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Dewey Richard Andersen
Iowa State University

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COATED DIATOMITE FOR TREATMENT OF RADIOACTIVE WASTES

by

Dewey Richard Andersen

A Dissertation Submitted to the
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The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Sanitary Engineering

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Dean of Graduate College

Iowa State University
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Ames, Iowa

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INTRODUCTION

Man has always been subjected to low levels of radioactivity from natural sources such as cosmic rays and the decay of radionuclides present in the air, soil and water. Since the discovery of X rays by Wilhelm Konrad Roentgen in 1895, man has also been exposed to additional sources of ionizing radiation. Within a few months after the discovery of X rays, man became aware of some of the damaging effects of ionizing radiation. However, due to the latent nature of much of this damage, many unfortunate incidents occurred before the present radiation safety standards were developed. Even today these standards are being revised as additional data is obtained from various sources regarding damage from radiation exposure.

Fortunately, however, studies were made of many of the incidents of known radiation damage, and recommended safety standards had been established prior to the advent of World War II and the atomic bomb. Thus, the nuclear industry recognized the need for radiation safety standards from its inception. Since wastes from the nuclear industry also contain varying levels of radioactivity, the need for close supervision and control over the storage, handling and disposal of such wastes was recognized.

There are three general concepts used for handling radioactive wastes. These are (1) dilute and disperse, (2) concentrate and contain, and (3) delay and decay. The first two concepts are also widely used in the treatment and disposal of other industrial wastes. However, the third concept, delay and decay, is primarily of importance to the nuclear industry. Temporary storage of radioactive wastes results in the natural decay of a portion of the radionuclides present. In the case of short-lived radionuclides, this may provide sufficient decay for the subsequent release of the wastes to the environment.

Radioactive wastes may be grouped into various classifications. However, the two more common classifications are based upon (1) the physical state of the waste and (2) the level of radioactivity. In classifying radioactive wastes according to their physical state, the three normal groupings, gaseous, liquid, and solid, are used. Gaseous radioactive wastes are generally vented to the atmosphere through tall stacks. In this manner, dispersion and available dilution is utilized. In some cases, pretreatment may be provided to remove specific radionuclides, or to reduce the overall level of radioactivity of such wastes to a level such that their release to the environment would not create a radiological health hazard.

Solid radioactive wastes are generally disposed of by burial in the ocean or in isolated land sites. Again, disposal of such wastes is closely supervised and controlled so as to prevent the release of excessive quantities of radionuclides to the environment. If such wastes are combustible or compressible, the bulk of such wastes may be reduced by incineration and/or compaction prior to final disposal. In addition, such wastes may be encased in concrete or other materials and sealed in steel drums. In land burial sites, compartmentized concrete cells may be constructed for burial of certain wastes. These burial sites are placed in areas which have good surface drainage and preferably relatively impervious soil.

The composition and the level of activity of liquid radioactive wastes vary considerably. As a result, the methods of handling, treating and disposing of such wastes are also quite diverse. The liquid wastes may be alkaline, acid, or neutral and may contain relatively large quantities of dissolved and suspended non-radioactive solids. The presence of such solids may or may not be of importance, however, in evaluating the indicated treatment process or disposal method.

In the nuclear or atomic energy industry, usage has resulted in the arbitrary classification of liquid radioactive wastes according to their level of activity as follows: (1) low-level for wastes having activities measurable in microcuries per liter or gallon; (2) intermediate-level for wastes having activities measurable in millicuries per liter or gallon; or (3) high-level for wastes having activities measurable in curies per liter or gallon (48).

This study was concerned with the development or modification of a method for converting an aqueous radioactive waste to a solid waste for disposal. It involved (1) coating diatomaceous earth with a base exchange material, (2) removing a specific radionuclide from solution with this material, (3) converting the used product into glass for final disposal, and (4) performing durability studies upon the final product.

PURPOSE

Where available dilution is sufficient, radioactive wastes may be released to the environment without treatment. However, the available dilution is often insufficient. In which case, some degree of treatment must be provided for the wastes prior to their release. This study was concerned with the modification of an existing method of treating low-level aqueous radioactive wastes.

For some aqueous radioactive wastes, filtration and ion-exchange serve as partial or complete treatment. Normally, this treatment is provided in two stages or units. Thus, the incorporation of these treatment units into a single stage could be advantageous because of its simplicity, convenience, and ease of operation.

Most of the significant, longer-lived radionuclides are cationic. Therefore, the incorporation of a base exchange medium into the filter should result in the removal of the soluble radiocations by the base exchange process while radionuclides associated with the particulate matter would be removed by the filtration process. The combined removal processes should provide significant treatment or decontamination for wastes passing through the filter.

Since diatomite (diatomaceous earth) is often used as the filter medium for aqueous radioactive wastes, this study was concerned with the development of a suitable base exchange coating for this material.

In the proposed treatment process, the removed radionuclides would be concentrated in the used filter cake. Therefore, the disposal of this material must also be considered. This material may be disposed of by various methods. Some of these methods are (1) storage of the used "diatomite", which will henceforth be referred to as coated diatomite, (2) incorporation of the used, coated diatomite in concrete, asphalt, plastics, or other suitable materials, or (3) the conversion of the used, coated diatomite into glass.

Since diatomite is primarily composed of silica, one logical process for the final disposal of this material might be the conversion of the used coated diatomite into glass. This process should also provide for maximum volume reduction. As a result, this is the method of disposal studied in this project. In addition to converting the coated diatomite into glass, a limited study was also made to determine the chemical durability or apparent corrosion rate of the resulting glass.

PROCEDURES

Preparation of Coated Diatomite

The base exchange coating used for the diatomite in this study was an inorganic zeolite. The procedure finally adopted for sample preparation was as follows:

1. 422.5 ml of 40° Baumé sodium silicate solution was mixed with distilled water to make five liters of solution.
2. 1000 g of flux calcined diatomite filter aid, Celite 545, which is a product of the Johns-Manville Corporation, was added to the solution and the resulting mixture was stirred for approximately 15 minutes.
3. 1667 ml of solution containing 20 g of NaOH and 181.67 g of sodium aluminate, NALCO 680, which is a product of the Nalco Chemical Company, was added to the mixture with stirring.
4. At the onset of gellation, the mixture was poured into shallow pans to form "cakes" approximately one inch thick. These were left at room temperature for approximately two hours.
5. The samples were then frozen at -20°C., thawed, and washed.
6. The washed samples were dried at approximately 65-80°C.
7. Finally, the samples were sieved through a 35 mesh

screen to obtain a more uniform particle size.

(See Figure 1 for a picture of the final product.)

Base Exchange Capacity Determinations

It is questionable whether base exchange material such as that prepared in this study would be regenerated and reused. Therefore, it was felt that the determination of absolute base exchange capacity or of the operating exchange capacity by the normal procedure was of limited value.

As a result, the base exchange capacity was determined in the following manner. Twenty grams of the coated diatomite were placed in a vertical, glass column 1.3 inches in diameter. The coated diatomite was supported on a pad of Pyrex wool. The softening or flow-through rate was regulated by means of a stop cock assembly, which was connected to a one hole rubber stopper inserted in the base of the column. Hard water was introduced into the top of the column through tygon tubing connected to a 20 liter, overhead water reservoir. (See Figure 2.)

In order to obtain a uniform bed of coated diatomite, a small volume of distilled water was placed in the columns prior to the addition of the coated diatomite. Particles which adhered to the sides of the column were washed down with distilled water. When necessary, a glass stirring rod was used to smooth the surface of the bed. In addition, the first

Figure 1. Uncoated diatomite, Celite 545 filter aid (No. 1) and coated diatomite, Sample 136D (No. 2)

