A Method for the Solidification of Radioactive Aqueous Liquid Wastes

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Radiation
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ABSTRACT

Progress is reported on a successful method for the solidification of radioactive liquid waste. Portland cement, mixed with expanded vermiculite, is added to the waste until all liquid is absorbed. The solidified waste is handled and stored as a solid waste package. Procedures in applying this method to various wastes are described. Quantities of waste, special circumstances, and economic considerations will determine where this method is most applicable.

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I. INTRODUCTION

The storage, transportation, and disposal of radioactive liquid waste is rapidly becoming one of the factors influencing the use of atomic energy in areas where storage and treatment facilities are at a premium.[1, 2, 3] Unless it is desired to keep the waste in liquid form for ultimate recovery of one or more of its components, it usually becomes necessary to find some means of treating the waste, either for removal of the radioactive contaminants or (by solidification) to permit storage without the danger due to container failure.

Treatment of the waste by removal of the contaminant is feasible actually only when the chemical makeup of the waste is more or less constant (as found in production facilities) and an economically justified system may be designed for the treatment of a specific waste.[4, 5] However, in a research laboratory where chemists work with many different radioactive isotopes, experiments may produce liquid wastes of totally disparate chemical makeup. Such wastes, although usually limited in volume (a few ml to several gallons), can present a serious problem when it comes to the final disposition of the waste. Storage or transportation of radioactive liquids requires special containers and special care in handling.[6, 7]

It is advantageous, therefore, to be able to solidify these liquids so that they may be stored or shipped as packages of solid waste without the danger resulting from container failure.[8, 9, 10]

A method which permits the solidification of small quantities of aqueous liquid radioactive wastes without external agitation has been developed by researchers at the Lawrence Radiation Laboratory (University of California). This method, which has been in use for some time, evolved from experiments utilizing various gelling agents in the solidification of liquid wastes. The use of these gelling agents (various commercial starch preparations) was abandoned because of several difficulties encountered. First of all, there was the need for mechanical mixing, which involved either the recovery of a contaminated stirring paddle after the solidification was complete or the use of disposable paddles that would remain in the gel. Further, it was found that high salt concentrations in the waste or the presence of small amounts of water-immiscible organics often prevented gel formation, or occasionally caused a breakdown of the gel after solidification had been completed. Another difficulty was that starch is an excellent medium for bacterial growth, so that it was necessary to add some sort of bacterial poison to the gel to prevent bacterial decomposition. It was found also that the finished waste package did not stand up under pressure when test drums were lowered to various depths in ocean tests.[11] Last, but by no means least, the gels were found to be reversible when exposed to salt water.

Research was therefore directed towards a solidifying medium which could be added with little or no mixing, the action of which was not reversible, and which, in its final form, would impart sufficient structural strength to the final package.

II. DEVELOPMENT OF METHOD

Preliminary Experiments

1. Use of Portland Cement

Experiments using Portland cement for the neutralization and solidification of acids showed that only small amounts of cement are needed to set up concentrated acids. These concentrated acids, when solidified, appeared to be fluffy, white-yellow solids and were of little structural integrity.

With 100-ml samples of HNO_3, H_2SO_4, and HCl the following minimum values were obtained:

Concentration of acid	Weight of cement (g/100 ml of acid)		
(normality, N)	HNO_3	H_2SO_4	HCl
12	14	16	
8			29
6	25	55	
4		96	117
1	172	103	198
0.1	220	228	231
0.01	245	236	252
0.001	260	252	242
0.0001	269	242	248
0.00001	246	253	
H_2O	220		

This information is presented graphically in Fig. 1.

