EVALUATION OF A LOW-LEVEL

RADIOACTIVE LIQUID WASTE GELATION PROCEDURE

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of

Master of Science

in

The Department of Nuclear Engineering

by

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B.S., Louisiana State University, 1971

August, 1973

DEDICATED TO
Sheryl, my wife

ACKNOWLEDGEMENT

I express my gratitude to the staff of the Nuclear Science Center for their patience and understanding while I was preparing this thesis. Special thanks go to Dr. Robert C. McIlhenny, my major professor, for his guidance, patience, and encouragement, especially in editing my rough drafts; to Dr. John C. Courtney, for his assistance and practical advice; and to Dr. Frank A. Iddings, for his availability and helpfulness.

The time-saving hints from Jim Robinson, Nelson English, and John Phillips, were very much appreciated.

To Sheryl, my wife and secretary, I am deeply indebted for the long and strenuous hours spent typing this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Although there are a number of liquid-waste solidification methods described in the literature, they are designed for large-volume applications which do not meet the special needs of a typical university where small volumes of aqueous and organic low-level wastes are generated. This project was undertaken to develop a waste-solidification procedure that would be applicable to both types of waste liquids to avoid the expense of renting special double-walled shipping containers, and would have a lower density than concrete, which is a commonly used solidification matrix. Safe-T-Set, a commercially available hydrophilic organic polymer, which gels readily with water, was found suitable for gelling toluene when the toluene is first emulsified with an equal volume of water and one-fifth volume of Triton X-100, a nonionic surfactant. Open-cup, ambient-temperature evaporation tests of the pure water- and toluene-emulsion gels were conducted, from which it was found that toluene evaporates first, but that both systems ultimately dry completely to a small residual solids volume. Open-cup evaporation at $105^{\circ}C$ is complete within 25 hours. Tracer retention tests in a vacuum system established that tritiated water and toluene-^{14}C were poorly retained by the gel (less than 23%), but that water-soluble ionic materials (lysine-^{3}H and $H_2^{32}PO_4$) were reasonably well retained (greater than 90%). Typical liquid-scintillation wastes were successfully gelled in gallon-quantity batches. The gelled wastes had characteristics suitable for shipment as solids. Further research will be required, however, in such areas as inflammability and biodegradability.

CHAPTER I

INTRODUCTION

As the nuclear power industry grows due to the shortage of fossil fuel, the amount and complexity of radioactive waste also increases.

To the present date, the wastes (solids, liquids, and gases) have been usually either buried, stored, or dispersed into the environment, but as the nuclear power industry grows in the future, so will the waste problem. Presented in Table 1 is the prediction that by the year 2000 approximately 77,000,000 gallons of high level waste is expected.[1] The Environmental Protection Agency (EPA) and other environment factions are pressuring the nuclear industries to find better methods of waste treatment or not build at all. The Atomic Energy Commission (AEC), also realizing the problem of waste, has formed a Division of Waste Management to find a workable solution to the waste problem.

The biggest contributor to the radioactive waste problem is liquid waste, especially the high activity level waste, from fuel reprocessing plants. Storage in underground tanks has been a solution for a number of years, but now because of more limited space and expected waste volume increase, other methods such as solidification of liquids must be considered. The prime reason for waste solidification is that great volume reduction can be obtained. Solidification and then storage in appropriate sites (see Appendix) must now be a prime consideration for present and future waste management, to conserve the limited storage site space.

TABLE 1

Estimated Wastes from Nuclear Power*

	Calendar Year		
	1970	1980	2000
Installed electricity, 10^3 MW(e)	6	150	940
Fuel Processed, 10^3 metric tons/year**	0.055	3.0	19
High-level liquid wastes, 10^6 gal/year+	0.017	0.97	5.8
Accumulated high-level wastes			
As liquid, 10^6 gal+	0.4	4.4	77
As solid, 10^6 gal‡		0.33	5.8
Accumulated fission products			
Weight, metric ton	2	550	14,000
Beta activity, MCi	2000	19,000	267,000
Heat-generation rate, MW	0.7	55	730
Sr-90, MCi	4	960	12,000
Cs-137, MCi	5	1,280	20,000

* From Reference 1
** Based on 33,00 MWd/metric ton
\+ At 100 gal/10,000 MWd(t).
‡ At 1 ft^3/10,000 MWd(t).

2

Solidification and/or fixation can be accomplished in high level liquid wastes in several ways, such as the methods of pot calcination, spray solidification, fluidized bed calcination, and phosphate glass solidification. These techniques will be considered in detail in Chapter II.

One obvious advantage of a successful solidification program would be the reduced transportation cost from the point of origin to the disposal sites. A second advantage is that the safety requirements for packaging would be less stringent since the shipment would be a solid instead of a liquid.

Sources of Radioactive Wastes

There are three primary sources of radioactive wastes. The first consists of the mining, milling, and fuel manufacturing operations which produce only the naturally occurring radioisotopes. The second is made from the irradiation of nuclear fuel and its reprocessing. The greatest amount of activity is from the fission product radioisotopes. The third is due to irradiation of non-fuel materials, and purposely produced radioisotopes for experimental use. This also includes the user of the preceding sources of radioisotopes.[2] Figure 1 is a simplified presentation of the basic sources of the radioactive waste cycle.

In the mining process, for a normal 1000 tons of ore processed a day, there are low level liquid wastes discharged into ponds and lagoons averaging 300 to 500 gallons per minute. For each ton of uranium that is processed there are approximately 1000 gallons of liquid wastes of intermediate level activity produced in the milling cycle of fuel fabrication.[3]
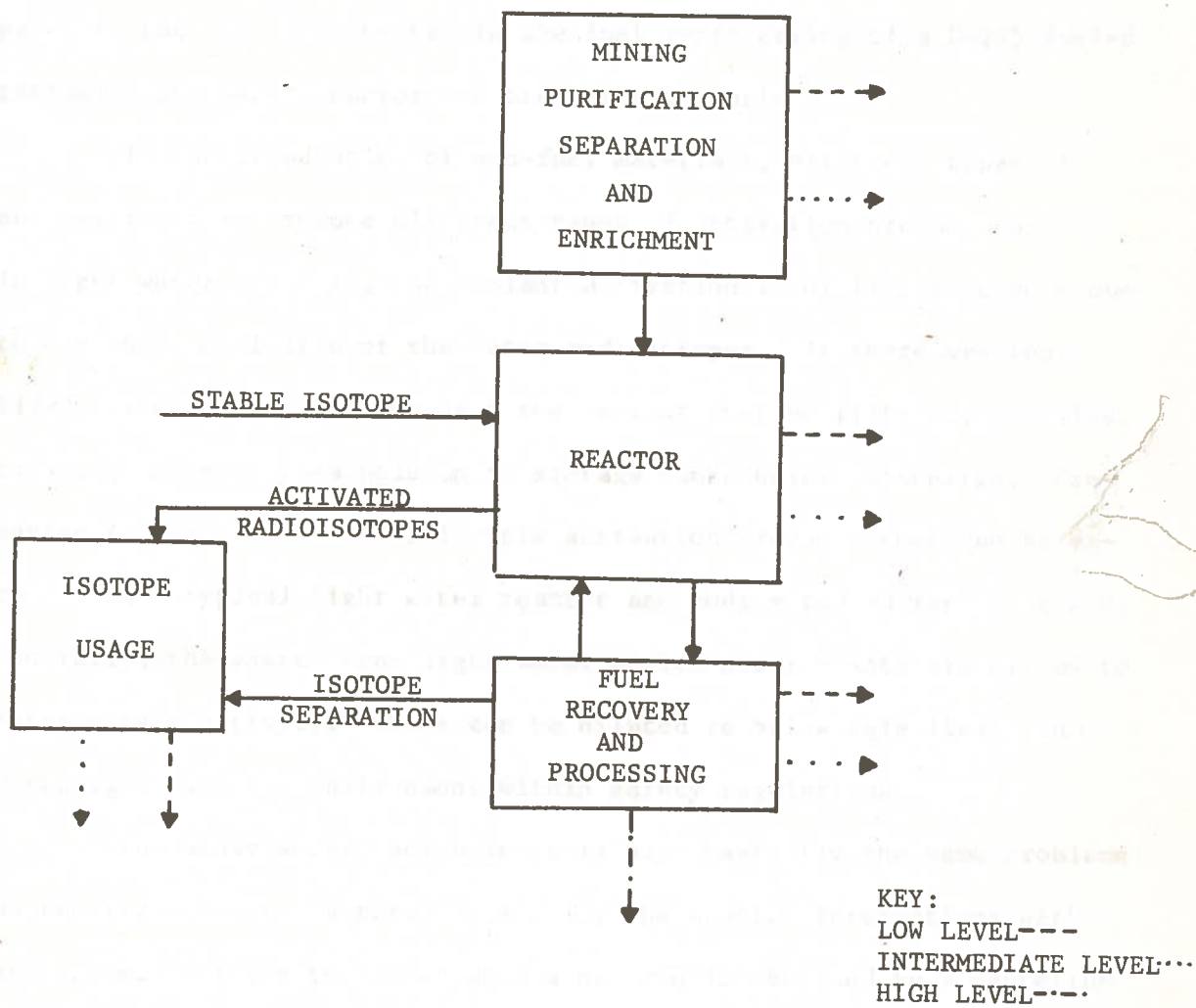
FIGURE 1. Sources of Radioactive Wastes

MINING
PURIFICATION
SEPARATION
AND
ENRICHMENT

STABLE ISOTOPE

REACTOR

ACTIVATED
RADIOISOTOPES

ISOTOPE
USAGE

ISOTOPE
SEPARATION

FUEL
RECOVERY
AND
PROCESSING

KEY:
LOW LEVEL---
INTERMEDIATE LEVEL⋯
HIGH LEVEL-·-·

4

Fuel reprocessing is the major source of high activity liquid wastes. From 1 to 100 gallons of high level liquid wastes can be expected from each kilogram of uranium processed.[3] The principle fission products that can be expected in the fuel reprocessing of a U-235 fueled thermal light water reactor are presented in Table 2.

In the irradiation of non-fuel materials, different types of nuclear reactors produce different types of activation product wastes. In light water reactors, the coolant activation is of little concern due to the short half-life of the activated isotopes. If there are long lived corrosive products present the coolant must be filtered, purified, treated, and sometimes held up in storage tanks before discharge. Presented in Table 3 are the principle activation products that can be expected in a typical light water reactor and sodium cooled reactor cases. Generally, the wastes from light water cooled power plants are of low to intermediate activity. These can be diluted to below safe limits and discharged into the environment within safety regulations.[2]

The heavy water cooled reactors have basically the same problems as the light water reactors, except for the neutron interactions with deuterium. Tritium is formed when a neutron is absorbed by a deuterium atom. But again this is not a major source of tritium. The major sources are fission product escape and fast neutron reactions on the boron shim, used in reactor control.[4] The coolant must be monitored and treated to keep the tritium release within safety regulations. In gas cooled reactors, the coolant is usually helium gas. The major problem that could occur in using this gas would be the neutron interaction with

TABLE 2

SOME IMPORTANT FISSION PRODUCTS*

Nuclide	Half-life	Yield,%**
Kr-85	10.4 years	0.3
Sr-89	50.4 days	5.3
Sr-90	28.9 years	5.8
Y-91	59 days	5.9
Zr-95	65 days	6.4
Tc-99	2.12×10^5 years	6.2
Ru-103	39.8 days	3.7
Ru-106	1 year	0.5
I-131	8.05 days	2.9
Xe-133	5.27 days	6.1
Cs-137	30.2 years	6.3
Ba-140	12.8 days	6.2
Ce-141	32.5 days	6.0
Pr-143	13.76 days	6.0
Ce-144	285 days	5.6
Nd-147	11.06 days	2.6
Pm-147	2.64 years	2.6

*   From References 2,3.
** For thermal neutron induces fission of U-235

6

TABLE 3

IMPORTANT ACTIVATION PRODUCTS

FOUND IN POWER REACTOR COOLANT WASTES*

Radioisotope	Half-life	Activated Source
Light-water-cooled reactors		
N-16	7 sec	water
N-17	4 sec	water
O-19	30 sec	water
H-3	12.0 years	lithium hydroxide, D_2O
Al-28	2.0 min	aluminum
Ar-41	1.8 hr	air
Cr-51	27.0 days	steel
Mn-56	2.6 hr	steel
Fe-55	2.9 years	steel
Fe-59	45.0 days	steel
Co-58	71.0 days	steel
Co-60	5.2 years	steel
Cu-64	12.8 hr	17-4 steel and Cu-Ni alloy
Zr-95	65 days	Zr fuel structure
Ta-182	111.0 days	steel
Sodium-cooled reactors		
Na-24	15.0 hr	sodium
Na-22	2.6 years	sodium
Ru-86	19.5 days	coolant impurities
Sb-124	60.0 days	coolant impurities

* From Reference 2, 3.

7

helium-3 to form tritium by an (n,p) reaction. But since the abundance of He-3 is small (0.00013%) this is not a major problem.

The use of radioisotopes by educational, research, and industrial users also results in radioactive wastes. These radioisotopes, such as P-32 and Fe-59, are used mainly in hospitals and laboratories for injections and tracer studies. These wastes may total 100 mCi/day for only a few patients. Most of the isotopes have short half-lives and are allowed to decay, but a few need to be disposed of.

Sources such as Cs-137, Co-60, and Ir-192 are commonly used for non-destructive testing and other industrial purposes. Since these sources are encapsulated solids, the problem of radioactive wastes is minimal. But special precautions must be taken in the manufacturing of the sealed sources containing Cs-137, because of its highly reactive nature and its tendency to "creep" or move along any surface with which it makes contact.

Types and Classification of Wastes

There are several ways to classify wastes. One way is by their physical form, that is: liquid, solid, gaseous, or aersol. A second way is to classify wastes by the level of activity present, such as low, intermediate, and high. And a third way is by the decontamination factor required to reduce the activity of a substance to within safe limits. The decontamination factor is used interchangeably with the previously mentioned waste classification.