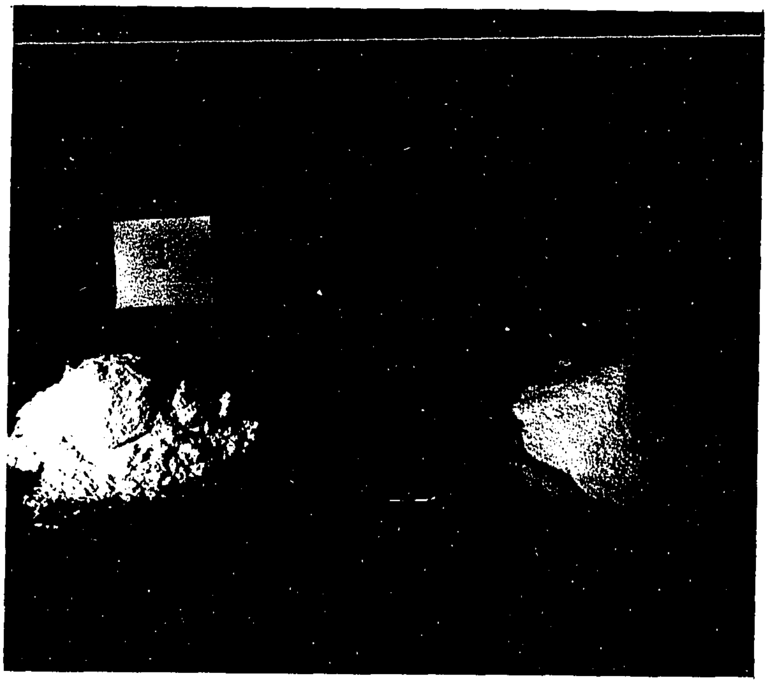
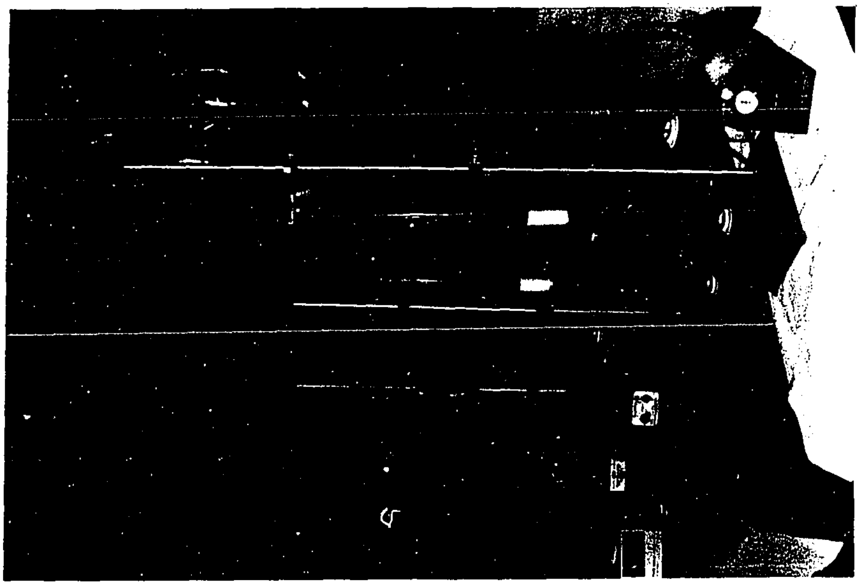
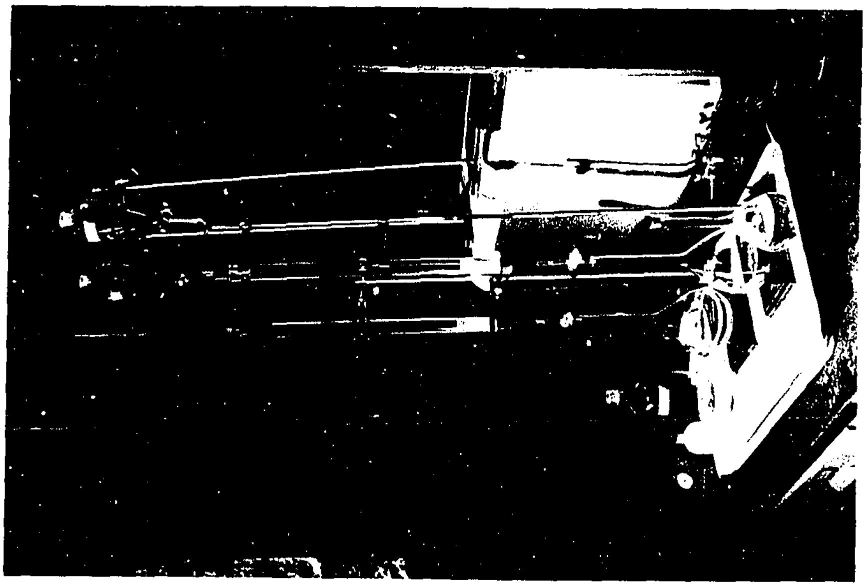


Figure 3. Apparatus used for radioactivity removal study

Figure 2. Apparatus used for base exchange capacity determinations





150 ml of distilled water passing through each column were recirculated, thereby, minimizing the loss of fines. Before determining the base exchange capacity of the coated diatomite, the distilled water in the column was drained to the top of the bed. Thus, dilution would be negligible and was ignored in determining the base exchange capacity. The depth of the coated diatomite bed was approximately 3.4 inches.

Hard water was prepared according to recommendations set forth in a bulletin published by the National Lime Association (27). The hardness of the water used for the base exchange determinations was approximately 400 mg/l as $CaCO_3$, of which approximately two-thirds was due to calcium chloride and the remainder was due to magnesium sulfate. The calcium hardness was determined prior to the addition of the magnesium sulfate. The hardness was determined with standard TitraVer solution and MonoVer indicator (25).

During the test, effluent from the column was collected in 250 ml graduated cylinders. The rate of flow was adjusted to approximately 34-35 ml per minute, which was equivalent to approximately 1 gallon per minute per square foot of bed area. This value is comparable to filtration rates commonly used for diatomite filters. The runs were terminated when the effluent hardness increased to 10-15 mg/l as $CaCO_3$.

Removal of Radionuclides on the Coated Diatomite

Strontium-89 was used to determine the removal efficiency of the coated diatomite for radionuclides. The apparatus used for this portion of the study was similar to that used in determining the exchange capacity of the coated diatomite (see Figure 3). However, the runs were terminated prior to breakthrough. Also, the effluent from each column was collected in a 2000 ml volumetric flask. A separatory funnel served as overhead storage for each column. Again, each column contained 20 grams of coated diatomite.

For each column the strontium-89 was diluted to 1010 ml with hard water. Three 10 ml aliquots of this solution were pipetted into counting planchets. These were evaporated to dryness and counted in an end-window proportional counter. The remaining solution was passed downward through the column of coated diatomite. Since the effluent was collected directly in volumetric flasks, flow measurements and adjustments were not made during the runs. Instead, the average rate of flow was determined at the conclusion of each run and varied from 0.6 to 1.4 gallons per square foot per minute. Due to a variation in the available head, there was some variation in the rate of flow during the run. At the conclusion of each run the equipment was rinsed with distilled water. This rinse water passed through the column and was collected in the same receiving flask. However, the rinsing operation was not considered in determining the average rate of flow. The effluent was diluted to 2000 ml and three 20 ml aliquots were pipetted into planchets. These were evaporated and counted for radioactivity thereby enabling the determination of the removal efficiency of the exchange bed for the strontium-89. All planchets were two-inch diameter, concentric ring, stainless steel planchets.

The used coated diatomite was removed from the columns and dried for use in the glass disposal studies. Water used for rinsing the columns was added to the respective radioactive, coated diatomite samples. The coated diatomite was then dried in a drying oven at 98°C.

Glass Preparation

One phase of this study involved converting the coated diatomite into glass. Two of the final glass samples prepared contained the coated diatomite used in the strontium-89 removal study. A comparable nonradioactive glass sample was prepared at the same time and was analyzed for chemical composition. In all cases, the components were mixed dry and were melted in a muffle furnace. Whenever the mixture contained strontium-89, the container used for mixing the components was rinsed with distilled water. The rinse water was added to the mixture in the crucible thereby minimizing the loss of strontium-89 from the mixture. Melted glass samples were air cooled at room temperature. All final samples were melted in fire clay crucibles.

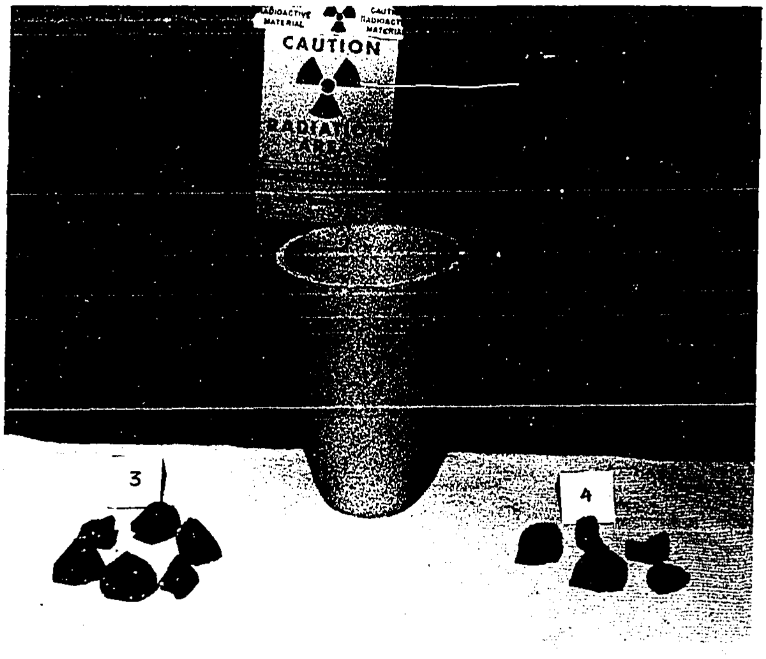
Chemical Durability Study

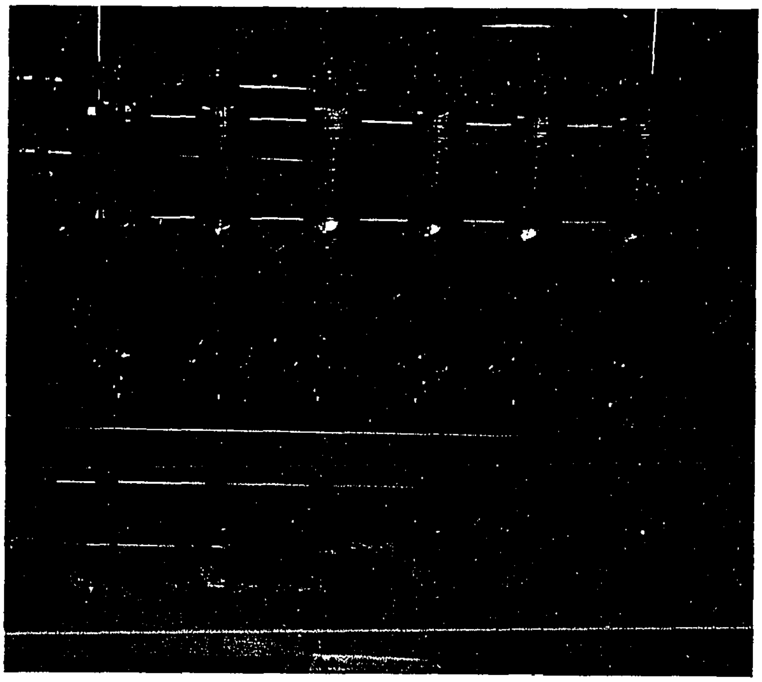
A study was made to determine the chemical durability or apparent corrosion rate of two radioactive glass samples (see Figure 4). Sample preparation involved crushing the glass samples in a steel mortar and pestle, sieving by hand for 15 minutes, and retaining the -40+60 mesh size portion for the leaching study. Following sieving, the retained glass portion was backwashed with distilled water in a Büchner-style, fritted disc, filtering funnel to remove adhering dust particles. The glass particles were then washed with acetone and dried at 110°C.