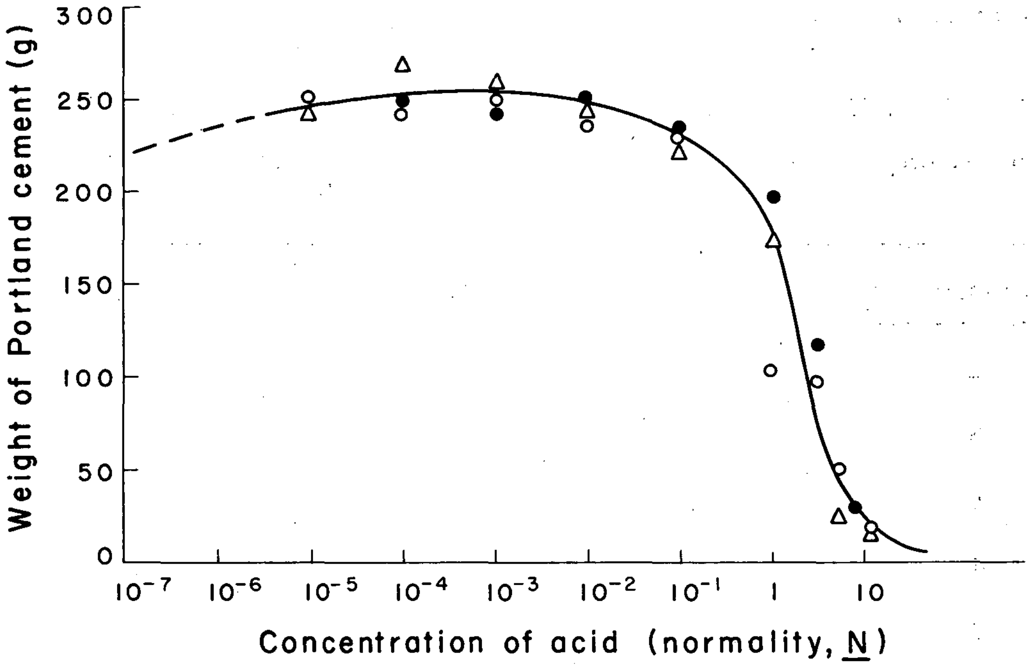

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Fig. 1. Neutralization and solidification of various acids with Portland cement.

The values in the above table are approximate, and were obtained by the following method: 100-ml samples of each acid concentration were placed in beakers and weighed. Enough cement was added to solidify each sample so that there was no free liquid left. The cement was added slowly, and the mixture was not stirred. (Note: any stirring of the mixture, however slight, reduces the amount of cement necessary to solidify the sample.) After the cement had set, the beaker was reweighed and the difference in weight recorded as the weight of Portland cement added.

The measurements are more exact for samples of low H^+ concentration because there is no violent chemical reaction. In samples of 1 to 12 N acids there is considerable heating and gas evolution and therefore a slight loss of weight.

2. Temperature Rise in Solidification of 1 to 12 N Acids by Portland Cement

When cement is used to neutralize acids (HNO_3, H_2SO_4, HCl) of greater concentration than 1 N there is a considerable rise in the temperature of the mixture. The rate of the temperature rise is correlated to the rate of addition of the cement to the acid. In these experiments the cement was added slowly to the acids (starting temperature approximately 22°C), and the final temperatures were recorded as follows:

	HNO_3	H_2SO_4	HCl
1 N	35°C	37°C	35°C
4 N	55°C	65°C	75°C
6 N	90°C	100°C	85°C
8 N	100°C	100°C	100°C

3. Gas Evolution

The gas evolved during the neutralization of the concentrated acid was identified as water vapor given off because of the rise in temperature. The water vapor was identified by the following experimental method: A measured amount of acid was placed in a glass container. This container was then placed in a bomb with a pressure gage. Portland cement was placed around the glass container in the bomb and the bomb sealed. The glass container was then broken by jarring the bomb against a cement slab. The acid then reacted with the cement and the rise in pressure inside the bomb was noted.

In all but one of these experiments the gas pressure returned to zero after an overnight wait. In one test some of the acid reacted with the metal wall of the bomb before it was neutralized by the cement. This resulted in the formation of hydrogen gas and a residual pressure of 20 lb/in.^{2}

4. Use of the Portland Cement—Vermiculite Mixture

Vermiculite was chosen as the absorbent for the solidification mixture for several reasons. It is porous, permitting the infiltration of dry Portland cement into the crevices in its particles; it is light in weight; it is available in various screen sizes and easily obtainable at very reasonable cost.

The vermiculite used in these experiments and in later waste-disposal applications was "Vermiculite-Expanded Form, 60 Mesh or Smaller."