Low levels of waste are commonly designated as having uCi/gal, intermediate as mCi/gal, and high levels as Ci/gal. This method does

not distinguish between the different types of radioisotopes, hence Eisenbud proposes the following deinition.[5] Low level wastes are those which may be discharged into the environment within safety regulations. The intermediate level wastes are those which may be discharged into the environment with only some dilution, or after some decontamination. And the high level wastes are those too intensely radioactive to be discharged safely into the environment without storage for decay.

Another method of classifying radioactive wastes is by the required decontamination factor, DF, which is defined as the unitless ratio of the initial concentration of activity to the final concentration of activity. This term may be used with any process that compares the input activity or concentration to the output activity or concentration. As an example, if the input stream of liquid wastes going into a filter system contains 10 mCi/cc and the output stream has an activity of 1 μCi/cc, the system DF is 10^4. Low level wastes are classified as requiring a DF of less than 10^3, intermediate a DF of $10^3 - 10^5$, and high level a DF greater than 10^5, before release into the environment.[3,6]

CHAPTER II

RADIOACTIVE WASTE TREATMENT PROCESSES

Radioactive waste treatment depends mainly on the forms of wastes (solids, liquid, gases) being handled. Each type of waste has its own peculiar problem that must be taken into consideration.

Solid Wastes

Solid wastes are usually processed in two ways: compression and incineration. From nuclear power plants the solid wastes are generally low level items like paper, plastic, etc. They are usually placed in containers and then compressed by a hydraulic press. Then the solid is bailed to keep it from expanding. A 3:1 to 7:1 volume reduction can easily be achieved at a cost of $2.00 to $3.00 per cubic foot. If incineration is used, the volume reduction can be up to 40:1.[3,6] However, the use of absolute filters and air scrubbers to trap and clean the particles makes this process much more expensive than simple compression and bailing, because the filters also become solid waste.

Gaseous and Aerosol Wastes

For gaseous and aerosol wastes the processes can vary quite decisively depending on the waste in question. These processes include adsorption, absorption, filters, and gas scrubbers.

Adsorption. Adsorption is the chemical or physical adhesion of a molecule to a surface that it contacts. Activated carbon, silica gel, and alumina are common adsorbents. The latter two can only be used in a dry gas stream. Activated carbon is mainly used to trap iodine; it can

remove up to 99.9% of the iodine passing through it. Also it is used to
contain and detain xenon and krypton long enough for decay to stable
nuclides. [3,7]

Absorption. Absorption is the molecular interaction between
two substances. It has been successfully used to scrub gases containing
$^{14}CO_2$ or ^3HHO into a liquid for further treatment.

For radioactive aerosols there are several different types of
filters in use now. Depending on the type of particles under consider-
ation, the filters that are used include fiberglass, bag filters, and
cellulose absolute filters. To be defined as an absolute filter by the
Atomic Energy Commission it must have 99.9% removal efficiency for a
0.3 μ particle. [3,7]

Centrifugation. With centrifugation, particles down to 5 μ can
be removed. Spray scrubbers are used for particles greater than 5 μ,
and Venturi scrubbers are used for sub-micron particles. [3]

Liquid Wastes

The main waste treatment processes for low and intermediate
level liquid waste are filtration, ion exchange, evaporation, foam sep-
aration, and biological uptake.

Filtration. Filtration is used to remove suspended solids from
liquids being processed. A high percentage of the insoluble corrosion
products present in light water reactor coolants can be removed by fil-
tration. Two types of filters are generally used: cartridge and pre-
coat types. The cartridge filter is generally disposable, and is made
from cellulose resin-bonded into a high porosity filter. The pre-coat

filter is rechargeable and can be used again with each new coating of finely-divided inert material such as diatomite, perlite, asbestos, or cellulose.[6]

Ion-exchange. Ion-exchange is only applicable to aqueous wastes having a total solid content of less than 2500 ppm. The resin works most efficiently for a solid content of less than 1000 ppm. The decontamination factors (DF) range from 50 for cation resins to about 10^5 for mixed bed resins.[8] The ion-exchange resin may be regenerated by use of an appropriate acid or base. The cost of resin is in the range of $60.00 to $80.00 per cubic foot.[6] Baetsle and Dejonghe showed that using a special mineral ion-exchange bed consisting of zirconium phosphate and ferrocyanide molybdate, a decontamination factor of at least 10^6 can be obtained for Cs-137 and Sr-90.[9]

Evaporation. Evaporation is a highly effective method of liquid waste treatment, which can be either partial with a concentrated slurry, or complete with a dry powder residue. Decontamination factors can be as great as 10^6 to 10^7 for vapor compression evaporators. Due to extensive gas cleaning and process safety equipment the cost can be from $50.00 to $100.00/1000 gallons, compared to $0.20/1000 gallons for a simple desalination evaporator.[3] As a typical example, the Knolls Atomic Power Laboratory (KAPL) in Schenectady, N.Y., has a 400 gal/hr forced-feed flash evaporator. The feed activity is 3×10^{-2} $\mu ci/cm^3$ and the overall decontamination factor is $10^4 - 10^5$.[8]

Foam separation. Foam separation has been proposed by the Oak Ridge National Laboratory (ORNL) as a method for removal of strontium and cesium from low to intermediate level liquid wastes. The ions have

a tendency to concentrate in the liquid at the bubble surface and hence are carried off. A decontamination factor of 10^3 has been obtained.[3]

Biological Uptake. Biological uptake is of interest because certain plants have an affinity for certain isotopes. The average aquatic plant can concentrate up to 60 ppm of Zn-65 without harm being done to its ecosystem.[10] It has also been found that virtually complete removal of cerium can be expected in oxidation ponds by biological uptake. Oxidation ponds as a polishing agent can be used effectively for low level waste water. Short-lived isotopes are consequently detained and diluted in this type of biological waste treatment.[8]

High Level Liquid Wastes

High level liquid wastes must be treated differently than the low to intermediate level liquid wastes. There are two main processes of handling the high level wastes: calcination and fixation. The calcination process includes pot, spray, and fluidized-bed calcination. The fixation process includes concreting, asphalt and polyethylene fixation, vitrification, encapsulation, and polymerization.

In all three methods of calcination (pot, spray, and fluidized-bed) the process is basically the same. The waste is heated from 400°C to 1200°C so that essentially all the volatile constitutents are driven off and either the solid (or a melt that will cool to a solid) is left.

Fluidized-bed. In the fluidized-bed solidification process (see Figure 2), the liquid waste is injected through pneumatic atomizing nozzels into the side of a heated (400°C to 600°C) bed of grannular solids. The solids are continously agitated (fluidized) by a gas flowing upwards through the fluidized bed reactor. When the waste makes
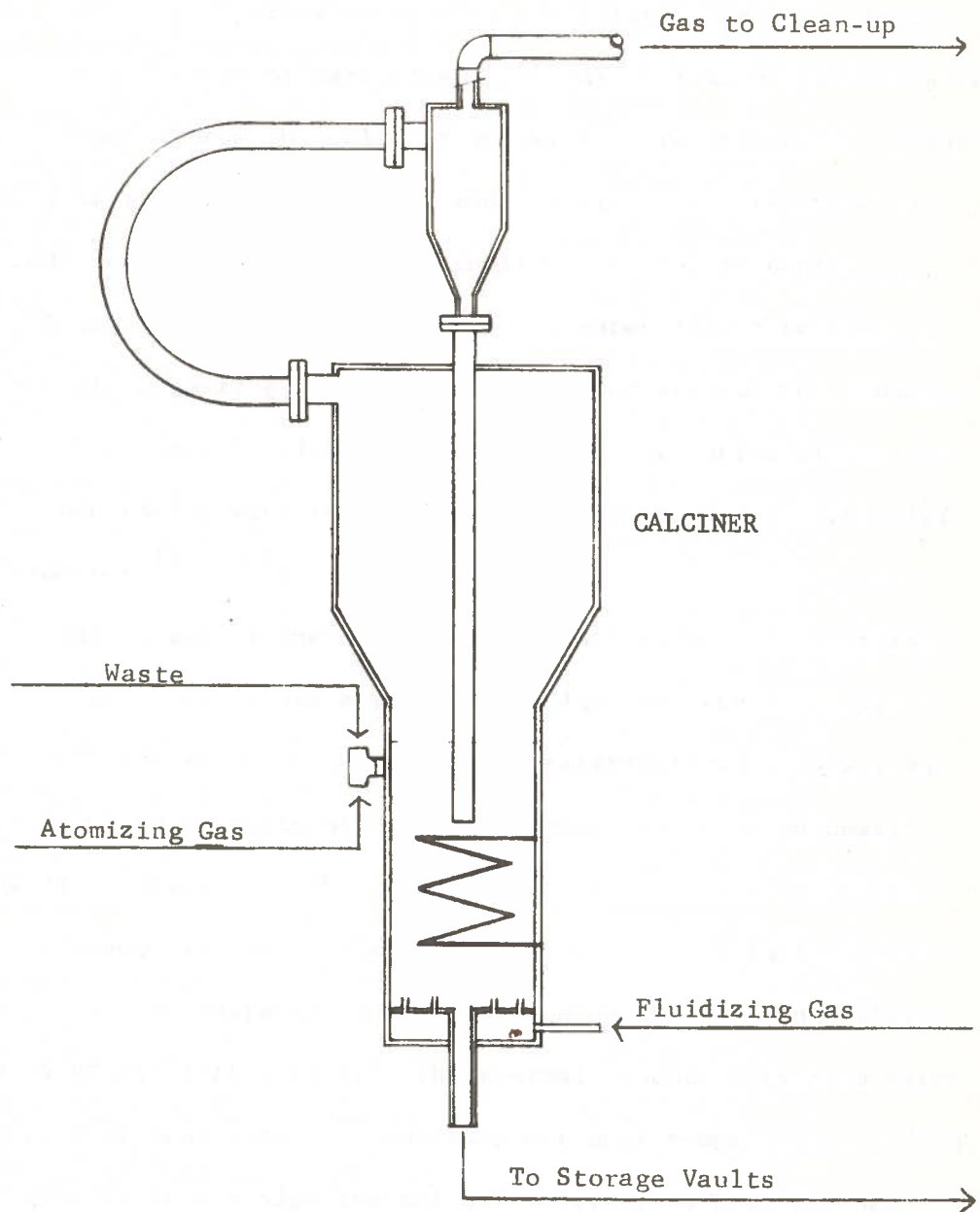
FIGURE 2. Fluidized-bed calcination

14

15

contact with the hot, grannular bed the results are evaporation and calcination of the feed as coating on the bed particles. The calcium entrained (trapped) with the process gases from the calciner is removed from the gas stream by cyclone separators and filters, and then is returned to the main stream of particles. The main stream of particles is continuously removed from the calciner vessel and transported to storage tanks. The storage tanks are usually made of stainless steel and can either be individual pots or large cylindrical or annular containers.[1] It has been found by Buckman and McBride that rates from 5 to 100 liters/hr per air atomizing nozzel can be achieved without the tendency of caking.[11] The particle size is controlled by regulation of the air-to-liquid volume ratio, with the desirable size being 0.5 to 0.6 millimeters in diameter.[12]

The advantages of the fluidized-bed process are: (1) it is a continous process, (2) it has a relatively high capacity for a given equipment size, (3) scale-up technology is relatively well known, and (4) solidified waste products are readily transportable by pneumatic means. The disadvantages of the process are: (1) it is a moderately complicated system, (2) solidified waste products are relatively water soluble, and (3) the waste has a relatively poor thermal conductivity (0.17 to 0.25 BTU/(hr)(ft)(^{o}F)).[1] The thermal conductivity of a material is the rate of heat flow by conduction per unit temperature gradient. It is desirable to have a high thermal conductivity so that the heat generated by the fission products decay is not retained within the waste, but escapes into the surrounding environment.

Pot Calcination. In pot calcination, the principle processing vessel, the pot, is also the final container for the solidified waste (see Figure 3). The liquid waste is added to a pot that is heated in a multiple-zone heating and cooling furnace. The waste is concentrated at a constant volume to the point that a scale of calcine cake forms on the walls of the pot. The scale grows in thickness and hence reduces the heat transfer from the pot wall to the boiling sludge. Therefore, the feed rate must be reduced accordingly. The feed is shut off when it drops below 5 liters/hr. At this point the scale should have grown inward from the pot wall and upward from the bottom of the pot to fill the pot, except for a small liquid containing space in the upper 3 to 5 feet of the salt cake. Heating is then continued until the liquid is boiled to dryness and all the waste in the pot has been calcined (about 850-900°C). The pot is then cooled in a furnace, removed, sealed, and taken to storage.