After drying, one gram portions of each glass sample were placed into crimped bags of 250 mesh stainless steel wire cloth. Three one gram portions were used of each of the two initial glass samples. Each of the stainless steel bags was made from a piece of cloth 3 inches by $1\frac{1}{4}$ inches. Each bag was then suspended by a constantan wire in a reflux condenser and submerged in 100 ml of distilled-demineralized water in the 250 ml Pyrex receiving flask (see Figure 5). The water was boiled continuously until its removal and replacement with fresh water. After a short initial leaching period, all subsequent water samples were boiled for seven continuous days

Figure 4. A fire clay crucible and radioactive glass samples 3 and 4

Figure 5. Apparatus used for chemical durability tests on radioactive glass samples


RADIOACTIVE MATERIAL
CAUTION RADIOACTIVE MATERIAL
CAUTION
RADIATION AREA
3
4



prior to being replaced. After each run, the flasks were rinsed with 10 ml of 0.1 M HNO_3 followed by two 10 ml rinses with distilled-demineralized water. These rinses were added to the leachate, which was evaporated and counted for radioactivity.

The leaching study was terminated after completion of six seven-day leaching runs. The glass was then removed from the bags, dried and weighed. At the conclusion of the leaching study, the receiving flasks and condensers were rinsed with dilute HF to remove any radioactivity which might not have been removed during the normal rinsing operation. These rinses were evaporated separately and counted for radioactivity. Throughout this study relative values are used for comparing radioactivity determinations.

BACKGROUND INFORMATION

Treatment, Handling, and Disposal of Aqueous Radioactive Wastes

As previously mentioned, there are various methods which are being evaluated or utilized for the disposal of aqueous radioactive wastes. Several of these methods are modifications of processes used at other installations and are, thus, quite similar.

High-level wastes

Storage of liquid radioactive wastes, particularly wastes having high levels of radioactivity, has been practiced as a means of handling such wastes since the early development of the nuclear industry during World War II. Initially this method was used because adequate methods of treatment were not known and the development of the atomic bomb was of prime importance (43). Storage or containment in this manner deferred treatment until acceptable methods of treatment could be developed and at the same time protected the public against excessive radiation exposure. Although this method of handling high-level aqueous wastes is, and was, considered a temporary solution, it is still the primary method of handling such wastes.

Wastes handled in this manner may be concentrated prior to storage. They are then stored in stainless steel tanks, which are in turn enclosed in concrete or stainless steel tanks or saucers designed to retain all possible leakage. In addition, monitoring is provided so that corrective action can be taken if a leak should develop. Some tanks are designed with heating coils or hot air to enhance the evaporation and self-concentration and solidification of stored wastes (44). Cooling coils may also be provided to prevent excessive temperature rises (17). Effluent vapor is condensed and monitored for radioactivity. Sufficiently decontaminated condensate may be wasted or diverted to lower-level radioactive waste treatment facilities. The remaining condensate is returned to the storage reservoir. The actual design and construction of the required storage tanks vary depending upon the nature of the waste and the hydrological, geological and climatical characteristics of the region.

In most cases, the anticipated useful life of the storage tanks is insufficient to provide for the natural decay of the contained wastes to levels of radioactivity suitable for release to the environment. Therefore, additional containment or treatment will need to be provided. Thus, although this is the method which has generally been used for storing high-level wastes, it does not usually provide for "ultimate" or final disposal in the original container. However, as previously mentioned, some studies are being made on in-tank solidification, ITS, which—if successful—might serve as a means of final disposal.

Pot calcination, Potcal, is one process being investigated as a method of final disposal. This process involves the continuous introduction of concentrated aqueous radioactive wastes, together with possible chemical additives to minimize the volatility of radionuclides, into a calcination pot where further evaporation occurs. When the pot is filled with solids, the feed is stopped and the contents are heated to provide calcination. The temperature required for calcination depends upon the waste being treated. Some reported temperatures varied from 350°-900°C. (15,19,20). Disadvantages of this process are progressively poorer heat transfer, non-uniform rate of off-gas release, and the possibility of foaming, dusting, and exothermic reactions (36). However, final disposal is quite simple since the porous calcined waste may be sealed in the calcination pot for burial. Reportedly, some of the pots used for storing calcined wastes are 5-24 inches in diameter and 78-88 inches long (6,11).

There are several modifications to this process. In one of these, spray calcination, atomized waste is introduced at the top and passes downward along walls heated to approximately 800°C thereby calcining it (36). The calcined droplets are collected in a pot below the heated column and may be contained for final disposal, or they may go to a continuous melter. Spray calcination has the advantage of having only a small volume of material in the heated column at any given time and is, therefore, safer from exothermic reactions. It also provides a more constant flow of off-gases. However, unless the product is converted to glass, it has a low density.

Another modification of the calcining process is the fluidized bed calciner (2,22). In this process the waste feed is mixed with air and is injected into the fluidized bed by means of spray nozzles spaced around the periphery of the calciner. The fluidized bed consists of alumina particles which are maintained in a fluidized state by means of hot air introduced into the calciner through a porous bottom. Additional heating coils may be placed in the bed. The temperature in the bed is maintained at approximately 400°-500°C and serves to oxidize the spray as it is deposited on the suspended alumina particles. Excess solids are either withdrawn from the bottom or from an overflow line. Difficulties encountered with this process are the large quantity of off-gas, fines, limited operating temperature, and the inability to handle self-heating wastes (36).

Reportedly, the world's first production facility for converting high-level liquid wastes to solids was a fluidized bed calciner (10). From December 1963 to October 1964, about 512,000 gallons of waste containing up to 40 curies per gallon were calcined in an air fluidized bed at 400°C at the Idaho Chemical Processing Plant. The final product was essentially amorphous alumina. It had an average bulk density of 57.1 lb/ft^3 and a total volume of 7,500 ft^3, which represented a volume reduction of 9.3. Off gas was decontaminated by spray quench towers, a venturi scrubber and associated entrainment separators, silica gel adsorbers and high efficiency filters. The feed wastes were from processing aluminum-uranium alloy fuel.

The Rising-Level-Potglass, RL-Potglass, process is similar to the Potcal process. However, in this process, glass forming additives are either added directly to the pot or to the wastes entering the pot (11,15). Thus, upon sufficient heating, hopefully at $\leq$900°C., glass is formed directly. (In the Potcal process, glass forming additives may or may not be added.) In the RL-Potglass process there are three phases present during the filling operation. These are liquid glass on the bottom, a small solid interface in the middle, and a small pool of aqueous supernatant on top. Overhead vapors are condensed and returned to the evaporator (15).

The RL-Potglass process is largely in the developmental stage. Difficulties associated with this process are corrosion, volatilization of radionuclides, foaming, localized overheating, and the production of a suitable glass at a relatively low melting temperature. However, products from this process should be safer and more economical to store than those from the Potcal process because the glassy solids have a higher degree of thermal conductivity and are less soluble (11). Studies are also being made toward the development of a suitable continuous glass melting process.

Other processes are also being considered for fixing radioactive wastes in glass. One of these processes involves the addition of phosphoric acid to aqueous fuel recovery wastes (54). Additional metal ions, such as iron, may be added to reduce the leachability of the glass. A two stage heating process is used with the final melting temperature at 1100-1200°C. The off-gas is condensed and filtered.

Leaching studies have been made upon phosphate glass containing high level radioactive wastes. Initial tests indicated a leaching rate of 2×10^{-5} g/cm^2-day, which is comparable to window glass (54). However, subsequent leaching studies indicated that leaching rates of 4.4×10^{-5} g/cm^2-day were obtained using typical ground water at Hanford, Washington, which had a pH of 7.8 and a total hardness of 125 ppm as $CaCO_3$, as compared to a leaching rate of 2.3×10^{-5} g/cm^2-day after 38 days of leaching when double distilled water was used (52). It was also found that dry storage was essential if low leaching rates were to be maintained for phosphate glass. It was found that the leaching rate of glass which had been stored under water was twice that for similar glass which had been stored in dry air. Likewise, the leaching rate of glass stored in moist air conditions was ten times that of similar phosphate glass which had been stored in dry air.

One study made using phosphate glass reported a volume reduction of 15-20 fold and a glass density of 2.68 g/cm^3 (51). The melting temperature was approximately 1200°C. It was found that a sodium to iron ratio of one improved the chemical durability of the glass without greatly increasing the melting temperature. Studies made with double distilled water and well water at 25°C indicated leaching rates of $0.2\text{-}2\times10^{-5}$ g/cm^2-day. These values were believed to be high due to insufficient area measurement. Leaching studies were of four-hour duration. However, it was felt that economic storage of the glass product would require containers of sufficient size as to result in a liquidus temperature at the center of the container due to heat evolved from the radioactive decay process. This would result in devitrification and may necessitate consideration of storage as ceramics or porcelains which may be more stable.