Data were obtained for the following experiments:

a. Hundred-milliliter samples of water were solidified by using various mixtures of Portland cement and vermiculite.

Two base points were used in the experiment.

For Portland cement the 100% value to set up 100 ml of water was taken at 220 g.

For vermiculite the 100% value (i.e., amount of material needed to absorb 100 ml of water so that there is no visible free liquid) was taken as 30 g. (Note: If pressure is put on the vermiculite, water is squeezed out.)

The results of the experiment are summarized in Fig. 2.

b. Series of 100-ml samples of 1N HNO_3 and 0.1 N HNO_3 were solidified with various mixtures of cement-Vermiculite, using the same base points as before.

The experimental results are summarized in Fig. 3.

From these and other trials it became apparent that a mixture of ten parts of Portland cement (by weight) and one part of vermiculite (by weight) generally gave a good set. This mixture was found to be approximately equal to a 1:1 ratio by volume, and this ratio has been used in all subsequent work done with this solidification mixture.

Experimental work showed that the presence of vermiculite resulted in a better mixing of the cement with the liquid, thus leading to a better final set. The vermiculite particles act like a sponge, absorbing the liquid and thus presenting more surface for the cement to act upon.

In all test solutions, there was usually an increase of about 50 to 75% in volume when the liquid was solidified.

It was also found that aqueous wastes containing up to 3% water-immiscible organics could be solidified in this manner without detriment to the setting quality of the cement.

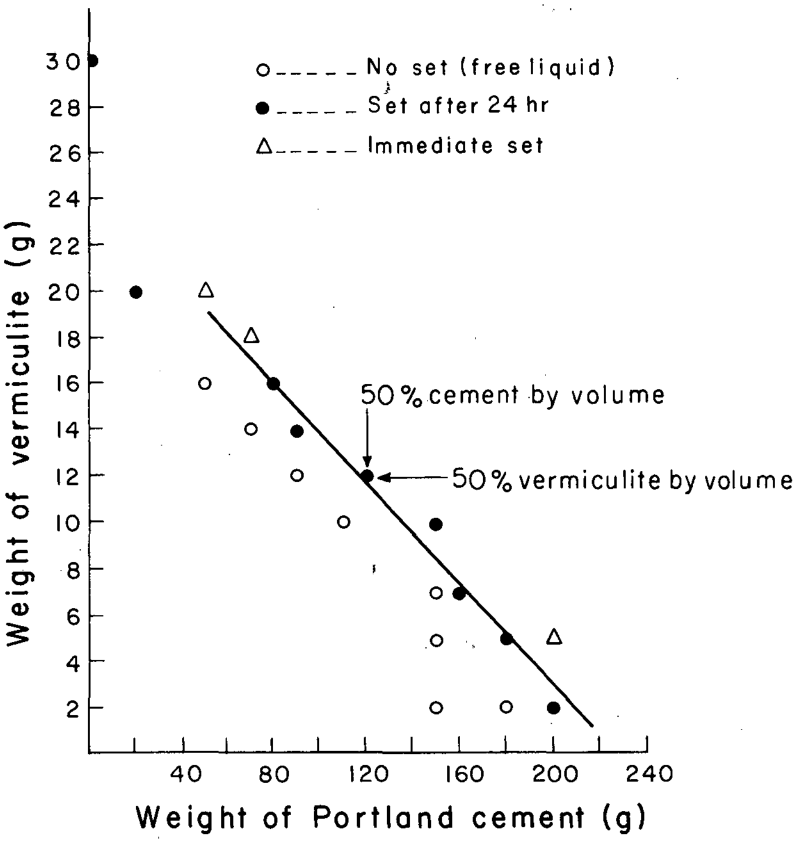

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Fig. 2. Solidification of 100-mil samples of water with various mixtures of Portland cement and vermiculite.

