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WASTE TREATMENT AND DISPOSAL SEMIANNUAL PROGRESS REPORT JULY - DECEMBER 1966

R. E. Blanco

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MASTER

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CHEMICAL TECHNOLOGY DIVISION

HEALTH PHYSICS DIVISION

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JULY-DECEMBER 1966

R. E. Blanco

F. L. Parker

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Oak Ridge, Tennessee
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ABSTRACT

High-Level Fluidized-Bed Fluoride-Volatility Process Waste. We are developing a process for preparing the waste powders from the fluidized-bed fluoride-volatility process for ultimate storage. The solids can be (1) sealed in a stainless steel pot, as such, (2) mixed with a getter to decrease production of volatile components, or (3) dispersed in a glassy matrix. A pilot plant is being designed for testing the applicability of these processes to radioactive wastes produced in the ORNL Fluidized-Bed Volatility Pilot Plant. Laboratory tests with nonradioactive simulated wastes showed that the addition of 10 wt % CaO to the fluidized-bed wastes reduced the weight loss at 850°C from 4.7 to 1.3%, or the weight loss attributable to moisture. In initial tests of a continuous process designed to disperse all types of powdered waste products in glass, fluidized-bed wastes and Purex wastes (produced in a spray calciner) were successfully dispersed in a glassy matrix.

Incorporation of Intermediate-Level Waste in Asphalt. A process for incorporating all types of intermediate-level wastes in asphalt is being developed. The types of wastes studied included: (1) ORNL intermediate-level waste, (2) second-cycle solvent extraction raffinates, and (3) aluminum cladding wastes. In this process, the wastes are mixed with emulsified asphalt (~ 35% H₂O), the water is volatilized, and the product is heated to 160°C. The leach rates of cesium from the asphalt products were reduced by factors of 2 to 10 by adding 2 wt % grundite clay and 2 wt % water glass to the original wastes. These additives also increased the ignition temperature of the product by at least 65°C.

The effect of radiation on the asphalt product is being studied using samples that contain 2 to 52 curies of mixed radionuclides per gallon of asphalt product and 60 wt % waste salts. No evidence of swelling, evolution of gases, or increase in the leach rate of the salts was noted at dose rates up to 4×10^7 rads over a 7-month period.

A pilot plant was constructed to determine the feasibility of using a wiped-film evaporator for the incorporation of intermediate-level wastes in asphalt. The equipment operated for 62 hr at rates up to 11 gal of nonradioactive simulated waste per hour, yielding a product that contained

as much as 64 wt % waste salts. No serious operating difficulties were encountered, and no appreciable wiper-blade wear has been detected. In all tests the sodium decontamination factor between the waste feed and the distillate was greater than 3000, usually 6000 to 8000, as compared with the original waste solution.

The capital cost of an asphalt plant for annually treating 400,000 gal of ILW containing as much as 5 curies/gal was estimated to be \$330,500; the operating cost, including amortization and burial at ORNL, was estimated at \$0.37/gal.

Water Recycle Process. Several important factors that could affect the treatment of recycle water by the Water Recycle Process were considered. When the concentration of dissolved solids is low, the amount of alum needed for clarification should not be significantly affected by the turbidity (concentration of suspended solids) of the feed water; it may be a function of both the specific conductance of the feed and the zeta potential of the suspended solids in the feed. In the presence of polyphosphates, alum floc formation is hindered unless an adequate amount of Ca^{2+} is present. The presence of low concentrations of alkylbenzene sulfonate (the foaming agent) in raw waste does not significantly affect the zeta potential of the suspended solids; however, the amount of coagulant required for clarification is greater.

Engineering, Economic, and Safety Evaluations. The operating experience in waste management is reviewed at the Dresden-I, Big Rock Point, Humboldt Bay, Elk River, Yankee, and Indian Point-I power-reactor stations and is used as a basis for estimating future radioactive waste production by the power industry over the remainder of this century. However, the conclusions and data presented here are preliminary and are subject to revision.

All the plants have been able to operate within their authorizations for release of radioactive wastes to the environment without undue difficulty. The Dresden, Big Rock Point, and Humboldt Bay reactors have been able to operate with substantial numbers of defective fuel elements without exceeding the permissible off-site dosage limit of 0.5 rem/year. The Elk River, Yankee, and Indian Point reactors, which operate with closed primary circuits, have released gaseous activity at less than 0.1% of the permissible concentrations given in Code of Federal Regulations 10CFR20.

Releases of liquid wastes have generally been made on the conservative assumption that these wastes contain unidentified isotopes, with radium known not to be present. Normally, except for tritium, ^{58}Co is the principal radioactive constituent present. The average amount of activity released annually has varied from 0.01 curie at the Elk River and Yankee power stations to 11.3 curies at the Indian Point station. An additional 10 to 100 curies of tritium per year is estimated to have been present in the discharged wastes from each reactor.

The annual volumes of solid wastes have ranged from several hundred to several thousand cubic feet; for the most part, the material has been of a very low activity level. These wastes are routinely shipped off site for disposal in commercial burial grounds by licensed contractors.

Assuming that the wastes from future reactors will not differ greatly from those of contemporary plants, it is estimated that the ^{85}Kr activity released annually from the United States will increase from 16 curies in 1970 to about 1100 curies in 2000, and that the activity, neglecting tritium, released in liquid wastes will increase from 80 to 5670 curies/year. The annual volume of solid waste will increase from 80,000 ft^3 in 1970 to 5.6 million ft^3 in 2000, and a total of about 534 acres of land will be required for its disposal.

Separation of Noble Gases from Air Using Permselective Membranes.

Krypton and xenon may be separated from air by using a cascade of thin silicone-rubber membranes. Preliminary design studies indicate that this process may be economically competitive with other separation methods that have been proposed. The permeabilities of pure xenon, krypton, oxygen, and nitrogen were determined using a single membrane.

Earthquakes and Reactor Plant Design. A state-of-the-art discussion paper on earthquakes and reactor plant design is being prepared jointly with the Reactor Division. Principal efforts are being directed toward the evaluation and interpretation of all relevant data on earthquakes from the standpoint of reactor siting and design.

Disposal in Natural Salt Formations. The second and third sets of ETR fuel assemblies have been installed in the arrays in the mine at Lyons, Kansas. The first set has been returned to Idaho. Both the second and third sets contained about 1.5 million curies at the time they

were installed. Radiation doses to personnel were low, and no serious problems were encountered.

Doses to the salt are expected to exceed the minimum goal of 5×10^8 rads by next May. Peak array temperatures have reached about 150 to 160°C; a planned power boost should allow a temperature of 200°C to be attained.

Salt flows (thermal expansion and plastic flow) resulted in increased separation (sag) rates of the 2-ft-thick salt layer in the roof. The installation of roof bolts in the entire experimental area appears to have eliminated any possible hazard from this source as a result of startup of the heated-pillar test. The heated-pillar test was started November 14 with a power input of 33 kw and is proceeding in expected fashion; that is, the transverse expansion rates of the pillar have increased greatly, producing pillar spalling and large vertical thermal expansion of the flow in the adjoining rooms.

Small quantities of water trapped in negative crystal cavities in the salt have been found to migrate toward a heat source. The rate of water inflow in the main and electrical arrays appears to be between 0.3 and 3 ml per day per hole. In the array in the old mine floor, the rate of water inflow is about 40 to 90 ml per day per hole because of the presence of water in the interbedded shale.

The array in the old mine floor is behaving similarly to the other arrays, except for slightly higher temperature rises, more water inflow, and no roof separation (due to a thicker roof beam).

Calculations of the gross salt mine space for the projected United States nuclear power economy indicate that by the year 2065 an area of about 7 miles square (49 square miles, a very small portion of the available area) will have been committed for waste disposal. Only about a third of that will have actually been used at that time.

Disposal by Hydraulic Fracturing. The ultimate capacity of a facility for disposing of radioactive wastes by hydraulic fracturing is governed primarily by the integrity of the rocks overlying the injected wastes. The objective of this study was to analyze theoretically the stresses and strains generated by the injected wastes in an effort to understand the behavior of the system sufficiently well that the failure

mechanism can be predicted and the capacity of an injection well can be estimated.

The most probable mechanism of failure of the rock appears to be by the formation of a vertical, instead of a horizontal, fracture. Fracture orientation is controlled primarily by the orientation of the principal stress field in the rock. Each successive waste injection slightly modifies this stress field toward a condition more favorable to the formation of a vertical fracture. The effect of the injections was evaluated for various assumed original stresses, and the minimum ultimate capacity of the formation was estimated as 4 million gal. Based on this analysis, it was also possible to make certain recommendations for the operation of the plant that would avoid, as far as possible, the conditions leading to failure and would subsequently increase the formation capacity.

The first waste injection of ORNL evaporator concentrate was completed; approximately 65,000 gal were successfully injected using 6 lb of solids per gallon. Excellent control of proportioning was maintained by the mass flowmeter and the densimeter.

Fate of Radionuclides in Terrestrial Environment. After 2 years of operation, ^{137}Cs loss from the 8 by 8-ft plots was 42.8% on the bare soil (plot 1), 19.4% on clipped meadow (plot 2), and 6.8% on tall meadow plot (plot 3). The ^{137}Cs loss during the second year was 2.5 times less on the bare soil, 4.4 times less on clipped meadow, and 23.9 times less on the tall meadow plots than the first year's losses. Cesium loss as a function of soil loss and of time was derived from the data.

Data on cobalt adsorption by minerals and soils are reported. Results to date suggest that cobalt sorption is greatly influenced by small amounts of sesquioxides and that the cobalt fixation is due to these sesquioxides rather than to the clay minerals.

Application of Mineral Exchange. The behavior of sulfur hexafluoride (SF_6) and methyl iodide (CH_3I) in an Idaho soil was studied. The SF_6 showed little, if any, interaction with the soil material. The CH_3I was retained to the extent that its movement was about 0.6 that of air.

Curium solutions of various pH levels were passed through columns of hydrobiotite. Instead of normal chromatographic breakthroughs, a constant leakage of curium occurred. The distribution of the curium along the column indicates that a radiocolloid is formed and that the hydrobiotite column acts as a low-grade filter.

1. INTRODUCTION

This report is the sixteenth of a series* of reports on progress in the ORNL waste treatment and disposal program, the objective of which is to develop and demonstrate, on a pilot plant scale, integrated processes for the treatment and the ultimate disposal of radioactive wastes resulting from reactor operations and reactor fuel processing. The wastes include those containing high, intermediate, and low levels of radioactivity in liquid, solid, or gaseous forms.

Under the integrated plan, low-activity wastes that consist of very dilute salt solutions, such as cooling water and canal water, would be treated by scavenging and ion exchange processes or foam separation to remove radioactive constituents; then the water would be discharged to the environment, or recycled and reused. The retained waste solids or slurries would be combined with the high-activity wastes or incorporated into asphalt or concrete before disposal in concrete vaults, salt mines, or burial pits. Alternatively, the retained solids or the untreated waste could be discharged to the environment in deep geologic formations. The high-activity wastes could be stored at their sites of origin for desired periods to allow for radioactive decay and artificial cooling.

Methods investigated for the permanent disposal of high-activity liquid wastes include conversion to solids by high-temperature "pot" calcination or glass formation in the final storage container (pot) and formation of a glass or ceramic in a continuous melter. High-activity solid wastes from nonaqueous fuel processing methods, such as the fluidized-bed fluoride-volatility process, could be packaged directly as solids or incorporated in a glassy matrix. The solids from either process would be stored in a permanently dry place such as a salt mine. This is undoubtedly the safest method because control of radioactivity can be ensured, within present technology, during treatment, shipping, and storage.

*ORNL-CF-61-7-3, ORNL-TM-15, ORNL-TM-49, ORNL-TM-133, ORNL-TM-169, ORNL-TM-252, ORNL-TM-376, ORNL-TM-396, ORNL-TM-482, ORNL-TM-516, ORNL-TM-603, ORNL-TM-757, ORNL-TM-830, ORNL-TM-1081, and ORNL-TM-1465; see also annual reports for 1962-1966, ORNL-3452, ORNL-3492, ORNL-3672, ORNL-3697, ORNL-3830, ORNL-3849, ORNL-3945, and ORNL-4007, from the Chemical Technology and Health Physics divisions.

Tank storage or high-temperature calcination of intermediate-level wastes may be unattractive because of the large volumes involved, and thus other disposal methods will be studied. One of these, the addition of solidifying agents prior to direct disposal into impermeable shale by hydrofracturing, has been investigated. Particular attention was given to the engineering design and construction of an experimental fracturing plant to dispose of ORNL intermediate-level wastes by this method. A second method is incorporation (and dehydration) of intermediate-level wastes in asphalt.

Environmental research on the Clinch River, motivated by the need for safe and realistic permissible limits of waste releases, is included in this program. The objective is to obtain a detailed characterization of fission product distribution, transport, and accumulation in the physical, chemical, and biological segments of the environment.

2. TREATMENT OF HIGH-LEVEL RADIOACTIVE WASTE

The development of the ORNL Pot Calcination and Rising Level Pot-glass processes has been completed and reported elsewhere. The treatment of high-level waste powders from the fluidized-bed fluoride-volatility process is now receiving major attention. These solids can be sealed in a storage pot without further treatment, or they can be dispersed in a glassy matrix in the storage pot. Similarly, powders obtained by spray or fluidized-bed calcination of aqueous high-level wastes can also be dispersed in a glassy matrix to decrease solubility and increase thermal conductivity.

2.1 Fluidized-Bed Fluoride-Volatility Process Waste

2.1.1 Chemical Development (H. W. Godbee, C. L. Fitzgerald, N. M. Davis, W. E. Clark)

The principal effort in laboratory studies has involved the problems associated with canning; that is, sealing the untreated powders in a stainless steel pot for long-term storage. Since the waste powders consist of aluminum oxide plus aluminum fluoride, stainless steel fluorides, and various fission product fluorides, the volatilization of fluorides poses a potential problem at storage temperatures above about 250°C. Thermochemical calculations indicate that alkaline-earth oxides should convert volatile metal fluorides, such as AlF_3 , in the waste powder into stable metal oxides plus the more-stable alkaline-earth fluorides. Addition of 10 wt % CaO to waste from an HF-O_2 volatility process reduced the weight loss of the powder at 850°C from 4.7 to 1.3%. According to the vapor pressures reported in the open literature, AlF_3 should volatilize at a temperature somewhat greater than 500°C. This volatilization was observed in samples held at 550°C and at 850°C for up to 74 hr. Samples of AlF_3 held at 850°C for 74 hr lost as much as 15.4% of their original weight.

Two arrangements of apparatus are used to determine the weight losses of waste powders (and pure fluorides making up the waste powder) as a function of time and temperature. In one, an analytical balance and carefully

controlled temperature programming are used to yield differential and integral weight losses on small samples (≤ 1 g) as a function of time and temperature by thermal gravimetric analysis (TGA). The other arrangement uses gross, integral weight losses on large samples (several grams) as a function of final temperature and time at that temperature.

TGA experiments have been made using waste powders obtained from both the HF-O_2 and HCl volatility processes. Weight losses for waste powder from the HF-O_2 process indicated weight losses of 0.998%. Each of the samples was heated at a rate of $4.7^\circ\text{C}/\text{min}$ to 850°C and then held at this temperature until a constant weight was attained. A flowing argon atmosphere was used; the off-gases were passed through two caustic scrubbers. Results of the analyses of the scrubber solutions are not conclusive but indicate that hydrolysis of the fluorides is occurring at the elevated temperatures, giving HF as the primary off-gas.

Plots of differential weight losses with time ($\Delta \text{weight}/\Delta \text{time}$) vs temperature for the HF-O_2 powder experiments gave peaks at 130, 465, and 660°C in one instance, and at 475 and 675°C in the other. The 130°C peak corresponds to the dehydration of $\text{Al}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$. The difference in weight loss, 0.21%, between the two samples can be explained by the difference in the amounts of Al_2F_6 that is hydrated. The peaks at 465 and 475°C correspond to the dehydration of $\text{Al}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$. The peaks at 660 and 675°C have not yet been identified. Plots of $\Delta \text{weight}/\Delta \text{time}$ vs temperature for the experiments with the waste powder from the HCl process gave peaks at 130 and 650°C . Again, the 130°C peak corresponds to the dehydration of $\text{Al}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$; the 650°C peak has not yet been identified. Approximate compositions of the two waste powders are shown in Table 2.1.

Integral weight losses as a function of time at temperature were determined using approximately 2-g samples. The samples were contained in an alumina boat resting in a 1-in.-diam nickel tube. This tube was heated in a tube furnace, and flowing argon was used to carry the off-gases into caustic scrubbers. In these experiments, samples of pure anhydrous AlF_3 that were heated at 250°C for periods of time up to 74 hr exhibited no weight losses. At 550°C , weight losses averaged 0.9% after 18.5 hr and 3.5% after 74 hr. Aluminum fluoride held at 850°C for 18.5

Table 2.1 Approximate Composition^a of Waste Powders from Fluidized-Bed Fluoride-Volatility Processes

Component	Waste Powders ^b Obtained From	
	HF-O ₂ Process	HCl Process
Al	50.4	52.8
Cr	0.12	
F	11.8	2.23
Fe	0.97	
Ni	0.15	
Sn		0.024
U	0.11	0.015
Zr		0.12

^aIn wt %.

^bORNL-TM-1441.

and 74 hr showed average weight losses of 4.9 and 15.4%, respectively. These results verify the vapor-pressure data recorded in the literature for AlF_3 and lead to the conclusion that the volatility of AlF_3 can present a problem in waste storage at high temperatures.

Waste powders obtained from the HCl process (Table 2.1) were tested for fluoride volatility. The weight loss of the untreated powder was 0.91% which agrees well with the data obtained in the TGA experiments above when we consider the difference in samples, sample sizes, and the manner in which the experiments were carried out.

Theoretical considerations indicate that the addition of alkaline-earth oxides should convert the metal fluorides in waste powder to stable metal oxides plus the more stable alkaline-earth fluorides. Experiments were performed in which CaO was added to inhibit the fluoride volatility. When it was added to the waste from the HF-O₂ process (Table 2.1) in weight ratios of 1:19 and 1:9, the weight losses were 2.4 and 1.3%, respectively. When it was added to the waste powder from the HCl process

(Table 2.1) in a weight ratio of 1:49, the weight loss was 0.2%. The above data lead to the conclusion that CaO does serve as an adequate fluoride getter. When CaO is added in sufficient quantity to hold the fluoride present, the weight losses observed correspond to the moisture content of the powders. Additional studies are in progress using various CaO:waste weight ratios. Also, studies using magnesium and barium oxides as fluoride getters are under way.

Something more than canning of the untreated waste powders from the fluidized-bed process or any waste treatment process that yields a powder may be desirable, or required. These waste treatment processes include spray calcination and fluidized-bed calcination. The powders may be unstable or poor thermal conductors at the storage temperatures to be used or they may be too soluble to be transported safely to storage. To improve the stability and thermal conductivity, as well as to decrease the solubility of the powders, they can be dispersed in a glass matrix. Thirteen experiments were conducted in which spray-calcined Purex wastes and simulated waste powders from the fluidized-bed process were incorporated in lead-silicate glasses. In seven of these experiments, the pots were filled by a rising-level technique (i.e., the mixed powders were added continuously to the pot, at a rate approximately equal to that at which the glass powder was melting, until the pot became full). In all experiments, the waste powder and glass powder were mixed in a weight ratio of about 1:2. (No further experiments are planned with this system since the responsibility for the dispersion of fluidized-bed waste in glass has been assigned to Brookhaven National Laboratory.)

The experimental apparatus consisted, basically, of a stainless steel pot in a controlled-temperature furnace, with ancillary equipment such as a powder mixer-feeder and scrubbers for trapping and analyzing the off-gases from the pot. A schematic diagram of the 2-in.-ID and 12-in.-long pot in the 5-kw furnace with three independently controlled zones is shown in Fig. 2.1. The feed rates of mixed powders ranged from about 1 to 5 g/min. The temperature of the material in the pot was increased to 800 to 850°C. In some experiments, the temperatures of all zones of the furnace were increased to 800 to 850°C before the feed was started; in others, the bottom zone was heated to 800 to 850°C and the

ORNL Dwg. 67-5197

Fig. 2.1. Schematic Diagram of Apparatus for Dispersion of Waste Powders in Glass.

top zone was heated to about 400 to 450°C before the feed was started. Then, as the level of the material in the pot rose, the temperature of the top was gradually increased to 800 to 850°C. Glass powder (< 200 mesh) with particle sizes less than those of the waste powder (80 to 100 mesh) was used in some of the experiments. In others, a glass powder with particle sizes about the same as those of the waste powder was used.