The pots, because they also serve as storage containers, must be made of corrosion-resistant materials. Type 304L stainless steel is usually used (less than 0.0003 in./day of corrosion) during processing.[1]

Pot calcination is a batch process and has the advantage of being a simple process that is adaptable to a wide variety of feed compositions. It has these disadvantages: (1) a stainless steel pot is required, (2) the thermal conductivity of the calcine is low (0.15 to 0.25 BTU/(hr)(ft)(°F)), (3) multiple pot lines must be used to increase the capacity of the system, and (4) the solidified waste is quite leachable in water (1.0 to 10^{-1} g/cm^{2}day).[1] The feed rate can vary from 8 to 30 liters/hr, with below 5 liters/hr being unprofitable.[13]

Waste   →   Gas to Clean-up →
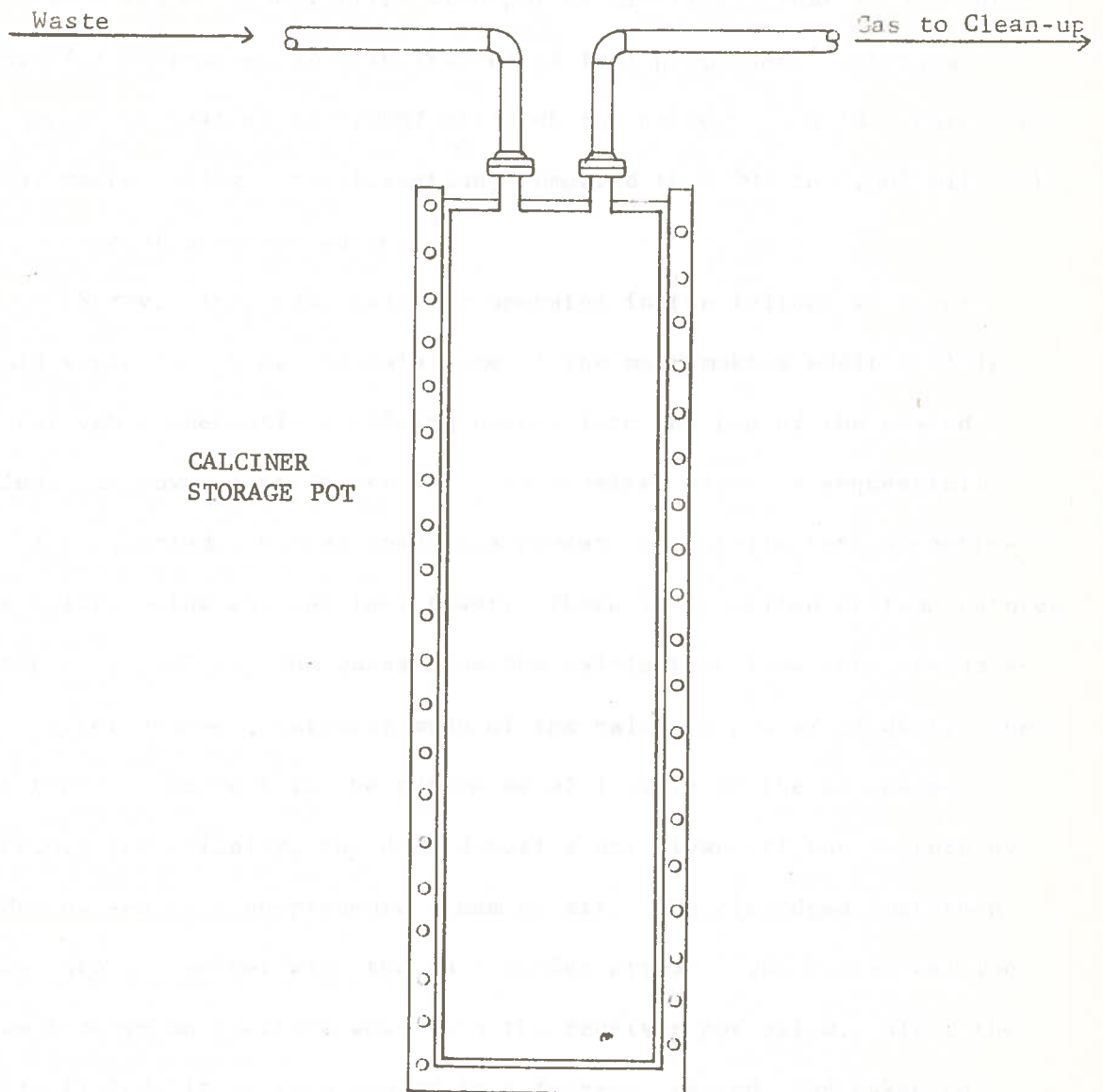
CALCINER
STORAGE POT

FIGURE 3. Pot Calcination

17

Waste Solidification Engineering Prototypes (WSEP) test runs at Battelle-Northwest produced these results. With nine runs completed, 7.7 megacuries were solidified with pot calcination. That is an equivalent of 13.8 tonnes (2205 lb./tonne) of fuel processed.[14] Perona estimated the cost to be 0.0087 mill/KWh for processing acidic Purex and Thorex wastes using pot calcination, compared to 0.002 to 0.009 mill/KWh for storage of the same waste.[15]

Spray. The spray calciner operates in the following manner. Liquid waste (which may contain some of the melt making additives) is fed through a pneumatic atomizing nozzle into the top of the heated cylindrical tower (see Figure 4). The atomized waste is sequentially evaporated, dried, and calcined to a powder as it falls into a continuous melter below the calciner tower. There it is melted at temperatures of $800^{o}C$ to $1200^{o}C$. The gases from the calcination flow into the adjacent filter chamber, carrying much of the calcined powder as dust. The dust tends to collect in the porous metal filters as the gas passes through. Periodically, the dust deposits are blown off the filters by sudden pulses of high-pressure steam or air. The dislodged dust then falls into the melter with the main powder stream. The molten calcine flows through an overflow weir into the receiver pot below. After the pot is filled, it is then cooled in a furnace, sealed, and taken to storage.[1]

Spray solidification has several advantages: (1) it is a continuous process with low hold up volumes, (2) it is adaptable to a moderately wide variety of feed compositions, (3) it produces a variety of good-quality solids (leach rates of 10^{-3} to 10^{-6} $g/cm^{2}day$), and
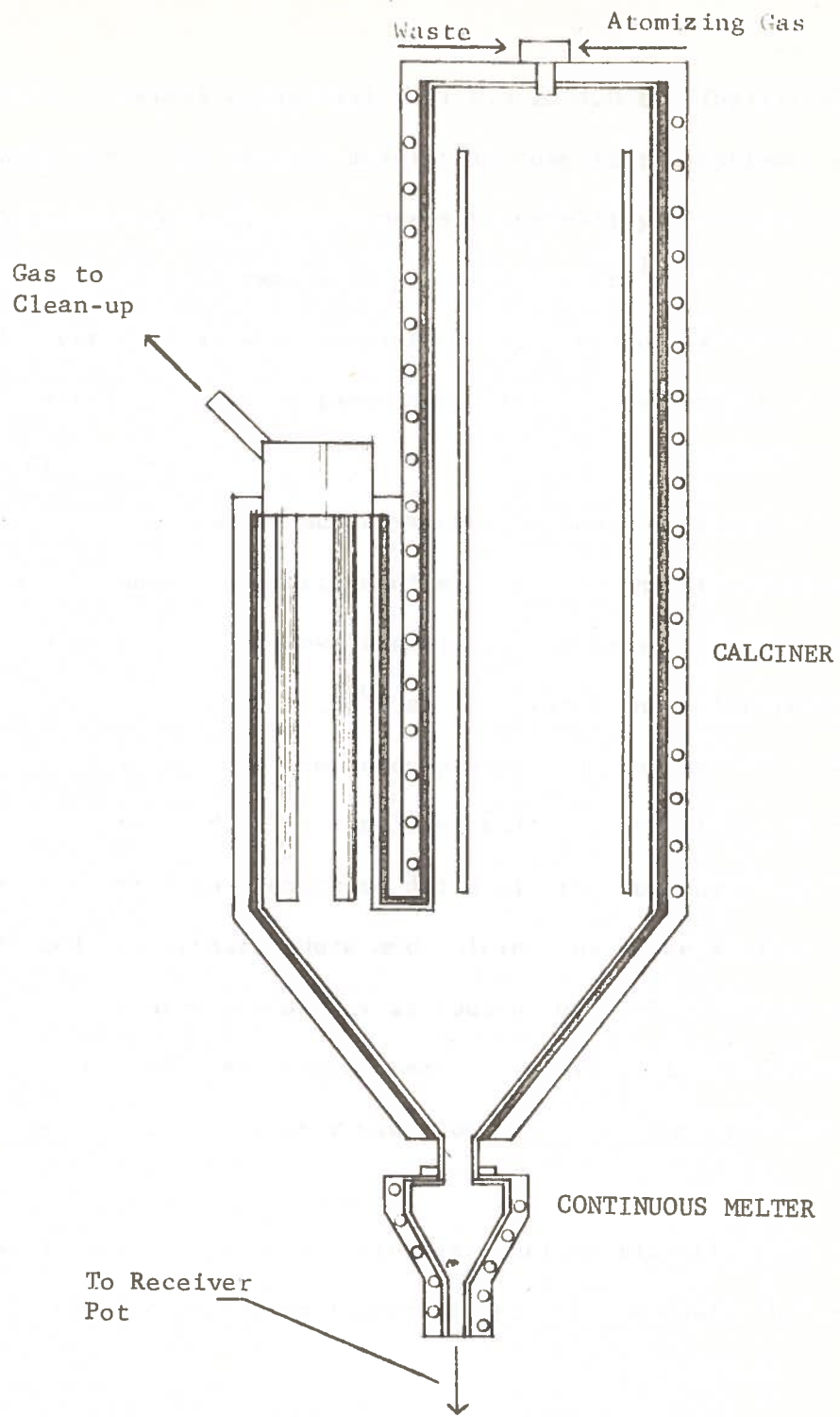
FIGURE 4. Spray Solidification

19

(4) the solid has a thermal conductivity of 0.5 to 1.0 BTU/(hr)(ft)(^{O}F).
The disadvantages are: (1) it is a moderately complicated system, (2)
it requires good flow control, (3) it needs high-quality atomizing, and
(4) at present it demands an expensive platinum melter.[1,14]

With 13 test runs at WSEP completed, 25.3 megacuries were solid-
ified using the spray calcination technique. That represents 16.6
tonnes of fuel processed.[14]

A novel idea, originated and developed at Savannah River
Laboratory, uses the unique properties of sulfur for converting radio-
active waste to a solid form of low solubility. Aqueous acidic wastes
are reacted with molten sulfur at 150°C so that water and volatile acids
are driven off and the chemical compounds present in the waste are cal-
cined and chemically reduced. The resulting sulfur-waste slurry is then
heated at 400-444°C for 1 to 5 hours to drive off the sulphuric acid and
residual water, and to further reduce and calcine the waste slurry.
After heating, the sulfur-waste slurry is cooled to 120-150°C and trans-
ferred as a liquid to the final containment vessel where it is allowed
to solidify. The leaching of tracer was found to be on the order of
0.01 to 0.02 in./year.[16]

The solidification process could also include vitrification.
Vitrification is the incorporation (immobilizing) of the waste into a
glassy solid.

Vitrification. Phosphate-glass and borosilicate-glass solid-
ification are the two main processes used. ORNL has extensively used
the borosilicate-glass process, whereas Brookhaven National Laboratory
uses the phosphate-glass method.[1,17] The processes are almost identical

except for the feed additives, H_3PO_4 for the phosphate-glass process, and B_2O_3 and SiO_2 for the borosilicate-glass process.

In the phosphate solidification process, liquid waste containing all the melt-making additives is first fed to the evaporator (see Figure 5) where it is concentrated and denitrated by factors of 2 to 10 to a thick, syrupy, aqueous phosphate slurry. The slurry is fed to a continuous melter where the remaining water, nitrate, and other volatile constituents are driven off. The material is then heated from $1000^{\circ}C$ to $1200^{\circ}C$ to form a molten glass. The molten glass flows through an overflow weir or freeze valve into the receiver storage pot below. After the pot is filled, it is cooled in a furnace, sealed, and then taken to storage. This process can also apply to the borosilicate-glass solidification process.

The advantages of phosphate and borosilicate glass solidification are: (1) it is a continuous process, (2) the solid has a high thermal conductivity (1.05 to 1.6 BTU/(hr)(ft)($^{\circ}F$) and 1.25 BTU/(hr)(ft)($^{\circ}F$) for phosphate and borosilicate glass, respectively),[17,18] (3) it produces a good quality glass product, and (4) the solid has been found to have a very low leach rate on the order of 10^{-7} g/cm^2-day.[19] It has these disadvantages: (1) it is a moderately complicated process, (2) it requires operations with slurries that are difficult to handle, and (3) at present it needs a platinum melter which is relatively expensive.[14]

Borosilicate glass can hold up to 60 percent by weight (43 percent by volume) of solids from simulated wastes that arise from fuel reprocessing, whereas the phosphate glass process can hold up to 20
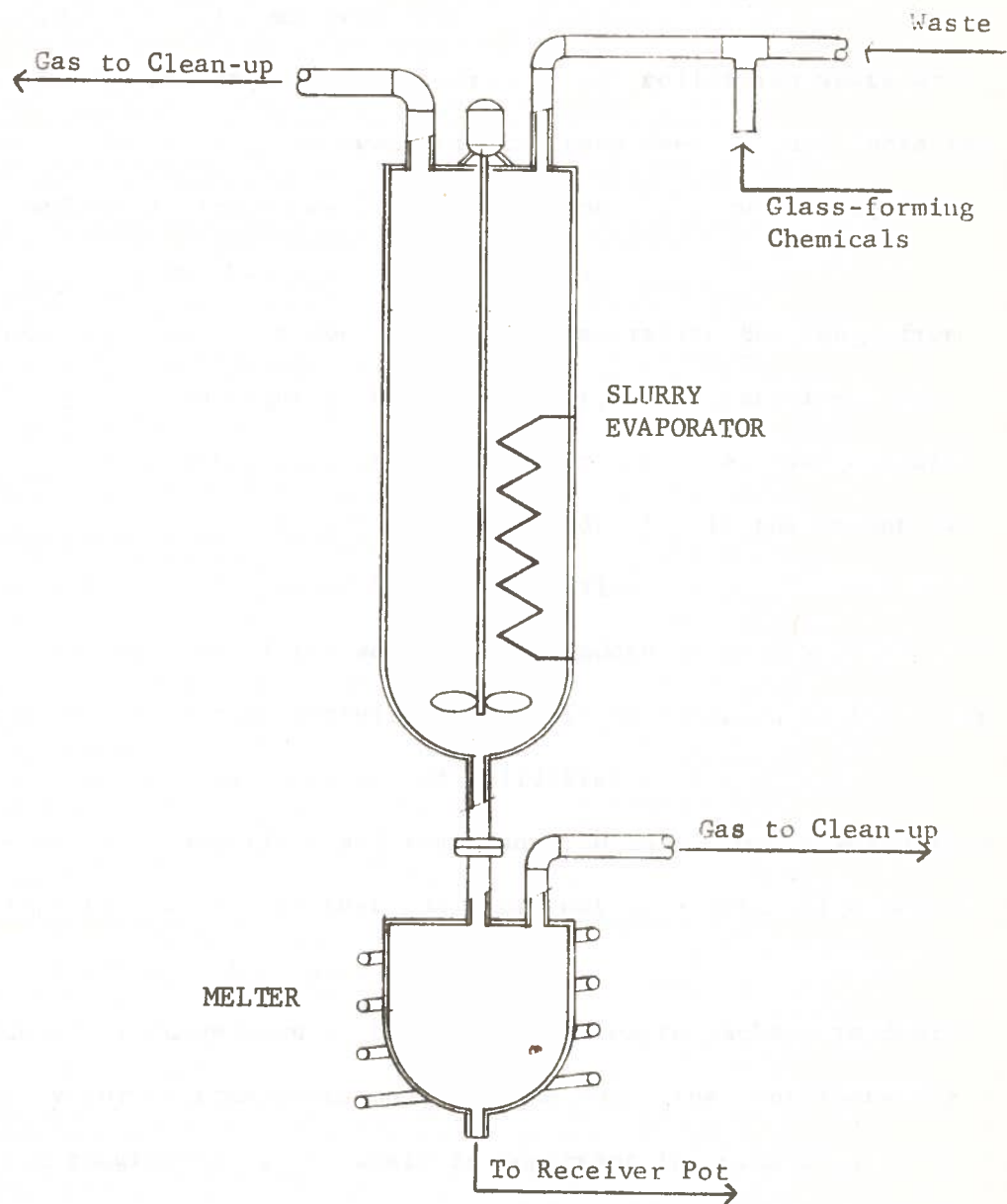
FIGURE 5. Phosphate-glass Solidification

22

percent by weight of fission products.[18]   Test runs held at WSEP num-
bered 11 for the phosphate glass solidification process. In these runs,
19 megacuries were solidified using the phosphate glass method, which
represents 9.8 tonnes of fuel reprocessed.[14]

In general the desired characteristics of solidified waste are
good thermal conductivity, low leachability, good chemical and radiation
stability, mechanical ruggedness, noncorrosiveness to containers, mini-
mum volume, and minimum cost.[1]

Since the fission product decay heat generation can range from
85 to 205 W/liter in an eight inch diameter pot,[14] the net effect of
high thermal conductivity is to increase the amount of allowable heat
stored in pot. This characteristic permits reduction in the amount of
time liquid waste must be stored before solidification.