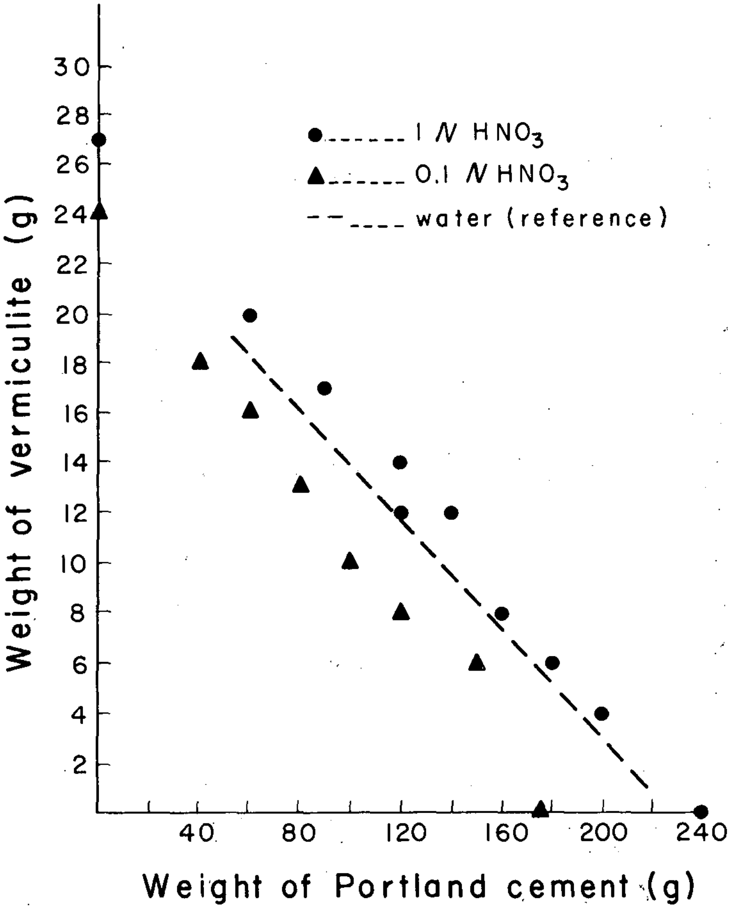

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Fig. 3. Solidification of 100 mil samples of 1N HNO$_3$ and 0.1 N HNO$_3$ with various mixtures of Portland cement and vermiculite.

III. USE OF CEMENT-VERMICULITE MIXTURE IN SOLIDIFICATION OF RADIOACTIVE LIQUID WASTE

The first trial run with radioactive liquid waste was made during the fall and winter of 1955-1956, when about 150 gallons was solidified. During this run about 70 gallons of low-level waste (less than 10^7 d/m/l) was solidified in one batch in a steel tank. The remaining 80 gallons (activity above 10^7 d/m/l) was solidified in the containers.

Since this run a total of about 2550 gallons of low-level wastes collected in 5-gallon carboys has been solidified by the use of cement-vermiculite.

About 160 gallons of high-level active α, β, and γ liquid waste from chemistry runs involving kilocuries of fission products and curies of α-particle emitters have been solidified also.[12] The procedures used with these wastes are described in Section IV.

IV. PROCEDURES USED IN THE SOLIDIFICATION OF RADIOACTIVE LIQUID WASTES WITH CEMENT-VERMICULITE

Solidification of liquid with the cement-vermiculite mixture is basically a simple addition of the solid material to the liquid without additional mixing. A sufficient quantity of the dry cement-vermiculite mixture is added to absorb all the liquid.

The equipment used in solidifying the various types of liquid waste is so designed that during the operation there is no exposure of the radioactive material to the outside atmosphere.

A. Procedure for Low-Level Wastes

These wastes are collected in the various chemistry laboratories in 5-gallon glass carboys.

1. Preparation of the Waste Drum

A 30-gallon steel drum, coated on the inside by the manufacturer with a baked phenolic corrosion-resistant coating, is anchored in a 55-gallon open-top oil drum by setting the 30-gallon drum into 4 to 6 inches of concrete. The lid of the 30-gallon drum, which has been modified in the shop, is clamped on the drum by means of a lock ring. The drum is now ready for filling. (See Fig. 4).