The experiments showed that this dispersion-in-glass process works equally well for Purex calcine (essentially Fe_2O_3 and Na_2SO_4) and fluidized-bed waste (essentially Al_2O_3 and AlF_3). Further, they showed that increasing the temperature of the material in the pot as the level of material rises, and that matching the particle sizes of the glass powder with those of the waste powder yielded products having fewer voids (2 or 3 vol %) than were noted for the products (20 to 30 vol %) obtained by using other modes of operation.

2.1.2 Pilot Plant Design (E. J. Frederick)

The FBVPP Waste Treatment Pilot Plant will be installed in cell 1, Building 3019, and will be used to demonstrate optimum processes that have been developed at ORNL and BNL for treating alumina waste emanating from the fluidized-bed primary reactor.

In the present conceptual design, which is the result of a detailed investigation of the operating capabilities in cell 1, the pilot-plant process equipment is installed in a cubicle that will be located on a platform in cell 1 approximately 8 ft above the existing cell floor. A 5-ft-wide operating corridor is provided between the south face of the steel-shielded cubicle wall and the concrete shielding wall of cell 1. In-cell process operations and a limited amount of in-cell maintenance will be performed by a bridge-mounted crane and manipulator. Major equipment maintenance will be accomplished by removing the faulty equipment from the cell. Lead glass windows will be installed in the steel shielding wall at appropriate locations to permit direct viewing of in-cell operations.

The waste will be discharged from the bottom of the primary reactor, located in cell 3, into the final disposal waste pot, which will contain

the necessary chemical or glass-making additives. The pot will be transferred from cell 3 to cell 1 in the volatility-waste transfer cask. The pot will be lowered into the product receiving station in cell 1 and then moved by the manipulator and crane to a tumbler-type mixer. After the chemicals or glass-making additives have been thoroughly mixed with the waste, the pot will be placed in a resistance furnace that will be mounted on a transfer dolly. The dolly will be moved to the heating station, and the pot will be connected to the off-gas system. Upon completion of the heat cycle, the pot will be disconnected and then moved to the product storage station for observation.

By using the PHOEBE and CRUNCH codes, shielding calculations were made for waste generated in "hot" runs of the FBVPP. These calculations indicate that 15 in. of steel shielding will be sufficient to reduce the radiation level at the surface of the operating face of the cubicle to less than 2 mr/hr for all runs except the short-cooled fluidized-bed volatility process demonstration runs, in which a maximum of 5 mr/hr is possible.

Calculations of fission product heating were made in order to size the waste disposal pots and to determine whether heat or cooling would have to be provided during storage and observation. Data obtained with the PHOEBE code indicated that fission product heating will be insignificant in all instances, and that, in fact, supplementary heating will be required during storage in order to approach the level given previously.^{2.1}

Since fission product heating is not limiting, a 12-in.-diam size was arbitrarily selected for the waste disposal pot. The average volume of waste that will emanate from a volatility run will be about 1 ft³, which will require a bed height (in the pot) of about 15 in. If the bed height allowed for chemical and glass-making additives is assumed to be equal to that for the waste, the overall height of the pot should be about 36 in. This is well within the 40-in. space limitation that is imposed by the process installation in cell 3.

2.2 Pot Calcination of Radioactive Purex Waste

The first test of the ORNL Pot Calcination process with radioactive Purex waste (PW2 type) was successfully made in November 1966 at the Waste Solidification Engineering Prototype (WSEP) Pilot Plant at Hanford, Washington.^{2.2} The pot contained about 83,000 Ci of gross activity. Two additional runs at higher levels of activity are planned for February 1967. Details of these tests will be presented in reports that will be issued by the Pacific Northwest Laboratory of Battelle Memorial Institute.

Final reports summarizing the development of the ORNL Pot Calcination and Rising-Level Potglass processes were issued.^{2.3, 2.4}

3. TREATMENT OF LOW- AND INTERMEDIATE-LEVEL RADIOACTIVE WASTE

3.1 Incorporation of Intermediate-Level Waste in Asphalt

The intermediate-level wastes generated in nuclear installations generally have been stored in tanks or mixed with cement. These wastes include second- and third-cycle raffinates; solutions from decladding, solvent cleanup, and off-gas scrubbers; and slurries and solids from processes for decontaminating process waters. They are characterized by modest levels of radioactivity (heating and radiation dose levels are not serious problems) and by high concentrations of salts or dissolved solids, which prevent their efficient treatment by a conventional method such as ion exchange or precipitation. Still, neither tank storage nor solidification in cement is completely satisfactory. Tank storage is only a temporary measure, and the products formed by mixing the waste with cement are only moderately insoluble and represent a volume increase. In addition, most operations with cement are dusty, good mixing is difficult to achieve, and the operations are cumbersome.

A promising recent development is the use of asphalt to solidify and insolubilize these wastes. Immobilization of wastes by incorporation into this cheap, insoluble material before burial or other storage can reduce not only treatment costs but also the flow of radioactivity to the environment. Plants for incorporating intermediate-level waste in asphalt are already in operation at Mol, Belgium,^{3.1-3.3} and Marcoule, France,^{3.4-3.6} while a plant similar to that in Belgium is being constructed at Harwell, England.^{3.7} At Mol, a batch process is used to incorporate wastes (incinerator ashes, concentrated aqueous solutions, or filtered sludges with variable water content) in hot asphalt (about 250°C) by a method that requires simultaneous gradual addition and violent stirring. Most of the work at Mol has involved sludges. At Marcoule a continuous process has been developed for mixing sludges, to which emulsifying agents have been already added, with hot asphalt (about 125°C). The major portion (80 to 90%) of the water in the sludges is exuded and thus separated from the coated wastes. The residual water in the asphalt mixture is then volatilized, and the mixture is heated to about 130°C.

Since exuded water would contain most of the soluble radiation emitters, the process is applicable only to wastes in which the latter are bound in the sludge solids.

In the process being developed at Oak Ridge National Laboratory (ORNL),^{3.8, 3.9} wastes are introduced into an emulsified asphalt at any convenient temperature below the boiling point of the solution, water is volatilized by heating, the temperature of the product is increased until the product flows freely, and finally, the product is drained into a steel drum for preliminary storage and shipment. Attractive features of the process include: (1) use of emulsified asphalt, which flows readily at room temperature; (2) evaporation at low temperatures to minimize degradation of the asphalt; (3) low agitation rates, which provide adequate mixing and keep the heated surfaces of the evaporator clean; (4) operation in either a batch or continuous manner; and (5) incorporation of soluble or insoluble solids with equal effectiveness.

3.1.1 Chemical Development (H. W. Godbee)

Asphalt products containing 10 to 80 wt % salts from waste have been prepared with ORNL intermediate-level waste (ILW), an aluminum cladding solution (ACS), and a Purex second-plutonium-cycle waste (2CW) with added caustic (Table 3.1). As reported previously, no apparent difference, other than hardness of the product, was observed in the mixture obtained with a given waste. Products made with 2CW are harder than those made with ILW or ACS having the same concentration of incorporated solids. Leaching tests with distilled water show that the leaching rates of strontium and ruthenium from asphalt products are sufficiently low, that is, 0.1% or less is leached out in 1.5 years; however, the leach rate of soluble cesium is 50 to 100 times higher than this.^{3.10} Results of initial experiments with mineral additives to improve cesium retention indicate that the addition of grundyte clay should have the desired effect. Tests were made with ORNL ILW that contained 2 wt % grundyte and 2 wt % water glass. The purpose of the water glass, Na_2SiO_3 , is to hold or suspend the grundyte in the waste. An asphalt product containing 60 wt % solids from this waste was prepared. After two months of leaching, the leach rate of ^{137}Cs from this product was about one-half that

Table 3.1 Compositions of Simulated Wastes Used
In Emulsified Asphalt^a Incorporation Studies

Component (M)	1 ILW ^b	2 ACS ^c	3 2CW ^d	4 2CW1 ^e	5 2CW2 ^f
Na ⁺	6.61	4.16	0.64	6.64	7.01
NH ₄ ⁺	0.19	--	--	--	--
H ⁺	--	--	6.2	--	--
Al ³⁺	0.22	--	--	--	--
Fe ³⁺	--	--	0.54	0.37	0.36
NO ₃ ⁻	4.64	2.2	6.2	4.26	4.14
OH ⁻	2.06	0.06	--	1.94	2.44
AlO ₂ ⁻	--	1.9	--	--	--
Cl ⁻	0.056	--	--	--	--
SO ₄ ²⁻	0.35	--	1.13	0.78	0.76
Density at 25°C (g/ml)	1.34	1.21	1.31	1.33	1.34
Total solids in waste (wt %)	39.1	28.5	38.8	39.4	39.9

^aThe emulsified asphalts used were the types used in the surface treatment of roads (type RS-2, a rapid-setting, high-viscosity emulsified asphalt; type SS-1, a slow-setting, low-viscosity emulsified asphalt). Both contained about 63 wt % asphalt, 35 wt % water, and 2 wt % emulsifying agent.

^bORNL intermediate-level waste solution (alkaline evaporator concentrates).

^cSolution from dissolution of aluminum cladding with NaOH-NaNO₃.

^dPurex second-plutonium-cycle waste.

^ePurex second-plutonium-cycle waste with 455 ml of 51.5% NaOH added to each liter of 2CW.

^fPurex second-plutonium-cycle waste with 497 ml of 51.5% NaOH added to each liter of 2CW.

of a similar product without grundite, namely, 7×10^{-5} vs 1.4×10^{-4} fraction leached $(\text{cm}^2/\text{g})^{-1} \text{ day}^{-1}$. Similarly, the leach rate of ^{137}Cs from a product containing 20 wt % salts (from ILW plus 2 wt % grundite) was reduced by a fraction of 10, that is from 6.5×10^{-5} to 6.5×10^{-6} . Additional experiments are in progress to determine the effect of increased amounts of grundite on cesium retention.

As part of a continuing program to evaluate the safety of asphalt-nitrate salts mixtures, large samples (150 g) of 60 wt % salts-asphalt products contained in stainless steel beakers were heated in air on a hot plate to about 400°C . Four of the five samples containing 2% grundite and 2% water glass would not ignite under these conditions. The fifth sample only smoldered. Similar samples without the grundite-water glass additive ignited at about 335°C under these conditions. It is worthy of note that these additives seem to inhibit the burning of the products; this inhibitory effect is being studied further as a function of the amount of grundite, the amount of water glass, and of the ratio of these additives.

3.1.2 Radiation Stability (J. H. Goode, J. R. Flanary)

Hot-cell tests are being conducted^{3.11, 3.12} in which three typical intermediate-level wastes, along with large quantities of aged, mixed fission products, were incorporated into asphalt to accelerate possible effects resulting from radiation. These effects are being measured by observation of swelling and/or radiolytic gas evolution from the asphalt products and as a function of the leach rates of sodium and fission products. Samples of an actual ORNL-ILW evaporator concentrate, a neutralized raffinate from the second plutonium cycle of the Purex process, and a simulated sodium aluminate fuel decladding waste (Table 3.1) were adjusted to four levels of radioactivity (approximate concentrations: 1, 2, 5, and 25 curies per gallon of waste) by adding desired amounts of a high-level waste concentrate. The concentrate contained a mixture of fission products that had decayed longer than 2 years. The wastes were then incorporated in asphalt, and the temperature was increased to 165°C . The final asphalt product had one-half the volume of the original waste and contained 60 wt % solids. Thus, the fission product activity in the products was about twice that of the feed.

The condensates that were collected during the evaporation of the water from the asphalt product were slightly radioactive ($9 \mu\text{c}$ to 0.7 mc/gal) because of entrained fission products. Our laboratory-scale fixation apparatus, however, had no deentrainment devices. Separation factors between the total beta-gamma activity in the wastes and that in the condensates ranged from 6.4×10^3 to 2.6×10^5 , which are higher than earlier estimates that were based on nonradioactive tests. Essentially all the radioactivity in the condensates could be attributed to ^{137}Cs . Ruthenium was almost nonvolatile, contributing less than 10% of the total gamma in the condensate from the most radioactive sample (52 curies per gallon of product). These condensates normally receive further treatment at a facility designed to process low-level waste.

Degradation of the asphalt products as a result of radiation appears almost negligible. We have not observed any swelling or gas evolution from the samples during the past 7 months. The maximum internal dose to the most radioactive sample was about 4×10^7 rads.

The static water leaching rates for sodium, gross beta activity, gross gamma activity, ^{90}Sr , ^{106}Ru , ^{137}Cs , and rare earths confirmed the results established in earlier tracer and nonradioactive experiments^{3.8} and hot-cell experiments made at the 5 Ci/gal level.^{3.11} Figure 3.1 illustrates typical rate curves for leaching evaporator-bottoms-in-asphalt containing 52 Ci of product per gallon. Sodium and the principal gamma emitters (gross gamma), primarily ^{137}Cs , were dissolved at equilibrium rates of 1 to $3 \times 10^{-4} \text{ g cm}^{-2} \text{ day}^{-1}$, while the rates for strontium, ruthenium, and the rare earths were orders of magnitude lower. Recent tracer experiments^{3.8} have shown that the incorporation of grundyte clay into the asphalt-waste mix reduces the leaching of cesium by 1 or 2 orders of magnitude and, in turn, the leaching rate of the gross gamma activity to at least the range of that of the ruthenium and the rare earths. We are planning further tests in which radioactive wastes will be incorporated in samples containing grundyte clay.

3.1.3 Pilot Plant Tests

A pilot plant was constructed in 1966 to evaluate the ORNL process for incorporating intermediate-level wastes (ILW) in asphalt. Nonradioactive simulated wastes were used in tests that were made, primarily, to

Fig. 3.1. Leaching of Fission Products from ILW Fixed in Asphalt (61% solids in asphalt; 52 curies/gallon of asphalt).

determine the applicability of a continuous wiped-film evaporator to the incorporation step. Other objectives of these tests were: (1) to verify the laboratory results, particularly the limitation of 60 wt % salts in the final product and the operating temperature of 160°C; (2) to determine the operational characteristics of the evaporator for periods up to 100 hr; (3) to determine the capacity of the equipment; (4) to examine the effect of operating variables, particularly the speed of rotation of the wiper blades and the steam pressure in the evaporator jacket; and (5) to determine the amount of organic and inorganic materials entrained or volatilized in the vapors and subsequently appearing in the condensate.

Pilot Plant Design (A. M. Rom, J. C. Suddath). The pilot plant was designed to yield approximately one drum (55 gal) of asphalt-waste salts product per day. This product was obtained by feeding emulsified asphalt and nonradioactive simulated ILW into a wiped-film evaporator.^{3.13}

The wiped-film evaporator, which was purchased from the Pfaudler Company, has 4 ft² of evaporating area (1 ft in diameter). The parts that contact ILW, emulsified asphalt, or a mixture of the two (Fig. 3.2) are made of austenitic stainless steel. The two feed streams (nonradioactive simulated ILW and asphalt emulsion) fall onto a spinning distributor plate; from there, they pass through weirs onto the heated surface. Four wiper blades continually blend a thin layer of film, and grooves in the wiper blades (Fig. 3.3) help force the product downward. The distributor plate supports a rotating cylinder that holds the wiper blades; it also contains baffles for deentraining the vapor. At a rotational speed of 285 rpm, the wiper blades move at a peripheral speed of 15 fps (i.e., a wiper blade passes a given point on the circumference every 0.053 sec). Other items of equipment include a 750-gal asphalt storage tank, a 120-gal ILW tank, a 75-gal emulsified asphalt feed tank, three pumps, a heat exchanger, and accessories.

The nonradioactive simulated ILW for use in the experiments contained 38.75 wt % salts and 61.25 wt % water, and was 6.61 M in Na⁺, 0.22 M in Al³⁺, 0.19 M in NH₄⁺, 4.64 M in NO₃⁻, 0.35 M SO₄²⁻, 0.056 M in Cl⁻, and 2.06 M in OH⁻. It had a specific gravity of 1.335. The

Fig. 3.2. Cutaway Drawing of Wiped-Film Evaporator (courtesy of the Pfaudler Company).

Fig. 3.3. Configuration of Grooves in Wiper Blades.

emulsified asphalt selected for the tests was type RS-2* (Federal Specification SS-A-674b), which contain 63 wt % base asphalt, 35 wt % water, and 2 wt % anionic emulsifying agent. Based on laboratory development work, the asphalt-waste salts product contained 60 wt % salts. Products with higher concentrations of salts (up to 80 wt %) have been formed; however, they have poorer flow and temperature characteristics than the 60 wt % product, which flows readily from the evaporator at 265°F.

An engineering flowsheet of the waste-asphalt process is shown in Fig. 3.4; a photograph (Fig. 3.5) shows the equipment installed in the pilot plant.

Process Development (J. C. Suddath, J. T. Long). An asphalt paving emulsion* was pumped into the feed tank from the storage tank as needed. Simulated ILW (See Table 3.2.) was made up in 400-liter batches and pumped into the waste feed tank. The emulsion feed rate was controlled by the dc voltage on the drive to a gear pump and was monitored by measuring the pump rotation rate. The pump rotation rate was periodically compared with the actual flow rate, which was determined by the time needed to pump a measured amount into a graduated cylinder. The waste feed rate was controlled by a needle valve in the feed line, and was measured by a calibrated rotameter. During startup and shutdown, only emulsion was fed to the evaporator. Thus, no waste salts were left in the evaporator body when it cooled off, and none were added until the evaporator was again at operating temperature.

Since the temperature of the product is well above the atmospheric boiling point of water, failure to remove all the water can be detected by bubbles of steam breaking at the surface of the product, or by flecks of salt left on the surface when the bubbles break. Unless the ratio of waste to emulsion was too high or the capacity of the evaporator was exceeded, the product always had a smooth, glossy appearance. Therefore, the appearance of the product was a rapid and infallible indicator of the suitability of operating conditions during the experimental

*Type RS-2 was obtained from the Chattanooga Rock Products Company, Knoxville, Tennessee, plant. This emulsion reportedly was made from Venezuelan crude base asphalt and probably contained a nonionic emulsifier.

INTERMEDIATE LEVEL WASTE-ASPALT PROCESS

Fig. 3.4. Engineering Flow Diagram.

Fig. 3.5. Wiped-Film Evaporator as Installed for Development of the Waste-Asphalt Process.

Table 3.2. Routine Conditions for Waste-Asphalt Wiped-Film Evaporator Tests

	Design Conditions	Operating Conditions
Composition of ILW Concentration:		
Na^+ , mg/ml	152	167
Al^{3+} , mg/ml	5.93	5.36
Cl^- , mg/ml	1.98	3.50
NO_3^- , mg/ml	276	288
OH^- , N	2.06	2.17
SO_4^{2-} , mg/ml	33.6	35.8
ILW feed rate, gal/hr	7.25	7.75
Solids in asphalt emulsion, wt %	65	70
Waste salts in product, wt %	60	58
Wiper rotation rate, rpm	---	285
Steam supply pressure, psig	200	200
Temperature in evaporator body, °C	160	Unknown
Temperature in steam jacket, °C	---	192
Temperature of product outlet nozzle, °C	---	110-120
Decontamination factor for sodium	---	> 4000

program. Because of the large heat capacity of the equipment, a period of about 30 to 60 min was required in order to reach full operating temperature. However, the heat capacity of the equipment, as well as the small amount of material in the equipment, was advantageous because any change in operation caused only a momentary departure from steady-state conditions.

1. Verification of Laboratory Tests. No problems were experienced in operating at feed rates that resulted in a product containing 60 wt % waste salts. (In fact, at waste feed rates up to 11 gal/hr, the equipment operated perfectly, yielding a product with up to 64 wt % salts; however, this was very near the upper limits of its capability.) At higher waste:asphalt ratios, the salt particles were no longer infinitesimal but appeared as discrete crystals coated with asphalt. The product had a definite granular appearance or, in worse cases, was lumpy.

Since the temperature of the mixture in the wiped film of the evaporator could not be measured, we could not verify the optimum temperature of 160°C that had been set by laboratory tests. However, the temperature was approximately in this range. The temperature of the steam jacket was about 190°C. The temperature of the product was somewhat greater than 120°C since this temperature was measured on the outside of the product nozzle after the product had partially cooled. The product also flowed easily when it contained 64 wt % waste salts.