Low leachability of the solidified products is desirable to
minimize the amount of radioactivity that could be released in the event
water contacts a breached container of solidified waste.

The chemical stability and resistance to radiation of solidified
waste are important to assure that gases are not generated which may
affect the integrity of the waste container.

Mechanical ruggedness of the solidified waste package is desir-
able primarily during transportation. In the event the containers are
breached, the ruggedness of the waste is important in terms of its
tendency to disperse.

Minimum volume is desirable primarily for economic reasons.
Generally reducing the volume will reduce the size and cost of contain-
ers, container storage areas, shipping equipment, and land for storage

areas. Minimumized cost, without affecting quality, is an obvious ad-
vantage.

To prove that solidification was practical, WSEP using the high-
level solidification processes (pot, spray, and phosphate glass) solid-
ified a total of 52 megacuries of mixed radionuclides in 75 days of
actual processing time. This is equivalent to the waste from about
335,000 MWd of electrical power.[14] With further improved technology
these statistics can be improved greatly. Presented in Table 4 are the
characteristics of the Solidified High Level Wastes found in the WSEP
program.

Fixation is the actual placing of the wastes into a medium and
fixing (sealing) it into a homogenous solution, preferably a solid.

Concreting. Concreting was used extensively in the early days
of nuclear waste disposal. The waste is either mixed with the aggregate
to form a solid, or concrete is placed around a container of liquid
wastes and then dumped into the ocean for disposal.[3]

Encapsulation. Encapsulation must be used for solids such as
the residue of the pot, spray and fluidized bed calcinators. Stainless
steel is a good material because it has good thermal conductivities,
non-leachability, and structural integrity. The corrosiveness of the
solids stored in the stainless steel must also be taken into consider-
ation. For the solidified waste stored in stainless steel, the corros-
ive life time limit is determined only by the oxidation rate of the air
on the outside of the containers.[1,2]

Asphalt and Polyethylene Fixation. The process of asphalt and
polyethylene fixation of intermediate level waste was studied in some

TABLE 4

CHARACTERISTICS OF SOLIDIFIED HIGH LEVEL WASTE*

	Pot Calcine	Spray Melt	Phosphate Glass
Form	Scale	Monolithic	Monolithic
Description	Calcine cake	Microcrystalline	Glass
Chemical composition, wt%			
Fission product oxides	up to 90	up to 25	up to 20
Inert metal oxides	5 to 60	30 to 50	15 to 35
Sulfur oxides (if in waste)	0 to 40	0 to 40	0
Phosphorous oxides	0 to 5	25 to 50	60 to 70
Bulk density, g/ml	1.1 to 1.4	2.7 to 3.3	2.7 to 3.0
Thermal conductivity, W/(m °C)	0.3 to 0.5	1.0 to 1.4	0.8 to 1.3 **
Max. heat, W/liter solid (8-in. pot)	85	205	190 **
Leachability in cold H_2O g/(cm^2 day)	10^{-1} to 10^{-2}	10^{-3} to 10^{-5}	10^{-4} to 10^{-6}
Hardness	soft	hard	very hard
Friability	crumbly	tough	brittle
Residual nitrate, wt% of product	0.05	0.005	0.005
Volume, liters/1000 MWd(t)	1 to 2.5	1.2 to 3	1.5 to 5
Maximum stable temperature, °C	900	phase separation at 900	devitrifies at 500
Container material	stainless steel	mild or stainless steel	mild or stainless steel

*From Reference 14.
**317 W/liter attained in a 6-in.-diameter pot

25

detail at ORNL. The wastes are added directly to a stirred evaporator that contains the emulsified asphalt or molten polyethylene. The mixture is stirred at a temperature of 70°C to 125°C to evaporate the water. Then the mixture is raised to 138°C to 180°C before draining to an appropriate storage vessel for solidification. It has been found that the polyethylene can accommodate up to 40 percent by weight of organic liquid, whereas the asphalt is not recommended for incorporating wastes containing oxidants. Asphalt or polyethylene containing up to 60 percent by weight of non-oxidizing inorganic solids have a chemical resistance similar to that of pure asphalt and pure polyethylene. Leak rates projected over 200 years show that approximately 5% of a soluble element (sodium or cesium) or 0.6% of an insoluble nuclide (Ru-166) would be leached from a suitable container (55 gal drum) underwater.[20]

Polymerization. Mercer at Battelle Northwest Laboratory found that by incorporating the soil or salt waste into a suitable resin matrix the water leach rates of radioisotopes can be reduced by 99.9%. The objective is to incorporate radioactive solid (e.g. fluidized-bed and pot-calcine waste) into an organic monomer, and to inject the resulting slurry into a containment vessel, where it may be polymerized by a suitable catalyst. This would lead to a reduction of the leachability of the radioactivity contained in the soil and/or salts.[21]

PROBLEM STATEMENT

Generally the majority of universities that use radioactive materials extensively have a problem of disposal of low level liquid wastes, many of which are organic materials. If the wastes are not transported to storage sites, they build up and occupy valuable storage space. Transportation of the liquid waste is expensive since the wastes must be shipped in special double-walled containment vessels which meet rigid safety requirements to guard against leakage in case of an accident. Since most universities are on a low budget, and alternative would be to solidify the liquid wastes and ship the waste inexpensively as solids. Of course, solidification and shipment as a solid must be cheaper than shipping the wastes as liquids if this is to be a practical approach.

The preceding chapters describe several solidification processes that could be used, but the cost of equipment makes them impractical for university usuage.

Chemical treatment of the liquid waste, especially if the chemical is inexpensive, nontoxic, and easy to use, would solve the problem of equipment cost. The use of an appropriate thickner to gel the liquid waste into a solid form could be an inexpensive solution for university application.

This research includes the evaluation of a commercially available gelling agent for solidification of aqueous and organic low level liquid wastes.

27

EXPERIMENTAL PROCEDURES

General Materials

All chemicals used throughout the experimental work (acetone, ethyl alcohol, toluene, sodium chloride) were reagent grade. Aqueous solutions were prepared with singly distilled water.

Samples were weighed with a Mettler Model H4 single-pan analytical balance. For those samples which exhibited weight loss during weighing, the weight was recorded approximately one minute after the sample was placed on the balance.

The gelling agent used for this study was a commercially available organic polymer sold under the trade name of Safe-T-Set by Oil Research Center, Lafayette, Louisiana. Triton X-100 (Hartman-Leddon, Philadelphia, Pa.), a nonionic surfactant, was employed for emulsifying immiscible liquid systems.

Liquid scintillation counting was accomplished with a Beckman Model LS 250 spectrometer. All radioactive samples were counted with the same channel settings (wide C-14 Channel A, wide P-32 in Channel B) in the external standard mode; the instrument was preset to 10 minute counting time and 0.2 percent standard deviation. A dioxane-base cocktail (100 g naphthalene, 1.67 g PPO, and 0.5 g POPOP per liter) was used for counting.

Phase Integrity Experiments

Ethyl alcohol and acetone were tested as intermediate solubilizing

agents for water and toluene by pipetting specified volumes of each of the components into 5-ml test tubes. Each tube was stoppered and shaken for approximately 30 seconds, then allowed to stand for approximately 3 minutes, after which it was examined for phase separation. Only one intermediate solubilizing agent was employed at a time.

For the emulsification test, equal volumes of water and toluene were pipetted into 5-ml test tubes. Specified volumes of Triton X-100 were added to each of the tubes, which were then shaken and allowed to stand. The individual tubes were examined for phase separation for periods up to 72 hours.

In determining the maximum ratio of ethyl alcohol in water to gelling agent, specified volumes of water, ethyl alcohol, and gelling agent were added to 20 ml vials. The vials were capped and shaken for 30 seconds, and then allowed to stand for 15 minutes, after which they were examined for solidification. The experiment was repeated replacing the ethyl alcohol by acetone.

Gel Stability Experiments

The effect of high temperatures on evaporation of a gelled sample was accomplished by placing the samples in a constant temperature drying oven at 105°C. Equal amounts of water were placed in 100 ml beakers. Specified amounts of gelling agent were added to each beaker and stirred to solidification. The beakers were then placed in a drying oven. The samples were periodically taken from the oven and weighed. The weight and time were recorded until complete evaporation occurred.

The study of the effect of natural evaporation of the solid was

made by exposing the samples in an air-conditioned room. Equal amounts of water were placed in a 100 ml beaker, specified amounts of gelling agent were added to each beaker, and the contents were then stirred to solidification. The beakers were weighed periodically, and the weights and time of weighing were recorded.

Isotope Retention

System Description and Operation. A vacuum trap system was set up as shown in Figure 6. The glassware (traps, stopcocks, sample holder, sample catcher) were interconnected with Tygon plastic tubing.

A vacuum, using a two-stage, rotary vane, high vacuum pump, was applied to the traps through the three-way stopcock.

With the system under continuous vacuum, the traps were immersed in liquid nitrogen.

The sample solid containing radioisotopes was made up in the sample holder (50 ml wide mouth glass jar). The sample holder was then placed into the system via a vented rubber stopper.

A vacuum was applied for 15 minutes to the sample by opening the stopcock between the trap and the sample holder. The sample holder was then placed in a 1000 ml beaker containing hot water (approximately 80°C).

The sample was disconnected after the prescribed time by turning the stopcock off.

The vacuum pump was then isolated from the collected radioactive condensate by turning the three-way stopcock in such a manner as to form a closed system between the traps and the sample catcher. The sample catcher was a 20 ml liquid scintillation vial.
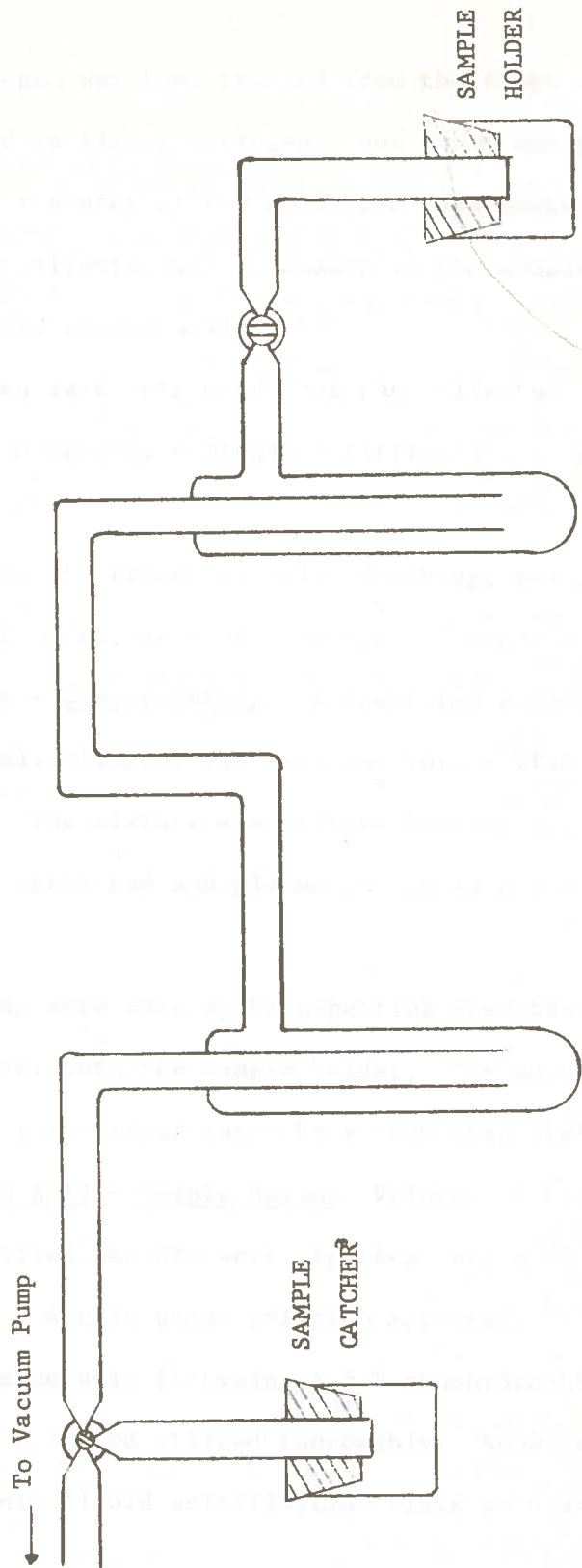
SAMPLE HOLDER

To Vacuum Pump

SAMPLE CATCHER

FIGURE 6. Vacuum Trap System Arrangement

The liquid nitrogen was then removed from the traps and the sample catcher immersed in liquid nitrogen. Hot water was placed around the traps to implement transfer of the collected condensate.

The vapors were collected as condensate in the sample catcher, which was then capped and placed aside.