2. Filling of Drum with Liquid Waste

Just prior to the filling, a vent hose is attached to the short pipe near the edge of the lid. This vent hose exhausts the air displaced by the addition of the cement-vermiculite mixture through a high-efficiency particulate filter. The solids-filling funnel assembly is placed in the center hole in the lid, and

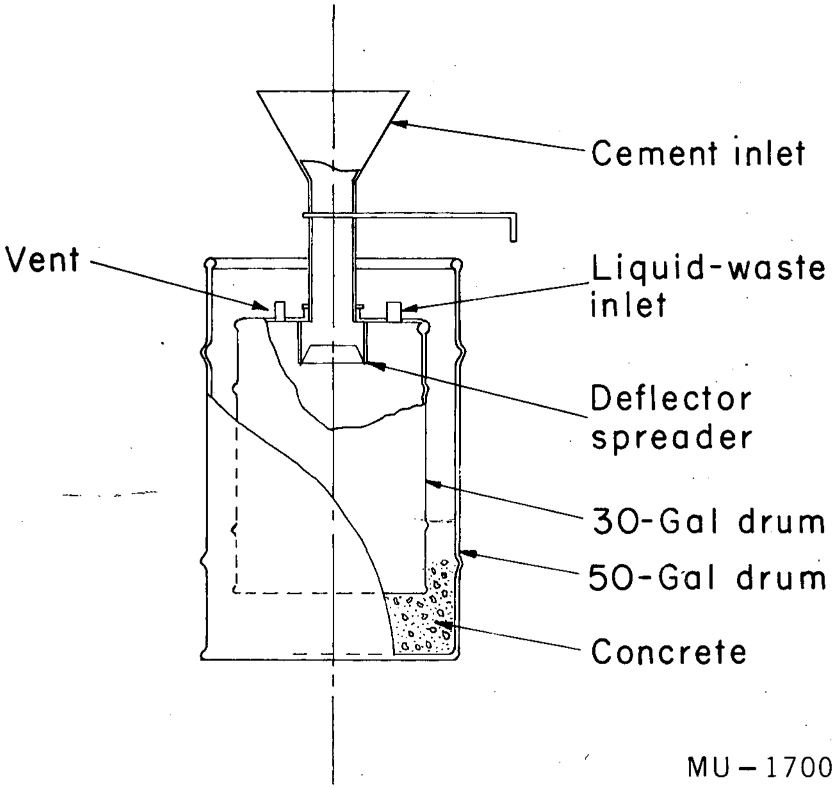

Fig. 4. Cross section of UCRL liquid-waste drum assembly.

the 3/8-in. i.d. Tygon tubing used for the addition of the liquid waste is pushed through the small pipe next to the solids funnel. The solids funnel is filled with cement-vermiculite. From 15 to 17 gallons of aqueous liquid wastes is then transferred into the drum from the 5-gallon glass carboys. Each carboy is checked for pH prior to transferring, and an attempt is made to combine the wastes in such a way that the final acidity of the waste in the drum is kept below 2 N. Where pumping is required it is accomplished easily through 3/8-in. i.d. Tygon tubing with a "Sigma Motor" pump. This type of pump has been found very useful because the liquid does not come in contact with parts of the pump, thus eliminating problems of corrosion and contamination. (Fig. 5).

3. Addition of Cement-Vermiculite

After the desired amount of waste has been put into the drum the filling tube is disconnected and the filling pipe closed with tape.

The addition of the cement-vermiculite now proceeds very slowly. At first only a handful or two of the mix is added by opening and closing the butterfly valve on the funnel. The cement-vermiculite must be added slowly to prevent generation of excessive heat in the drum, which may result in a boilover. During the first hour not more than one funnelful (about 10 liters) of the dry mix should be added.

After the first 10 liters has been added, the addition may be speeded up, but care must be exercised until 30 to 40 liters of the dry mix have been added. The rest of the solid mix (i.e., until the 30-gallon drum is filled) can be added rapidly.

4. Finishing of Drum

After the liquid waste has been solidified the solids funnel and vent line are removed. The drum is then permitted to sit for at least 24 hours before concrete is poured into the space between the 30-gallon drum and the 55-gallon drum. The top of the 30-gallon drum is covered over with concrete. After the concrete sets the package is handled as solid waste for storage and disposal.