2. Operating Duration. The equipment was operated for 62 hr at conditions similar to those shown in Table 3.2. No operating difficulties were encountered, and wear of the wiper blades was negligible. The equipment can be started up and stopped easily and, when disassembled, shows only an oily film on the evaporating surface.

3. Equipment Capacity. The equipment operates satisfactorily at waste feed rates up to 11.4 gal/hr, but at higher waste rates, the proportion of asphalt must be increased appreciable (Table 3.3). The evaporator could not be operated satisfactorily with a waste feed rate greater than 13.1 gal/hr, using any proportion of asphalt. The limiting conditions are determined by both the rate at which water is evaporated (i.e., waste feed rate) and by the waste:asphalt ratio (i.e., the wt % solids) in the product.

Table 3.3. Operating Limits for the Wiped-Film Evaporator

Waste Feed Rate (gal/hr)	Percentage Waste Solids in Product		Water Evaporation Rate (gal/hr)	
	Satisfactory Operation	Unsatisfactory Operation	Satisfactory Operation	Unsatisfactory Operation
11.1	64.5	---	10.0	---
11.3	64.4	65.0	10.1	10.1
11.4	64.0	---	10.3	---
11.6	62.6	---	10.5	---
11.9	52.5	58.4	11.6	11.1
12.7	48.6	54.1	12.7	12.2
13.5	---	50.0	---	13.3

4. Changes in Operating Conditions. Two ranges of wiper rotation rate can be used, 150 and 285 rpm. The higher rate is required for operation at waste feed rates greater than 8 gal/hr; however, the rate appears to be unimportant at lower feed rates.

The steam pressure could not be decreased below 185 psig, probably because the temperature inside the evaporator body was too low. We could not increase the steam pressure above 200 psig because of supply limitations.

5. Carry-Over of Organic Matter. A trace of oil appeared in samples taken at the exit of the condenser, but the amount was not sufficient for analysis. No oil appeared in the distillate leaving the knockout drum.

6. Decontamination Factor. The measurement of the decontamination factor (DF) for cesium was impractical, but the DF for another alkali metal, sodium, was readily obtained. In all tests the sodium DF between the waste feed and the distillate was greater than 3000; in most instances, it was in the range of 6000 to 8000.

3.1.4 Economic Evaluation (A. M. Rom)

A conceptual design and a preliminary cost estimate for a plant^{3.14} to immobilize ORNL ILW (an alkaline evaporator concentrate) were prepared as a part of the development of the waste-asphalt process at ORNL. Fundamental design considerations were:

1. In the process, a wiped-film evaporator with 50 ft² of heat-transfer area would be used to produce one volume of homogeneous asphalt-waste salts mixture when fed with two volumes of ILW and one volume of emulsified asphalt. The ILW would contain 0.1 to 5 Ci/gal and up to 40% dissolved salts; it would be processed at a rate of 60 gal/hr for 278 days per year. The emulsified asphalt would be composed of 63 wt % base asphalt, 35 wt % water, and 2 wt % emulsifying agent. The asphalt-waste salts product, containing 62.5 wt % salts and 37.5 wt % asphalt, would be collected in 55-gal drums. A schematic process flowsheet is shown in Fig. 3.6.

2. A new building, conforming to ORNL double-containment standards, would be provided to house the process. The building would include a central cell (10 x 10 x 16 ft) and 3-ft-thick concrete walls, a shielding

Fig. 3.6. Schematic Flowsheet--ORNL Asphalt-Waste Salts Process.

window, a pair of master-slave manipulators, a shielded tunnel for handling product drums remotely, and crane bay with a 5-ton bridge crane. The conceptual building design is shown in Figs. 3.7-3.9.

The capital and operating costs were estimated for a plant with an ILW capacity of 400,000 gal/yr. The total capital cost was \$330,500 (Table 3.4). The unit operating cost was \$0.34 per gallon of waste, assuming 20-year amortization of capital without interest, or \$0.37/gal, assuming 20-year amortization and 4% interest. The plant operation was assumed to be 3 shifts per day, 5 days per week, and 52 weeks per year (Table 3.5).

3.2 Water Recycle Process

W. C. Yee

The reuse of water is the objective of the Water Recycle Process for treating low-level radioactive waste (LLW). Instead of conventional treatment, which involves partial decontamination and which relies on discharge to streams and on dilution to maintain radionuclide concentrations at below MPC_w requirements, waste water containing low concentrations of dissolved solids is completely decontaminated and demineralized, and returned for plant reuse, thus providing a closed circuit. Fresh water is demineralized before entering the circuit.

The process includes zeta-potential-controlled flocculation-clarification, cation-anion exchange, and sorption by activated carbon. Overall decontamination factors of 10^3 to 10^4 are achieved for all major radionuclides, including the troublesome ^{106}Ru and ^{60}Co , for up to 2400 volumes of recycle water treated per volume of cation resin.

The laboratory work has included a survey of a number of important factors that could affect the treatment of recycle water. These include turbidity (concentration of suspended solids) and the presence of polyphosphates and alkylbenzene sulfonate, the two main components of synthetic detergents. A comparison of a number of micro pilot plant runs indicates that optimum clarification of recycle-type water does not appear to be attained simply by zeta-potential-controlled (ZP) additions of coagulants and coagulant aids. The data are summarized in Table 3.6.

Fig. 3.7. Waste-Asphalt Building, Overall View.

Fig. 3.8. Waste-Asphalt Building, Plan Views.

Fig. 3.9. Waste-Asphalt Building, Views of Section A-A and B-B.

Table 3.4. Capital Costs of Waste-Asphalt Plant

	Construction Costs	Total Costs
Improvements to land	\$ 3,000	
Building	41,000	
Hot cell	74,300	
Process equipment and piping	69,400	
Carrier	10,000	
Process instrumentation	14,200	
Radiation monitoring instruments	10,500	
Outside utilities	7,500	
Total construction costs		\$229,900
Engineering, design, and inspection (15% of construction cost)		34,500
Contingency (25% of construction cost and engineering, design, and inspection)		66,100
		<u>\$330,500</u>

Table 3.5. Operating Costs of the Asphalt-Waste Salts Plant

	Annual Costs
Asphalt, 200,000 gal, at \$0.12/gal (delivered)	\$ 24,000
Steam, 586 lb/hr, at \$0.97/1000 lb	3,550
Barrels, 4240, at \$3/bbl	12,720
Burial ground storage space (includes transportation), 11.6 ft ³ /bbl, at \$0.57/ft ³	28,000
Direct labor, 1 operator/shift, 3 shifts/day	20,500
Overhead (including supervision), 140% of direct labor	28,700
Maintenance of building, 1% per year of original cost	1,150
Maintenance of process equipment, 5% per year of original cost	5,200
Depreciation of capital by straight-line method, assuming 20-year life and no interest	16,525
	<u>\$140,345</u>

Table 3.6. Effect of Turbidity in Recycle Water on Coagulant Dose

Feed	Feed Turbidity (JTU) ^a	Initial ZP ^b of Feed Particles (mv)	Specific Conductance of Feed (micromhos/cm)	Alum Dose ^c [ppm Al ₂ (SO ₄) ₃]
ORNL-LLW	15	12-15	300-350	20-30
Diluted LLW 1 ^d	5	15-19	50-60	2-3
Diluted LLW 2 ^e	20-25	15-19	50-60	2-3

^aJackson Turbidity Units.

^bZeta potential.

^cAmount of alum necessary to bring zeta potential to ZP = 0 ± 5 mv.

^dORNL-LLW diluted five times with decontaminated and demineralized LLW.

^eSame as (d), except LLW solids added to increase turbidity.

Feeds used in the micro pilot plant runs included (1) ORNL-LLW, (2) ORNL-LLW diluted fivefold with completely decontaminated and demineralized LLW, and (3) ORNL-LLW diluted as in (2) but with additional LLW solids to increase the turbidity. The amount of alum [expressed as $\text{Al}_2(\text{SO}_4)_3$] necessary for clarification of (2) and (3) was one-tenth of that used for (1). Interestingly, both (2) and (3) required the same amount, even though the turbidity of (3) was four to five times that of (2). These data suggest that, in recycle waters, where the specific conductance is low, the amount of alum needed is proportional to the specific conductance (total dissolved solids) of the feed water and is not significantly affected by the turbidity (concentration of suspended solids) of the feed water. Further work on clarifying recycle waters is needed in order to describe the system adequately.

When a polyphosphate (the builder of a synthetic detergent) is present, alum flocculation and clarification are difficult, particularly in water that has a low calcium content (e.g., recycle water). This is illustrated by jar tests at pH 7, the optimum pH for alum floc formation (Fig. 3.10). Since the average total phosphate concentration in waste effluents is reported to be 25 ppm of phosphate (as PO_4^{3-}),^{3.15} each solution in the tests contained 25 to 30 ppm of ortho-, pyro-, tripoly-, or hexametaphosphate (as PO_4^{3-}) in distilled water. Alum floc formed in orthophosphate solutions with or without calcium present and, subsequently, orthophosphate was removed from solution. However, in polyphosphate solutions without calcium, no floc formed even with the addition of sufficient alum to produce a solution containing 60 ppm of $\text{Al}_2(\text{SO}_4)_3$. Although this is twice the amount of alum normally required for clarifying ORNL-LLW, none of the forms of polyphosphate tested was removed from solution. With 30 ppm of Ca^{2+} in solution (the concentration present in the water treated by the Water Recycle Process), alum floc formed immediately when the solution contained 60 ppm of $\text{Al}_2(\text{SO}_4)_3$, and, subsequently, 80 to 95% of each of the polyphosphates was removed. In all tests, greater than 90% of the particular phosphate in solution was removed when the solution contained 120 ppm of $\text{Al}_2(\text{SO}_4)_3$.

Similar results were obtained in column sorption tests at pH 7 with activated alumina, which is, essentially, dehydrated alum floc with less

Fig. 3.10. Alum Flocculation. Effect of calcium ion on phosphate removal at pH 7.

surface area. In detailed studies, it was found that polyphosphate sorption was significantly higher when the calcium:phosphate molar ratio was at least 1. In the jar tests, this ratio was either 0 or 2.5 to 3.0. Thus, the implication is that, when polyphosphates are present in recycle water, adequate Ca^{2+} must also be present in order to achieve satisfactory flocculation and clarification with a minimum amount of alum. Hydrolysis of the polyphosphates to the ortho form prior to the addition of alum should be a method of preventing this potential difficulty.

The presence of less than 500 ppm of alkylbenzene sulfonate (the foaming agent of synthetic detergents) in raw waste does not significantly affect the zeta potential of the waste; however, the amount of coagulant needed for clarification is greater.

4. ENGINEERING, ECONOMICS, AND SAFETY EVALUATIONS

4.1 Power-Reactor Waste Management

J. O. Blomeke

F. E. Harrington

The management of wastes produced at nuclear power plants may become increasingly significant in an economy that is expected to grow to 50 times its present size within the next 13 years. As a preliminary step in assessing future implications, the operating experience in waste management at Dresden-I, Big Rock Point, Humboldt Bay, Elk River, Yankee, and Indian Point-I power stations has been reviewed and will be published as ORNL-4070. The conclusions and data presented below are preliminary and are subject to revision.

4.1.1 Sources and Characteristics of the Wastes

Most of the routine waste effluents from power reactors originate as by-products of repurifying the primary reactor coolant. The radioactive constituents of the coolant are derived, primarily, from the activation of corrosion products, chemical additives, natural impurities in the water, and of the water. In addition, some fission products are invariably present in the primary circuits as a result of the presence of as much as several milligrams of ^{235}U in "tramp uranium" contamination on the outer surfaces of the fuel cladding. Fission products may also leak into the coolant through defective cladding.

There are many other sources of wastes, which are generally of small routine importance but which, under special circumstances, can become significant problems. Examples are the large volumes of water used for shielding during refueling operations; liquid wastes from decontamination operations, the laundry, and analytical laboratory; and solid wastes ranging from replaced reactor components and instruments to contaminated tools, laboratory ware, laundry, and miscellaneous trash.

Gaseous Activities. Fortunately, many of the radioactive species in the coolant have such short half-lives that they are of little or no consequence shortly after reactor shutdown or following separation from the reactor water. This is particularly true of gaseous wastes which, after

several minutes' holdup for decay, contain primarily the activation products, 1.8-hr ^{41}Ar and 10-min ^{13}N , and isotopes of the noble-gas fission products, krypton and xenon. Della Rocca^{4.1} reports that the ^{13}N production rate in the SENNBWR varies from 1.2 to 2.4 μc per second per megawatt (thermal). The release rate of the stack, following the customary 20- to 30-min delay, is about one-fourth to one-eighth of the production rate. The only long-lived noble-gas fission product is 10.5-year ^{85}Kr ; and, based on known ^{235}U fission yields and decay schemes, this isotope contributes only about 0.02% of the total activity after a decay period of 30 min. After 2 hr, the total noble-gas activity decreases to about half the original value, with 9.2-hr ^{135}Xe and 2.8-hr ^{88}Kr contributing more than 50% of the total. After 60 days, ^{85}Kr contributes more than 99% of the remaining activity.

Pressurized-water reactors (PWRs) operate with "closed" primary circuits and do not need to release gaseous activity continuously, as is required in the case of BWR's. The same isotopes are present in PWR gaseous wastes; however, since their removal rate from the primary coolant is low, they can generally be stored for decay of short- and medium-lived nuclides before being released.

Some radioactive particulates appear in the gaseous wastes as a result of entrainment or decay of noble-gas precursors. The particulates have generally been of less consequence than the radioactive gases; and, after filtration through "absolute" filters, their activity is less than one-millionth of that of the gases. But any iodine present in the gaseous effluents is often associated with the particulate matter; and, therefore, all particulate activity is conservatively attributed to ^{131}I .

Primary-Water Chemistry. When no cladding failures are present, the activity in the reactor water after several days' decay is attributable mainly to activated corrosion products. Although the surfaces in contact with the coolant are predominantly austenitic stainless steels, other materials that can contribute importantly to the corrosion product spectrum are invariably present. Brutschy *et al.*^{4.2} estimate that, even if the coolant contacted only stainless steel, a large water-cooled power plant would produce, each day, about 100 g of corrosion products that could become activated in the core. From radiochemical analyses of the

Dresden and SENN primary coolants, Brutschy et al. and Della Rocca found that the most significant short-lived activities were ^{16}N , ^{13}N , and ^{18}F (from activation of the water) while the short-lived corrosion products were dominated by ^{64}Cu , ^{56}Mn , and ^{187}W . The significant long-lived radionuclides found in solution and in the crud are given in Table 4.1. The major activated corrosion products in solution are ^{99}Mo - ^{99}Tc , ^{58}Co , $^{110\text{m}}\text{Ag}$, and ^{51}Cr , while the dominant activity in the crud is ^{58}Co . The average concentration of iron in the coolant was 0.20 mg/liter at Dresden, and between 0.5 and 1.0 mg/liter at SENN. Thus it can be seen from Table 4.1 that greater than 90% of the long-lived activity is associated with the crud. All these nuclides are found in other water-cooled reactors and may be expected to be present in the liquid and solid wastes.

Fission product levels are much less dependent on "tramp uranium" than on activation products; however, defective fuel cladding can result in more significant concentrations in the primary coolant. During 1964, when the Dresden-I reactor was operating with substantial numbers of defective elements, the annual average fission product content in the coolant was: ^{131}I , 0.025 $\mu\text{Ci/ml}$; ^{133}I , 0.1 $\mu\text{Ci/ml}$; other iodine, 0.25 $\mu\text{Ci/ml}$; other fission products, 0.25 $\mu\text{Ci/ml}$.

Tritium. The production of tritium (12.3-year ^3H) and its behavior in power-reactor streams have been reviewed informally by Smith.^{4.3} Tritium has been identified in the primary coolant of several power plants at levels ranging from 5×10^{-4} $\mu\text{Ci/ml}$ in the SENN reactor (Zircaloy-clad fuel) to about 3 $\mu\text{Ci/ml}$ in the Yankee reactor (stainless-steel-clad fuel). From an analysis of these data and the particular reactor systems involved, Smith concludes that, in BWR's, tritium is principally derived from fission and appears in the coolant after having leaked through defective cladding. The higher levels of tritium found in PWR primary coolants can probably be attributed to its production by fast-neutron reactions with boron, which is used as a chemical shim control.

Because of its relatively long half-life, and because no effective treatment is available for its removal, the ^3H in reactor water is eventually released to the environment. Tritium has not been a major waste disposal problem, largely because of its rather liberal discharge limit (3×10^{-3} $\mu\text{Ci/ml}$) in water. This is 30,000 times more liberal

Table 4.1. Activated Corrosion Products Poured in Dresden
and SENN Primary Coolants 30 Days After Sampling

Isotope	In Solution (dis/min/ml)		In Crud (dis/min/mg Fe)	
	Dresden ^a	SENN ^b	Dresden ^a	SENN ^b
			x 10 ⁶	
⁵¹ Cr	120	14.2	3.79	0.71
⁵⁹ Fe	0.15	0.8	1.27	0.34
⁵⁴ Mn	2.5	35.5	0.67	0.12
⁵⁸ Co	252	527	55.9	61.8
⁶⁰ Co	27.4	22.9	4.86	3.04
^{110m} Ag	203	1.1	0.11	0.002
³² P	55.9	----	----	----
⁹⁹ Mo- ⁹⁹ Tc	586	----	0.61	----
⁶⁵ Zn	----	3.0	----	0.30

^aData of Brutschy et al. (ref 4.2) for operation after 3675 equivalent full-power hours (EFPH). Apparent steady-state equilibrium is reached by 1500 EFPH.

^bData of Della Rocca (ref 4.1) for operation after 5160 EFPH, adjusted for a decay period of 30 days.

than the 10^{-7} $\mu\text{C}/\text{ml}$ disposal limit that is frequently used for unanalyzed aqueous wastes. The future implications of ^3H to reactor waste management are somewhat obscure. If future use of Zircaloy-clad fuels results in the expected fewer incidences of cladding failure, ^3H will probably become an even less important consideration in BWR's than it has been in the past. However, the present trend toward greater reuse of both the reactor water and condenser cooling water for all new reactors, could result in the production of individual batches of waste having concentrations of ^3H as much as an order of magnitude greater than those currently encountered, and the availability of proportionately smaller quantities of water for on-site dilution before release.

4.1.2 Operational Experience

Waste management experience at Dresden-I, Big Rock Point, Humboldt Bay, Elk River, Yankee, and Indian Point-I power-reactor stations is summarized in Table 4.2. The first four reactors are BWR's; the latter two are PWR's.

The power ratings of these stations vary from 24 Mw (electrical) for Elk River to 270 Mw (electrical) for Indian Point-I. (The latter rating includes 110 Mw from a fossil-fueled superheater.) The periods of operation considered range from 3 to 5 calendar years. These plants have been termed "prototypes," and, as such, their performances have been studied carefully by both the utility companies and the designers. In some instances (notably the Dresden and Yankee reactors), they have been used to test innovations in reactor components, controls, and fuel technology. This accounts for occasional extended periods of down time and generally lower capacity factors than would have been expected otherwise. Also, fuel cladding failures have been more prevalent than is expected in the future. In spite of these "special circumstances," no serious limitations or deficiencies have arisen in the waste management systems as originally installed. All the stations have been able to operate within their authorized limits, and releases to the environment have, in general, been made on the conservative assumption that the released material contained unidentified radioisotopes, with ^{226}Ra and ^{228}Ra known not to be present.

