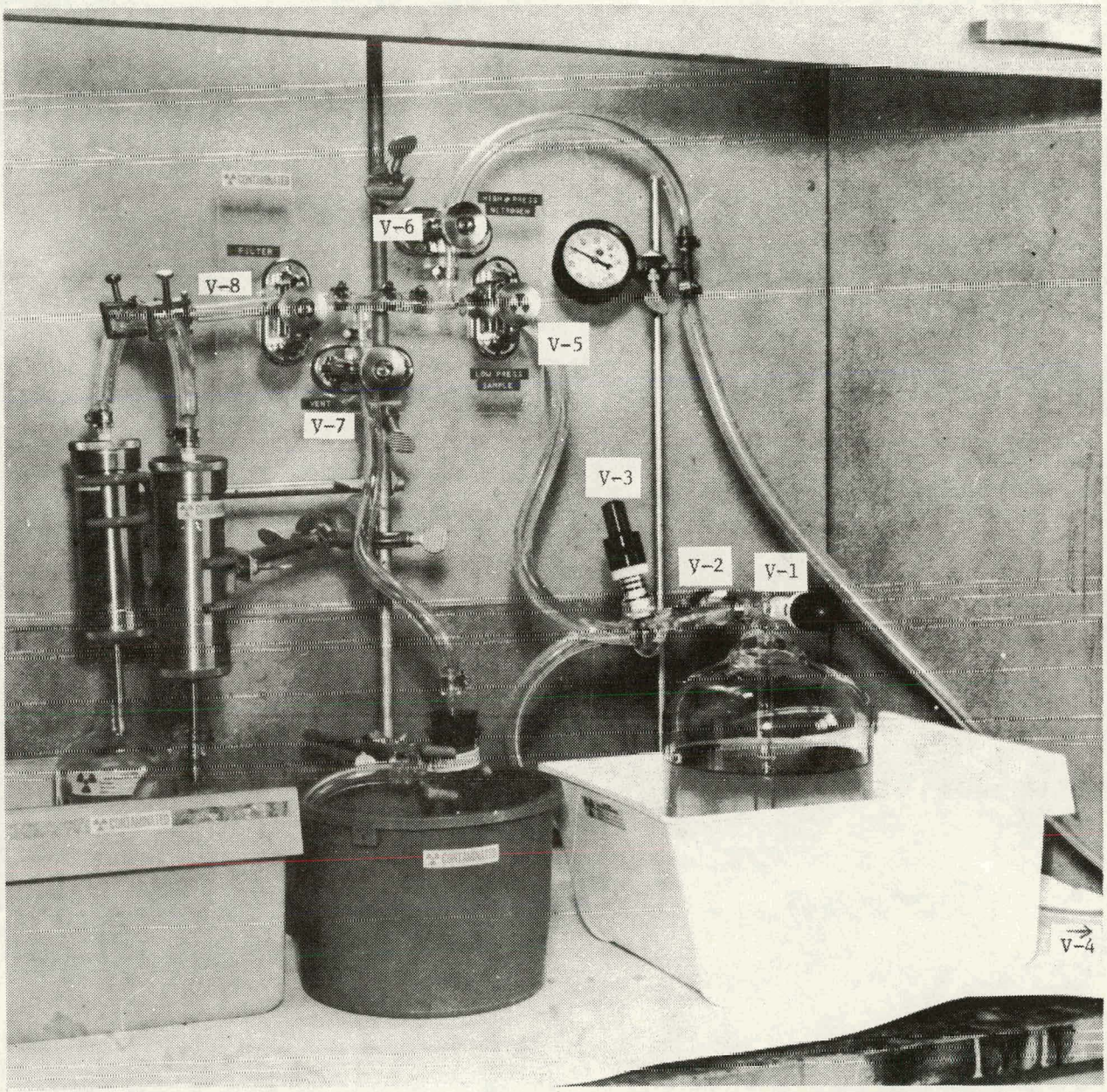


Figure 7. Laboratory Filtration of Trench Water Samples.



11. Close V-7
12. After the water in the filtration vessel is displaced by N_2, close V-6
13. Open V-7 to reduce the pressure in filtration vessel to slightly above atmospheric pressure
14. Close V-7

C. Transfer of sample to filtration vessel

15. Close V-3
16. Open V-2
17. Open V-1
18. Open V-5
19. When the transfer automatically stops; close V-5
20. Open V-6 slowly to initiate filtration

D. Refilling filtration vessel

21. Close V-6
22. Open V-7 (see step 13)
23. Close V-7
24. Repeat steps 18-23

E. If filter change is required

25. Open V-7
26. Close V-8
27. Disassemble unit, replace filter
28. Repeat procedure from step 3

More than one filtering vessel may be used simultaneously in this system. Each vessel requires a hose clamp to perform the function of V-8. This procedure may be used with either the plastic or stainless steel filtering units. The plastic unit is used for the inorganic and radiochemical samples and the stainless steel unit is used for the organic samples.[5] During the filtration of the organic samples both the sample and the filtrate collection bottles are kept on ice.

The trench water samples collected and filtered by the procedures described above did not form any brown precipitate up to the time they were filtered (approximately two to three weeks after collection). In some instances, where only part of the sample was filtered, the trench water remaining in the bottle under nitrogen and stored in a refrigerator did not form any visible brown precipitate five months after collection.

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