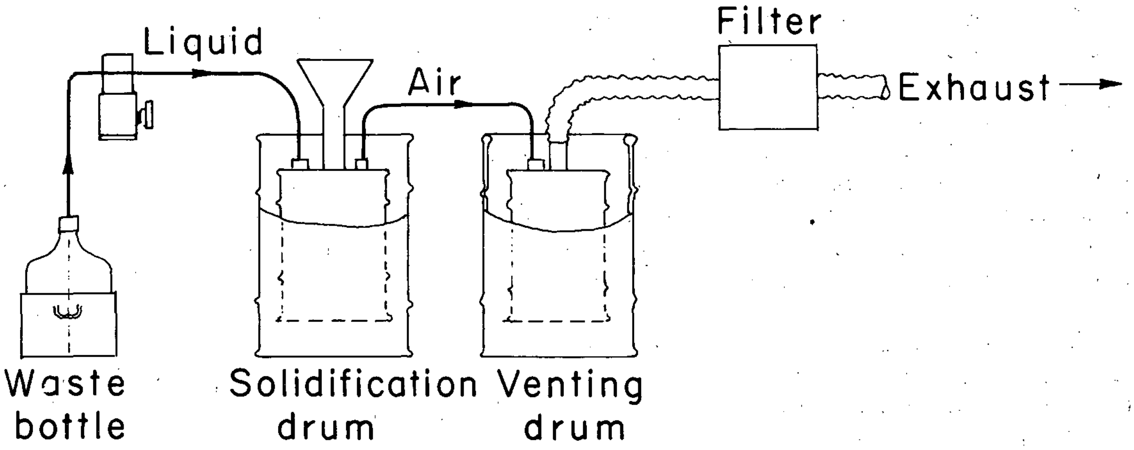

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Fig. 5. Representation of 30-gallon-drum setup for liquid-waste solification.

B. High-Level Wastes

1. High-Level Wastes from 6-Inch Lead Cave Runs

These wastes are collected in shielded containers during the cave operations. About 40 liters of high-level wastes (α emitters about 10^{10} to 10^{12} dpm, β, γ to 150 mr/hr through 4-inch lead) are produced during a run.

a. In early days a 55-gallon steel drum coated with 4A plastic and provided with a modified lid was anchored in the center of a concrete block so that at least 15 inches of concrete surrounded the drum except for the access funnels and piping on the top.

Liquid waste was pumped into the drum drom portable shielded waste containers and solidification proceeded as described above. The block was then sealed with a layer of cold concrete.

b. Recent improvements in the design of the portable shielded waste containers used in the 6-inch lead cave runs have made it possible to add the cement-vermiculite directly into the removable waste container. Thus the disadvantages of the extra step of pumping the waste (radiation exposure while handling lines, connection and disconnection of lines, etc.) are eliminated. (Fig. 6)

After the wastes have been solidified inside the shielded waste container, the waste container is removed from its lead shield and placed in a special concrete block for disposal. The portable lead shield is returned for reuse.

2. High-Level Small-Volume Liquid Wastes

Preplanning and avoidance of dilution frequently result in limiting the waste produced in gloved boxes or other work enclosures to volumes of 500 ml or less. These wastes are solidified with cement-vermiculite, either in their own containers or in 1-quart mayonnaise jars, in the enclosures where they are produced. Thus only solid waste is removed from these enclosures by means of the sealed-plastic-bag technique.[13]

C. High-Level Wastes Stored in 5-Gallon Carboys

During a recent solidification run about 60 gallons of high-level liquid wastes containing a total of 10^{12} dpm α were processed in a specially designed solidification box which permitted the whole process to be carried out without exposing any of the waste to the outside atmosphere. The waste had been collected in 5-gallon glass carboys connected to the work enclosure by means of Tygon tubing.