Table 4.2. Power-Reactor Waste Management Experience

	Boiling-Water Reactors				Pressurized-Water Reactors	
	Dresden-I	Big Rock Point	Humboldt Bay	Elk River	Yankee	Indian Point-I
Power rating	700 Mw(th), 200 Mw(e)	157 Mw(th), 50 Mw(e)	165 Mw(th), 52 Mw(e)	58 Mw(th), 24 Mw(e)	392-600 Mw(th), 125-185 Mw(e)	615 Mw(th), 270 Mw(e)
Operational period reported	October 1959--December 1965	September 1962--April 1966	February 1963--February 1966	October 1961--March, 1966	January 1961--December 1965	August 1961--January 1966
Electricity generated, Mwhr gross	5,126,000	670,000	847,000	259,000	4,991,000	2,809,000
Approximate capacity factor, %	65	41	83	70	69	~ 50
Fuel cladding	Stainless steel and Zircaloy	Stainless steel	Stainless steel and Zircaloy	Stainless steel	Stainless steel	Stainless steel
Max. assemblies with defective cladding, %	~ 5	~ 15	~ 25	~ 0	~ 0	~ 0
Gaseous Wastes:						
Stack dilution air, scfm	44,000	30,000	12,000	3,000	15,000	280,000
Holdup time	20 min	30 min	18 min	30 min	As much as 60 days	As much as 120 days
Type of treatment	Delay, filtration, dilution	Delay, filtration, dilution	Delay, filtration, dilution	Delay, filtration, dilution	Delay, filtration, dilution	Delay, filtration, dilution
Permissible release ^a						
Activation and noble gases	700,000 $\mu\text{C}/\text{sec}$	10 ⁸ $\mu\text{C}/\text{sec}$	50,000 $\mu\text{C}/\text{sec}$	600 $\mu\text{C}/\text{sec}$	2000 $\mu\text{C}/\text{sec}$	100 $\mu\text{C}/\text{sec}$
Halogens and particulates	0.006 $\mu\text{C}/\text{sec}$	3.6 $\mu\text{C}/\text{sec}$	0.18 $\mu\text{C}/\text{sec}$	3 x 10 ⁻¹⁰ $\mu\text{C}/\text{cc}$	3 x 10 ⁻¹⁰ $\mu\text{C}/\text{cc}$	3 x 10 ⁻¹⁰ $\mu\text{C}/\text{cc}$
Range of average release during operation						
Activation and noble gases	< 100 to 25,000 $\mu\text{C}/\text{sec}$	~ 60 to 27,000 $\mu\text{C}/\text{sec}$	34 to 16,000 $\mu\text{C}/\text{sec}$	10 ⁻⁴ - 6 $\mu\text{C}/\text{sec}$	2 x 10 ⁻³ to 22 curies/year ^d	0 to 24 curies/year ^d
Halogens and particulates	0.002 to 0.003 $\mu\text{C}/\text{sec}$	< 3 x 10 ⁻⁷ $\mu\text{C}/\text{sec}$	2 x 10 ⁻⁶ to 3 x 10 ⁻² $\mu\text{C}/\text{sec}$	< < 3 x 10 ⁻¹⁰ $\mu\text{C}/\text{cc}$	< < 3 x 10 ⁻¹⁰ $\mu\text{C}/\text{cc}$	< < 3 x 10 ⁻¹⁰ $\mu\text{C}/\text{cc}$
Liquid Wastes:						
Volume collected						
Annual average, 10 ³ gal	10,855	~ 1060	600	72	~ 740	7710
Total, 10 ³ gal.	67,846	~ 3900	1800	323	~ 3700	27,000
Principal type of treatment	Deminerlization, filtration	Deminerlization, filtration	Filtration	Deminerlization, filtration	Filtration, evaporation	Deminerlization, filtration
Percent returned to reactor use ^b	84	~ 80	0	0	~ 0	~ 0
Activity range before dilution, $\mu\text{C}/\text{cc}$	< 10 ⁻⁴ to 10 ⁻²	< 10 ⁻⁴ to 10 ⁻²	< 10 ⁻⁴ to 10 ⁻²	6 x 10 ⁻⁸ to 10 ⁻⁴	10 ⁻⁸ to 10 ⁻⁵	3 x 10 ⁻⁸ to 2 x 10 ⁻³
Condenser water for dilution, gpm	115,000	50,000	100,000	28,000	140,000	260,000
Activity discharged ^b						
Concentration range, $\mu\text{C}/\text{cc}$	10 ⁻⁸ to 5 x 10 ⁻⁸	10 ⁻⁸ to 9 x 10 ⁻⁸	10 ⁻⁸ to 1.5 x 10 ⁻⁸	10 ⁻¹⁰ to 2 x 10 ⁻⁷	3 x 10 ⁻¹⁰ to 2 x 10 ⁻⁸	3 x 10 ⁻⁸ to 1.8 x 10 ⁻⁷
Total curies, annual average	3.0	4.4	1.0	0.01	0.01	11.3
Total curies, accumulated	18.7	16.1	2.9	0.05	0.054	39.6
Shielded interim storage capacity, gal	50,000	5000	10,000	0	0	6700
Solid Wastes:						
Average annual vol and activity content ^c						
Resins	774 ft ³ and ? curies	242 ft ³ and 119 curies	50 ft ³ and ? curies	4 ft ³ and 3 curies	3280 ft ³ and 21 curies ^e	?
Other	3357 ft ³ and 107 curies	257 ft ³ and ~ 0.3 curie	1025 ft ³ and 310 curies	340 ft ³ and 5 curies	300 ft ³ and 24,000 curies	580 ft ³ and 0.5 curie ^f
Total volume and activity						
Resins	4835 ft ³ and ? curies	768 ft ³ and 378 curies	150 ft ³	18 ft ³ and 10 curies	16,400 ft ³ and 106 curies ^e	---
Other	20,983 and 666 curies	815 ft ³ and ~ 1 curie	3330 ft ³ and ~ 1000 curies	1532 ft ³ and ~ 21 curies	~ 1500 ft ³ and 120,000 curies	203 ft ³ and 1.6 curies ^f
Shielded interim storage capacity, ft ³						
Resins	6680	1300	1300	0	250 ft ³	800 ft ³
Dry solids	2400	1200	1200	0	0	0

^aPermissible average release during periods of reactor operation.^bExclusive of tritium which may average an additional 10 to 100 curies/year.^cSolid waste activities are "best estimates" at time of shipment. They vary on a "unit volume" basis over many orders of magnitude.^dReleases from stack are < 0.1% of permissible concentrations.^eThis waste is mainly evaporator bottoms and incinerator ashes mixed with cement but also includes resins.^fQuantities of waste shipped off site for disposal.

Gaseous Wastes. The stations are licensed to release different quantities of gaseous activation and fission products, depending on the meteorological conditions and the population distribution at the individual locations. While the limits of these licenses exceed the permissible concentrations specified in 10CFR20, Appendix B, environmental monitoring indicates that they are adequately conservative, since measured radiation dosages have been less than one-tenth of the permissible 0.5 rem/year at any ground-level location in the environs.

The Dresden, Big Rock Point, and Humboldt Bay reactors have operated for extended periods of time with substantial, though imprecisely known, numbers of defective fuel elements. Subsequently, the average noble-gas release rates have been observed to increase from a normal level of less than 100 $\mu\text{Ci/sec}$ to about 25,000 $\mu\text{Ci/sec}$. Instantaneous release rates have approached 100,000 $\mu\text{Ci/sec}$. The release rates of halogens and particulates have been somewhat below those defined by the AEC license limits and, on the average, very near the permissible concentration for ^{131}I as stated in 10CFR20.^{4.4}

The Elk River reactor, which generally operates with a closed primary circuit, is more typical of a PWR than a BWR in its waste management practices. The Elk River, Yankee, and Indian Point reactors have released radioactive noble gases, after dilution with ventilation air, at less than 0.1% of permissible concentrations as stated in 10CFR20.

Liquid Wastes. Although all the plants have the capability of conditioning the liquid wastes for reuse by filtration, demineralization, and evaporation, only the Dresden and Big Rock Point stations have found it expedient or economically desirable to follow this practice to any appreciable extent. At both these stations, wastes containing low concentrations of dissolved solids are segregated, filtered, and demineralized, and then returned to reactor use. More than 80% of all liquid wastes collected have been treated in this manner. After filtration, the remaining wastes, which contain activity in the range 10^{-4} to 10^{-2} $\mu\text{Ci/ml}$, are diluted to 10^{-7} to 10^{-8} $\mu\text{Ci/ml}$ with condenser cooling water and then released. On several occasions at the Big Rock Point station, individual batches of waste containing between 10^{-7} and 10^{-6} $\mu\text{Ci/ml}$ were discharged after analysis had

verified that more than 90% of the activity was attributable to ^{58}Co and ^{65}Zn .

At the Humboldt Bay station, wastes are treated only by filtration and dilution prior to discharge, while at the Elk River station, they are filtered and demineralized before dilution and discharge.

Liquid wastes at the Yankee and Indian Point stations contain boric acid from chemical shim control and "cold" shutdowns. Yankee is the only plant among those studied at which substantial volumes of waste are evaporated; and this is done, primarily, to avoid releasing boron. As a result, the activity released in liquid wastes is quite low. At the Indian Point station, boron is not removed. Essentially all liquid wastes are released after analysis and dilution.

The average activity released annually in liquid wastes has varied from 0.01 Ci at the Yankee and Elk River stations to 11.3 Ci at the Indian Point station. This does not include tritium, which, in the past, has not been routinely determined. Based on what is now known concerning the concentration of tritium in reactor coolants, it is estimated that, on the average, an additional 10 to 100 Ci of this isotope is released annually in the liquid effluents from each station. Its concentration ranges from 1 to 10% of its permissible concentration, $3 \times 10^{-3} \mu\text{Ci/ml}$.

Solid Wastes. The solid wastes vary widely in nature, volume, and activity level. The annual volumes range from several hundred to several thousand cubic feet. Most of this material has such a low activity level that it can be shipped without external shielding. Spent resins and filter cartridges are the most radioactive routine wastes; however, occasionally replaced reactor components such as control blades, poison curtains, and in-core ion chambers are the most concentrated radiation sources and must be shipped in heavily shielded containers.

4.1.3 Estimated Future Waste Production

The quantities of radioactive wastes to be produced at the power stations over the remainder of this century will depend not only on the growth of the nuclear power economy but also on the types of reactors that come into use. For the next 10 years, light-water reactors will most certainly predominate; however, after that time, breeders and probably some

types of advanced converters will be installed as rapidly as the technology can be made available. A meaningful analysis of waste production by these as-yet-underdeveloped reactor types cannot very well be made, but, as a first approximation, it may be assumed that wastes from future reactors will not differ greatly in volume and characteristics from those of contemporary light-water reactors.

For present purposes, it is assumed that nuclear power is generated entirely by light-water reactors, each of 750-Mw (electrical) capacity. The estimated quantities of waste produced by each reactor are based on the experience of existing power stations (Table 4.2); and, consequently, the continuation, for the most part, of present waste management practices is assumed.

It is assumed that each 750-Mw reactor will release noble-gas activity at an average rate of 200 μ Ci/sec during operation. If the reactor operates at its rated capacity 70% of the time (capacity factor of 0.7), this is equivalent, annually, to 4000 Ci, of which 1 Ci is attributable to ^{85}Kr . Although appreciably higher rates than this have been experienced at the Dresden, Big Rock Point, and Humboldt Bay stations as a result of defective fuel, it is expected that cladding failures will be less common in the future than they have been in the past. Also, at least half the plants may be PWR's, which have much lower gaseous releases than do BWR's.

The activity, exclusive of tritium, that is released in the liquid wastes from each reactor is assumed to average 5 Ci/year. Experience indicates that greater than half of this activity is attributable to 70-day ^{58}Co . In addition, the liquid wastes from each reactor will contain an estimated 300 Ci of 12-year ^3H annually. The latter figure is based on an estimated release of 100 Ci/year from the Dresden and Indian Point stations.

The annual production of solid wastes is assumed to be 5000 ft³ for each reactor. Although the activity in this waste stream will vary over many orders of magnitude, most will be of a very low level. The greatest problem associated with the solids should stem from their volume rather than from their radiation level.

Projections of nuclear power growth in the United States have been revised frequently in the light of announced intentions on the part of many utility companies to install nuclear-fueled plants within the next few years. In this study it is assumed that the installed capacity will rise from 12,000 Mw (electrical) in 1970 to 85,500 Mw (electrical) in 1980 and that it will reach 850,000 Mw (electrical) in 2000. Assuming an average capacity factor of about 0.7, the electricity generated by this economy will increase from 74 billion kwhr in 1970 to 5460 billion kwhr in 2000. The number of 750-Mw plants required will increase from 16 in 1970 to 1133 at the end of this century. The krypton activity released annually will increase from 16 Ci in 1970 to about 1100 Ci in 2000; and the activity released in liquid wastes, neglecting ^3H , will increase from 80 to 5670 Ci/year. The ^3H in liquid effluents is projected to be 4800, 34,200, and 340,000 Ci in 1970, 1980, and 2000, respectively. The annual volume of solid wastes will increase from 80,000 ft^3 to more than 5.6 million ft^3 , representing a total accumulated volume of 53.4 million ft^3 over this 30-year period. Using the same burial-ground usage factor as has been found to apply at Oak Ridge National Laboratory, namely, 1 acre of ground for each 100,000 ft^3 of waste buried, the total area required for the disposal of solid wastes from power reactors will increase from 16 acres in 1970 to 534 acres by the end of the century.

5. SEPARATION OF NOBLE GASES FROM AIR USING PERMSELECTIVE MEMBRANES

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W. L. Carter

The removal of krypton and xenon from off-gases during reactor emergencies and during the routine processing of fuel has been studied in great detail by various contractors of the AEC. The processes currently in use or under development either require temperatures of less than -70°C or occupy a large volume.^{5.1} For more than 100 years, it has been known that the rates of permeation of gases through semipermeable membranes are not equal.^{5.2} However, separations have become practical only during the last few years because of the development of thin plastic sheets that are free of holes.^{5.3}

A joint program by the Oak Ridge Gaseous Diffusion Plant (the K-25 Plant), General Electric, and ORNL has been initiated to investigate the use of a cascade of thin (~ 1 mil) silicone-rubber membranes with Dacron backing for removing xenon and krypton from either the atmosphere of a reactor containment vessel following a reactor accident or from the off-gas normally obtained during the dissolution of reactor fuel elements. The criterion for the reactor containment vessel study is that krypton is separated from $3 \times 10^6 \text{ ft}^3$ of contained air by a factor of 100 in 1 week to yield a product gas having a volume of $50,000 \text{ ft}^3$, which is enriched in xenon and krypton. Preliminary studies indicate that the cost of this operation by a cascade of permselective membranes may be competitive with that of other proposed decontamination systems.^{5.4} The permeabilities of pure xenon, krypton, oxygen, and nitrogen through an unbacked dimethyl silicone rubber membrane at room temperature, as originally measured at General Electric, were 203×10^{-9} , 98×10^{-9} , 60×10^{-9} , and 28×10^{-9} , respectively, where permeability is defined as gas flow (cm^3/sec) through a 1-cm-thick membrane per square centimeter of surface area, divided by the difference in pressure (cm Hg) across the membrane.

Preliminary design studies based on theoretical separations, the above permeabilities, and other simplifying conditions indicate that a

minimum of 31,300 yd² of membrane allocated into 17 stages of various sizes would be required for the separation. The construction cost would be on the order of \$1.1 x 10⁶, and the power requirement would be about 2 Mw. This cascade separator would occupy about 6000 ft³ and could be constructed in three semitrailers that could be air-lifted to the site of a reactor accident.^{5.4}

Recent data from General Electric, the K-25 Plant, and ORNL, using a single dimethyl silicone rubber membrane with a Dacron backing, show permeabilities approximately one-half those obtained using the unbacked membrane for the pure gases. The values measured at General Electric showed decreasing permeability with pressure, but this trend was not observed in the ORNL data (Fig. 5.1). Simple volume observations have been satisfactory for measuring the permeabilities of pure gases. However, precise analyses of the components in gas mixtures are required when permeabilities are determined in complex systems. The mass spectrographic analyses of gas samples were not satisfactory because of the total error involved in the sampling technique, the interruption of the process caused by removal of the sample, and the limited accuracy of the results. Equipment has now been installed that will be used to determine permeabilities by the in-line analyses of mixtures of air and radioactive noble gases (Fig. 5.2). In future work, this equipment will be used to study the effects of water vapor, nitrogen oxides, and iodine on the characteristics of the membrane.

Fig. 5.1. Comparison of Pure Gas Permeabilities Between General Electric and ORNL.

Fig. 5.2. ORNL Equipment for the Determination of the Permeability of Xenon and Krypton by the In-Line Analysis of Radioactive Gases.

6. EARTHQUAKES AND REACTOR PLANT DESIGN

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Herbert Robertson^{6.1}

A discussion paper entitled, "Earthquakes and Reactor Plant Design," which is one of a series of papers on water-cooled reactor safety, is currently being prepared under the auspices of the Nuclear Safety Information Center. The preparation of the paper is a joint venture between the Radioactive Waste Disposal Research Group of the Health Physics Division, which is responsible for the earth science portion of the paper, and the Reactor Division, which has assumed responsibility for the design or structural response portion. Private consulting firms have been employed by both groups to aid in data collection, etc., for the document. Review committees representing the Laboratory, the USAEC, and "outside" experts have been formed to guide the preparation of the paper.

In general, the paper will present a state-of-the-art discussion of earthquakes and reactor plant design and will specifically point out gaps in our present knowledge and possible solutions as noted by accepted experts. Areas of primary interest in the earth science part of the report include faulting, shaking, tsunamis, soil behavior, and instrumentation.

The siting and the design of reactors to take into account transient ground motions and differential ground displacements that are associated with earthquakes are perhaps two of the most perplexing problems that face the nuclear power industry today. In general, the problem of earthquakes as it relates to reactor design can be divided into two rather distinct phases: determination of the expected ground vibrations and displacements, and design of reactor structures to withstand these movements. Ideally in siting, the expected ground motions and permanent displacements are described and defined, and then the structures are designed accordingly. In the past, however, there has been considerable controversy concerning the expected vibrations and, especially, the expected ground displacements at some sites. Also, structural designs to accommodate displacements have not been proved. The recent controversies over the Bodega Head and

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Malibu sites attest to this. Clearly, for many parts of the country, where seismic activity is very low and, indeed, even within some parts of California and Nevada, where a high degree of seismic activity is experienced, earthquake effects are not generally regarded to be critical in the siting and design of reactors. There are also other well-defined sites, such as those astride the San Andreas fault trace, where reactor structures, if built at all, would certainly have to be designed so as to withstand maximum shaking and very great horizontal, perhaps even vertical, ground displacements. These extreme cases, however, do not present a problem, since in one instance the structure could be constructed with little or no modifications to accommodate earthquake effects and, in the other, the reactor structures would simply not be located in the areas under consideration. The main problem, then, is to define and describe the expected earthquake ground effects and design the structures accordingly for those areas that lie near major faults (where movements are likely to occur), or even for those areas where it cannot be reasonably determined whether movement will occur. It appears that, in most cases, the major breaks can be defined in siting; however, in general, it is much more difficult to define the location and extent of the so-called subsidiary or minor faults that accompany a major fault movement.

7. DISPOSAL IN NATURAL SALT FORMATIONS

7.1 Project Salt Vault

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Project Salt Vault is a demonstration disposal of high-level radioactive waste solids, with irradiated Engineering Test Reactor fuel assemblies being used in lieu of actual solidified wastes. This demonstration is being carried out in the Carey salt mine at Lyons, Kansas. Major objectives are the confirmation of feasibility and safety of disposal in salt mines, including the demonstration of required waste-handling equipment and techniques, and the collection of rock mechanics data sufficient to establish the basis for the design of a disposal facility.

7.1.1 First Two Fuel Assembly Changeouts

The first set of irradiated fuel assemblies stored in the relatively pure salt floor in room 1 was transferred in June 1966, without incident, to the new experimental facility in room 5 to determine the effects of shale and its included moisture. The second set of 14 irradiated Engineering Test Reactor fuel assemblies from the National Reactor Testing Station was shipped from Idaho to Lyons, Kansas, and on June 13 to 15 was lowered, without difficulty, 1000 ft into the mine and placed in the experimental facility in room 1. No undue exposures were received. The new shipment contained about 1.5 million curies. The radiation fields in the test holes were found to be higher than in the previous run. No personnel exposures greater than 70 mrem were incurred during the transfer operations. Negligible contamination of the shipping cask was found after the discharge of the fuel assemblies.

^{7.1} Guest scientist from France.

In October 1966, the first set of fuel assemblies was removed from room 5 and returned to Idaho. The second set of ETR fuel assemblies (which had been installed in the array of holes in the relatively pure salt of room 1 in June) was moved to the array in room 5, in the original mine floor, during the first week of November. On November 7-10, 1966, the third set of ETR fuel assemblies (containing a total of about 1.5 million curies) was lowered into the mine and placed in the holes vacated in room 1. The chief difficulty encountered was mechanical and was attributed to pieces of rubber from the inside of the hydraulic hoses causing malfunctions in the hydraulic system of the underground transporter. No excessive personnel radiation exposures were received during the operation.