Specified volumes were extracted from the collected condensate and placed in 10 ml of dioxane-base liquid scintillation cocktail for counting.

Between each run, the traps, associated tubing, and glassware were cleaned by rinsing with water, acetone, toluene and ethyl alcohol.

H-3 Tagged Water - Sample Makeup. A specified volume of tritiated water (2.72×10^6 dpm/ml, 3/19/65) was pipetted into a vial containing a known amount of water. The mixture was stirred thoroughly, after which specified volumes were extracted and placed in liquid scintillation cocktails as a standard.

The sample solids were made up by pipetting specified volumes of water and tritiated water into the sample holder. The solution was stirred to solidification, then placed into the vacuum trap system.

H-3 Tagged Amino Acid - Sample Makeup. Volumes of toluene, water, and emulsifier in specified amounts were pipetted into a vial. The mixture was stirred until a single phase solution appeared. A specified volume of H-3 tagged amino acid (L-Lysine 4,5 T monohydrochloride 1 mCi/ml) was added and then the solution stirred thoroughly. Known volumes were extracted and placed into liquid scintillation vials as a standard for counting.

The sample solid consisted of specified amounts of water, toluene, emulsifier, tagged amino acid and gelling agent. The constituents were placed in the sample holder, and stirred to solidification. The sample holder then was placed in the vacuum trap system.

The collected condensate in the sample catcher was a partially separated two phase solution. Sodium chloride was added to enhance the separation, and both phases were sampled for counting.

C-14 Tagged Toluene - Sample Makeup. A solution containing known amounts of toluene, water, emulsifier, and C-14 tagged toluene $(4.36 \times 10^5 \text{ dpm/ml}, 12/67)$ was mixed in a vial until a single phase solution appeared. From this solution specified volumes were transferred to liquid scintillation vials for counting as a standard.

Into the sample holder were placed specified volumes of water, toluene, emulsifier, and C-14 tagged toluene. The mixture was stirred until a single phase solution appeared. From this solution specified volumes were extracted and placed into liquid scintillation vials for counting as an individual standards. After withdrawal of the individual standard, know amounts of gelling agent were added to the solution in the sample holder and stirred to solidification. The sample holder then was placed in the vacuum trap system.

The collected condensate was a partially separated two phase solution. Sodium chloride was added to enhance the separation, and both phases were sampled for counting.

P-32 Tag in Water and Water-Toluene Base Solids. Phosphorus-32

(H_3PO_4 diluted to 1 μCi/ml) was used in a water-toluene base solid and in a pure water base solid.

In a 20-ml vial, specified volumes of water, toluene, emulsifier, and P-32 tag were placed. The mixture was stirred until a single phase solution appeared. From this solution specified volumes were pipetted and placed in liquid scintillation vials for counting as standards. Also from this solution a know volume was transferred to the sample holder.

Known volumes of water, toluene, and emulsifier were added to the tagged solution, and stirred until a single phase solution appeared. From this solution a specified volume was removed and placed in liquid scintillation vials for counting as a individual standard. The gelling agent was added in known amounts to the sample holder, and the mixture was stirred to solidification. The sample solid was then placed in the vacuum trap system.

The collected condensate was partially separated, hence sodium chloride was added to separate the two phases further. Both phases were sampled for counting.

Specified volumes of water and P-32 tracer were pipetted into a 20-ml vial. The solution was stirred thoroughly, and then specified volumes were transferred to liquid-scintillation vials with cocktails for counting as a standard. Also transferred were known volumes of this solution which were then placed in the sample holder.

Specified volumes of water were added to the sample holder containing the P-32 tagged solution. This solution was stirred, after which known volumes were extracted for the purpose of counting as individual

standards.

Known amounts of gelling agent were added to the sample holder. The resulting mixture was stirred to solidification. The sample holder was then placed in the vacuum trap system.

Vapor Pressure Change Experiment

To determine the effect of a gelling agent on vapor pressure, a simple mercury manometer system was arranged as shown in Figure 7.

With the main stopcock controlling the vacuum, known volumes of toluene were placed in one sample holder, while a known volume of water was placed in the other sample holder. With the other stopcocks open, a partial vacuum was applied by turning the main stopcock on and off five times. After an initial reading was taken of the mercury level of both sides of the manometer, the samples were isolated from each other by simultaneously turning the two stopcocks off. Periodic readings of the mercury level were taken over a period of 12 hours.

The samples of toluene and water were interchanged, and the experiment was repeated.

Specified volumes of toluene, water, and emulsifier were placed in one sample holder. The mixture was stirred until a single phase solution appeared. A known amount of gelling agent was added, and the resulting mixture stirred to solidification. Specified volumes of water and gelling agent were placed in the other sample holder. Again, the mixture was stirred to solidification. The two samples were then placed in the manometer system and a partial vacuum applied by turning the main stopcock

To Vacuum Pump

SAMPLE

HOLDER

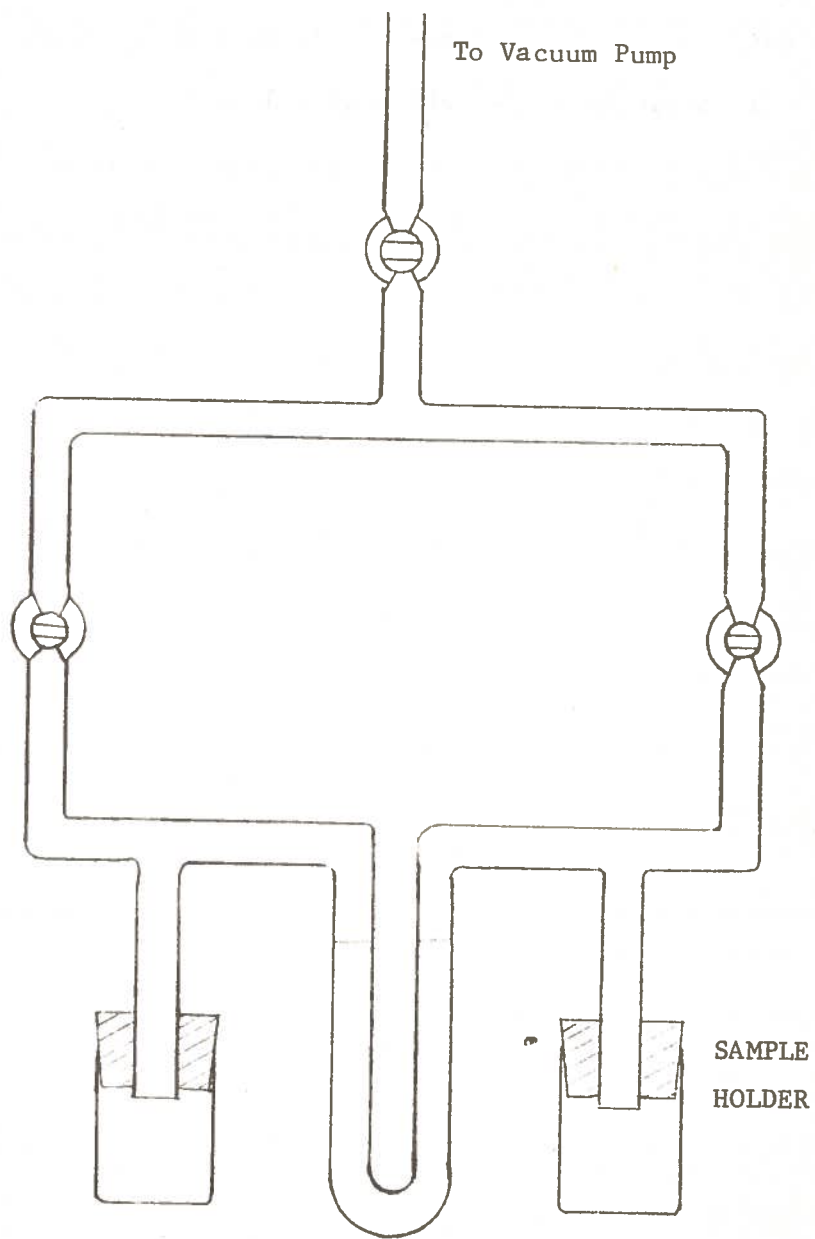FIGURE 7. Mercury Manometer System Arrangement

36

on and off several times. After an initial reading was taken of the
mercury level, the samples were isolated from each other. Several
readings of the mercury level were taken over a period of 12 hours.

Reversing the position of the sample solids in the apparatus, the
experiment was repeated. This provided a check for possible leaks in
the vacuum system.

CHAPTER IV

RESULTS AND DISCUSSION

The intent of this research was to establish simple procedures for using a single gelling agent to convert aqueous and organic liquid wastes into a non-liquid form suitable for shipping without expensive precautions. A hydrophilic agent was selected because the majority of the waste liquids are aqueous.

Of several possibilities for gelling agents, Safe-T-Set was chosen because it was locally available, easy and safe to use, non-toxic, and has a variable gelling time depending on the mixing ratio. The cost of the Safe-T-Set is fairly inexpensive, $2.70/lb. The actual cost of solidification of one gallon of aqueous solution was on the order of $1.25 for a 16:1 ratio. The gelling agent has an infinite shelf life, a density of 54-56 lb./ft.^{3} and is in a powder form.

Phase-Integrity Studies

While gelation of aqueous wastes presented no problems, direct treatment of non-aqueous liquids was not possible. As a first approach to the use of hydrophilic agent, it was thought that if the organic liq-uid could be made miscible with water, successful gelation could be achieved. Two techniques were investigated for feasibility: use of an intermediate solubilizing agent, which would lead to a true single-phase solution, and emulsification, which would approximate a single-phase system if the micelles were sufficiently small.

38

Toluene was employed as a model organic liquid because it forms the base of liquid scintillation cocktails, a major source of waste in a university. Ethyl alcohol and acetone were used as intermediate solubilizing agents for the first set of experiments.

First, equal volumes of toluene and water were placed in a test tube, then increasing increments of acetone were added and the test tube was shaken vigorously. The results were always the same: separation of water and toluene. Equal volumes of acetone and toluene were placed in the test tubes and various volumes of water added. Separation occurred in all cases. The addition of 0.1 ml of water to 1 ml of toluene and 1 ml of acetone produced a two-phase system.

The acetone was replaced by ethyl alcohol and the experiment repeated. The results were the same: after adding 0.1 ml of toluene to 1 ml of ethyl alcohol and 1 ml of water a distinct two phase solution appeared.

The solubility of toluene in water is on the order of 0.0542 ml of toluene in 100 ml of water at 16°C.[22] The maximum water in ethyl alcohol-toluene solution has been reported to be on the order of 10%.[23]

Although a single-phase system with a practical water content was not found with the intermediate solubilizing technique, it was decided that a test of the four-component system toluene/solubilizer/ water/gel was worthwhile.

First, the ethyl alcohol or acetone:water:gelling agent ratio was found for good solidification. The various ratios of ethyl alcohol-water to gelling agent that were tried and the results are

presented in Table 5. Up to 66% ethyl alcohol in water can be solidified using a liquid-to-solid volume ratio of 1:1. The gelation time ranged from several minutes to hours. The results of the acetone experiments are summarized in Table 6.

Toluene was added to the solution of ethyl alcohol, water, and gelling agent, and the mixture was shaken. The results were consistent in that a distinct two-phase system appeared, and gelation failed to occur.

Emulsification studies using Triton X-100 were conducted with toluene and water, and the results presented in Table 7. A 1:1 ratio of toluene to water was chosen as the base for various increments of emulsifier. With the addition of 0.08 ml of emulsifier to 1 ml of toluene and 1 ml of water, an emulsion formed readily after shaking. Over a period of 24 hours, the test tube containing 0.2 ml of emulsifier, 1 ml of toluene and 1 ml of water showed the least amount of phase separation. The addition of 0.4 ml of emulsifier to 1 ml of toluene and 1 ml of water led to a system with a thick, syrupy consistency.

The ratio of 0.2 ml of emulsifier to 1 ml of toluene and 1 ml of water was chosen as the standard mixture of the three constituents. It was the least amount of emulsifier added for a single phase mixture that showed good emulsification over a period of 24 hours.

The mixture was then tried with different ratios of gelling agent to produce stable solids. The ratios of 2:1, 3:1, 4:1, 8:1, and 16:1 of mixture of gelling agent were tried. All the ratios produced

TABLE 5

GELATION WITH INTERMEDIATE SOLVENT ETHYL ALCOHOL

Sample	Water (ml)	Ethyl Alcohol (ml)	Thickener (gm)	Ratio of Solution to Gelling Agent*	Alcohol in Water (Percent)	Gelled (24 hr.)
1	2	–	.5674	4:1	–	yes
2	2	–	.2837	8:1	–	yes
3	2	–	.1418	16:1	–	yes
4	2	.1	.5958	4:1	4.7	yes
5	2	.1	.2979	8:1	4.7	yes
6	2	.1	.1489	16:1	4.7	yes
7	2	.2	.7084	4:1	9	yes
8	2	.2	.3121	8:1	9	yes
9	2	.2	.1560	16:1	9	yes
10	2	.3	.681	4:1	13	yes
11	2	.3	.34	8:1	13	yes
12	2	.3	.17	16:1	13	no
13	2	.6	.7377	4:1	23	yes
14	2	.6	.368	8:1	23	no
15	2	.6	.184	16:1	23	no

TABLE 5 -- <u>Continued</u>

Sample	Water (ml)	Ethyl Alcohol (ml)	Thickener (gm)	Ratio of Solution to Gelling Agent*	Alcohol in Water (Percent)	Gelled (24 hr.)
16	2	.8	.7944	4:1	28	no
17	2	1	.8512	4:1	33	no
18	2	1.2	.9079	4:1	37.5	no
19	2	1.4	.9647	4:1	41	no
20	2	1.6	1.021	4:1	44	no
21	2	1.8	1.078	4:1	47	no
22	2	2	1.134	4:1	50	no
23	2	1	.9728	3.5:1	33	yes
24	2	1	1.134	3:1	33	yes
25	2	1	1.361	2.5:1	33	yes
26	2	1	1.702	2:1	33	yes
27	1.5	1.5	2.269	1.5:1	50	yes
28	1.5	1.5	3.4	1:1	50	yes
29	2	2	3.4	1:1	66	yes

* Calculated with the thickener density being .8811 gm/cc

42

TABLE 6

GELATION WITH INTERMEDIATE SOLVENT ACETONE

Sample	Water (ml)	Acetone (ml)	Thickener (gm)	Ratio of Solution of Gelling Agent*	Acetone in Water (Percent)	Gelled (24 hr.)
1	2	.2	.6242	4:1	9	yes
2	2	.3	.6525	4:1	13	yes
3	2	.6	.7377	4:1	23	yes
4	2	1	.8512	4:1	33	no
5	2	1	1.134	3:1	33	yes
6	2	1	1.361	2.5:1	33	yes
7	2	1	1.702	2:1	33	yes
8	1.5	1.5	3.4	1:1	50	yes
9	2	2	3.4	1:1	66	yes

* Calculated with the thickener being .8811 gm/cc

43

TABLE 7

TOLUENE-WATER EMULSIFICATION*

Emulsifier (Triton X-100) volume, ml	Observation
0.08	Emulsification, reseparation within 24 hours
0.12	Emulsification, reseparation within 24 hours
0.16	Emulsification, reseparation within 24 hours
0.2	Emulsification, no reseparation within 24 "
0.28	Emulsification, no reseparation within 24 "
0.32	Emulsification, no reseparation within 24 "
0.4	Emulsification, viscous solution
0.6	Emulsification, viscous solution
0.8	Emulsification, viscous solution
1.0	Emulsification, viscous solution

* Volume of Toluene = 1 ml, volume of water = 1 ml

44

solids.   The 8:1 and 16:1 ratios required 10 to 20 minutes for gelation.