Another method of fixing fission products in glass consists of the use of nepheline syenite, an igneous rock having a chemical analysis as follows: SiO_2-60%; Al_2O_3-24%; Na_2O-10%; K_2O-5%; and CaO, Fe_2O_3, MgO, and $TiO_2 \leq 1\%$ (56). This process was developed in Canada. It involves mixing 85 percent weight nepheline syenite with 15 percent by weight CaO, which is in turn mixed with an acidic aqueous radioactive waste which reacts with the nepheline to release silica and form a gel

(55,57). The resulting gel is then dried and denitrified before being fired to 1300-1350°C to form a glass. Studies indicate that the leaching rate of the resulting glass is strongly dependent upon the temperature of the leaching solution. One test showed that the leaching rate at 80°C was 100-200 times that at 25°C (55). Also, the leaching rate for cesium was 10 times that for strontium. Similarly, the leaching rate for sodium was 30 times that for calcium.

In Britain a process dubbed Fingal's Cave has been developed for the disposal of radioactive wastes (16). FINGAL stands for Fixation in Glass of Active Liquors. In this process the fission product waste solution containing nitric acid is mixed with slurried borax and silica. This mixture is pumped into a 6-inch diameter, 5-foot long steel cylinder where it is heated to 1050°C in an electric furnace. After the molten glass has reached a depth of 40 inches, the operation is stopped, the glass is cooled, and the cylinder is replaced and stored. Off-gases pass through a series of filters for decontamination.

Another method of providing for final disposal of aqueous radioactive wastes uses porous ceramic sponges which are soaked in the waste and dried. Some sponges made with diatomaceous earth have a porosity of 66 percent (8,29). By repeated soaking and drying cycles, the sponges may accumulate an equivalent volume of solution of 200-300 percent. The sponges are then fired to approximately 1300°C to obtain a final porosity of approximately zero and to fix the retained radionuclides for final disposal. As usual, treatment of evolved gases is required.

Another somewhat similar method of proposed treatment consists of stirring diatomaceous earth or other solid silica material of similar porosity into a solution of high level wastes (45). After the elements in the solution are absorbed on it, the silica material is separated, dried, and melted. The silica material may be pretreated with a binder such as clay prior to the absorption step.

For glass containing high level radioactive wastes, leaching studies indicate that unprotected storage, particularly under moist conditions, would be unsafe (53). For instance it is estimated that for such a glass containing strontium-90 exposed to moist conditions, a dilution flow of 2000 gal/min-ft^2 would be required. Therefore, disposal of wastes in dry oil wells, dry mine shafts, dry salt mines, or similar locations, or burial in frozen tundra, the desert, or deep areas of the ocean is also being studied. The wastes may be pre-processed by methods such as those previously described, or they may be concentrated and/or mixed with a solidifying material such as cement before disposal (39). Evaporation is commonly used for concentrating high-level wastes. Some lower level wastes may also be handled in this manner.

It should be noted that in all of the previously mentioned processes, the emphasis is on the fixation or containment of the radioactive materials so as to prevent or minimize their release to the environment and does not remove or destroy the radionuclides except by the natural decay process.

Probably the ultimate in radioactive waste disposal, outside of recovery and reuse, would be the actual destruction or conversion of the radionuclides into isotopes which are stable or have short half lives. At least one such method is being studied at the present time (46). This method would involve the use of a "burner" reactor to convert some of the more hazardous radionuclides to stable or short-lived products. In this process, cesium and krypton from a reactor are passed through gaseous diffusion plants where the cesium-137 and krypton-85 are each enriched to 90 percent. They are then mixed with unenriched strontium-90 and fed into the "burner" reactor. After suitable burning times, the irradiated radioisotopes are recycled through the separation processes and back into the "burner" thereby essentially destroying three of the more troublesome radionuclides.

Intermediate and low-level wastes

Whenever adequate dilution is available, the lower level wastes are generally diluted and released to the environment. Also, because of their lower initial activity, the concept of delay and decay finds more applicability to these wastes. At suitable locations, such as at the Hanford Atomic Products Operation in the State of Washington, large quantities of lower-level wastes have been discharged to the soil environment (48). In the soil environment, ion exchange reactions, and the slow rate of ground water movement combine to detain the radionuclides and, thus, to provide for natural decay. In addition, dilution is provided. In certain selected areas, the combined effects provide sufficient decontamination before the wastes reach any area of concern to the general environment.

Once the radioactive wastes have been released to the soil environment, man has lost much of his control over their movement. Therefore, soil discharge should not be initiated in an area until after extensive studies have been made of the geological, hydrological, and demographical characteristics of the area, and these studies have confirmed that no potential hazard exists. Also, an extensive monitoring program should be provided wherever soil discharge is practiced. Such a program is necessary to detect any undesirable movements of the released wastes so that corrective action may be taken.

The concept of concentrating and containing also finds wide use for the lower level radioactive wastes. In some cases, these concentrated wastes may be added to high level wastes for disposal. In other instances, they are handled separately. One method being studied for handling low-level process wastes involves the use of a recycle-scavenging-precipitation-ion-exchange process (30). In this method the process wastes are passed upward through an activated alumina bed to remove phosphate. They are then passed through a precipitation-clarification stage consisting of a conventional type flash mix and coagulation unit followed by an upflow clarifier. This effluent passes through anthracite filters and ion exchange columns before being monitored and released to the environment. Regenerant from the exchange columns is mixed with Grundite clay and returned to the flash mix. Thus, all of the radioactivity is retained in one sludge stream which is then concentrated and air dried prior to being packaged and buried.

Another process which provides for the final disposal of intermediate and low level wastes consists of the use of columns of extruded clay pellets (42). The clay has a base exchange capacity of approximately 1 meq/g. After the exchange capacity of the column has been exhausted, the clay is fired to approximately 950°C, thereby, fixing the removed radionuclides in the fired clay. The fired clay may then be placed into a suitable container for final disposal. If the waste being treated contains significant concentrations of nonradioactive ions, it may be provided with pretreatment to remove these ions and, thereby, obtain maximum utilization of the available exchange capacity in the clay. A similar process used in Britain consists of two columns of treated Fuller's earth. The exchange capacity of the treated Fuller's earth is 0.8 meq/g (24).

Numerous studies have been made using various ion exchange materials. Depending upon the characteristics of the wastes and the availability of exchange materials, natural or synthetic, acidic or basic, inorganic or organic materials have been used. In one study, 100-400 mesh zeolites were used as filter precoat medium on a diatomite filter (5). Also, a mixture of diatomaceous earth and zeolite (clinoptilolite) was used successfully on a pilot plant scale for removing particulate matter and cesium. The degenerated exchange material may be contained and stored or it may be regenerated and reused, thereby creating a concentrated waste solution.

There are also various other methods being investigated for treating lower level radioactive wastes. These include conventional water and waste water treatment processes, phosphate coagulation, chemical precipitation, solvent extraction, clay treatment, metallic dusts, foam separation, evaporation, and electrodialysis.

In all of these processes the bulk of the solution is released to the environment or is reused. However, the concentrated liquid or solid wastes are retained and require additional handling. The concentrated wastes may be contained and stored or buried as is, or they may be given additional treatment. One method which has been used extensively for disposing of these wastes consists of mixing the wastes with cement and burying it in a suitable container in designated burial sites on land or in the ocean.

Asphalt is being studied as a substitute for cement in waste disposal and appears to offer some advantages. One study indicated that the volume reduction for asphalt was twice that for cement and that the leaching rate for the asphalt mix was only about one-hundredth that of cement mix for sodium and cesium-137 (11,18). The asphalt used was a rapid setting, high viscosity, emulsified asphalt. It contained 35 percent water and is defined in Federal Specification SS-A-674b (Emulsion Paving Asphalt) as Type RS-2. After mixing the mix is heated to 160°C to volatilize the water thereby leaving the solids encased in asphalt. Asphaltic products have been prepared which incorporated 20-80 percent waste solids by weight (15). Static leaching rates determined at 25°C were 3×10^{-4} g/cm^2-day for 60 percent (wt) solids for either cesium-137 or sodium and 1.5×10^{-4} g/cm^2-day for 20 percent (wt) solids. These values were the apparent steady state leaching rates.

Some of the attractive features of the use of asphalt are (1) the emulsified asphalt flows at room temperature, (2) the low evaporation temperature minimized the entrainment of radioactive material in the off-gases and the degradation of asphalt, (3) the mixing or agitation rates are relatively low, 100-300 rpm, (4) the process may be operated continuously or on a batch basis, and (5) the soluble and insoluble solids are incorporated into the final product with equal effectiveness (5). Possible disadvantages to this process are the low melting temperature of the asphalt and its relatively unknown stability toward radiation (11).

Ion Exchange

Water has been one of the major factors influencing civilizations throughout history, and, as a result, methods for treating it were devised and successfully employed during the early periods of history. These methods included the use of clays, sands, and chars—substances that owe some of their purifying powers to their ion-exchange properties (31). However, it wasn't until 1845 that Harry Thompson and J. Thomas Way, two English agricultural chemists, recognized ion exchange as a physical-chemical phenomenon. As the name implies, ion exchange is the exchange of an ion, cation or anion, for another similarly charged ion.

After the ion-exchange phenomenon was recognized, numerous investigators studied various natural ion-exchange materials as well as synthetic inorganic zeolites. (Strictly speaking, the term zeolite refers to naturally occurring hydrous silicates present in the cavities of lavas. However, through usage, it is frequently used to refer to all inorganic ion exchange materials and has been loosely applied to all cation exchangers [14].) However, it wasn't until 1935 that Adams and Holmes discovered that crushed phonograph records also exhibited ion exchange properties, and thereby, started the development of synthetic organic ion-exchange materials (26). Today, ion exchange materials are used for numerous applications in industry, including the nuclear industry. These materials may be liquid or solid, acid or base exchangers, and organic or inorganic.