7.1.2 Radiation Dose to Salt

The measured peak radiation dose to the salt, at the junction between the two ETR fuel assemblies, was about 3.7×10^8 rads, as of November 1, 1966 (see Fig. 7.1, bottom curve). Based on the extrapolation of the first set of dosimeter measurements with the third set of assemblies, we should accumulate another 1.6×10^8 rads by next May, which will bring the total to about 5.3×10^8 rads (Fig. 7.1). Generally, the accuracy of the dose measurements is believed to be within about 20%. However, the point at which the measurements of the incident dose to the salt are made (the junction between the assemblies) is such that dose values are produced that are lower than the average incident salt dose (over the 6-ft length of the tandem fuel assemblies) by about 35%, and lower than the peak dose (near the centers of the individual fuel assemblies) by nearly a factor of 2. The reason for this may be seen in Fig. 7.2, which shows the actual dose distribution measured on the outside of an array hole liner, along a line that is about $4 \frac{1}{4}$ in. from the center of the liner. The measurements appear reasonable, since the power in the lower fuel assembly was reported by ETR operations to be about 15% higher than in the upper assembly. (Other cans show similar profiles.) For comparison purposes, the incident dose measured in the normal manner is shown. This point is 6 in. from the center of the liner, and the relationship between this reading

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Fig. 7.1. Comparison of Measured and Calculated Doses to Salt in Project Salt Vault.

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*TWO ETR FUEL ASSEMBLIES IN CANISTER IN HOLE IV, ROOM 1 ON DEC. 14, 1966. MEASUREMENTS MADE WITH 3 GLASS ROD DOSIMETERS AT EACH POSITION TAPED TO A ROD INSERTED THROUGH EAST CALIPER PORT. DOSIMETERS ABOUT $4\frac{3}{4}$ in. FROM THE ϕ OF THE CANISTER AND ABOUT $1\frac{3}{4}$ in. FROM THE HOLE LINER.

Fig. 7.2. Dose Distribution Along ETR Fuel Assembly Canister.

and the one closer to the hole liner is approximately what would be expected when the distance from a cylindrical source is considered.

It should be noted that the measured doses for salt depths up to about 5 cm would also be expected to be lower than the maximum, because all of the dosimeters, except the incident one, are located at varying distances above or below the junction of the two fuel assemblies. The 10- and 20-cm dosimeters are located near the points of maximum dose, and thus should be approximately correct.

It should also be noted that, in the following discussions, corrections based on the above considerations have not been taken into account. Thus, in particular, the incident salt doses may be assumed to be quite conservative.

From Fig. 7.1 it may be seen that if the fourth set of fuel assemblies is assumed to be identical to the third, the peak dose accumulated to next November would be about 6.8×10^8 rads. This compares favorably with the calculated theoretical curve (Fig. 7.1), which was based on the nominal ETR fuel history used in the design of the experiment. The chief difference lies in the fact that the peak dose rate appears to be at the salt surface rather than at a depth of about 2 cm. This appears to be of no consequence.

Our original goal was to achieve a dose of at least 5×10^8 rads. This goal will have been met at the time of our final changeout (May 1967). The 5×10^8 minimum was based on the fact that at 10^8 rads there was no indication of any change in the physical properties of salt, while at 5×10^8 there was an indication of small changes in properties such as the compressive strength. On the other hand, a hypothetical Acid Purex solid waste of the future would deliver a calculated peak dose of about 4×10^9 rads in 2 years, and more than 10^{10} rads ultimately. We could not hope to reach these levels until actual waste solids become available. In any case, only the first few inches of salt adjacent to the containers would be exposed to such levels.

Since both field and laboratory studies now confirm that radiation effects on salt do not appear to have any detrimental effects for waste disposal, the need for bringing in the fourth set of fuel assemblies is questionable. The approximately 30% increase in total dose that

would accrue with the fourth set of fuel assemblies would be unlikely to produce any new results. For example, even if the salt around the waste containers were to lose all its structural strength, the extent of the damaged zone (even for the future wastes) is small enough that it should have no significant effect on mine stability.

7.1.3 Array Temperatures and Heat Effects

Peak temperatures in the centers of the arrays have approximated 150°C (except in the array in the old mine floor, where the peak temperature is about 160°C). More heat was being lost to the room air than would be conducted through the salt if the room were backfilled with salt, or if there were a solid mass of salt. Consequently, each array was insulated over an area of about 16 ft square in an effort to increase the peak temperature significantly. Results showed higher temperatures in the salt above the centers of the arrays but no appreciable increase in the peak temperature at the periphery of the holes.

The objectives of the experiment included achieving a peak temperature of about 200°C . The chief reason that this level has not been reached is that the salt appears to have somewhat better heat dissipation properties than those assumed in the theoretical calculations (200°C values of Birch and Clark). (These somewhat pessimistic values were used for the calculations to ensure that the temperatures did not increase prohibitively.) In order to reach the desired 200°C , it is now planned to boost the total power input (fission product plus electrical) by about 40%, probably in January 1967. This will allow sufficient time for the temperature change to approach equilibrium before the changeout in May.

The effects of the heat from the arrays have been essentially as expected, with two exceptions. The first exception was the rate at which the effects of thermal stresses produced in the floor were transmitted to the roof, causing accelerated sag of the roof slab. This accelerated sag, although posing no problem for the demonstration, could cause difficulty in an actual disposal facility. A series of tests have indicated that this potential problem can be solved economically and effectively with conventional roof bolts. These studies will be discussed in the next section.

The second exception was the discovery that the small quantities of water normally trapped in small cavities in rock salt migrate toward a heat source. The possible effects of this water migration will also be described in a following section.

7.1.4 Rheological Measurements and Roof Bolts

Figure 7.3 shows the vertical thermal expansion of the floor (floor uplift) as a function of time for the radioactive array (room 1) at the center and 25 ft from the center. The uplift at the center has now reached about 1 1/2 in.

Figure 7.4 shows the uplift profiles for room 1, along the north-south and east-west axes of the room, as of the middle of July 1966. It is apparent that significant thermal expansion (greater than 0.1 in.) extends to more than 50 ft from the center of the array. The north-south uplift profile shows the restraining effect produced by the presence of the adjacent pillars. The data for the control array (room 4) are essentially the same.

Since the salt pillars act as restraints on the thermal expansion of the salt in the floor, one might expect to find some effect on the behavior of these pillars. This was indeed the case; we found that the normal horizontal expansion rate (about 0.3 in. per year) of the pillar had increased to about 0.6 in. per year. This increase in expansion would be of no concern per se; however, movements in the pillars are reflected in the roof. The net result is shown in Fig. 7.5 by the curve labeled 111-A-U-3, which was plotted using data from a gage located in the center of the array room (room 1). This curve shows that a separation is taking place between a 2-ft-thick layer of salt in the roof and the strata above. In the 150-day period prior to startup of the demonstration in room 1 (the radioactive array room), the gap between layers had increased about 0.04 in., but the rate of separation was decreasing with time. Immediately after startup, the separation rate increased fivefold, but then decreased over a period of time. This separation rate in the roof is not such that it should pose a hazard during the 2 years that we will be operating in the mine. We became concerned only from the standpoint of what might happen to the roofs of the two rooms

Fig. 7.3. Floor Uplift in Room 1.

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Fig. 7.4. Uplift Profiles of Room 1 as of July 15, 1966 - 1046 Standard Days.

Fig. 7.5. Roof Movement in Rooms 1 and 3.

that border the pillar in the center of the experimental area. These rooms are wider than the array rooms, and the pillar is narrower (by design); we also anticipate applying three to six times as much heat there as in the array rooms.

The curve designated as 150-A-U-3 in Fig. 7.5 shows the sag of the 2-ft-thick roof slab in one of these center rooms (room 3). Notice that the separation rate was initially about three times that of room 1, because of the wider unsupported span. Consequently, we decided to attempt bolting the 2-ft-thick slab to the strata above it. On March 9, we successfully completed this operation for an area in the center of room 3; the result is shown on the curve designated as 150-A-U-3 (Fig. 7.5) for the period between March 9 and May 14. Not only was the separation halted, but the gap in the roof was reduced by about 0.1 in. In May and June, the roof of the entire experimental area was bolted; results similar to that just described were obtained; that is, the existing gap decreased and no further increase in separation was noted.

7.1.5 Water Release and Possible Effects

We have found that the small quantities of water trapped in negative crystal cavities in the salt migrate toward a heat source. This is apparently attributable to a small increase in salt solubility with increasing temperature, and diffusion of salt from an area of high concentration (the hot side of the brine cavity) to that of a lower concentration (the cold side). Based on some approximate calculations and a simple laboratory test, we would anticipate that the migration rate through the temperature gradients that exist around the holes in the arrays might range from approximately a fraction of an inch per year to as much as 3 or 4 in. per year. Previous measurements have indicated that the water content of the salt is around 1/4 vol %, which should produce maximum daily inflow of water of 2 ml per hole per day. We have not yet ascertained the exact rate at which water is being released into the radioactive and control array holes, but we do know that it is at least 0.3 ml per day per hole and probably not more than 3 ml per day per hole. This small quantity of water poses no problems for the demonstration, since it is removed (as vapor) by the off-gas system.

In an actual disposal facility, the waste-container holes will be backfilled with crushed salt. In that case the water coming into the hole would move upward as vapor, through the void spaces in the crushed salt, where it would condense as it reached cooler regions. It is possible that the temperature of the upper regions of the waste containers (filling neck, void-space zone, etc.) will remain below the boiling point for some extended period of time and that the water will corrode through the container. In the event that this did occur, no problem would exist as long as the container did not contain appreciable quantities of gases at a positive pressure and the waste product was relatively nonleachable. (As long as most conversion-to-solids processes are functioning properly, no gas buildup should occur. However, in a routine production operation, occasional exceptions should be anticipated. These containers might release oxides of nitrogen, hydrogen, volatile fission product fluorides, ruthenium, or perhaps other unknown compounds. Most of these materials would be expected to remain in the 7 to 8 ft of crushed salt above the waste containers.) As the 100°C temperature front moves higher, the water would be expected to move with it, thus eventually finding its way up into the room. In the relatively pure salt (such as is normally mined), which is free of significant quantities of interbedded shale (which contains several percent water), the water content is generally on the order of less than 1/2 vol %. Quantities such as this should pose no problem in a disposal operation since the rate of inflow is very low.

The two modified pillar heaters (heaters in sealed cans in holes backfilled with salt as in an actual disposal operation) are expected to be helpful in evaluating the effects of the water in the relatively pure salt. One of these (made of plain carbon steel pipe) has been operating since June 1966 and is still maintaining pressure. The other (made of stainless steel) was started in November 1966.

More accurate values for the rates of water inflow are now being determined. Also, it is planned to try to calculate the theoretical migration rates of the brine cavities in order to determine the quantities of water that might accumulate in a given hole over any specified period of time. Some laboratory tests may be required in this connection. (It also seems desirable to calculate the rate of diffusion of chlorine as

well, even though the field tests have failed to confirm the release of any significant quantities.)

As a result of the presence of shale, the water inflow rate in the array in the original mine floor is about 40 to 90 ml per day per hole, a much more significant volume than in the other arrays. Since in some situations it may not be possible to find suitable salt that does not contain some shale in the region where the holes would be drilled for the waste containers (or one might want to use an old mine area that would almost invariably contain such shale layers), it would be very desirable to run a few tests with containers made of various materials by placing them in holes in the floor of the original mine at Lyons. These holes would be backfilled with crushed salt to see what happens to both the integrity of the containers and the fairly large quantities of water. These tests would be similar to the modified pillar heater tests, and would be run in a previously cleaned area somewhere in the vicinity of (or in) room 5.

7.1.6 Radioactive Array in Old Mine Floor

In the array in the old mine area (room 5), temperature rises are running a few percent higher than in the other arrays (indicating poorer heat transfer properties) because of the presence of the layers of shale and anhydrite. Thermal expansion of the floor is similar to that in the other arrays. Thermal stress transfer to the pillars is also about the same as in the other arrays, except that there is no indication of separation taking place in the roof. Actually, none was expected, since the distance from the floor to the first significant shale layer is at least 8 ft.

7.1.7 Heated-Pillar Test

The heated-pillar test was started November 14, 1966, with a power input of 33 kw and is proceeding in expected fashion. After about 6 months of operation (next May) two-thirds of the area beneath the center pillar should be at or above 75°C, based on theoretical calculations. If the expected temperatures are not reached, or if salt flow is less than anticipated, the power input may be boosted to as much as 66 kw.

It is expected that the power will be turned off after about 9 months (August 1967) so that the behavior on cooling may be observed. Should the effects of the pillar heating cause incipient stability problems, the test may be terminated earlier. (An early termination is not anticipated, however.)

The objectives of the heated-pillar test are to determine large-scale temperature effects, particularly the transient temperature case that cannot be duplicated in the laboratory pillar models, on pillar behavior.

7.2 Salt Space Requirements for Projected Nuclear Power Economy

R. L. Bradshaw

An estimate has been made of the gross area required in salt formations to dispose of high-level wastes from the projected United States nuclear power economy to the year 2065. The estimates of installed nuclear electrical generating capacity up to the year 2000 were assumed to be the same as those developed by J. O. Blomeke and W. J. Boegly, Jr., in July 1966.^{7.2} From 2000 to 2060 the figures were derived from the projections shown in Fig. 3, page 44, of the 1962 AEC Report to the President on Civilian Nuclear Power.^{7.3} A comparison of the installed electrical capacity derived from this figure for the year 2000 with that of Blomeke-Boegly indicated that the AEC figures were about 14% lower. Thus the numbers derived from the 1962 AEC Report, up to the year 2060, were multiplied by a factor of 1.14. The results are shown as the lower curve in Fig. 7.6. All curves were extrapolated to the year 2065.

The upper curve of Fig. 7.6 shows the installed nuclear thermal capacity. Again, the thermal efficiency assumptions of Blomeke-Boegly were used to obtain this curve; that is, a thermal efficiency linearly increasing from 30% in 1965 to 44% in 2000 was assumed. Beyond 2000 the efficiency was assumed to remain constant at 44%.

The middle curve of Fig. 7.6 shows the expected thermal generation, considering load factors; this, too, is based on Blomeke-Boegly Assumptions that the reactor load factor is constant at 80% until 1980, then linearly decreases to 70% by 2000, and is constant at 70% thereafter.

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Fig. 7.6. Nuclear Power Projections to 2065.

Calculations of mine space requirements were previously made for the joint Health Physics-Chemical Technology waste management economics study.^{7.4} In that study it was found that the overall economics are best when the waste is stored for about 30 years before disposal. At the end of this period, essentially only ^{137}Cs -Ba and ^{90}Sr -Y are left as significant heat producers. (The same is true for wastes at least 10 years old.) Therefore, only the total megawatt-days of operation and not the residence time of the fuel in the reactor (1 year in the prior economic study, and perhaps 2 or more years in future reactors) is important in determining the generation rate of waste heat. Thus the future requirements for salt mine space can be derived directly from the previous study.

The assumptions in the previous economic study represented the continuous operation of 56,000 Mw (thermal) [15,000 Mw (electrical) continuous operation at 27% efficiency]. In that study the peak allowable temperature at the walls of the holes containing the waste cans was assumed to be 200°C. (Based on considerations of the effects of elevated temperature on mine stability and other variables, this figure appears to be realistic, although perhaps slightly conservative.) For the temperature calculations, the cesium and strontium were assumed to be a single isotope having a 30-year half-life. Other assumptions were that the mine is located at a depth of 1000 ft, which is typical of many of the deposits in the United States, and that conventional mining practices are used, modified by the special requirements for handling radioactive materials. (Deeper mines would require more gross space; shallower ones would require less.)

The gross mine space requirements (storage rooms, access tunnels, and all unexcavated salt left for overburden support, barriers, etc.) for disposing of the 30-year-old waste from the continuous operation of the 56,000 Mw (thermal) amounted to 5.25 acres per year. Thus the yearly space committed in any given year can be determined by dividing the megawatts required for continuous operation (from the middle curve of Fig. 7.6) by 56,000 Mw (thermal) and multiplying by 5.25 acres. Results obtained from these mathematical operations are shown in Fig. 7.7.

Also shown in Fig. 7.7 is the cumulative gross salt formation space committed up to any given year. This curve was obtained by a graphical integration of the previous curve.

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Fig. 7.7. Salt Formation Space Requirements for Disposal of High-Level Waste Disposal to the Year 2065.

The third curve of Fig. 7.7 shows the gross salt area that might actually be used by any given date. It is merely the second curve shifted 33 years to the right--30 years for the interim storage period and 3 years for the period from the time the fuel went into the reactor until the time it was processed.

It is of interest to note that by the year 2065 only about 30,000 acres (an area less than 7 miles square) will have been committed, and only about one-third of this will have actually been used. Considering that about 250,000 to 500,000 square miles of the United States is underlain by salt, no scarcity in available land is expected in the foreseeable future, even though only a small percentage of the area might be suitable for waste disposal. Also, in some of the formations, where the salt deposits are several hundred feet thick, more than one level might be used.

As a point of interest, if the waste were to be stored for only 10 years instead of 30, the gross space commitments would be increased by about a factor of 1.6. In that case the "space-used-to-date" curve would be shifted back to the left by 20 years; for example, the space used to the year 2045 would then be about 16,000 acres.

7.3 Dome Deposits and Other Geologic Formations

T. F. Lomenick

R. L. Bradshaw

7.3.1 Dome Deposits

The widespread occurrence of rock salt over the United States has been commonly accepted as one of the principal advantages for the use of these rocks as storage sites for radioactive waste materials. Salt deposits underlie a portion of 24 of the 50 states;^{7.5} however, from recent laboratory and field studies on the flowage of rock salt at elevated temperatures and high overburden loads,^{7.6, 7.7} it is apparent that many of these deposits are unsuitable for disposal sites. At present there are perhaps three principal areas in the United States where disposal in salt would appear to be highly desirable: (1) the Silurian salt deposits of the Northeast, which underlie parts of New York, Pennsylvania, West Virginia, Ohio, and Michigan; (2) the Permian basin

salts, which underlie parts of Kansas, Oklahoma, Texas, and New Mexico; and (3) the Gulf Coast Embayment salts, which underlie parts of Louisiana, Texas, Arkansas, and Mississippi. The first two areas are bedded deposits, while the latter contains only salt domes at reasonable depths.

Most of the other deposits throughout the United States are less suitable because of their great depths below the surface, their numerous inclusions of other rock types, or a general lack of knowledge concerning their extent, depth, etc. (In general, mine workings at great depth in salt are initially expensive to open and, because of the greater overburden load, accelerated deformation of the salt occurs. The presence of other rock types with the salt beds may accelerate further the deformation of the salt.) For instance, in the Williston basin, which underlies a part of North Dakota, salt is located at a minimum depth of 3600 ft; in addition, the bed is only about 20 ft thick. Thicker deposits occur; however, they lie between 4300 and 7000 ft below the surface. Also, in Florida, salt beds are present, but they are only about 30 ft thick and occur at depths of 10,000 to 12,000 ft. Even in the Permian basin, much of the salt occurs at great depths and contains numerous inclusions of other rocks.

Perhaps the principal concern in the disposal of waste in bedded deposits is the stability of the structure at elevated temperatures and stresses. This has been found to be especially significant when shale beds occur interbedded with the salt.^{7,8} These shale beds are usually absent in dome deposits; thus, in this respect, domes may be favored over bedded deposits for waste-disposal sites. From recent laboratory and field tests, it appears that we can now design an efficient and safe operation in bedded rock salt; however, there are several problems unique to salt dome deposits that will require investigation before a similar operation can be designed for these structures.

More than 300 salt domes are now known to be present in the Gulf Coast Embayment. In addition to the lack of shale beds and the higher salt content of these deposits as compared with bedded formations, these domes often occur relatively near the land surface. Many lie between 500 and 1000 ft below the surface, and, of course, in all, the salt extends to depths of many thousands of feet. A large part of the available mined-out space in salt deposits also exists in salt domes. Approximately 40%

of the total space vacated by rock salt mining each year results from workings in the domes of the Gulf Coast region.^{7.5}

Our principal technical concern in the disposal of waste in salt domes is in ensuring that migrating waters do not reach stored waste. The recent flooding of the Winnfield, Louisiana, dome mine may serve to illustrate the concern. Also, in Germany, where domal-type salt structures have been mined for many years, at least 20 mines have been reported to have been flooded by groundwaters.^{7.9} At present, apparently little is known about the movement of groundwater in the vicinity of salt domes;^{7.10} thus, investigations should be initiated to ascertain the geohydrological factors or other parameters that were, or appeared to be, instrumental in the flooding at Winnfield and other salt domes. Here a critical review of the German floodings, as reported in the literature, would appear to be especially helpful. In addition, a thorough search for general information regarding groundwater characteristics around salt domes should be undertaken. It is obvious that the distance between mine workings and aquifers is important, but, at present, we are not able to estimate, for example, the minimum distance for specified conditions of mine depth, structural and stratigraphic conditions of the intruded country rocks, etc. Once the important parameters that bear most directly on mine flooding are identified, laboratory and/or field investigations will, if necessary, be initiated to demonstrate that safe and efficient disposals can be made in salt domes.