In order to prevent any exposure the sealed bottles were placed in specially modified metal cans in a polyvinyl bag. The bag was then attached to one of the two flanges in the bottom of a specially designed work enclosure. An empty 5-gallon carboy in can and bag was attached to the other flange. The bottles were raised into position in the work enclosure by means of automobile jacks. (Fig. 7)

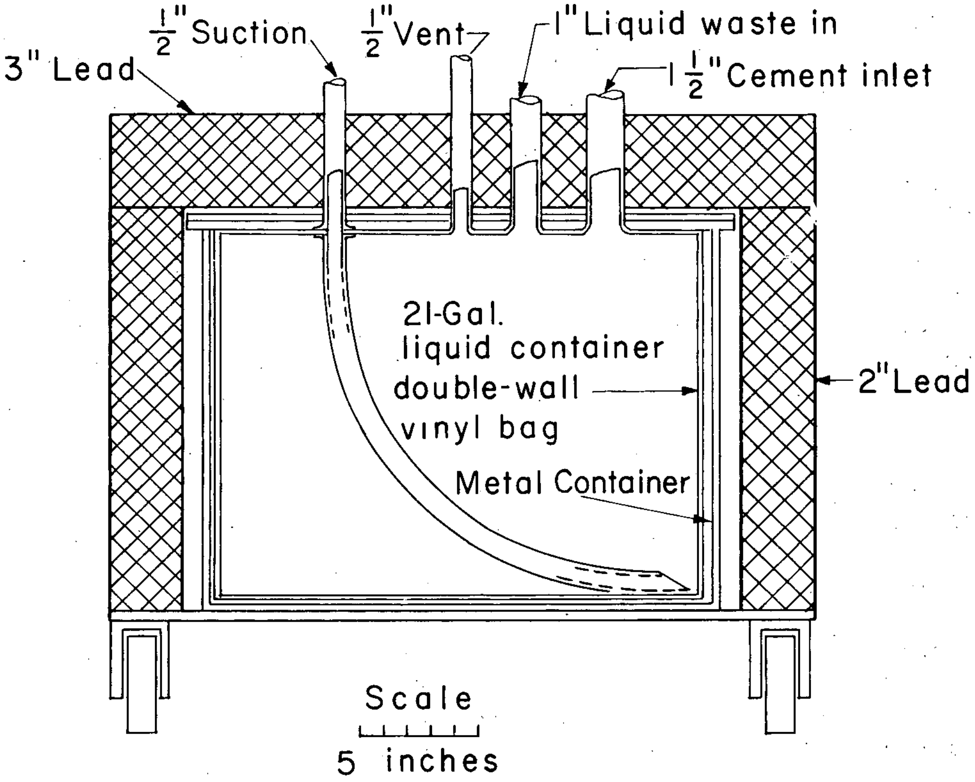

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Fig. 6. Mobile shielded liquid waste container for high-level chemistry runs.