Upon contact with an electrolytic solution, ion exchange materials exchange their replaceable or exchangeable ions for a stoichiometrically equivalent quantity of ions of the same electrical sign or charge. This exchange of ions is usually reversible and may be represented by the following typical equation for cation exchange materials:

$$\underline{2NaZ} + CaCl_2(aq) \rightleftharpoons \underline{CaZ_2} + 2NaCl(aq)$$

where NaZ represents the exchange material in the sodium form and CaZ_2 represents the exchange material following the exchange of cations. Cl represents the corresponding anion in solution and does not enter into the reaction. The underlined compounds are in the solid form. Materials having replaceable or exchangeable cations are called cation or base exchangers while those with replaceable anions are called anion or acid exchangers.

In this study an inorganic cation exchange material, sodium-alumino-silicate, was used. The general formula for this compound is $Na_2O \cdot Al_2O_3 \cdot XSiO_2 \cdot nH_2O$ (7). However, the basic principles involved in the exchange process are the same for organic cation exchange materials and probably for anion exchange materials although they have not been studied as extensively. Various theories have been advanced regarding the mechanisms involved in and controlling the ion exchange process. The ion exchange process will be discussed briefly in this dissertation.

Basically for an ion exchange reaction to occur between a porous solid and an electrolytic solution, there must be (1) a diffusion of the ions in solution to the surface of the solid, followed by (2) a diffusion of the ions into the structure across a depleted film around the particle, (3) an exchange of the ions, (4) a diffusion of the exchanged ions toward the surface, and (5) finally the diffusion of the exchanged ions into the bulk of the solution (31). Thus, there are essentially three diffusion processes. These are diffusion in the solution itself, diffusion across the film surrounding the solid particles, and the diffusion of the ions in the solid particle itself. Generally, diffusion in the solution is not the rate controlling factor unless non-porous solids or very viscous solutions of ionic species of high molecular weight are involved. In very dilute solutions, the diffusion of the ions across the film layer is the rate-controlling process. At somewhat higher concentrations the kinetics is determined by both the diffusion across the film and the diffusion in the solids, and at still higher concentrations diffusion in the solid becomes the sole rate-determining step (31).

Since ion-exchange reactions are reversible, the favored direction is determined by the relative affinity of the ion exchanger for the ions entering into the reaction. There are several factors affecting the affinity of an ion exchanger for ions. Some of these factors are temperature, pH, concentration, valence, and atomic number. Generally, the following empirical rules may be used as a guide in predicting ion exchange reactions (32):

(1) At low concentrations (aqueous) and at ordinary temperatures, the degree of exchange increases with increasing valency of the exchanging ion: $Na^+ < Ca^{+2} < Al^{+3} < Th^{+4}$.

(2) At low concentrations (aqueous), ordinary temperatures, and constant valence, the extent of exchange increases with increasing atomic number of the exchanging ion: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$;

$Mg^{+2} < Ca^{+2} < Sr^{+2} < Ba^{+2}$. (This sequence is the same as that of the decreasing radii of the hydrated ions.)

(3) At high concentrations the differences in the exchange "potentials" of ions of different valence (Na^+ versus Ca^{+2}, etc.) diminish, and in some cases, may reverse.

(4) At high temperatures in non-aqueous media, or at high concentrations, the exchange "potentials" of the ions of similar valence do not increase with increasing atomic number but are very similar, or even decrease.

(5) The relative exchange "potentials" of various ions may be approximated from their activity coefficients —the higher the activity coefficient, the greater the exchange "potential".

Some of the factors which affect the ion exchange process will be discussed briefly in the following discussion. In this discussion, counter ions refer to the mobile ions associated with the ion exchange material or similarly charged ions present in the surrounding solution which may replace or exchange with these ions. Co-ions refer to stationary or fixed charged sites on the framework of the ion exchanger or similarly charged ions present in the surrounding solution.

Probably the largest single factor responsible for the selectivity or affinity of ion exchangers for various cations may be explained by the ionic hydration theory (32). Since ion exchange is controlled by electrostatic forces, presumedly coulombic, the adsorbability of the various counter ions will depend on their relative charges and ionic radii. According to this theory, it is assumed that ions in aqueous solutions are hydrated and that the degree of hydration for cations increases with increasing charge and decreasing crystallographic radius. Thus, the counter ions having the higher valences and smaller hydrated radii are preferentially selected by the ion exchanger.

In some cases, the larger organic ions and inorganic complexes may be excluded from the ion exchange material by screening or sieve action. Likewise, molecular sieving or screening may occur. In fact, molecular sieves are manufactured for this purpose in a manner similar to that used for preparing the coated diatomite used in this study (33).

There are also interactions in the ion exchanger which affect its behavior. For instance, solvation results in charge-dipole interactions between the ions and solvent molecules. Also, ion-pair formation and association between the counter ions and the fixed ionic groups is important. In this case, the ion exchanger prefers the counter ion which forms the stronger ion-pairs or bonds with the fixed ionic groups.

In order for the ionogenic groups of an ion exchanger to act as fixed charges requiring counter ions, they must be ionized. Thus, nonionized groups do not contribute to the exchange capacity of the material. In the case of strong-acid and strong-base groups, they are essentially completely ionized under all conditions. However, the weak-acid and weak-base groups are predominantly nonionic at low and high pH values, respectively. The degree of ionization of the ionogenic groups depends on the acid or base strength of the groups and on the pH in the exchange material. Thus, their exchange capacity depends upon the pH.

Ion exchange materials have a reservoir or supply of exchangeable counter ions or ionogenic groups. This reservoir may be characterized in quantitative manner by the capacity which, in common usage, is defined as the number of counter-ion equivalents in a specified amount of material. On a weight capacity basis, the capacity is given in milliequivalents per gram or equivalents per pound; on a volume capacity basis, it is given in terms of equivalents per cubic foot. For weight capacity evaluations, the weight of the material is determined when the material is completely converted to a specific ionic form and is devoid of sorbed solutes and solvents. Reported exchange capacities of inorganic ion exchangers range up to 12 meq/g for some zirconium phosphates (26).

The strength of a polymer, whether organic or inorganic, is a function of the degree of crosslinking of its polymeric structure. In sodium-alumino-silicates, such as used in this study, silica is the crosslinking component. Thus, the higher the silica content the stronger the product is mechanically. However, increasing the silica content also reduces the exchange capacity and, as a result, a compromise is usually made to obtain the best over-all product. Studies with zeolites indicate that the ratio of silica to alumina also affects the cation selectivity (1). Since all zeolites have approximately the same anionic radii, it is believed that anionic site separation distance becomes the controlling factor in cation selectivity. Alumino silicate ion exchange material used at the Oak Ridge National Laboratory in 1962 had an exchange capacity of 1.84 meq/g. Inorganic zeolites are generally more stable under radiation exposure that organic resins.

There are various methods used for preparing sodium-alumino silicates. Variations include the method of gellation, the proportions of the various chemicals, and the handling and temperature during the curing, dewatering, and drying stages. Considerable work has been done at Iowa State University involving the use of freezing for dewatering the gell (4,23, 50). Also, some work was done towards perfecting the use of pressure for dewatering the gell. Reportedly, pressure dewatering is currently used for this type of ion exchange material (7,14). In this study, the freezing method was used for dewatering the gell.

Basic Glass Composition—Property Relationships

Although several plausible theories have been advanced, the origin of glass manufacturing remains in doubt. The oldest glazes and glass discovered are believed to date back to 12,000 and 7000 B.C., respectively (3). However, the art and science of glass making has often been jealously protected by guilds and, to some extent, by governments. Even today, advances in the technology of glass making are often closely guarded secrets.

All known glasses are undercooled liquids. On cooling from the molten state, all glasses pass through a temperature or temperature range in which the liquid becomes unstable with respect to one or more crystalline compounds. At and below this temperature the glass can be devitrified, that is, crystallized by appropriate heat treatment (37). Devitrification is the chief factor limiting the range of glass compositions. Devitrification may occur quite readily if errors are made in the composition of the mix or in the technique of glass making.

Silica glass possesses many desirable properties. However, the high melting point of pure quartz and the difficulty of working the resultant glass limit its use. As a result, other oxides are added to flux the silica and to reduce the viscosity of the molten glass. In this respect, soda, Na_2O, is relatively cheap and is a very effective flux. The addition of 25 percent by weight of soda to the mix lowers the melting point from 1710°C to 793°C. However, the resultant sodium silicate glass having this composition is readily soluble in water. Therefore, if a more permanent or durable glass is desired, other stabilizing oxides must be added. Normally, lime, CaO, is used for this purpose since it is effective and relatively cheap. If too much lime is used, however, the mix is hard to melt and tends to devitrify. Phase equilibrium diagrams of the ternary system Na_2O-CaO-SiO_2 are very useful in determining the desired compositions. These soda-lime-silica glasses, which are often called "lime" glasses, comprise the majority of all glasses melted today (40).

In addition to the three main oxides—silica, soda and lime—various other chemicals are usually present. These may be a result of impurities in the raw materials and corrosion of the pots or refractories, or they may be deliberately introduced into the mix. These impurities serve various functions. Some of these are (1) to further depress the melting point or to increase the rate of melt, (2) to act as fining agents, (3) to add brilliance, color or lustre, (4) to improve the chemical durability, (5) to change the coefficient of expansion, (6) to improve the workability, or (7) to reduce the tendency to devitrify.

The addition of alumina generally improves the chemical durability, reduces the tendency toward devitrification, and lowers the coefficient of expansion of the resultant glass. In low concentrations, it may also lower the melting point. Potash, barium oxide, and fluoride also tend to increase the chemical durability and to reduce the tendency toward devitrification, but they increase the viscosity of the melt. Boric oxide increases the melting rate and acts as a fining agent in addition to lowering the coefficient of expansion of the resultant glass and increasing its chemical durability. Titania, TiO_2, lowers the viscosity of the melt and increases the chemical durability of the resulting glass.