Gel Stability

The gelling agent stability as a solid was studied by placing
different sample sets under various environmental conditions, using an
open-cup technique.

A set of three gelled samples with different ratios of
water to gelling agent was placed in an oven at 105°C to simulate
extreme conditions. The percentage loss due to evaporation as a
function of time is shown in Figure 8, from which it is apparent
that the water was driven off readily. The curves peaked at 103% less
evaporation loss because of residual water content in the original
gelling agent.

A set of unswelled dry samples containing 5 mg, 10 mg, and
20 mg of gelling agent was placed in the oven. As shown in Figure 9,
up to 24% loss due to inherent water content was found in the 5 mg
sample.

A set of samples with the same mixing ratio of water to
gelling agent as the samples in the oven was allowed to evaporate at
room temperature to evaluate evaporation of a sample solid under
natural conditions. The results, loss due to evaporation versus time,
are shown in Figure 10. Ambient-temperature evaporation took almost
100 times longer than the forced evaporation off the samples in the
oven for 100% evaporation. The lighter ratio, 16:1, reached 100%
evaporation first, followed by the 8:1 ratio and then the 4:1. This
is expected since water-gelling agent bonding should increase with the
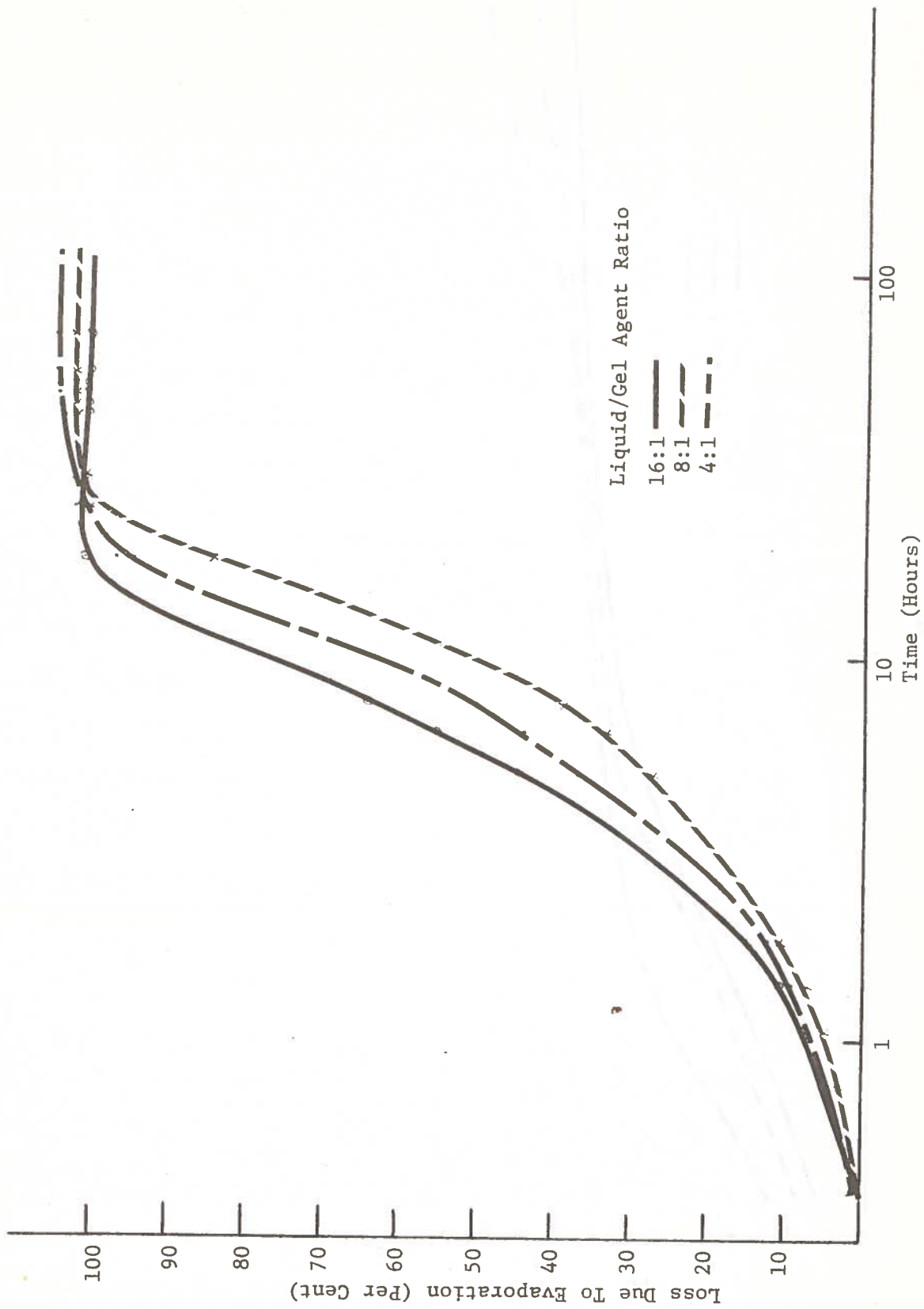amount of gelling agent.

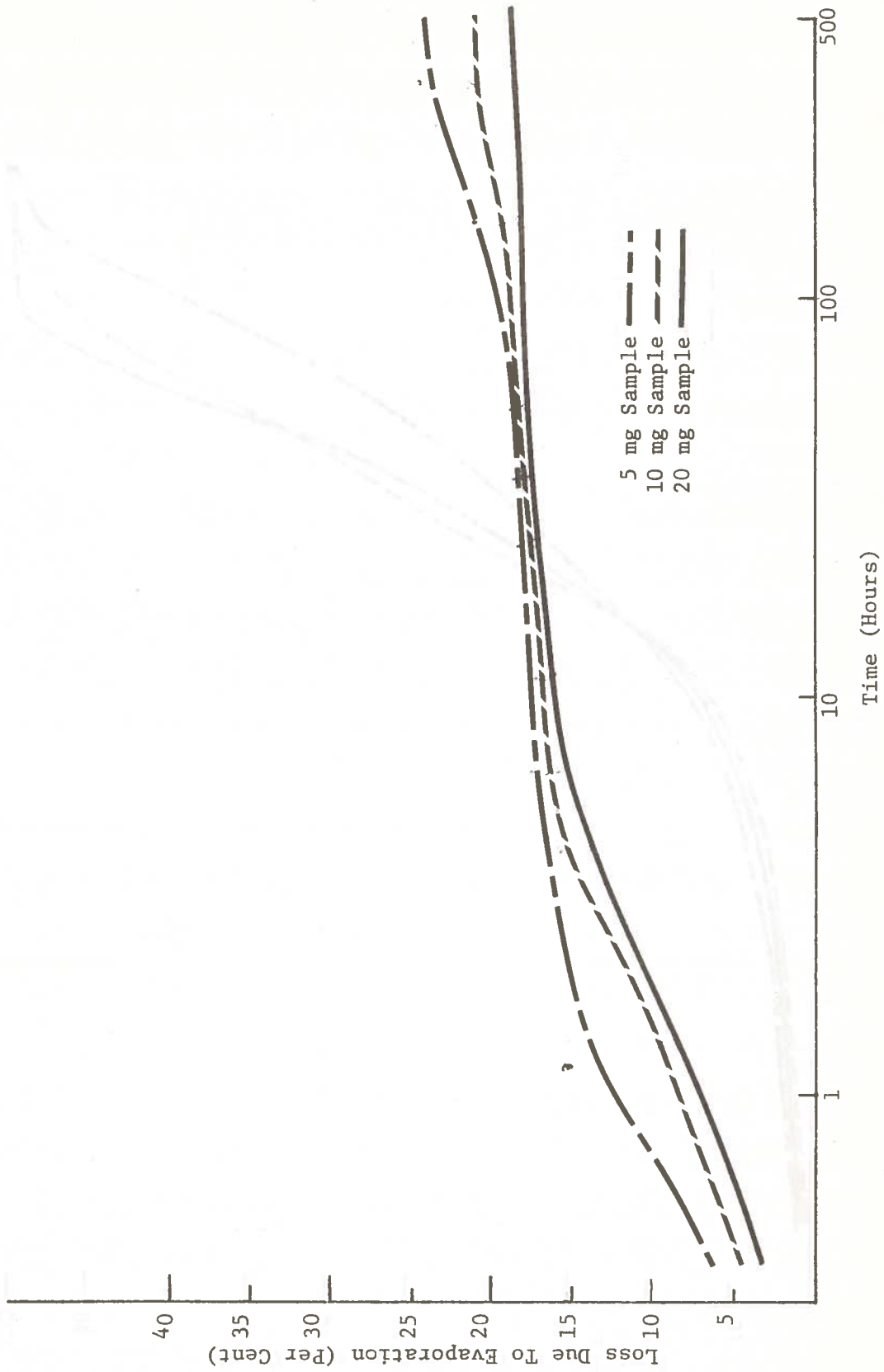FIGURE 8. Open-cup Evaporation Loss from Water-base Gel at 105°C

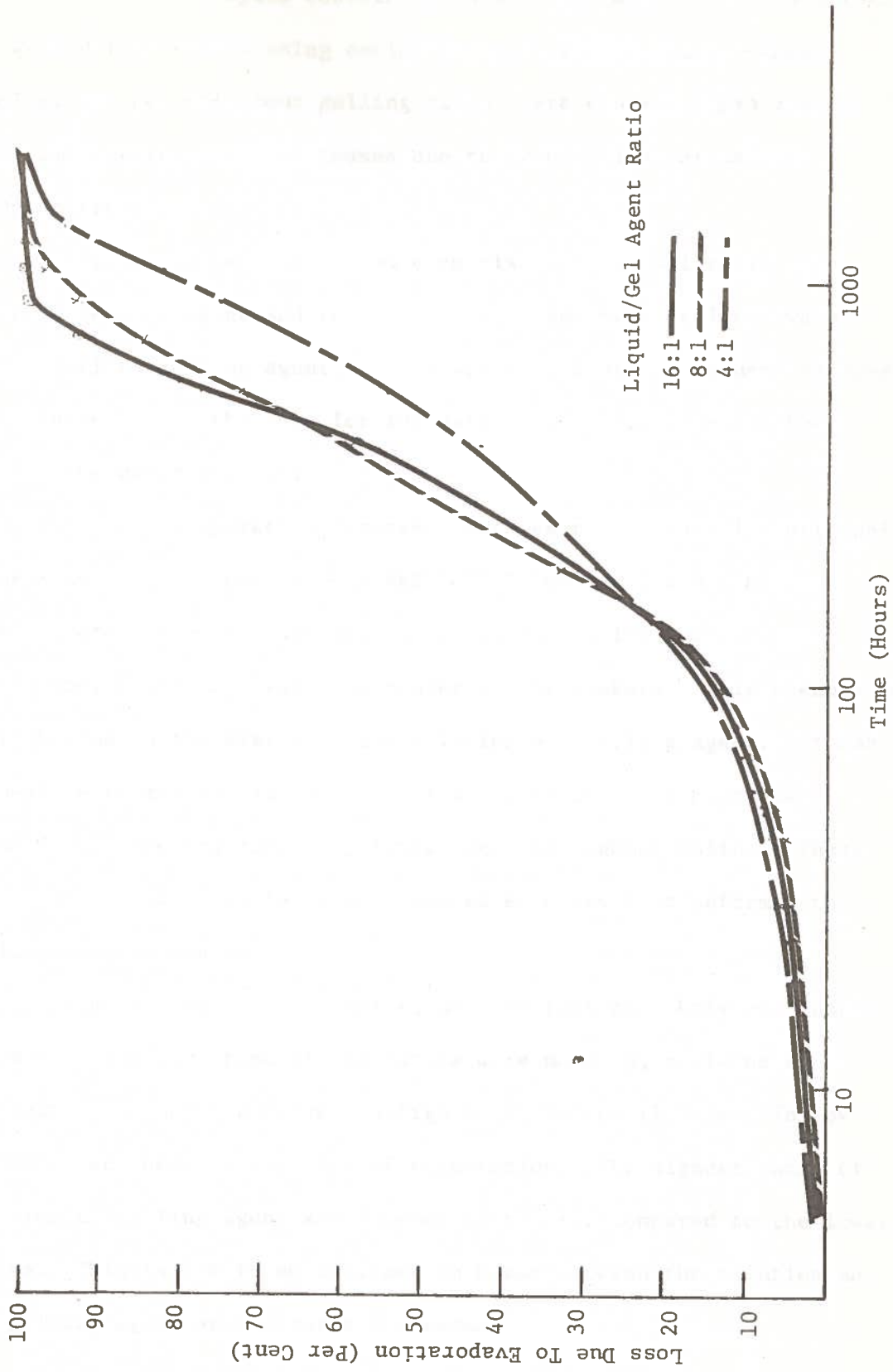FIGURE 9. Open-cup Evaporation Loss from Dry Gel Agent at 105°C

47

FIGURE 10. Open-cup Evaporation Loss from Water-base Gel at Ambient Temperature

48

A set of samples containing equal volumes of toluene and water was gelled into solids using emulsifier and gelling agent. These samples, one per different gelling ratio, were exposed (open cup) to room temperature, with the losses due to evaporation versus time shown in Figure 11.