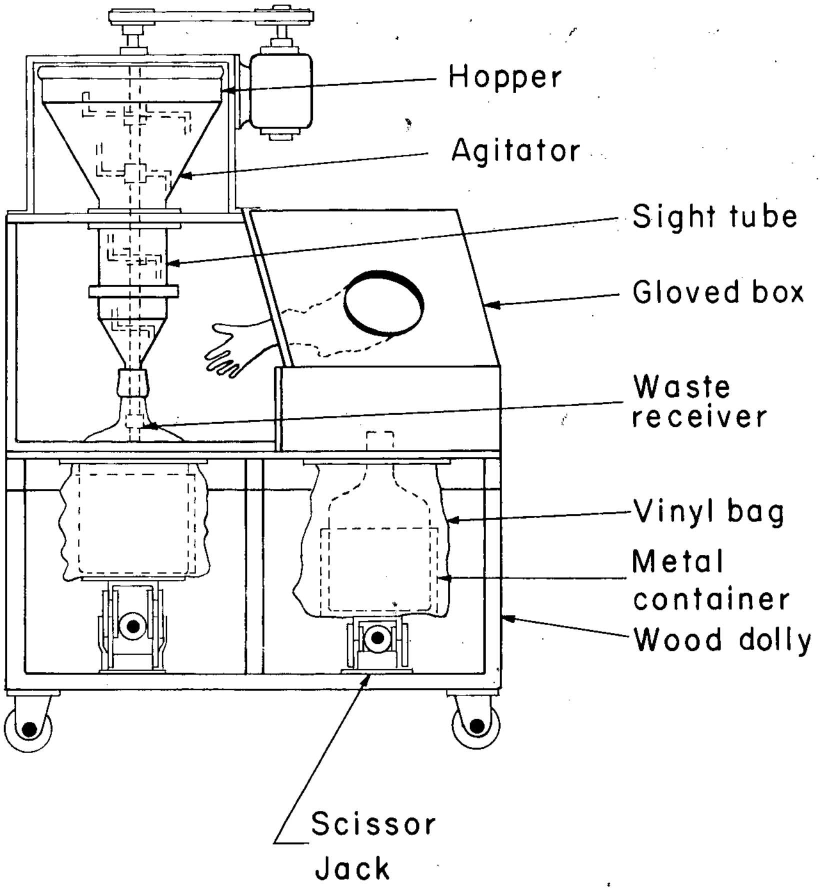

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Fig. 7. Enclosure for solidification of liquid waste in 5-gallon carboys.

Once in position, the full waste bottle was opened and the waste checked for acidity by visual check with pH paper, and, if necessary, a sample was titrated with a standard NaOH solution.

Wastes found to be above 1 to 2 N in acidity were neutralized by the slow addition of concentrated NaOH solution. After neutralization, about 3 gallons of waste was pumped into the empty bottle and solidified by the addition of cement-vermiculite. (The 3 gallons is the maximum volume of waste that can be solidified in a 5-gallon carboy with the addition of cement-vermiculite and allowing for the increase in volume.)

The bottle filled with the solidified waste was lowered, and the plastic bag sealed off by use of a heat welder. A fresh bottle and bag were then attached to the flange over the stub of the old bag and the old bag pulled inside the work enclosure. This process was repeated until all waste had been processed.

V. DISCUSSION

Although the cement-vermiculite method for the solidification of liquid waste has been used successfully at this laboratory for several years, work is being carried out to improve the efficiency of the process.

Most of this work is directed along two lines:

1. Incorporation of safety feature in waste handling.

The main difficulty encountered in the solidification of small amounts of active waste is the possibility that the wastes are of a highly concentrated nature (concentrated acids, cleaning mixtures, organics, etc.) which, when mixed indiscriminately, could cause an explosion inside the solidification enclosure. A simplified system for the assay and batch neutralization of wastes is planned so that only wastes of 1 to 2 N (or less) acidity will be solidified by the addition of the cement-vermiculite mixture.

2. Reduction of cost of equipment used in the solidification of various types of liquid waste

The cost for the materials used in the solidification (i.e., cement-vermiculite) is relatively low per unit volume (about $0.20/gallon). The cost per solidified gallon of waste rises because of the use of specific equipment used in the specific process. This equipment consists of 1-quart mayonnaise jars for the solidification of small volumes of liquid waste, 5-gallon glass carboys for larger volumes, 30-gallon steel drums with special lids, special enclosures, etc. These raise the total cost per gallon of solidified waste to from $1.00 to $2.00. Efforts in this line will be in the design and use of simpler equipment and the utilization of less costly substitute materials for final disposal containers.

The method for the solidification of aqueous radioactive liquid wastes described in the preceding sections has been found satisfactory for use with most of the wastes produced at Lawrence Radiation Laboratory. Because experiments are planned under the concentrate-and-confine policy practiced at the Lawrence Radiation Laboratory, the volumes of liquid waste to be solidified are kept small.[14]

As stated previously, liquid wastes produced in a research laboratory can be of a great variety, and thus a method which can be adapted for the disposal of most of these without extensive modification is of advantage as far as cost and labor are concerned. The use of cement-vermiculite in the solidification of liquid wastes may be of interest in the land burial of wastes. Recent work at the Oak Ridge National Laboratory using cement-vermiculite and radioactive waste as makeup liquor showed that the concrete could be sintered at high temperatures. Leaching tests then determined the retention of the radioactivity in the concrete.[15]

The cement-vermiculite method of solidification of aqueous radioactivity liquid waste is useful in areas where liquid-storage facilities are limited and permanent disposal of the waste is desired.

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