When glass is used for fixing radioactive wastes, additional ingredients may be added to reduce the volatility of certain radionuclides. For instance, the addition of formaldehyde and/or sugar reduces the volatility of ruthenium by reducing the amount of free acid in nitrate wastes (9). Other possible inorganic reducing agents are phosphite and hypophosphite, which would be oxidized to phosphate, which is a glass former. Sulfate volatilization may be controlled by adding an excess of a volatile acid or by adjusting the amount of other elements such as sodium and magnesium (19).

Likewise, sulfate may be added to reduce sodium or cesium volatility. The atmosphere in contact with the molten glass may also be adjusted to minimize volatility of specific radionuclides. For instance, a nitric oxide atmosphere has been used to reduce the volatility of ruthenium.

The average composition of container glasses manufactured in 1960 was as follows: silica, 71.7 percent; stabilizing oxides, 13.55 percent; and fluxes, 14.85 percent (56). Of the stabilizing oxides, 11.50 percent was due to CaO, MgO and BaO with the remainder due to the R_2O_3 group. The fluxes consisted of 14.50 percent as Na_2O, K_2O, and B_2O_3 and 0.35 percent as SO_3 and fluorine.

Basically, the glass melting process involves forming sodium silicates and then dissolving the remaining silica, limestone, etc. to form the final glass (35). The homogeneous molten melt is then carefully cooled. During the cooling process, stresses build up in the solidifying mass. As a result, a carefully controlled annealing process is often required to reduce these stresses to acceptable levels.

Chemical Durability or Leaching Tests

At the onset of the nuclear industry and its interest in glass as a means for disposing of radioactive wastes, there were various standardized tests for determining the chemical durability of a glass. The tests varied depending upon the intended use of the glass and served to provide an accelerated means for evaluating the quality of the glass (37). However, none of the tests were considered adequate for evaluating the quality of glass for radioactive waste disposal. As a result, different criteria were established by different investigators and the comparison of results was difficult, if not impossible.

Finally, a committee was formed to establish a standard leaching test for radioactive glass (49). Basically, the recommendations of this committee were that a reflux condenser apparatus consisting of a Soxhlet extractor, a Vycor receiving flask, and "hyper-pure" water be used. Furthermore, the glass sample should be placed in a teflon thimble located in the neck of the receiving flask. The thimble would receive the condensate from the glass finger condenser and would be emptied periodically by means of an intermittent siphon. The temperature of the leaching solution should be maintained at around 70°C. Reportedly, these standards were later simplified to provide for the use of Pyrex in place of Vycor and Teflon and a temperature of 92-98°C in the extraction thimble (21).

Apparently, the proposed standard leaching test has not been widely adopted since recent studies show a considerable variance in the leaching conditions. For instance, one study used glass coupons ground to nominal dimensions of $1 \times \frac{1}{2} \times \frac{1}{4}$ inches and used distilled water at 25°C for leaching studies (53). At least two other studies used -40+60 mesh glass particles for leaching studies (21,41). This powdered glass was washed in distilled water and acetone and dried. One gram samples were then placed into crimped bags of 200 mesh stainless steel wire cloth. The cloth used for each sample was 3 x $1\frac{1}{4}$ inches. Each bag was suspended in 100 ml of boiling, distilled water contained in a 250 ml Pyrex flask fitted with a reflux condenser. After one week of continuous boiling, the leachate was removed, evaporated, and counted for activity. The flask was rinsed and refilled with 100 ml of fresh water. In one study, the flask and bag were rinsed three times with distilled water. In another, the flask was rinsed with two 10 ml portions of 0.1 $\underline{M}$ HCL and two 10 ml portions of distilled water. The rinses were added to the leachate.

In the latter two studies, the mean leaching rate was calculated in terms of the apparent corrosion rate, i.e., the depth of a uniform volume increment at the surface of the product which would contain the weekly eluted activity at the initial volumetric activity concentration. The resulting equation was as follows:

$$\frac{\text{cm}}{\text{wk}} = \frac{\text{eluted activity (cpm/wk-g)}}{\text{(surface area-cm}^2\text{/g)(initial activity concentration,cpm/cm}^3\text{)}}$$

The indicated error for these values was determined by the standard deviation of the mean or standard error, $\sigma_{\bar{X}}$, where

$$\sigma_{\bar{X}} \approx \sqrt{\frac{1}{n(n-1)}\sum_{1}^{n}(X_i-\bar{X})^2}$$

where

n = the accumulated number of leachate samples (3× the number of weeks of the chemical durability study since three one gram specimens were used for each glass sample).

In one study, the surface area of the -40+60 mesh glass particles was determined by gas adsorption techniques (21). It was found that all glass having a specific gravity of 2.9-3.6 had a surface area of 125 cm^2/g ±5 percent. It was felt that this was due to a more crystalline structure in the denser material. This value was also used in the other study using this size particles.

In the leaching studies using powdered glass, there were several indicated sources of error (21). These included (1) inhomogenity of the samples, (2) errors in judging a satisfactory degree of fusion, (3) possible erosion as well as dissolution due to nucleate boiling on the submerged glass samples, (4) a variation in the exposed surface area due to possible vapor locks, agglomeration of particles, etc., (5) a possible variation in corrosion rate due to increasingly contaminated water during each weekly run, and (6) errors in measurements such as those due to low counting rates.

Reportedly, the variable erosive effect of nucleate boiling on the surface of the submerged glass leads to a somewhat greater and more variable apparent leaching rate (21). However, it was felt that this method represented a set of conditions more indicative of the effects to be expected if ground water contacted hot stored glasses. Also, it was felt that the sensitivity of the test could be improved by increasing the surface area, hence, the use of powdered glass.

These studies indicated that the corrosion rate in boiling water was 100-1000 times that at room temperature. Also, the corrosion rate varied with the isotope. For instance, for four mixes the corrosion rates for cesium-137 ranged from $(7.74 \pm 0.45) \times 10^{-6}$ cm/wk to $(1.27 \pm 0.08) \times 10^{-5}$ cm/wk while those for strontium-89 ranged from $(9.00 \pm 0.63) \times 10^{-6}$ cm/wk to $(5.47 \pm 0.37) \times 10^{-6}$ cm/wk. Also, the melting temperature and the cooling rate of the glass were very important. For the same mix, underfiring by even 50°C in 1400°C increased the solubility by 50 percent. Slow cooled products were found to be more soluble than those which had been rapidly cooled.

BASE EXCHANGE COATING STUDY

Introduction

Due to the developmental nature of this research, the majority of the samples prepared had limited significance other than to serve as aids in reaching a suitable, final product. Therefore, the results of most of these preliminary samples will not be included nor discussed. Generally, the samples were numbered chronologically.

In addition to the method of sample preparation finally adopted, a process was investigated which involved mixing diatomite with caustic soda followed by a heat treatment process to obtain a base exchange material. Difficulties associated with this process were the degradation of the diatomite and a product of low exchange capacity. As a result, this method of approach was discontinued and will not be included in this discussion.

As previously mentioned, sodium silicate solution, caustic soda and sodium aluminate were the chemicals used for the coating finally selected in this study. However, aluminum sulfate was substituted for sodium aluminate in some of the preliminary samples. The results indicated that the coating prepared with sodium aluminate had a higher exchange capacity. As a result, the use of aluminum sulfate was discontinued.

In the coating process selected, all samples were let set at room temperature for at least 20 minutes after gellation.

In some cases, samples were divided after this initial set and were given different subsequent treatment. Generally, frozen samples were left in the freezer overnight and were then thawed, washed and dried. Unless noted, all frozen samples were spread to a thickness of not over $1\frac{1}{2}$ inches prior to freezing. Non-frozen samples were generally dried at the indicated temperature, washed and re-dried. (A previous study on the preparation of zeolites showed that excessive drying temperatures lowered the exchange capacity of inorganic zeolites (28). As a result, the drying temperatures of most samples reported from this study were $\leq$85°C. The variations in the drying temperatures were due to the fact that the drying oven was being used by more than one investigator.) Prior to the base exchange capacity determinations, all reported samples were sieved through a 35 mesh Tyler Standard Screen to obtain samples of more uniform particles size.

Investigations were made of several factors affecting the exchange capacity of the coated diatomite and its intended use as a base exchange filter medium. The results of these investigations will be presented and discussed separately. However, a compilation of data for most of the coated diatomite samples is given in Appendix A.

Evaluation of Dewatering Processes

There have been at least three methods used for dewatering or drying inorganic zeolites. These are air or oven drying, pressure dewatering and freezing. In this study, air or oven drying and freezing were investigated as methods of preparing the coated diatomite. Reportedly, one of the problems associated with the freezing process was a large amount of fines resulting from the ice crystal formation (23). While this would normally be considered a disadvantage, it would probably be an advantage for the intended use of the coated diatomite.

For this study, the samples were generally divided. In this manner, identical samples could be subjected to various dewatering and/or drying procedures. Samples 89-92 were each divided into three portions. One portion of each sample was placed in a freezer at -5°C. The other two portions of each sample were heated in a water bath at 60°C for three hours. Afterwards, one portion was frozen at -5°C while the other portion was covered and placed on a steam bath at 100°C for 24 hours. Most of the preliminary samples were subjected to temperatures up to 100°C under moist conditions to complete the chemical reaction. This portion of the study was made to determine whether this was desirable or if freezing would be advantageous. The frozen samples were frozen overnight and were then thawed and partially dried at 25°-35°C. All of the samples were then washed and dried at 85°-100°C. The dried samples were sieved before making exchange capacity determinations.