The Health Physics Division Advisory Committee has raised a question about the effect of decay heat on stability of the dome (i.e., whether it will possibly accelerate or reinitiate upward movement of the salt). A check shows that, with waste concentrations such as those that may produce temperature rises compatible with safe operation, the average heat generation in a disposal mine would be about two orders of magnitude greater than the normal geothermal flux (assuming wastes interim stored for at least 10 years, until only the 30-year half-life cesium and strontium remained). Thus, it is conceivable that there might be some effect on dome movement. In Germany, it has been found that there is considerable variation in temperature gradients in salt structures. While some of these structures are known to be active, too little is known about the

type of salt deposits and the geologic environment of particular structures to allow development of meaningful temperature-movement relationships.

Another need is for the installation of a few plastic-flow gages in at least one dome mine in an effort to determine whether the creep behavior is the same as that in bedded deposits. True, pillar models behave in the same manner, but there are reasons to suspect that the in situ behavior may be different. One would suspect that there might be residual tectonic stresses in the salt, as well as differences in the way the overburden loads are transmitted into the interior of the dome; both of these would exert considerable influence on flow behavior.

7.3.2 Investigations of Other Geologic Formations

Excavations in rocks other than salt may be suitable for the ultimate disposal of high-level radioactive wastes. Impervious or dry excavations have been reported in limestone, shale, granite, and chalk deposits. However, their possible uses as disposal sites have not been investigated. With model specimens of mine pillars, it has been demonstrated that hard rocks like dolomite do not exhibit such accelerated flow characteristics at elevated temperatures and pressures as does rock salt.^{7,8} Thus it appears that the structural integrity of the excavated openings in these rocks would not be of primary concern in the event that these rocks are used as a disposal media; however, it is likely that such things as ensuring the isolation of these excavations from migrating groundwaters and the geographic location of suitable deposits and their vertical and lateral extents would be critical.

In order to investigate the possibilities of using "other" rocks as disposal media for high-level wastes, it is planned to delineate, on a regional scale those areas that appear most promising. For example, it is expected that, if suitable carbonate rocks and shales do occur, they should be found in relatively tectonically undisturbed areas, such as the mid-continent area. Too, loess deposits, which also may be considered a possibility, are found, among other places, along the lower and middle Mississippi River Valley. It is proposed to investigate a few local representative sites for evidence of such things as potential groundwater problems, depth of excavations, etc. Should the number and location of

suitable deposits be attractive, it would then be appropriate to conduct the necessary laboratory and/or field investigations to determine the actual feasibility of disposal of the high-level waste in these rocks.

8. DISPOSAL BY HYDRAULIC FRACTURING

W. C. McClain Tsuneo Tamura

8.1 Rock Mechanics

W. C. McClain

The initial phases of the theoretical investigation of the deformations induced in the host rock by the hydraulic fracturing technique have been described previously.^{8.1, 8.2} Based on this work, the most probable rock failure mechanism was postulated to be the formation of a vertical, rather than a horizontal, fracture. The orientation of a hydraulically induced fracture is controlled mainly by the orientation of the principal stress field in the rock;^{8.3} that is, the fracture will form perpendicular to the least compressive principal stress. Other factors, such as bedding plane weaknesses, stress concentrations around the borehole, and the configuration of the casing performance may affect the fracture orientation, especially when the value of the intermediate principal stress is approximately the same as that of the least stress.

In order to obtain an estimate of the ultimate capacity of the formation at the Shale Fracturing Plant, the analysis of the stresses immediately adjacent to the injected grout sheet was undertaken.

In this analysis, the original state of stress, the induced stress, and the tensile strengths of the shale are considered, while the other factors will be discussed later. The analysis is based on the assumption that a failure condition has been reached when the total stresses at any point in the rock mass are such that there is an equal probability of either a vertical or a horizontal fracture. This situation will occur when the total vertical stress exceeds the minimum total horizontal stress by an amount equal to the difference between the vertical and horizontal tensile strengths.

The vertical component of the primitive stress field is usually assumed to be a principal stress, and because of the weight of the overlying material,

$$S_z = -\delta H, \quad (1)$$

where

S_z = vertical component of original stress (negative sign indicating compression),

δ = density factor (usually about 1 psi per foot of depth),

H = depth.

The horizontal components of the primitive stress have been measured only in those areas where the behavior of the rock very nearly duplicate that of a perfectly elastic solid (i.e., granite or dense homogeneous limestone). Even then, the accuracy of the measurement is not good. In other localities, the value of the horizontal primitive stresses can only be estimated from elasticity [$S_x = \nu' / (1 - \nu') S_z$, where ν' = Poisson's ratio], plasticity ($S_x = S_y = S_z$), or geologic observations. For example, in the Oak Ridge area, the geological structure is dominated by thrust faulting and folding associated with the Appalachian Revolution. This suggests that large, compressive, horizontal stresses were once present; and, since there is no normal faulting of a more recent age, they probably still exist, although reduced in magnitude. The development of horizontal hydraulic fractures in the area, indicating that both of the horizontal stresses are larger (in compression) than the vertical stress, tends to confirm this conclusion.

Measurement, or even estimation, of the original state of stress is very difficult. In those few areas in the world where measurements have been made, the maximum horizontal stress has never been found to exceed three times the vertical stress.^{8.4} Since it is the intermediate stress, the lesser of the two horizontal stresses, that controls the fracture orientation, an upper limit of $S_y/S_z = 2.0$ is assumed for the Oak Ridge area. Geological evidence and the fact that horizontal fractures develop suggest that the horizontal stress is not less than the vertical stress; therefore, a lower limit of $S_y/S_z = 1.0$ is indicated.

The stresses induced in the host rock around an injected grout sheet can be analyzed by a modification of Sneddon's solution^{8.5} for the stress distribution around an elliptical Griffith crack in an infinite elastic body. This analysis indicates that, except for a small area near the tip

of the injection, the maximum difference between the induced vertical and horizontal stresses occurs along the line above the center of the grout sheet, that is, coincident with the injection well. Also along this line, the two induced horizontal stresses are equal and the induced vertical stress is a principal stress. The variation of these stresses, in terms of the internal pressure, P_o , with distance from the level of the injection is shown by the solid curves in Fig. 8.1. The internal pressure, P_o , in this case is the amount by which the static fluid pressure in the injection exceeds the overburden pressure. For a single injection this internal pressure, P_o , is very small. It can be estimated using:^{8.5}

$$P_o = \frac{\pi E \alpha}{8(1 - \nu^2)c} \quad (2)$$

where

c = horizontal radius of injection,

α = thickness of injection measured at the center,

E = modulus of elasticity, and

ν = Poisson's ratio.

For a 40,000-gal injection with $c = 500$ ft, $\alpha = 0.01$ ft, and using $E = 10^6$ psi and $\nu = 0.25$ (determined from laboratory tests), Eq. (2) gives an internal pressure (P_o) of 8.4 psi. The effects of each individual injection will be cumulative, however; and it is obvious that after a few score injections a sizable pressure, P_o , will be built up.

It is the difference between the induced vertical and horizontal stresses ($\sigma_z - \sigma_y$) that determines the influence of the prior injections on the stress field. This difference is plotted as the dashed curve in Fig. 8.1, where it can be seen that the most adverse location is $0.55c$ (where c = radius of injection) above the center of the injection. This critical point will be the first to satisfy the failure condition, and all of the following analysis is, therefore, based on its behavior.

It is now possible to write the equations defining the sum of the influences in the vertical (Σ_z) and horizontal (Σ_y) directions at any point in the rock mass:

Fig. 8.1. Vertical and Horizontal Stresses Induced by the Injections Above Its Center.

$$\begin{aligned}\Sigma_z &= S_z + \sigma_z - J_z, \\ \Sigma_z &= S_z + \alpha_z P_o - J_z,\end{aligned}\tag{3}$$

and

$$\begin{aligned}\Sigma_y &= S_y + \sigma_y - J_y, \\ \Sigma_y &= \beta S_z + \alpha_y P_o - J_y,\end{aligned}\tag{4}$$

where

α_z, α_y = coefficients of the induced stress (for the critical point shown in Fig. 8.1, $\alpha_z = -0.85, \alpha_y = -0.10$),

β = ratio of the original horizontal to vertical stresses ($S_y = \beta S_z$),

J_z = tensile strength in the z direction, that is, parallel to the bedding, and

J_y = tensile strength perpendicular to bedding planes.

When the sums of the influences in the two directions are equal at the critical point, by the previous definition, a failure condition exists. From this, it can be seen that the ratio Σ_y/Σ_z has the significance of an engineering safety factor for the system.

The variation of this safety factor as a function of the total thickness of injections for various radii of injection and various β values is shown in Fig. 8.2. The physical properties of the shale used in preparation of this figure were: depth = 870 ft, $E = 10^6$ psi, $\nu = 0.25$, $J_y = 900$ psi, $J_z = 300$ psi. These values were estimated, based on laboratory tests of specimens obtained from the experimental site. This shale is very variable, both vertically and laterally, and the samples were not originally for these tests. Therefore, these values for the physical properties can be considered only as estimates.

From Fig. 8.2 the maximum ultimate capacity of the Oak Ridge Shale Fracturing Site can be estimated. Table 8.1 shows the range of that ultimate capacity.

Fig. 8.2. Variation of Safety Factor as a Function of Total Thickness of Injection, Injection Radius (c), and Original Stress Ratio (β).

Table 8.1. Range of the Ultimate Capacity
of the Oak Ridge Shale Fracturing Site

Mean Radius of Injection (ft)	Maximum Total Capacity (millions of gallons)	
	$\beta = 1.0$	$\beta = 2.0$
300	0.9	2.0
500	4.1	8.0
700	11.3	20.0
1000	32.8	49.3

8.2 Disposal of Evaporator Concentrate

Tsuneo Tamura

Injection of approximately 65,000 gal of waste concentrated by the evaporator at ORNL was made in the same slot that was used in the previous injection at 872 ft. The injections were performed on two successive days, since waste storage capacity at the site was limited to 40,000 gal.

Since this injection marks the first use of actual ORNL concentrate, the concentrations of several of the elements and radionuclides in the waste are given in Table 8.2. The composition of this waste differed from that of earlier wastes mainly in hydroxide content. This lower caustic concentration reduced the amount of extender (delta gluconolactone) required to provide sufficient pumping time. The concentration of sodium (present primarily as sodium nitrate) is about twice that of IX waste, which was used in making earlier experimental injections.

The major radionuclide in the waste is ^{137}Cs ; its concentration is approximately 0.3 Ci per gallon. Its gamma radiation makes it the chief contributor to the radiation field. The concentrations of ^{90}Sr and the other radionuclides are lower because of the high pH, which serves to remove these radionuclides from the liquid phase by precipitation. As reported elsewhere, both ^{137}Cs and ^{90}Sr are fixed in the grout by the selected materials used in preparing the slurry.

Table 8.2. Composition of ORNL Evaporator Concentrate

Ion	Concentration (M)	Radionuclide	Concentration (mCi/ml)
Na^+	1.04	^{137}Cs	8.2×10^{-2}
NH_4^+	0.15	^{90}Sr	2.9×10^{-4}
OH^-	0.05	^{144}Ce	9.0×10^{-6}
Cl^-	0.05		
NO_3^-	0.75	^{60}Co	1.1×10^{-4}
SO_4^{2-}	0.18	^{106}Ru	1.4×10^{-4}

No major difficulties were experienced during the injection. A solid-waste proportioning ratio of 6 lb/gal was specified. The solid, which was blended a week in advance and stored in the bins, had the following components:

<u>Material</u>	<u>Parts by Weight</u>
Portland cement type II	2.0
Kingston fly ash (pozzolan)	2.0
Grundite	0.5
Attapulgate	0.9
Delta gluconolactone	0.002

In addition to using the solid with waste, it is used with water at the start of each injection to check plant operation (1000 gal), and at the end of each injection to reduce residual contamination in the system (1000 gal). To produce a slurry that will not develop phase separation upon setting, 7 lb of blend per gallon of water is used. The slurry density of this mix is 11.6 lb/gal as compared with 11.5 lb/gal when waste is used.

The mass flowmeter, which was installed to provide a second independent control of solid-liquid proportioning, performed well during

this injection. The calculations based on the flowmeter, as well as the densimeter, readings agreed to within 3% of the amount calculated using a known waste volume and solid weight.

Following the injection, the slot was not cemented to permit the well to be opened to measure bleedback of water. Occurrence of bleedback is an indication that undesirable phase separation occurred upon setting. This test was conducted to correlate laboratory blending techniques with field equipment. Preliminary data suggest that the mix was adequate, since less than 1000 gal of water was collected after 5 days. This volume can likely be attributed to the return of the water that was used to clear the well after the injection.

9. FATE OF RADIONUCLIDES IN TERRESTRIAL ENVIRONMENT

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The major long-term objective of the soil studies is to obtain information from field and laboratory experiments on the behavior of radionuclides in soils and to use this information to write a mathematical model that will provide a rational basis for predicting the fate of radionuclides released to the environment of a selected landscape.

9.1 Field Plot Studies

9.1.1 Comparison of Two-Year Results from Runoff Plots

The study of ^{137}Cs movement of runoff, erosion, and infiltration of three 5-m^2 plots, located on Captina soil, was continued. Each of the plots (bare soil, clipped poor meadow, and fertilized good meadow) had been dosed with 5 mc of ^{137}Cs in the fall of 1964. Initially, all of the ^{137}Cs was applied to the vegetation in the meadow plots, and to the soil surface in the bare soil plot. After 18 months of environmental exposure, it was found that 98% of the ^{137}Cs originally applied to the vegetation had been leached off. Most of the remaining ^{137}Cs was concentrated within the upper 2.5 cm of the soil profile, and less than 2% of the total applied (and less than 4% of that remaining) was at a depth greater than 10 cm.

Erosion losses of soil and radiocesium during the 2-year study period are shown in Table 9.1. Although the rainfall during the second year of study amounted to only 43.4 in. as compared with 53.1 in. during the first year, the erosion index^{9.1} (EI) values were 1.60×10^4 dynes/sec for the first and second years respectively. Despite the similarity in the erosion index values, an increase in soil loss on the bare soil plot 1 was observed. This increase can be attributed to the increase in runoff from the hard, smooth surface of the bare soil plot formed during the first year's rains and continuing during the second year of study. Such a

Table 9.1. Soil and Cesium Losses on Runoff Plots

Plot	First Year		Second Year		Total	
	Soil Loss (g/m ²)	¹³⁷ Cs Loss ^a (%)	Soil Loss (g/m ²)	¹³⁷ Cs Loss ^a (%)	Soil Loss (g/m ²)	¹³⁷ Cs Loss ^a (%)
1. Bare soil	2023	30.8	3235	12.01	5258	42.8
2. Clipped poor meadow	207	18.9	44	0.5	251	19.4
3. Fertilized good meadow	73	6.7	13	0.1	85	6.8

^aPercentage ¹³⁷Cs loss is computed on the basis of total ¹³⁷Cs applied originally to the plots.

surface inhibits infiltration, thereby increasing runoff and erosion. On the other hand, the fivefold reduction in the soil loss on the vegetation-covered plots is a direct result of heavy vegetative growth in the springs and summers of 1965 and 1966. The ^{137}Cs loss during the second year, computed on the basis of the soil loss during the first year, was found to be 2.5 times less on the bare soil, 4.4 times less on clipped-poor-meadow plot, and 23.9 times less on the fertilized-good-meadow plot.

9.1.2 Seasonal Distribution of Cesium-137 Loss

In Fig. 9.1, the seasonal distribution of ^{137}Cs loss is shown as a function of time following the application. Highest losses of cesium were observed on all plots during the winter and spring of the first year following the application of radionuclide in the previous fall. After 153 days the seasonal losses decreased markedly on the vegetation-covered plots as a result of new meadow growth. During the second summer and fall, an increase was observed in the total ^{137}Cs loss on the bare soil plot. This increase is related to high-energy and high-intensity thundershowers that are prevalent in Tennessee during the summer, and to the accompanying increase in runoff and soil losses from exposed areas.

9.1.3 Cesium-137 Loss as a Function of Soil Loss

An equation was fitted to the 2-year data for all values of cumulative ^{137}Cs and soil losses on the bare soil plot. The relationship derived is:

$$y = 1.37 (x/b)^{0.41}, \quad (1)$$

where

y is the cumulative ^{137}Cs loss (%),
 x is the cumulative soil loss (g/m^2), and
 b is a constant (g/m^2).

It was observed that the experimental values obtained after the spring of the second year fell below the values predicted by Eq. (1). Accordingly, the data were fitted by Eq. (2):

$$y = 2.22 (x/b)^{0.35}, \quad (2)$$

Fig. 9.1. Cesium-137 Loss as a Function of Time Following Application.

where y , x , and b are as defined for Eq. (1). The results are shown in Fig. 9.2. Although the standard error for Eq. (2) was ± 0.29 as compared with ± 0.23 for Eq. (1), the fit involving second-year data was good, as shown in Fig. 9.2.

Similar relationships, but with different values of the coefficients and exponents, were found to apply to the vegetation-covered plots. In particular, three distinct time phases--early, transition, and equilibrium--could be discerned on all plots (Table 9.2). The relationships for these time phases are shown in Table 9.2.

Overall, the rate of cesium loss as shown by the exponents (Table 9.2) decreased with time, as would be expected as a result of the cesium movement into the soil. During the first two phases, the rate, as shown by the exponents, increased with the amount of vegetation because of the washoff contribution from vegetation on meadow plots. After 153 days the rate of cesium loss decreased with the increase in the amount of vegetative cover.

The initial losses of cesium for 1 g of soil, as shown by the coefficients in Table 9.2, were highest on the clipped meadow plot containing large amounts of dead plant material. Also, considering the coefficients in Table 9.2, it appears that the initial losses for 1 g of soil would be relatively higher if the applied cesium was in the equilibrium phase rather than in the early phase. The results shown in Table 9.2 suggest that in a generalized model of cesium movement we might expect the coefficients to be a function of the absorption coefficient (K_d) values, whereas exponents might best be expressed as a function of the radionuclide downward movement (F_N) into the soil profile:

$$y = f(K_d) [(x/b)]^{f(F_N)}, \quad (3)$$

where both $f(K_d)$ and $f(F_N)$ are time-dependent rate functions.

9.1.4 Differential Movement of Cesium-137 and Cesium-134 on Runoff Plots

In the spring of 1966 a further study of radiocesium movement on three additional runoff plots, similar in size and construction to the original runoff plots, was initiated. These plots consisted of a bare

Fig. 9.2. Functional Relationship Between Cumulative ^{137}Cs and Soil Losses.

Table 9.2. Cesium-137 Loss^a as a Function of Soil Loss and Time

Plot	Time After Application of ¹³⁷ Cs (days)		
	< 72	72 to 153	> 153
1. Bare soil	$Y = 0.3 (x/b)^{0.7}$	$Y = 0.8 (x/b)^{0.5}$	$Y = 2.2 (x/b)^{0.4}$
2. Clipped meadow, unfertilized	$Y = 0.4 (x/b)^{0.8}$	$Y = 1.0 (x/b)^{0.6}$	$Y = 7.3 (x/b)^{0.2}$
3. Tall meadow, fertilized	$Y = 0.1 (x/b)$	$Y = 0.4 (x/b)^{0.7}$	$Y = 4.3 (x/b)^{0.1}$

^aY = cesium loss (%); x = soil loss (g/m²); b = units constant (g/m²).

soil plot, a fertilized-good-meadow plot, and a mulched plot on which the vegetation was moved, killed, and allowed to remain on the surface. The mulched plot was designed to simulate conditions on the clipped-poor-meadow plot in the original series. The bare soil plot was located on a steeper slope than the bare soil plot in the original series, and the fertilized-good-meadow plot was on a gentler slope and had undergone vigorous vegetative growth just prior to ^{137}Cs application as contrasted with a steeper slope and dead vegetation in the case of the original tall meadow plot. The plots were designed to serve as replicates of the original series and also to yield information on seasonal effects and on the origin of eroded cesium and soil material. Information on the seasonal effects was obtained by applying cesium in the spring rather than in the fall as was done previously. To determine the origin of eroded material, the plot was divided diagonally into two portions; the upper half was dosed with ^{137}Cs , and the lower half received an application of ^{134}Cs . Different rates of application were employed to establish whether dose rate had any relationship to the amount of material eroded. In Table 9.3 the pertinent initial data for each plot are shown.