Figure 12 is a graphical comparison of the 4:1 ratio of water to gelling agent and the 4:1 ratio of emulsion (toluene/water/ emulsifier) to gelling agent. It is apparent that the toluene escapes first, after which the loss for the water:organic gel approaches that of the water-only gel.

As the evaporation occurred, each sample changed its original shape into the weirdest forms possible. A few samples had hollow pockets, others formed thin layers of residue, while the toluene-based samples shrunk toward the center of the beakers. This phenomenon could be due to the mixing of the solution and gelling agent. It was impossible to mix all samples identically, hence there might be nonuniform concentrations of gelling agent throughout solids. These local concentration differences produced stresses that deformed the solid as it evaporated.

The mixing of the samples, and the fact that only one sample of each of the different mixing ratios were made up, could be an explanation of why the curves in Figures 8, 9, and 11 do not follow the expected theoretical order of evaporation. The highest ratio of solution to gelling agent should evaporate first compared to the lower ratios. This is due to an increase in bonds between the solution and the gelling agent as the ratio decreases.
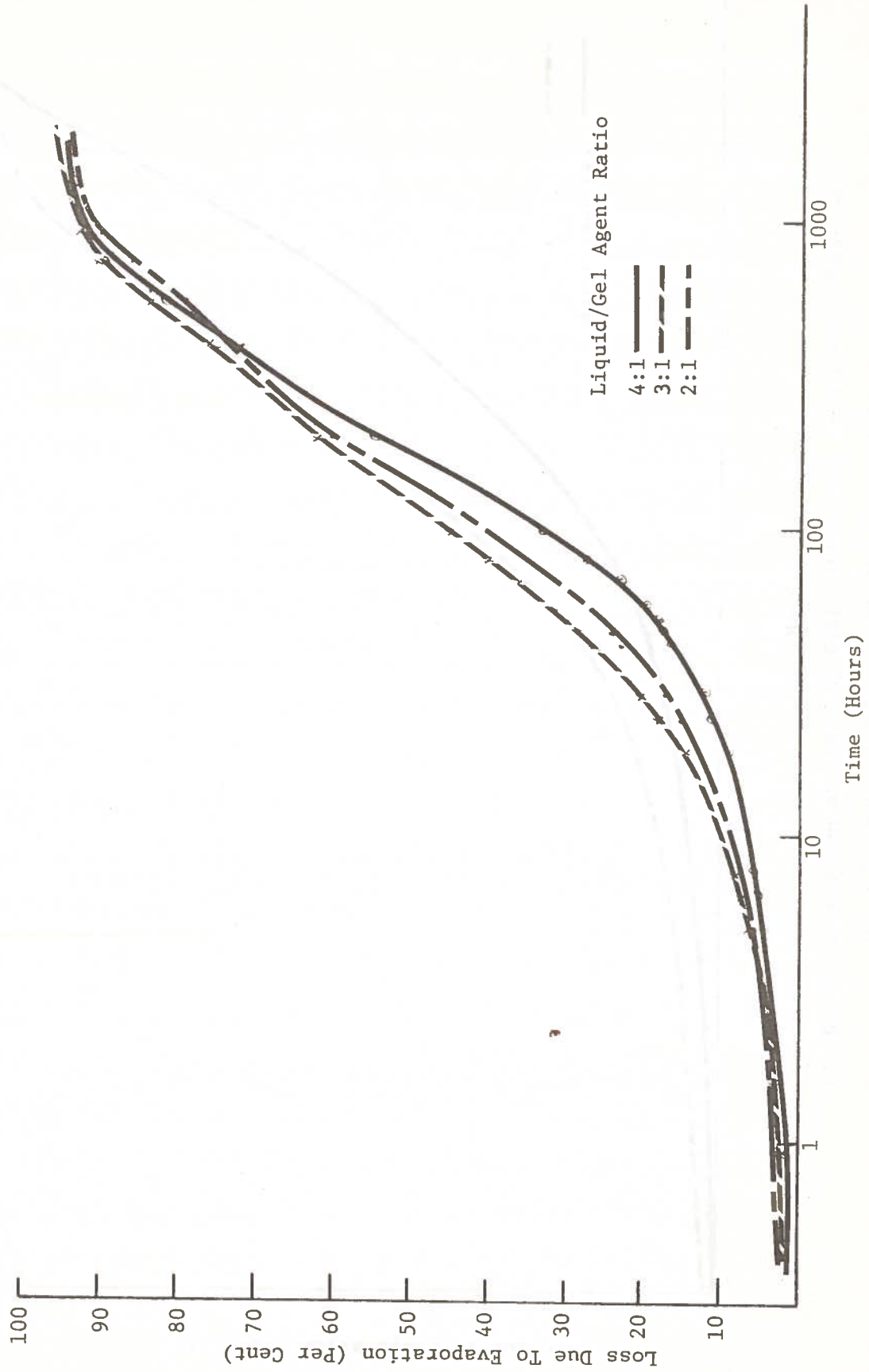
FIGURE 11. Open-cup Evaporation Loss from Toluene-base Gel at Ambient Temperature
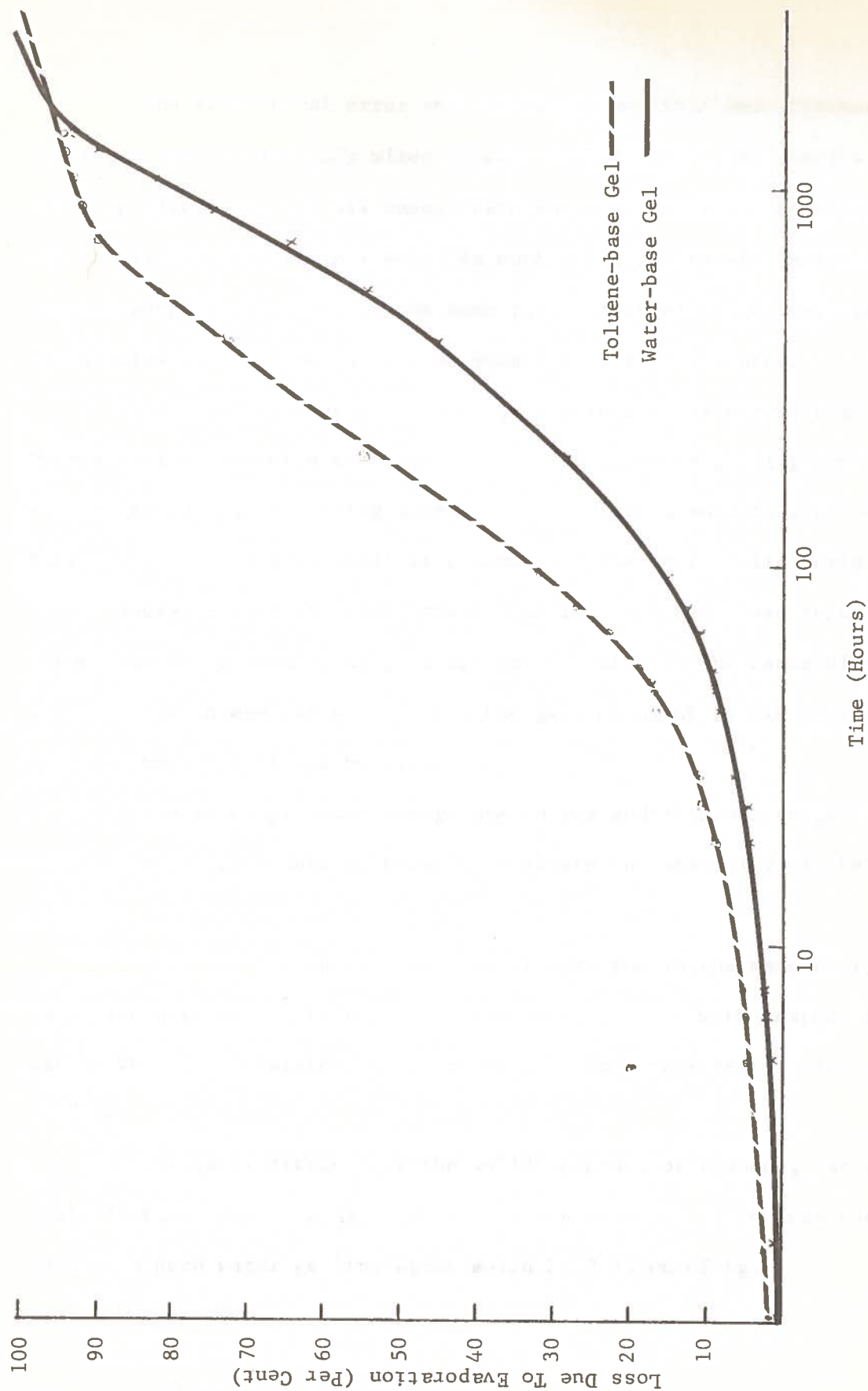
FIGURE 12. Comparison of Open-cup Evaporation Loss from a Water-base Gel and a Toluene-base Gel a Ambient Temperature

The statistical error and the mixing variable were checked by placing a set of uniformly mixed samples in the oven. The results are shown in Figure 13. In all cases there was a great variation between the individual samples in a set. As much as 16.2% average deviation between samples was found of the same ratio of water to gelling agent. The samples again formed grotesque shapes as they evaporated.

A set of samples was placed in zip-lock polyethylene bags. Over a period of months the highest ratio of water to gelling agent (100 ml to 13.4 g of gelling agent) began to form a mold on its solid surface. The mold grew until it encompassed the whole solid surface; then, slowly, the water phase appeared until completed phase separation between the water and moldy gelling agent occurred. The cause of this is not clear unless the mold caused the gelling agent to bio-degrade and release the water it was holding.

The vapor pressure change due to the addition of the gelling agent to a solution must be known to evaluate the stability of the gel properly.

When the toluene and pure water were run in the manometer, the vapor pressure of the toluene was 4 mm of Hg greater with respect to the water, which is consistent with the known vapor pressures of water and toluene.

The vapor pressure of the solid composed of toluene, water, emulsifier, and gelling agent, however, was measured to be less than that of a pure water-gelling agent solid by 2.75 mm of Hg.
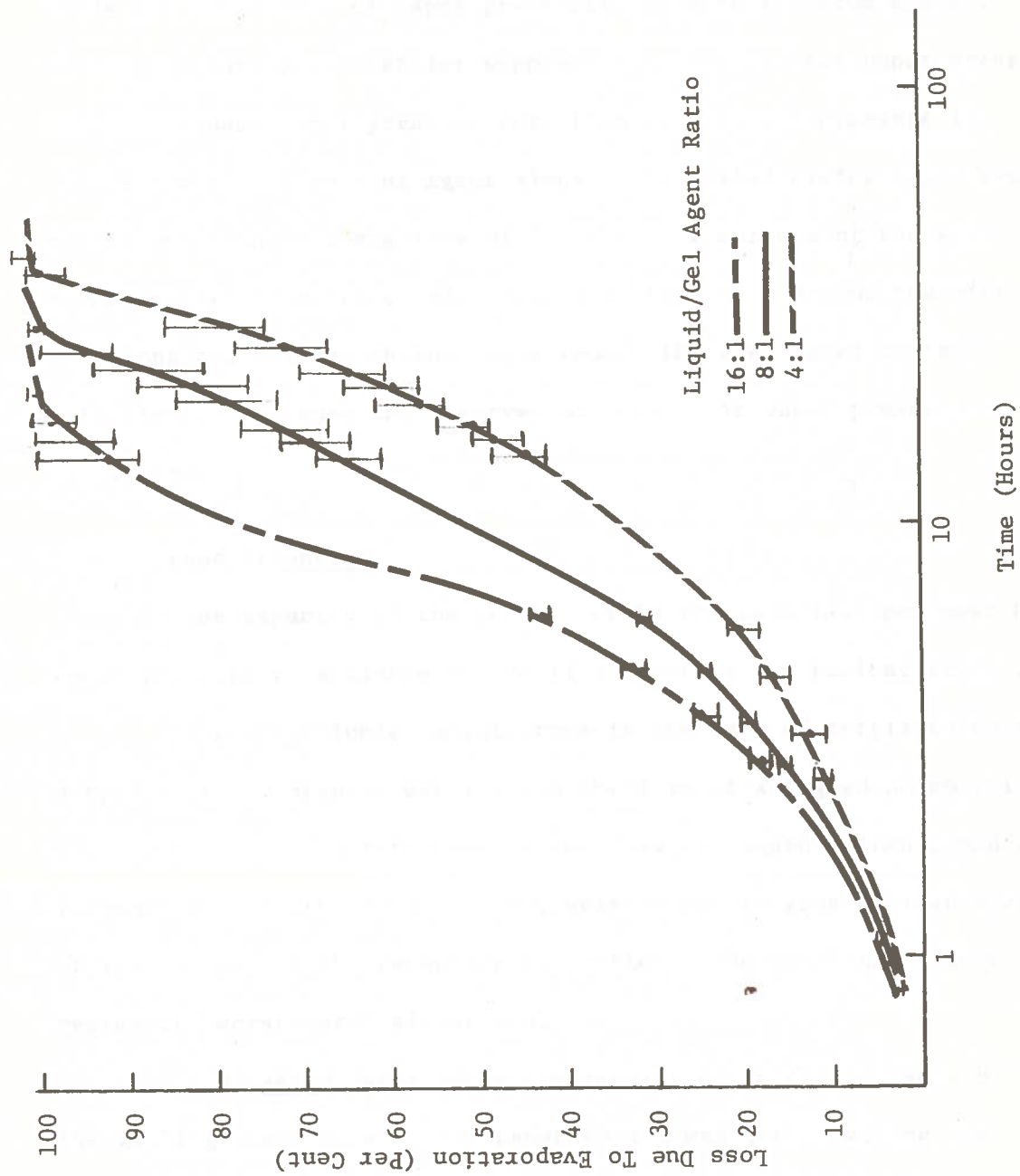
FIGURE 13. Open-cup Evaporation Loss from Uniformly Mixed Water-base Gel at 105°C

This behavior apparently contradicts the observation that the emulsified toluene-water gel loses weight more rapidly than the pure water gel. The latter, however, was determined by the open-cup method, while the comparison of vapor pressures is an equilibrium system. It may be that the emulsifier suppresses both the water vapor pressure and the toluene vapor pressure more than water vapor pressure is suppressed by the gelling agent alone. The gelled system could reduce diffusion of the toluene from micelles to the surface of the solid, and the ordering of the water molecules simultaneously around the micelles and along the polymer chains would reduce the free water content sufficiently to cause the observed difference in vapor pressure of the two systems.