Table 1. Comparison of dewatering processes

Sample No.	Exchange capacity, meq/g A[a]	 B[b]	 C[c]
89	0.48	0.46	0.42
90	0.36	0.34	0.36
91	0.28	0.26	0.25
92	0.45	0.47	0.42
93	0.50	0.51	0.46

[a] After the initial set, samples were frozen at -5°C.

[b] After the initial set, samples were preconditioned at 60°C for three hours before being frozen at -5°C.

[c] After the initial set, samples were preconditioned at 60°C for three hours before being heated in moist atmosphere for 16 hours at 100°C.

The exchange capacities of Samples 89-93 are given in Table 1. For these samples, the exchange capacities of the various portions of the same sample were quite similar. However, the frozen samples generally had a slightly higher capacity. This would indicate that, over the range tested, the temperature had a limited effect upon the final exchange capacity.

Based upon measurements of the depths of the 20 gram samples in the exchange column, the unfrozen samples had a higher bulk density than those which were dewatered by the freezing process. The depth of bed for unfrozen samples averaged about 2.8 inches. For samples dewatered by the freezing process, the depth of bed averaged about 3.4 inches.

During the washing process, the unfrozen samples tended to become gelatinous and to cake. However, samples which had been frozen retained the appearance of small kernels of rice. As a result, samples which had been frozen were more easily washed, dried and sieved. Since sample dryness was determined by visual appearance, it is quite possible that the frozen samples may have been drier than similar unfrozen samples at the time exchange determinations were made. If so, this could account for some of the differences in the exchange capacities and densities noted between frozen and unfrozen samples. However, these effects are believed to be quite small. Since samples which had been dewatered by freezing were easier to process, this was the dewatering process selected.

A comparative study was also made of samples frozen at two different temperatures, -6°C and -20°C (see Table 2). The results of split Samples 104 and 105 indicate that the variance in freezing temperatures had very limited effect upon the exchange capacity of the material. However, after washing, the samples which had been frozen at -20°C appeared to have a smaller particle size. Due to the intended use of the product, this was felt to be advantageous and all final samples were frozen at the lower temperature, -20°C.

Table 2. Comparison of freeze drying processes

	Exchange capacity, meq/g	
Sample No.	Frozen at -6°C	Frozen at -20°C
104	0.57	0.56
105	0.56	0.61

Effect of Washing Samples

For some uses, the coated diatomite may not need to be washed prior to use. Therefore, a study was made to determine the effect of washing upon the final exchange capacity. For this purpose, portions of Samples 115, 116, 122 and 123 were used. The unwashed samples were dewatered on a Büchner funnel prior to drying, however.

The results of this study are given in Table 3. In

Table 3. Effect of washing samples

	Exchange capacity, meq/g	
Sample No.	Washed portion	Unwashed portion
115	0.59	0.57
116	0.48	0.38
122	0.65	0.52
123	0.47	0.41

general, the exchange capacities of the washed samples were significantly higher than those of their unwashed counterparts. Some of the increase in exchange capacity may be attributed to the removal of excess alkalinity during the washing process. However, it is probable that most of this increase was due to other factors such as cleansing the exchange sites, thereby making them more readily accessible. Since the washing process was beneficial, and since this step was relatively easy for samples which had been frozen, all subsequent samples were washed.

Effect of Dewatering and Washing Prior to Freezing

After gellation there is a tendency for the excess liquid to separate from the gell. As a result, a limited study was made to determine if dewatering the sample prior to freezing would be advantageous. Samples 94, 99, 115 and 116 were split for this purpose. Samples were dewatered in a Büchner funnel.

The results of this study are given in Table 4. These results indicate that dewatering the samples prior to freezing had a negligible effect upon the exchange capacity of the final product. Therefore, the simpler procedure, freezing prior to dewatering, was used for subsequent samples.

A limited study was also made to determine the effect of washing the sample prior to freezing. Sample 103 was split for this purpose (see Table 4). It is felt that the results

Table 4. Effect of dewatering and washing samples prior to freezing

	Exchange capacity, meq/g	
Sample No.	Dewatered prior to freezing	Dewatered after freezing
94	0.41	0.48
99	0.38	0.37
115	0.59	0.60
116	0.48	0.45
103	0.53[a]	0.49

[a] Sample was also washed prior to freezing.

obtained from this one sample are insufficient to draw any conclusions as to the effect of this modification of procedure upon the exchange capacity of the product. However, the difficulties encountered in washing the unfrozen sample were sufficient to discourage the adoption of this process.

Effect of Rapid Freezing

Since freezing at a lower temperature appeared to be advantageous, at least from particle size considerations, a study was made to determine whether a change in the rate of freezing at the same temperature might also affect the final product. For this study, two samples were frozen in plastic beakers while two other samples were spread in pans upon gellation.

Samples 119 and 121, which were frozen in plastic beakers, were approximately three inches deep. The depth of the other comparable samples, Samples 117 and 120, respectively, were approximately $\frac{1}{2}$ inch. The results of this study are given in Table 5.

Table 5. Effect of rapid freezing

	Exchange capacity, meq/g	
Sample No.[a]	Spread samples	Frozen in beakers
117, 119	0.62	0.58
120, 121	0.66	0.63

[a] Samples 117 and 120 were spread at the onset of gellation.

This brief study indicates that a rapid freeze may increase the exchange capacity of the final product. After washing and drying, the spread samples appeared to have a smaller average particle size. Thus, even after sieving the spread samples may have had a smaller average particle size and, hence, possibly a slightly greater, readily accessible surface area. If so, this could account for the slightly higher exchange capacity. This same reasoning could be applied to the possible slight increase in exchange capacity for samples frozen at -20°C as compared to samples frozen at -6°C. Due to the intended use of the product, the smaller particle size was considered to be advantageous. As a result, all final samples were spread at the onset of gellation.

Effect of Sodium Hydroxide Additions

It was found that the addition of sodium hydroxide helped to stabilize the sodium aluminate solution. A previous study indicated that the addition of a limited amount of sodium hydroxide to the mixture increased the exchange capacity of the final product (4). Therefore, a study was made to determine whether the addition of sodium hydroxide to the mixture used in this study was beneficial and, if so, the approximate optimum addition. Except where noted, the sodium hydroxide was added to the sodium aluminate solution.

Before evaluating the results of this study, it should be pointed out that the processing and/or chemical additions were not the same for all of these samples. Therefore, a group comparison is impossible. Instead, each sample used in this study had a control sample which was similarly processed and had the same chemical additions, except for varying sodium hydroxide quantities. Sixty grams of diatomite were used for each sample. A compilation of the results of this study is given in Table 6.

Table 6. Effect of NaOH additions upon the exchange capacity

Sample No.[a]	Exchange capacity in meq/g for various additions of NaOH		
	<0.8g	0.8-1.2g	>1.2g
89-1, 94-1, 99-1		0.48; 0.48	0.37
117, 118[b]		0.62	0.58
121, 122-1[b]		0.63	0.65
124, 125[b]		0.34	0.34
128, 132	0.62	0.68	
129, 133	0.62	0.68	
130, 134	0.58	0.62	

[a] Similar samples are grouped together.

[b] The additional NaOH was dissolved in the sodium silicate solution.

It is apparent from Table 6 that the addition of NaOH does affect the exchange capacity of the product. For instance, Samples 128 and 129, which had 0.48 grams of sodium hydroxide added, had exchange capacities of 0.62 meq/g. Their comparative samples, Samples 132 and 133, each had 0.96 grams of sodium hydroxide added and had exchange capacities of 0.68 meq/g. The exchange capacity of Sample 99-1, which had an addition of 6.2 grams of NaOH, was only 0.37 meq/g as compared to 0.48 meq/g for similar Samples 89-1 and 94-1, which had NaOH additions of 0.8 grams and 1.2 grams, respectively. Thus it appears that there is an optimum sodium hydroxide addition.

The optimum sodium hydroxide addition could depend upon several factors such as the ratio of the chemicals added, the chemicals to diatomite ratio, and the quantity of dilution water used. Since the sodium hydroxide was a minor ingredient, 24 grams of sodium hydroxide were added to each mole of sodium aluminate. Thus, the amount of sodium hydroxide added would vary directly with the amount of sodium aluminate used. This simplified subsequent chemical adjustments. For the final mixture selected this amounted to 1.2 grams of sodium hydroxide per 60 grams of diatomite. Based upon the results of this study, this value would be in the upper range for the beneficial addition of sodium hydroxide. As mentioned previously, the optimum sodium hydroxide additions would probably vary somewhat with the mixture; however, additional studies of this effect were not made with the final mixture selected.

Effect of the Order of Chemical Addition

For sample preparation, the diatomite was mixed with one of the chemical solutions. The other chemical solution was then added to this mixture. Gellation occurred regardless of which solution was used initially. Therefore, a brief study was made to determine whether the exchange capacity of the final product was affected by the order of addition.

Two samples were prepared for this study, Samples 96 and

98. Sample 96, which had diatomite added to a sodium silicate solution, had an exchange capacity of 0.48 meq/g. Sample 98, which had diatomite added to a sodium aluminate solution, had an exchange capacity of 0.46 meq/g.

The results of this study indicated that the order of chemical addition had little, if any, effect upon the exchange capacity. All subsequent samples were prepared by adding and mixing the diatomite with the sodium silicate solution prior to adding the sodium aluminate solution.

Effect of Using Soft vs. Distilled Water

For convenience, distilled water was used for preparing and washing the coated diatomite samples. However, if large quantities were to be prepared, it would probably be more economical to use soft water if similar results were obtained. Therefore, one sample was prepared and washed with water softened by sodium-zeolite to determine whether similar coatings could be obtained.