In Table 9.4 preliminary results covering the period of 144 days after the applications are given; cesium loss--soil loss relationships first observed on the original runoff plots were further confirmed by the results obtained. A major loss of soil from the bare soil plot resulted in a major loss of cesium; a minor loss of soil from the fertilized-good-meadow plot resulted in a minor cesium loss. The cesium loss predicted by using the second phase equation in the middle column of Table 9.2 is shown for comparison. (The phase 2 equations were used to correspond to a 144-day study period.) Substantial losses of soil from the bare soil and mulched plots reflect the seasonal effect of summer thunderstorms. On the other hand, good vegetative meadow growth on the fertilized-good-meadow plot afforded adequate safeguard against cesium loss, in comparison with the 6.5% cesium loss observed during the initial 153-day period on the original plots where cesium was applied to heavy, but dead, vegetation.

Consideration of the ^{137}Cs loss/ ^{134}Cs loss ratios in Table 9.4 indicates that, on both the bare soil and the mulched plot, cesium was lost in about equal proportions from the upper and lower halves of these plots;

Table 9.3. Summary Data for Second Series of Experimental Runoff Plots
to Which Cesium-137 and Cesium-134 Were Applied

Type of Plot	Slope (%)	Total Area of Plct (m ²)	Amount of Vegetation ^a (g/m ²)	¹³⁷ Cs Applied		¹³⁴ Cs Applied	
				Amount (μCi/m ²)	Area (m ²)	Amount (μCi/m ²)	Area (m ²)
Bare soil	5	5.6	----	841	3.0	3869	2.6
Mulched	3	5.7	582 ^b ± 120	418	3.0	2397	2.7
Fertilized good meadow	7	5.1	802 ± 184	440	2.7	1462	2.4

^aVegetation expressed on dry-matter basis.

^bVegetation was in form of dead-grass mulch.

Table 9.4. Second Series of Experimental Runoff Plots: Data on Soil and Cesium Losses

Type of Plot	Soil Loss (g/m ²)	¹³⁷ Cs Loss (%)	¹³⁴ Cs Loss (%)	Cesium Loss (avg.)	¹³⁷ Cs Loss/ ¹³⁴ Cs Loss Ratio	Predicted ^a Cesium Loss (avg.)
Bare soil	7562	64.0	58.3	61.4	1.10	72.8
Mulched	436	26.8	28.7	27.7	0.93	31.1
Fertilized good meadow	5	0.1	2.84	1.41	0.04	1.08

^a Predicted on the basis of equations shown in the middle column of Table 9.2.

however, the cesium loss on the fertilized-good-meadow plot was primarily from the lower half of the plot.

The results to date on both the original and the differentially dosed cesium runoff plots support our original conclusions that heavy cesium losses can be expected from exposed areas where heavy soil losses occur. The results also suggest that heavy and vigorous vegetative growth provides good protection against excessive cesium movement by runoff and erosion in the initial period after deposition.

9.2 Laboratory Adsorption Studies

In the preceding progress report it was shown that sorption of cobalt by dioctahedral muscovite was greater than that by trioctahedral biotite from solutions containing tracer concentrations of cobalt in 0.1 N NaCl. This behavior was surprising, because, with other minerals, the trioctahedral varieties sorbed more than their dioctahedral analogs. It was further noted that, if the two minerals were acid washed, the muscovite lost its capacity, whereas the biotite did not. Further results, which have been obtained in recent studies of the sorption of cobalt by muscovite and related minerals, are discussed in this section.

9.2.1 Behavior of Muscovite in Distilled Water and Salt Solution

As noted earlier, the sorption of cobalt by muscovite was greatly reduced in the 0.1 N NaCl solution when the muscovite was acid washed. If the acid washing had destroyed the muscovite, greatly reduced sorption would be expected, even in distilled water, which does not contain competitive sodium ions. The results in Table 9.5 show that acid washing did not destroy the muscovite. Even at pH 5.2 to 5.4 more cobalt was sorbed from distilled water than from salt solution. When the pH was increased, the sorption of cobalt increased; however, the acid-washed muscovite did not sorb any cobalt in the pH range of 5 to 6 in 0.1 N NaCl. Further analysis of the data suggests that acid washing removed a component from the system that was responsible for sorbing cobalt in the presence of competing sodium ions.

Table 9.5. Percentage Sorption of Tracer-level Cobalt by Unwashed and Acid-washed Muscovite in Distilled Water and in 0.1 N NaCl

(Test using 0.15 g of 20 to 2 μ particles in 100 ml of solution containing 2×10^{-6} N cobalt. Sorption measured 7 days after initial contact and after adjustment of pH.)

Contact Media	Treatment of Muscovite	pH			Sorption of Cobalt (%)		
		Initial	After Addition of NaOH	After Addition of HCl	Initial	After Addition of NaOH	After Addition of HCl
Distilled H ₂ O	Unwashed	5.79	6.00	5.30	68.1	96.1	86.3
	Acid-washed	5.21	6.00	5.19	63.8	9.7	52.2
0.1 <u>N</u> NaCl	Unwashed	5.41	5.83	5.38	50.8	90.3	91.4
	Acid-washed	5.00	5.92	5.15	1.10	0.0	0.0

After the pH was increased and the amount of sorbed cobalt was measured, the pH was decreased to near its former value, and was redetermined. A difference in behavior was noted between the acid-washed and unwashed mineral. The acid-washed muscovite released the sorbed cobalt at the higher pH and retained approximately the same amount at equilibrium as originally present at the lower pH. On the other hand, the unwashed muscovite did not release the cobalt to the expected degree and, after 8 days, retained considerably more cobalt than originally measured at the lower pH (Table 9.5). These responses indicate that acid-washed muscovite sorbs cobalt by reversible ion exchange but that the component present in unwashed muscovite sorbs irreversibly or perhaps forms a new compound with cobalt.

9.2.2 Comparison of Acid-washed and Aluminum-Saturated Muscovite

To obtain the desired particle size of muscovite for testing, the original flakes are wet-ground in a mortar or wet-filed. The suspension of the ground or filed materials was found to have a neutral or an alkaline pH, presumably from the release of potassium from the muscovite (a potassium aluminosilicate). This observation also suggests that the muscovite could have been partially destroyed, releasing aluminum and silica as well to the system. The aluminum would hydrolyze and form a hydroxy polymer that could adhere to the muscovite surface. If this type of reaction had occurred during the grinding or filing process, the acid washing could have dissolved the aluminum hydroxides and removed them from the system. These considerations led to the preparation and testing of aluminum-saturated muscovite (Al-muscovite) that would give information on a system containing only a minimal amount of aluminum. To prepare the Al-muscovite, the acid-washed muscovite was treated with 0.5 N AlCl_3 solutions; the excess AlCl_3 was removed by rinsing with distilled water.

As shown in Table 9.6 the Al-muscovite sorbed much more cobalt at pH 7 than the acid-washed muscovite from which it was produced. The possible explanation for the improved adsorption is that the sodium ions replaced the aluminum, which hydrolyzed at pH 7. The cobalt was adsorbed

Table 9.6. Percentage Sorption of Cobalt by Acid-washed Muscovite
With and Without Aluminum Saturation

(Sorption of 0.15-g material in 100 ml of 0.1 N NaCl
containing 2×10^{-6} N cobalt)

Contact Time (days)	Acid-washed Muscovite ^a				Acid-washed Muscovite ^b			
	Without Al-Saturation		With Al-Saturation		Without Al-Saturation		With Al-Saturation	
	pH	Sorption (%)	pH	Sorption (%)	pH	Sorption (%)	pH	Sorption (%)
1	6.05	0.0	5.08	6.59	----	----	7.00	93.5
3	5.16	1.92	5.10	3.33	6.98	7.00	7.05	98.1
7	5.11	0.0	5.18	2.14	7.10	8.30	7.15	98.9

by the aluminum hydroxy polymer, since studies in this laboratory have shown that alumina and aluminum hydroxide precipitates can sorb cobalt selectively from sodium solutions. A similar improvement in cobalt sorption was found when pyrophyllite and vermiculite underwent this same aluminum treatment. In the case of vermiculite, iron saturation was also done and the results on cobalt sorption paralleled those for the aluminum form.

9.2.3 Cobalt Sorption by Soil Minerals

The objective of the laboratory tests with minerals is to provide an understanding of the reactions occurring in soil systems. Before one proceeds intensively in studying the "laboratory" system, the relation of the latter system to the environmental system should be considered. This is particularly true of cobalt since this element has been studied by soil scientists for many years. One of the more-recent explanations for selective cobalt sorption has been based on surface structural defects of minerals. Our results thus far suggest a sesquioxide reaction. Hence we felt it desirable to investigate soil minerals in contrast to pure reference standard minerals.

The B₁ horizon of several soils found in the southeastern United States was initially used to study the sorption of cobalt at different pH levels. Sorption was found to be high at pH 7 and low at pH 5; the latter value corresponds to the natural pH of most of the soils considered. Figure 9.3 shows the type of response observed with the soils, as well as the B₁ horizon of the Sequoia soil, which has a natural pH of 4.90 and a base exchange capacity of 5.40 meq/100 g. To measure the influence of the sesquioxides, the Sequoia sample was treated with sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) to remove the iron oxides. This sample was then tested using another Sequoia sample that had been treated identically except for the use of Na_2SO_4 instead of $\text{Na}_2\text{S}_2\text{O}_4$. The results are compared in Fig. 9.3, showing that the treatment which removed the iron oxide caused a significant reduction in cobalt adsorption.

Unfortunately, it was not possible to evaluate the role of aluminum oxides in these samples since the dithionite treatment does not quantitatively remove aluminum. Effects of the dithionite treatment were studied using alumina as well as ground muscovite; results showed that alumina was not affected and that ground muscovite sorbed about one-third as much cobalt as untreated muscovite. In the soil the hydrated alumina would be expected to be more stable than the "alumina" of the muscovite but less stable than pure alumina. Efforts are continuing on developing stabilized alumina on clay minerals so that a better understanding of the reaction can be obtained. The results thus far are encouraging, and a better understanding of the cobalt reaction would not only lead to predictable behavior of cobalt in soils but would contribute valuable information on microconcentration adsorption reactions of elements that are similar to cobalt and are vital micronutrients for plants and animals.

Fig. 9.3. Effect of pH and Iron Oxide Removal on the Sorption of Cobalt.

10. APPLICATION OF MINERAL EXCHANGE

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10.1 Behavior of Sulfur Hexafluoride and Methyl Iodide in an Idaho Soil

Sulfur hexafluoride and methyl iodide have been considered as possible gaseous tracers for evaluating the suitability of a site near the proposed LOFT test for containing radioactive gases.

Sulfur hexafluoride, although not a radioactive waste, seems to be a very good tracer for this project. It is inert, nontoxic, and sparingly soluble in water. This gas does not attack ordinary metals even at 110°C and 50 psi. It is stable to silent electric discharge, and no hydrolysis takes place under ordinary conditions.^{10.1} In addition to its chemical stability, SF₆ is the most sensitive compound available to detection by electron capture in gas chromatographic analysis.^{10.2, 10.3} It has been reported that SF₆ can be detected at levels as low as 10⁻⁹ ppm.^{10.4}

Methyl iodide has been suggested as a possible tracer, since it has been found to penetrate iodine adsorption columns and would likely present a major hazard in the case of a reactor incident.

In order to determine the magnitude of the interaction of CH₃I and SF₆ with soil materials, laboratory studies were conducted using columns of Idaho Falls subsoil that were provided by Bruce Schmalz, USAEC, Idaho Falls.

Adsorption of SF₆ at Room Temperature (26°C)

Twenty-mesh (or larger size) pieces of Idaho soil from a depth of 14 to 15 ft, with a moisture content of 3.8%, were packed in a glass column and flushed with 99% pure SF₆ at the rate of about 20 ml/min for an hour. A portion of the treated soil was leached with 0.2 M KOH. Both the treated soil and the leached solution were submitted to the Analytical Chemistry Division, ORNL, for analysis, but no satisfactory results were obtained. Infrared measurements showed contradictory results.

Three hundred forty-five grams of the same soil was packed in a glass column that was 61 cm long and 4.6 cm² in cross-sectional area.

The porosity was 56.2%. Sulfur hexafluoride was passed through the soil column at a rate of about 18 ml/min for 4 hr and subsequently was purged by helium at the same rate for 2 hr. The soil was then transferred to a 500-ml Erlenmeyer flask that was connected to a gas-sampling rubber balloon. The soil was heated to about 90°C for 1 hr, and the remaining gas in the flask was blown into the balloon with air. The gas sample was then analyzed by a gas chromatograph with an electron-capture detector. Sulfur hexafluoride air standards (0.1 to 10 ppm of SF₆) prepared by the Y-12 Plant failed to show any peak on the recording chart; thus pure SF₆ was used as a standard. Sampling was accomplished by using a 1-microliter syringe.

The gas chromatograph used was an Aerograph model 200 with an electron-capture detector. The glass column was 10 ft long and 1/4 in. in diameter glass, and packed with 20% silicone gum rubber SE-52 on 60- to 80-mesh Chromosorb W. It was operated at a 75°C column temperature and a flow rate of 50 ml/min, using N₂ as the carrier gas. The electron-capture anode potential was 90 v. With this column, the SF₆ peak overlaps with the air peak. Therefore, for experiment 2 the difference between the peak of the sample and that of the air was used for the computation of SF₆. For separation of air and SF₆ peaks, decreasing the flow rate and column temperature did not produce any favorable result. A silica gel column would have helped the separation.^{10.2, 10.5} Difficulties were also encountered in making standard SF₆-air mixtures and in sampling from a gas bulb or a balloon. It seems that both the glass surface and the rubber surface adsorb SF₆. Even the syringe needle may absorb an amount of SF₆ sufficient to give a substantial peak. For sampling devices, references 10.4, 10.6, and 10.7 should be consulted.

The sample collected by heating the soil after treatment with SF₆ and helium showed adsorption of 99 ppm. Because of the nonlinearity of the instrument at higher concentrations, the chromatographic peaks obtained from pure SF₆ are probably lower than they should be, and thus the resulting value of 99 ppm is probably too high.

Three hundred forty grams of soil was packed in the same glass column as in the above experiment; the porosity was 52.3%. The soil was first flushed with helium for 2 hr to displace all the air in the column, and

then SF_6 was admitted at the rate of 12 ml/min. Samples were collected in rubber balloons at 8-min intervals for 2 hr. The soil column was eluted with helium at the rate of 7.7 ml/min, and again the sample was collected in a rubber balloon at intervals of 5 min for 105 min. After the soil had been flushed with helium, it was transferred to an Erlenmeyer flask and heated as described above, except that the remaining gas in the flask was blown into the balloon by helium instead of by air. All the samples collected were analyzed chromatographically. The standards used for the sample obtained by heating were prepared by a dynamic method.^{10.8}

In this experiment the adsorption value of the sample collected from heated soil is 8 ppm. On the other hand, the curve in Fig. 10.1 shows that the half breakthrough point for the elution of SF_6 by helium is at 22.5 min. Correcting for half the sample size gives a retained volume of 148 ml, compared with an integrated value of 154 ml. The pore volume of the column was 147 ml; thus 4 ± 3 ml of SF_6 was adsorbed on the 340 g of soil. This amounts to 70 ± 52 ppm by weight and includes, of course, the loosely bonded, as well as the tightly bonded, SF_6 . Based on the fact that the solubility of SF_6 in water is 3.3×10^{-4} g/cc and the soil moisture is 3.8%, all of the first 13 ppm adsorbed would be dissolved in water.

Adsorption of CH_3I at Room Temperature (26°C)

A glass column, 29 cm long and 2.27 cm^2 in cross-sectional area, was packed with 86.1 g of CH_3I . The bed was 25.5 cm long, and its porosity was later determined to be 56.5%. A known quantity of CH_3I tagged with ^{131}I and contained in a 125-ml Erlenmeyer flask was attached to the glass column that is connected to a glass tube which extends above the scintillator of the counter and finally connects to a U-tube containing 1 M AgNO_3 solution. The setup is shown in Fig. 10.2.

After the connection was made, counts were taken at an interval of 5 or 10 min (except during the night) until a constant count was attained. Then the column was purged with air at the rate of 2.2 ml/min and a count was taken every 5 min until background was reached. The precipitate formed by the reaction of CH_3I and AgNO_3 was dissolved in KCN solution, and the volume of this solution was measured and counted. After the purging of loosely bound CH_3I , the soil column was dissected into five

Fig. 10.1. Elution of Sulfur Hexafluoride from a Column of Idaho Falls Soil Using a Helium Purge.

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Fig. 10.2. Schematic of Apparatus for Measuring Diffusion of CH_3I Through a Column of Idaho Falls Soil.

sections, crushed, and exposed to air for 10 min; then the adsorbed $\text{CH}_3^{131}\text{I}$ was counted.

The result of the air elution experiment is shown in Fig. 10.3. From this curve the half breakthrough point is found at 32 min after elution; therefore, the total volume of CH_3I retained is $2.2 \text{ ml/min} \times 32 \text{ min} = 70.4 \text{ ml}$ for 86.1 g of soil. Since the pore volume is 41.2 ml, the CH_3I adsorbed on the soil is 29.2 ml, which is 1940 ppm by weight. If, however,

the formula of $\bar{V} = \frac{\Sigma Q_i}{C_o}$ is used for computation, where $\bar{V}$ is the volume

adsorbed, including the pore volume, ΣQ_i is the total amount of gas adsorbed and $Q_i = C_i \Delta V$, and C_o is the initial concentration of the adsorbed gas, then the computed $\bar{V}$ for CH_3I is 74.8 ml, which is somewhat larger than the value 70.4 ml obtained from the curve.

The adsorption value obtained directly by counting the soil column, as shown in Table 10.1, is 577 ppm, which may be considered as water-dissolved and nonexchangeable CH_3I . Since the soil moisture is 3.8% and

Table 10.1. Mass Balance of CH_3I

Weight of CH_3I , g	19.7166
Weight of CH_3I after diffusion, g	18.8346
Total weight of CH_3I diffused, g	0.8820
Weight of CH_3I collected in AgNO_3 solution, g	0.7067
Weight of CH_3I remaining on soil, g	0.0497
Discrepancy, g	0.1256

the solubility of CH_3I in water is 1.4%, then 295 ppm of the retained CH_3I should be dissolved in water, assuming that Henry's law holds in this solid system (vapor pressure of CH_3I at 26°C is 410 mm). There is, however, a discrepancy of 0.1256 g between the amount of CH_3I diffused and collected. This discrepancy may be the result of adsorption of glass and possibly some loss of CH_3I during a short period of failure in making connections.

A plot of cumulative counts during the diffusion period vs time was made (see Fig. 10.4). The holdup time was found to be 9.2 hr. From

Fig. 10.3. Elution of CH_3I from a Column of Idaho Falls Soil Using an Air Purge.

Fig. 10.4. Cumulative Diffusion of CH_3I Through a Column of Idaho Falls Soil.

this value and according to the equation $t_e = \frac{d^2}{6\bar{D}}$ for holdup time, and the equation $t_a = 0.42 \frac{d^2}{\bar{D}}$ for time lag before a steady state is attained,^{10.9} the diffusion coefficient, $\bar{D}$, and the time lag, t_a , were estimated to be $3.3 \times 10^{-3} \text{ cm}^2/\text{sec}$ and 23.1 hr respectively. The experimental value for the latter, as can be seen in Fig. 10.5, is 22.5 hr. For the purpose of comparison, a value of the molecular diffusion constant, D , for CH_3I diffusing in air, was calculated with the Chapman-Enskog formula:^{10.10}

$$(D_m)_{AB} = 1.8583 \times 10^{-3} \frac{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}{P \sigma_{AB}^2 \Omega_{AB}} = 0.07 \text{ cm}^2/\text{sec},$$

where

T = absolute temperature, 299.2°K,

P = total pressure, 0.973 atm,

σ_{AB} = collision diameter, 4.218 Å (for CH_3I , estimated from atomic radii),

Ω_{AB} = Lennard-Jones molecular parameter 1.6 (for CH_3I , assuming $T_c \cong \frac{3}{2} T_b$),

M_A = molecular weight of CH_3I (142 g/mole),

M_B = average molecular weight of air (28.8 g/mole).