Radioisotope Retention

The capacity of the gel to retain the radioisotopes must be known in order to evaluate the gelling agent to its fullest extent.

A water soluble radioisotope in the form of tritiated water, a typical ionic organic material in the form of a tagged amino acid, a toluene soluble radioisotope in the form of tagged toluene, and an inorganic ion in the form of $H_2PO_4^-$ were chosen to give a broad spectrum of information of the retention capacities. The water and toluene represent "worst-case" situations.

H-3 Tagged Water. From the results presented in Table 8, the the gelling agent's retention capacity H-3 was very low, the best being 23.5% at a 2:1 water-to-gelling ratio.

As the gelling agent-to-water ratio increased, the capacity of the gelling agent to retain H-3 increased, as would be expected

TABLE 8

TRITIATED WATER RECOVERY

Ratio of Solution to Gelling Agent	Liquid Collected (Percent)	Radioisotope Collected (Percent)
8:1	*	97.5
4:1	100	90.8
2:1	81.5	76.5

*Insufficient data

55

from the reduction in "free" water with increased available bonding sites.

The data in the liquid collection column was derived by weighing the sample holder and sample catcher before and after each run of the vacuum trap system.

Tagged Amino Acid. A tagged amino acid was used because it represents wastes that can be expected from biological experiments.

In all cases the sample collected was slightly separated, therefore sodium chloride was added to enhance phase separation. The H-3 tag stayed with the water as shown by the data in Table 9, which is consistent with the solubility of amino acids in water.

In the 4:1 and 2:1 ratio runs the percent of activity that was recovered remained about the same; the 3:1 ratio was slightly less because of the small amount of sample collected. Of the vapors pulled off only 35% were collected, compared to 95% and 92% for the 2:1 and 4:1 ratios, because of a loss of vacuum during this particular run. Instead of collecting the vapors in the liquid scintillation vial, the vapors condensed on the tubing and glassware. The condensate had to be chased through the system by heating the tubing inch by inch to the final collection vial.

C-14 Tagged Toluene. Since toluene forms the base of many liquid scintillation wastes, the retention of a toluene soluble isotope must be considered.

As the result in Table 10 shows, the retention of toluene in general was very poor.

TABLE 9

TRITIATED AMINO ACID RECOVERY

Ratio of Solution to Gelling Agent	Total Liquid Collected (Percent)	Phase	Radioisotope Collected (Percent)
4:1	92	water	4.8
		toluene	0.41
3:1	35	water	1.4
		toluene	0.06
2:1	95	water	9.1
		toluene	0.02

TABLE 10

C-14 TAGGED TOLUENE RECOVERY

Ratio of Solution to Gelling Agent	Liquid Collected (Percent)	Phase	Radioisotope Collected (Percent)
4:1	93	water	0.17
		toluene	75.1
3:1	100	water	0.29
		toluene	107
2:1	100	water	0.18
		toluene	109

58

P-32 Tagged Toluene, Water. The results presented in Table 11 are for the tagged solids containing toluene, water, emulsifier and pure water. The gelling agent shows a very good retention capacity for P-32.

Actual Waste Treatment

A series of very low level liquid scintillation cocktail wastes were used to find a workable "recipe" for gelation.

A single vial containing 15 ml of cocktail was emptied into a 100 ml beaker. A few milliliters of water were added. If a single phase did not form three milliliters of emulsifier were added and the mixture was stirred. Then about 7.5 gm of gelling agent was added and the mixture stirred again. Finally, 25 ml of water was added and the mixture was stirred until solidification (about 5 minutes).

In the case when the water added to liquid scintillation cocktail formed a single phase solution, gelling agent (7.5 gm) was added first and stirred, water (25 ml) was then added, and the mixture was then stirred to solidification.

If the contents of the liquid wastes are known, the batch process can be increased greatly. Also the idea of making the gelation of the wastes a continuous process was given some thought, but it was beyond the scope of this research.

TABLE 11

P-32 TAGGED SOLIDS RECOVERY

Ratio of Solution to Gelling Agent	Liquid Collected (Percent)	Phase	Radioisotope Collected (Percent)
Toluene based			
4:1	97	water	0.109
		toluene	0.31
3:1	95	water	0.03
		toluene	0.41
2:1	99	water	0.15
		toluene	0.37
Water based			
4:1	100	water	0.733
3:1	100	water	0.3
2:1	100	water	0.15

SUMMARY AND CONCLUSION

Problem Development

Although a variety of large-scale liquid waste processes have been developed, none is suitable for university usage. Typically, a university generates low-level waste liquids in relatively small quantities as both aqueous and organic solutions from tracer experimetns. These waste solutions usually are cast as concrete (aqueous solutions), or shipped for burial in special small volume double-walled containers (organic wastes) which must be rented from a commercial disposal service. Disposal of the organic solutions costs on the order of $10 per gallon, and shipping concrete, which necessarily has a small liquid capacity, is needlessly expensive.

Aqueous wastes, and a few water-miscible organic solutions, can be diluted and discharged to the sanitary sewer system. However, the nuclides must be in a form not readily concentrated into biological systems, and only one curie per year can be handled this way.

The above factors prompted the research into finding a substance that is of lower density than concrete which converts aqueous and organic liquids into a form acceptable as shipments as solids.

Two candidate materials which could fill this requirement are Cab-O-Sil, a fine divided silica, and Safe-T-Set, a hydrophilic organic polymer. Cab-O-Sil is popular for developing a gel for liquid scintillation counting. The problems with this substance are that

61

(1) it is a hazardous material which can cause silicosis; (2) it is very difficult to handle, due to its light weight; and (3) it forms thixotropic gels that could easily be liquified by the shear stresses of a loose containment vessel. Therefore the Safe-T-Set became the prime material for investigation.

Experimental Results

Safe-T-Set usage as a gelling agent for aqueous systems was well established, but the application to organic wastes, especially liquid scintillation cocktails, was not apparent. The idea of using an intermediate solubilizing agent to make the organic liquid miscible with water proved to be futile --- the water and toluene would always form a two phase system. With the use of an emulsifier, the water and toluene produced an approximate single-phase system that would gel with the Safe-T-Set.

The evaporation from the gel could pose a problem. Even at ambient temperature, in an open vessel, the gel will ultimately dry out, with a substantial decrease in volume. At 105°C, in an open container, the water is evaporated completely within 25 hours.

Since loss due to evaporation was demonstrated, the importance of knowing the retention of radioisotopes by the gel under induced evaporation was evaluated. It was found that the retention of tagged toluene and tritiated water was poor, but that retention of ionic, water soluble radioisotopes was reasonably good.

The vapor pressure of the emulsified-liquid/gelling agent was found to be less than that of the pure water/gelling agent in a closed system.

Trial sample processing revealed that if the composition of the actual wastes is not known, the procedure is a vial-by-vial time-consuming process; but that if the contents are known, processing can be done in large batches.

Conclusions

The gel solid that resulted from the use of an emulsified organic solution with Safe-T-Set had acceptable characteristics for shipping.

The problem of evaporation from the gel could be solved by placing the gel in an airtight containment vessel, since excessive vapor pressure would not be encountered. Also the gel evaporation has potential advantages which make it attractive for burial. After arrival at the burial site, the liquid could be evaporated from the gel, with a great reduction in volume, and the dried material buried. This could be developed as a continuous process at the disposal site. With radioactive wastes, the vapors could be processed and cleaned before discharge at the disposal site.

The actual waste treatment was treated as a batch process, but large volumes of waste might justify the development of a continuous gelling process. The liquid waste could be emptied into a container where it is treated according to content, gelled, and then extruded into containment vessels.

Recommendations for Further Research

The application of Safe-T-Set with regard to other systems should be investigated further. The avenues of research are wide

open to the investigation of retention of other radionuclides, the use of other emulsifiers, the effects of acidity or basicity of aqueous solutions, the effect of corrosion by the solid wastes, the flammability of the organic gelled wastes, and the bio-degradability of the gelled wastes.

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WASTE DISPOSAL

A vexing problem is concerned with what to do with the wastes after processing. The disposal and storage of waste must be considered. This appendix covers storage in tanks, in-tank solidification, hydraulic fracturing, storage in salt-deposits, storage in ice, bed-rock storage, storage in man made vaults, ocean disposal, and ultimate disposal.

Storage in Tanks

Storage, as liquid waste, in tanks is not considered to be more than an interim technique. The potential consequences of failure could be large. Tank storage has been used in the United States for the past 25 years for aqueous high level wastes. Over 80 million gallons of wastes are stored in nearly 200 tanks at three AEC sites, Richland, Washington; Savannah River, South Carolina; and Idaho Falls, Idaho. Alkaline wastes are stored in mild-steel tanks and acidic wastes are stored in stainless steel tanks. The tanks are buried under 10 feet of earth to provide structural support, protection from surface weather conditions and inexpensive shielding. The latest design, a 1 million gallons capacity, has a mild-steel tank enclosed by another mild-steel tank for additional safety. Both tanks are surrounded by a concrete structure. To reduce corrosion, especially in stainless steel tanks, air circulators and cooling coils are used to keep the temperatures below $65^{\circ}C$. Laboratory tests show that mild-steel tanks corrode at a rate of 0.00002 in./year if stress corrosion cracking does not occur. Corrosion

Storage in Salt Deposits

The most extensively studied and the most practical method of waste disposal is in salt mines. The waste first must be solidified and encapsulated in a suitable container, then transported to the mine and placed in pre-excavated vertical holes in the mine floor. To limit the maximum salt temperatures from 200°C to 250°C the spacing of waste containers is typically 5 to 15 feet apart. Crushed salt is put into the 6 to 8 foot deep hole above the waste containers for shielding. Then excess salt chips from mining operations are used to fill the room containing the wastes. After a few decades, because of the overburden of weight the salt will plastic flow under pressure to form a monolithic formation. This will seal the wastes in the salt and keep it out of man's environment. Salt formations have these good properties: the salt formations (1) are usually dry and impervious to water, (2) are not associated with usuable water tables, and (3) are widely distributed and abundant. Also, salt has the ability to change shape under pressure and is a fair conductor of heat. [1,2]

Salt deposits underlie some 400,000 square miles of the United States. The estimated volume of high level waste solids produced by year 2000 would occupy less than 1% of the volume of salt now being mined each year. [2]

The estimated cost for disposal of solidified waste in salt mines ranges from about 0.003 mill/kW(e)-hr after 10 years of aging, to about 0.01 mill/kW(e)-hr after 2 to 5 years of aging. [1]

Storage in Ice

Zeller, Sounder, and Angine propose to store the encapsulated solid waste in the ice formation of the Antarctica. The waste would be encapsulated in a suitable container and be allowed to melt its own emplacement shaft, which would rapidly reseal by freezing and plastic flow. Calculation based on a 30 centimeter in diameter by 3 meter in length container with a thermal output of 5400 watts, indicate a sinking rate of 1 meter a day with an ambient temperature of ice in the range of -50°C. [24] This method should be studied further because the wastes are removed from the environment and the access to them would be difficult.

Bed-Rock Storage

The bed-rock storage of liquid waste was conceived by the Savannah River Plant in Aiken, South Carolina. In this concept, liquid waste is pumped through a pipe into one of several lateral tunnels carved out of deep, thick rock formation. When the tunnel is filled with waste, two thick concrete bulkheads are installed to seal off the tunnel.

Three principle mechanism delay the migration of wastes from the bedrock tunnels: low rate of natural water movement (1.5 to 7ft/year), the impermeability and ion-exchange properties of the natural clay present, and the ion-exchange properties of the top layers of earth. It is estimated that any one of the natural barriers is capable of confining the waste within the plant boundaries for at least 600 years. [1,2,25]

Storage in Man-made Vaults

In this concept the high level wastes are first converted to solids, placed in storage containers, then placed in large concrete rooms

built under about 10 feet of earth. The soil provides inexpensive shielding and safety from the surface environment. The heat is dissipated through the concrete, into the soil, and then to the surface. It can also be dissipated by forced or natural convection cooling, using air. This method should be used only for interim storage because of the surveillance and control required. The cost ranges from 0.03 to 0.07 mill/kW(e)-hr, or about 5 to 7 times the cost of salt mine storage.[1]

Ocean Disposal

Ocean disposal is mentioned because it used to be a prime disposal method. Solids were ballasted with concrete and damped in at least 6000 feet of water. England has put nearly 10,000 Ci/year into the ocean for the past 15 years with a 3 km long underwater pipeline.[1,3] The environmental impact of these discharges is not fully known at present, hence a moratorium on ocean disposal is in effect.

Ultimate Disposal

The permanent removal of a radioisotope from man's biosphere is called ultimate disposal. Such disposal may be accomplished in two ways: convert the hazardous material into a nonhazardous material, or dispose of the material so it cannot enter the environment.

Transmutation involves highly efficient separation of the long lived isotopes from waste, and then transmutation of the specific isotopes in a spallation reactor to form short lived isotopes. Not to mention the amount of mixed fission products generated using this process, the cost and practicality of this operation makes it unreasonable.

Space disposal is another way of ridding the environment of the

wastes.   The present limitations to this process are high cost and
unsafeness of the launching and propulsion system (chance of re-entry).
The cost ranges from about .3 mill/kW(e)-hr for a $1000 per payload
pound to 0.03 mill/kW(e)-hr for a $100 per payload pound.   But again,
these cost do not reflect the other waste management cost of processing,
interim storage, solidification, and transportation.[1]

VITA

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