This value corresponds closely to the diffusion constant of ^{131}I in air, $0.0784 \text{ cm}^2/\text{sec}$.^{10.11}

The value for the diffusion coefficient of CH_3I in air must be corrected for the porosity of the soil column and by a tortuosity, or path length, factor; this gives a value of $0.024 \text{ cm}^2/\text{sec}$ for the diffusion of CH_3I in the soil column. In addition, the total distance between the source of the CH_3I and the detector must be modified for the adsorptive properties of the soil for CH_3I . This would account for the additional difference of an order of magnitude between the extracted and the calculated values.

Fig. 10.5. Diffusion of CH₃I Through a Column of Idaho Falls Soil.

Movement of Curium in Soil Columns

Sodium nitrate solutions (0.1 M) tagged with ^{242}Cm were passed through 1-g columns of hydrobiotite preequilibrated with untagged solutions of the same chemical composition. Approximately 1 liter of solution was passed through each column. The concentration history of the effluent is shown in Fig. 10.6. The concentration did not follow a normal chromatographic breakthrough; instead, the leakage was fairly constant during the entire time. The average leakage through the columns was: pH 3 ($0.80 \pm 0.09\%$), pH 7 ($2.75 \pm 0.41\%$), and pH 10 ($15.0 \pm 2.5\%$). Also, as the pH was increased, ^{242}Cm precipitated from the stock solution, reducing the activity of the influent solution.

After the runs, the columns were disassembled to ascertain the distribution of activity along the column. Most of the activity was found in a glass wool plug above the column and in the first segment of the column. This indicates the importance of precipitation on the behavior of curium. The leakage of the curium through the column suggests that the mobile species is probably a radiocolloid that is small enough to avoid filtration by the hydrobiotite.

Fig. 10.6. Leakage of ^{242}Cm Through a 1-g Column of Hydrobiotite Using a Carrier Solution of 0.1 M NaNO_3 .

11. SAFETY EVALUATION: ESTIMATION OF DOSE TO MAN FROM RADIOACTIVE WASTE RELEASED TO THE ENVIRONMENT

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11.1 Krypton-85 and Tritium in an Expanding World Nuclear Power Economy

The complete release of ^{85}Kr and ^3H during the reprocessing of spent reactor fuel may impose unacceptable radiation exposures to man and his environment as nuclear power production increases. Study indicates that the worldwide distribution of these radionuclides in the year 2000 may result in a total body dose rate of 1.8 mrem/yr from ^{85}Kr and a body tissue dose rate of 2.1×10^{-3} mrem/yr from ^3H .^{11.1} However, the limits of permissible discharge and the requirements for treatment of effluent must be determined for local environments in which reprocessing plants may be sited.

Procedures for Estimating Permissible Release

Acceptable rates of ^{85}Kr and ^3H release are now being investigated for a hypothetical fuel-reprocessing plant located in the Oak Ridge environment. All critical pathways of internal and external exposure must be considered for both the hypothetical plant and current operations that result in the release of radionuclides.

Average annual downwind air concentrations are calculated by a modified Gaussian plume formula as follows:

$$X(\theta x) = \sum_{i=1}^S \sum_{j=1}^R \frac{2.032 F(\theta S)_i Q_{0j}}{\sigma(Sx)_z \bar{\mu}(\theta)_i x} e^{-\frac{h^2}{2\sigma(Sx)_z^2}}, \quad (1)$$

where

$X(\theta x)$ = average annual concentration along 22.5° arc at distance x , in direction θ (Ci/m^3);

$F(\theta S)_i$ = fraction of time wind is in direction θ , for stability S and wind speed group i ;

Q_0 = initial emission rate (Ci/sec);

$\sigma(Sx)_z$ = vertical dispersion coefficient at distance x , for stability $S(m)$;

$\mu(\theta S)_i$ = average wind speed in direction θ , for stability S and speed group i (m/sec);

h = stack height (m);

R = index denoting wind speed groups; and

S = index denoting stability parameter.

This expression is achieved by integrating the Gaussian plume formula over the cross wind direction and distributing the results uniformly along the entire arc. Since the average wind speed vector and its frequency of occurrence are used, calculations yield average annual air concentrations. Application of this technique was demonstrated previously by Culkowski.^{11.2}

Equation (1) is modified to include washout and fallout by multiplying by appropriate correction factors. Corrections for washout and fallout, based on the work of Chamberlain and Slade, respectively,^{11.3,11.4} are as follows:

$$Q_{\text{washout}} = e^{-\frac{Ax}{\mu(\theta S)_i}}, \quad (2)$$

where

A = washout coefficient, sec^{-1} ,

$$Q_{\text{fallout}} = e^{-\left[\left(\frac{2}{\pi} \right)^{1/2} \frac{V_g}{\mu(\theta S)_i} \int_0^x \frac{1}{\sigma(Sx)_z} e^{-\frac{h^2}{2\sigma(Sx)^2}} dx \right]},$$

where

V_g = deposition velocity, m/sec.

Equations (1), (2), and (3) are coded for the CDC 1604-A computer. Equation (3) can be evaluated numerically, based on curves of σ_z values given by Hilsmeier and Gifford.^{11.5}

Figure 11.1 shows the calculated air concentrations at the ground surface for a one-part-per-second release from a 100-m stack. The most recent meteorological data reported by Hilsmeier are used in these calculations.^{11.6} Concentrations shown in Fig. 11.1 will be compared with others that include fallout, washout, and changes in stack height; by this process, average annual dose estimates will be made for a variety of conditions.

Washout and Fallout Corrections

Dose equivalents have been projected for a 6-ton-per-day fuel-reprocessing plant sited in the Oak Ridge environment.^{11.7} These preliminary estimates of dose are being evaluated by incorporating the most recent meteorological data and the best estimates of washout and fallout coefficients in the computer program.

Washout. Washout coefficients for soluble gases have been calculated by Chamberlain, using the assumption that the rate of absorption was controlled by the rate of gas diffusion to the raindrop.^{11.3, 11.8} Since the solubility of krypton in water is low (1.85×10^{-10} g of krypton per g of water at equilibrium),^{11.9} it was assumed that the solubility limit controlled the amount of krypton absorbed. The solubility of ^{85}Kr in rainwater, even when the krypton is released at 1 Ci/sec, would be limited by the stable krypton in the atmosphere (about 4×10^{-3} g/m³ near sea level).^{11.10} It was further assumed that krypton was washed out of the atmosphere, beginning at an average height of 1 mile. This assumption was based on the height of rain-bearing cumulus clouds and the extent of vertical development of radioactive clouds released as a point source. The average intensity of rainfall is about 4 mm/hr in the Oak Ridge area,^{11.11} and, at equilibrium, 2×10^{-14} g of krypton per second could be absorbed in an atmospheric column that is 1 mile high and 1 cm² in area. About 4×10^{-4} g of stable krypton per square centimeter is contained in the atmosphere to a height of 1 mile. Based on these considerations, the average washout coefficient is calculated to be:

$$\Lambda = \frac{2 \times 10^{-14} \text{ g Kr/sec/cm}^2}{5 \times 10^{-4} \text{ g Kr/cm}^2} = 4 \times 10^{-11} \text{ sec}^{-1} . \quad (4)$$

Average Annual Surface Concentrations—Parts per Cubic Meter (Source Height $h=100$ meters, Source Strength $Q=1$ part per sec).

Fig. 11.1. Average Annual Air Concentrations at Ground Surface.

Fallout. If the sorption of a radionuclide by the ground surface is irreversible, the flux of the radionuclide to the surface does not depend on the amount already deposited.^{11.12} Chamberlain describes the rate of deposition for such a system in terms of a deposition velocity. The following equation is used to estimate the deposition velocity of gases or very small particles:^{11.8}

$$V_g(z_1) = \frac{ku^*}{\ln(ku^*z_1D^{-1})}, \quad (5)$$

where

V_g = deposition velocity, cm/sec,

k = von Karman's constant = 0.4,

u^* = friction velocity, cm/sec,

z_1 = reference height above ground surface at which the concentration of the radionuclide is measured, cm, and

D = molecular diffusivity, cm^2/sec .

By assuming $u^* = 40$ cm/sec (appropriate to Oak Ridge area),^{11.13} $z_1 = 100$ cm, and $D = 0.15$ cm^2/sec (diffusion coefficient of krypton in nitrogen),^{11.14} the deposition velocity of krypton is found to be 1.7 cm/sec.

The retention of krypton by the soil is assumed to be limited by the adsorption capacity of the soil for krypton. An estimate of krypton retention by soil is made by also assuming that the amount of krypton adsorbed is proportional to the surface area of the soil. From measurements of krypton adsorption on charcoal (2×10^{-6} g of krypton per g of charcoal at 25°C and 10^{-3} mm Hg partial pressure)^{11.15} and knowledge of the soil to charcoal surface area ratio $[(50 \text{ m}^2/\text{g})/(1000 \text{ m}^2/\text{g})]$ ^{11.16} the amount of krypton adsorbed by soil is estimated to be 10^{-7} of krypton per gram of soil (or 1.2×10^{-7} g of krypton per cubic centimeter for a soil density of $1.2 \text{ g}/\text{cm}^3$). The rate of krypton deposition to the soil is estimated to be the product of the deposition velocity ($V_g = 0.017$ m/sec) and the krypton concentration in the atmosphere ($X = 4 \times 10^{-3}$ g of krypton per cubic meter), or 6.8×10^{-5} g of krypton per square meter per second. At this rate of deposition and during geologic time, the soil has possibly become saturated with krypton and thus may not act as a perfect sink for

the deposited ^{85}Kr . The amount of ^{85}Kr adsorbed on the soil at equilibrium is assumed to be directly proportional to the ratio of radioactive krypton to stable krypton in the atmosphere. For a release rate of 1 Ci of ^{85}Kr per second, the soil load (at equilibrium) at the point of maximum ground-level air concentration would be:

$$1.2 \times 10^{-7} \text{ g Kr/cm}^3 \text{ soil} \times [4 \times 10^{-9} \text{ g } ^{85}\text{Kr/m}^3 / (4 \times 10^{-3} \text{ g Kr/m}^3 \text{ air})] \times 397 \text{ Ci/g } ^{85}\text{Kr} = 4.8 \times 10^{-11} \text{ Ci/cm}^3.$$

Since the adsorption of ^{85}Kr by the soil may not be an irreversible process, the net flux of ^{85}Kr to the soil ($\text{mg cm}^{-2} \text{ sec}^{-1}$) may change as the soil approaches saturation. The deposition velocity calculated from Eq. (2) can be used to estimate only the initial flux of ^{85}Kr to the soil (and cloud depletion by fallout). The flux to the soil would be expected to diminish with time until steady-state conditions were attained. Thus, the determination of the flux of ^{85}Kr to the soil during both transient and steady-state conditions would require further studies.

Krypton might be adsorbed on particulates in the atmosphere and then be deposited on the ground with these particles. The quantity of krypton associated with particles is estimated by assuming that the air contains $1.4 \times 10^{-4} \text{ g}$ of particulates per cubic meter (average for city atmosphere)^{11,17} and, as an upper limit, that the particles can adsorb as much krypton as charcoal does ($2 \times 10^{-6} \text{ g}$ of krypton per gram of particles). Adsorption of krypton on particulates is estimated to be $3 \times 10^{-10} \text{ g}$ of krypton per cubic meter of air, which is negligible compared with the krypton in the atmosphere ($4 \times 10^{-3} \text{ g}$ per cubic meter of air).

Deposition of ^{85}Kr on the ground surface is not likely to create any excessive radiation exposure to man; the critical exposure pathway for ^{85}Kr would be submersion in contaminated air. Similar considerations are now being given to the release of tritiated water vapor to the atmosphere.

11.2 Underground Disposal of Krypton-85

Continuous disposal of ^{85}Kr to suitable geologic formations is one possible means of reducing or avoiding atmospheric release. Although the apparent advantages of underground disposal are its relative simplicity

and its effectiveness, one severe requirement imposed on any disposal formation is that it must be essentially free of vertical channels.

The mechanisms considered by which ^{85}Kr may be retained underground include containment and adsorption. In the absence of convective transport, movement is influenced only by molecular diffusion. These mechanisms are evaluated for quantities of ^{85}Kr and volumes of off-gas assumed to be produced at a 10 metric ton/day reprocessing plant (i.e., a continuous release of 1 Ci/sec of ^{85}Kr in an off-gas stream of $80 \text{ ft}^3/\text{min}$).^{11.16}

Containment

Complete containment of the off-gas in a permeable layer requires an annual storage volume of about $4 \times 10^7 \text{ ft}^3$. In addition, the material overlying the disposal formation must be sufficiently impermeable to prevent the permeation of the gas.

Dynamic Adsorption

Although the adsorption capacity of underground material for krypton is very low, adsorption may be important in the delay of ^{85}Kr breakthrough because of the large mass of material available underground.

The following relation^{11.17} expresses the retention time, t (min), of a gas in the process of dynamic adsorption in a permeable disposal formation:

$$t = \frac{km}{F}, \quad (7)$$

where

$$k = \text{adsorption coefficient} \left[\frac{\text{cc(STP)}}{\text{g}} \right],$$

$$m = \text{amount of adsorbent (g)},$$

$$F = \text{flow rate of the carrier gas (cc/min)}.$$

Assuming an adsorption coefficient of 3 cc/g (the basis for this assumption is detailed in reference 11.16) and isotropic movement of ^{85}Kr , the required thickness of the disposal formation overlying the point of gas injection for a retention time of about 250 years (decay factor of 10^{-7}) is 250 m.

Molecular Diffusion

Vertical movement of ^{85}Kr is assumed to occur in a relatively impermeable formation (e.g., shale) overlying the disposal formation, in which convective flow is negligible as compared with molecular diffusion. Steady-state conditions are assumed as a first approximation. The average travel time, t (sec), of a gas moving by molecular diffusion over a distance, L (cm), and having an initial concentration much larger than the concentration at distance L can be expressed by a derivation of Fick's diffusion laws:^{11.18}

$$t = \frac{L^2}{2D}, \quad (8)$$

where

D = diffusion coefficient of the gas in the underground formation (cm^2/sec).

It is assumed that the diffusion coefficient D of krypton is $0.015 \text{ cm}^2/\text{sec}$. The thickness of the relatively impermeable formation required to reduce the initial radioactivity of the ^{85}Kr by a factor of 10^7 is computed to be 150 m.

Simultaneous Diffusion and Adsorption

The vertical flow of ^{85}Kr through a relatively impermeable formation, in which both molecular diffusion and adsorption take place, is assumed to be analogous to the flow of a contaminant in groundwater.^{11.19}

The following equation is used to estimate the rate of ^{85}Kr movement:

$$\frac{v_a}{v_d} = \frac{1}{1 + \frac{QS}{PC_0}}, \quad (9)$$

where

v_a = velocity of flow of ^{85}Kr retarded by adsorption,
 v_d = velocity of flow of ^{85}Kr moving by molecular diffusion
 (1.5 m/yr).

Q = sorption capacity of ground material (10^{-7} g of krypton per g of adsorbent) at C_0 ,

S = bulk density of medium (1.5 g/cc),
 P = porosity of medium (0.2),
 C_0 = initial concentration of ^{85}Kr (1.3×10^{-7} g/cc).

The thickness of a relatively impermeable formation required to reduce the initial radioactivity of the ^{85}Kr by a factor of 10^7 is computed to be 55 m.

Comparison Between Stack and Ground Level Releases

Some ^{85}Kr might reach the ground surface following underground disposal and be dispersed into the atmosphere as a ground-level source. Since the radioactivity of the ^{85}Kr is assumed to be reduced by a factor of 10^7 as the gas moves underground, air concentrations would be up to 7 orders of magnitude lower than those following a release from a 100-m stack.

Conclusions

The present evaluation indicates that, considering adsorption and molecular diffusion of ^{85}Kr , underground disposal of ^{85}Kr from reprocessing plants may be feasible, provided the right geologic setting is available at the plant site. Requirements for the complete containment of ^{85}Kr in a permeable layer are severe, and finding a suitable site for this operation would be extremely difficult.

11.3 Safety Evaluation of Tank Storage

In the event of a leak of radioactive liquids from a high-level waste storage tank or pipe line into the surrounding soil, localized "hot" spots, exterior to the primary container, are likely to develop. The consequences of such a leak are directly related to the temperature rise in, and adjacent to, the contaminated zone. Since tank leaks have occurred in actual practice, the probability of such a failure is finite. Fortunately, these leaks did not result in a major release of radioactivity. 11.19, 11.20

Tank studies for the Oak Ridge environment have thus far characterized hypothetical high-level wastes in storage, considered the loss of cooling accident and the resultant atmosphere transport and dose equivalents associated with the vented material, and estimated the underground movement of several radionuclides.^{11.21, 11.22} This study is concerned with the temperature rise in Conasauga shale resulting from fission products that may leak from a tank.

Information developed previously on the construction details and contents of a 1-million-gal acid waste storage tank is used as the starting point for the study. The tank, 85 ft in diameter by 35 ft high, is made of stainless steel and is contained within a steel-lined concrete vault. When filled, the tank contains 6.8 billion curies of fission products in a 5.7 M HNO_3 solution and produces heat at 72 million Btu/hr. Decay heat is removed to maintain the solution temperature at 140°F.

Steady-State Approximation

A spherical shell geometry and thermal equilibrium are assumed as a first approximation to estimate the magnitude of the thermal problem in contaminated Conasauga shale. Figure 11.2 shows the simplified model and the heat-generating capacity of the contaminated shale by zones. A solution to the spherical shell geometry is described by Etherington.^{11.23} The tank is ignored as a heat sink, and a heat sink is assumed to be located at the edge of a variable-sized non-heat-generating region. To define the limits of temperature rise, two cases are considered. The first assumes that liquid waste is retained in the shale pore volume, and the second assumes that liquid is not retained in this way. The source strength is listed for each zone, and the volume occupied by each zone is normalized to 1 gal of waste. For example, if a leak of 1000 gal occurs and liquid waste is retained by the shale pores, then the volume of zone 1 is 150 ft³ and the heat-generating rate in this zone is 30,000 Btu/hr.

When acid waste leaks from a tank, it will be neutralized by the buffering action of the shale (260 meq of H^+ per 100 g).^{11.21} Zone 1 depicts the acid zone; the remaining zones are neutralized. Soil loadings are estimated from studies (of radionuclide uptake by soils) conducted at ambient temperatures and from judicious application of these results to

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ZONE	LIQUID RETAINED		LIQUID NOT RETAINED	
	BTU/FT. ³ -HR.	FT. ³ /GAL.	BTU/FT. ³ -HR.	FT. ³ /GAL.
1	200	.15	61	.15
2	280	.05	220	.06
3	250	.09	140	.25
4	33	.18	4.7	2.80
5	.45	.01	.05	.73

Fig. 11.2. Configuration and Characteristics of Contaminated Soil Zones.

the analysis.^{11.21, 11.24} Values of thermal conductivity of unweathered Conasauga shale range from 1 to 2 Btu/m-ft-°F when measured at 30 to 33°C.^{11.25} Similar data do not exist at significantly elevated temperatures. For this study, it is assumed that the thermal conductivity of shale increases gradually with increasing temperature and follows the pattern observed in metal systems.^{11.26} In all likelihood the thermal conductivity of shale will decrease as temperature increases, especially when water is lost from the shale. Thus, the temperature rise estimated in this preliminary analysis is likely to be lower than that which may actually occur.

Figure 11.3 shows the temperature attained in the center of the spherical system as a function of leak volume. Maximum temperatures increase with the volume of leak, the retention of liquid in pore spaces, and the absence of a heat sink. For a leak of 1000 gal, temperatures range from 870 to 1250°F.

Transient Solution

Transient temperatures are now being investigated as a function of time and space for a system that includes a variable-sized cylindrical geometry representing the contaminated zone, and variably spaced heat sinks located at the tank, at the groundwater table, and at the ground surface.

A digital computer program, TOSS, contains many of the requisites for solving the transient problem for a multivariate system.^{11.27} This program has been adapted for our needs and has the capability of calculating the temperature distribution for a three-dimensional, multiregional problem having internal heat generation. A number of cases are now being analyzed. Studies are also under way to evaluate the diffusivity, or specific heat, and the thermal conductivity of Conasauga shale as functions of temperature.

Fig. 11.3. Steady-State Temperature for Spherical Geometry.

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