This sample, Sample 139, was prepared and washed with water which had been softened by previous coated diatomite samples. Based upon the initial hardness of 341 mg/l as $CaCO_3$, the sodium ion concentration of this water was 156 mg/l. For comparative purposes, Sample 137 was prepared the same as Sample 139, except distilled water was used. The exchange capacities of Samples 139 and 137 were 0.68 meq/g and 0.64

meq/g, respectively.

These results show that sodium-zeolite softened water may be used for preparing coated diatomite in place of distilled water. Furthermore, the exchange capacity of the final product should be as high as that for similar samples prepared with distilled water. Since only one sample was prepared with soft water, the increase in exchange capacity of this sample was not considered significant. Each of the samples had 0.96 g of sodium hydroxide added to the sodium aluminate solution. By calculation, an additional 0.05 g of sodium was present in the 343 ml of softened water used for preparing Sample 139. Thus, it is possible that, in this case, the additional sodium was beneficial. In actual practice, it may be desirable to adjust the sodium hydroxide addition to correct for the sodium present in the water used for coated diatomite preparation.

Effect of Diatomite Particle Size

Most of the samples were prepared with Johns-Manville Celite 545 diatomite filter aid. It was felt that the use of a coarser filter aid, such as Celite 545, would normally be advantageous since the resulting product would probably be more permeable. However, some samples were prepared from a finer grade of diatomite to determine what effect, if any, this might have upon the exchange capacity of the product.

Two samples, Samples 137 and 138, were prepared for this purpose. Johns-Manville Celite 535 was used for these samples. Celite 535 was also used for Sample 139, but since it was prepared with sodium zeolite softened water, it was not used for comparative purposes for this particular investigation. Comparative samples, which were prepared with Celite 545, were Samples 131 and 136. The results are shown in Table 7.

Table 7. Effect of diatomite particle size

	Exchange capacity, meq/g	
Sample No.	Celite 535	Celite 545
137, 131	0.64	0.62
138, 136	0.79	0.78

Reported mean particle sizes of Celite 545 and Celite 535 diatomite filter aid are approximately 21 microns and 16 microns, respectively. These values may differ somewhat from the current mean particle size of these filter aids, however, due to modifications in the manufacturing process.

These results indicate that slightly higher exchange capacities may be obtained by using diatomite having a smaller mean particle size. This may be due to a slightly larger surface area for coating purposes. Thus, for a given mixture the resulting coating would be somewhat thinner and have a greater surface area, which in turn might provide a slight increase in accessible exchange sites. However, the variance in exchange capacities between samples prepared from Celite 535 and Celite 545 was quite small. No comparison was made of the permeabilities of samples prepared from the two grades of diatomite. However, the permeability of the coarser grade diatomite sample would probably be greater. Since the use of a finer grade of diatomite did not result in a significant increase in the exchange capacity of the final product, and since the permeabilities of these samples were probably lower, all subsequent coated diatomite samples were prepared with Celite 545.

Effect Upon Permeability

Since the coated diatomite would probably be used as a filter medium, it is essential that the resulting filter cake be permeable. Therefore, a limited study was made to compare the permeability of Celite 545 with that of the coated diatomite. A laboratory-scale pressure filter, which had been used extensively for evaluating the permeability of diatomite filter aids, was used for this study.

The filter apparatus consisted of a 500 ml plastic precoat pot, a flat, circular filter septum placed in a vertical plane and a small centrifugal pump. The pump (Model No. 2) was manufactured by the Little Giant Pump Company, Oklahoma

City, Oklahoma, and had a capacity of 255 gph at 3 feet TDH. A magnetic stirrer was used to keep the diatomite in the precoat pot in suspension. During the precoating operation, the filter effluent is recirculated. Thus, any fines which may have passed through the filter during the initial phase of the precoating operation are recirculated and deposited on the filter. Tygon tubing was used for connecting piping. Although a flow meter was incorporated in the effluent piping, flow measurements were made by collecting the effluent in a 250 ml graduated cylinder. The temperature of the effluent was measured. A manometer was used for determining the pressure differential or head loss across the filter septum. Distilled water was used for all runs. If desired, additional information on the construction and/or operation of this filter may be obtained from other sources (13,38).

The results of these filter studies are generally expressed in terms of the resistance of the filter cake to flow and thus are a measure of the impermeability of the filter aid. The term which will be used to report the results of this study is the filter aid resistance index or ξ index. The ξ index was derived in a thesis by James Dillingham (12). It may be expressed as follows:

$$\xi = \frac{Hpg}{q\nu w}$$

where

ξ = filter aid resistance index or ξ index

H_p = head loss or pressure differential across the filter in terms of a water column

g = gravity constant

q = flow rate per unit of septum area

ν = kinematic viscosity

w = weight of the precoat per unit of septum area

ξ index determinations were made on Celite 545 and on coated Samples 89-1, 92-1, 93-2, 93-3, 115-1, 121, and 136D. In addition, the ξ index was also determined for samples of Celite 545 and coated Sample 121 which had been recirculated through the pump for varying periods of time prior to precoating. The ξ index values are compiled in Table 8. A typical

Table 8. ξ index determinations

	ξ index, ft/lb		
		With recirculation	
Sample No.	Without recirculation	10 min	15 min
89-1	331		
92-1	529		
93-2	472		
93-3	836		
115-1	449		
136D	409		
Uncoated Celite 545	828	893	928
121	426	796	802

calculation is given in Appendix B.

The results show that, except for Sample 93-3, the ξ index values of non-degraded coated samples were much lower than that for Celite 545. For instance, the ξ index value of Sample 136D, which was the coating selected for the radioactivity removal and glass studies, was only 409 ft/lb as compared to 828 ft/lb for Celite 545. Thus, the filter aid resistance index of the coated sample is only one-half that of Celite 545 for this filter. This indicates that in actual filter operation, the use of coated diatomite should materially reduce the pressure differential or headloss through the filter for a given filter cake thickness. This would permit the use of thicker filter cakes which may be advantageous for decontaminating wastes by the ion exchange process.

It is interesting to compare the ξ index values of Samples 93-2 and 93-3, which were 472 ft/lb and 836 ft/lb, respectively. These two samples were of the same initial mix. Both samples were heated in a water bath at 60°C for 3 hours following gellation. Sample 93-2 was then frozen at -5°C while Sample 93-3 was dried at 100°C. Both samples were then washed and dried. Admittedly, this constitutes a very limited study, but it indicates that the freezing step increases the permeability of the resulting product.

From a visual observation, the coated diatomite appeared to be more granular than the uncoated Celite 545 (see

Figure 1). A microscopic examination of the coated diatomite revealed a certain amount of clumping of two or more diatomite particles into a larger irregular mass. Therefore, it was felt that normal handling and filter operation might cause serious particle degradation which, in turn, might materially increase the ξ index of the material. As a result, a limited degradation study was made with Sample 121. A similar study was also made with Celite 545 for comparative purposes. For the degradation study the desired material was added to the precoat pot and kept in suspension in the normal manner. However, the resulting slurry was recirculated through the centrifugal pump prior to precoating the filter. In addition to ξ index determinations, degraded portions of Samples 117 and 121 were used for determining the effect of degradation upon their base exchange capacities. The results of this study will be discussed in another section of this thesis.

The results of the permeability-degradation study showed that the ξ index values of portions of Sample 121 which had been recirculated through the pump for 10 and 15 minutes were 796 ft/lb and 802 ft/lb, respectively, as compared to an initial ξ index of 426 ft/lb. For Celite 545, the ξ indices were 893 ft/lb and 928 ft/lb after recirculating through the pump for 10 and 15 minutes, respectively. The initial ξ index for the Celite 545 was 828 ft/lb. Thus, the ξ indices of degraded Celite 545 represented a change of only +8 percent and +12 percent for samples recirculated for 10 and 15 minutes, respectively. For Sample 121, the ξ indices of degraded samples recirculated for 10 and 15 minutes represented a change of +87 percent and +88 percent, respectively. However, it should be noted that the highest ξ index obtained for a degraded Sample 121 specimen, 802 ft/lb., was still lower than that obtained for non-degraded Celite 545, 828 ft/lb.

The limited difference in the ξ indices of the recirculated portions of Sample 121 indicates a high initial change in particle size and/or shape. This was probably due to the breakdown of the clumped particles mentioned previously, followed by a reduced rate of degradation. A microscopic examination of a portion of degraded Sample 121 showed a marked reduction in the number of "clumped" particles.

Thus, while the ξ index of the coated diatomite did increase significantly due to degradation, the study also indicates that the ξ index of coated diatomite would probably be less than that of similarly handled uncoated diatomite. Degradation studies were not made with samples of the final coating selected. However, it is felt that similar results could be expected.

Effect of Particle Degradation Upon Exchange Capacity

In addition to ξ index determinations, exchange capacity determinations were made on degraded portions of Samples 117 and 121. These samples had been recirculated through the filter pump for 10 minutes. The degraded samples were collected in Pyrex beakers. After settling, the supernatant was poured off, and the samples were dried and checked for exchange capacity.

The exchange capacities of degraded Samples 117 and 121 were 0.51 meq/g and 0.55 meq/g, respectively. The initial exchange capacities for these samples were 0.62 meq/g and 0.63 meq/g, respectively. Thus, the exchange capacities of these degraded samples were 0.11 meq/g and 0.8 meq/g lower than the initial values. These values represent reductions in capacities of 17 and 14 percent, respectively.

Thus, the exchange capacities of the degraded samples were substantially lower than their original values. However, the samples were probably more severely degraded than would occur in normal operation. Degradation tests were not made with the final coating selected. However, comparable results would probably be obtained.

Coated Diatomite for Body Feed

Before being placed into operation, the filter septa of diatomite filters are coated with a layer of diatomite which serves as the filtering media. This initial coating is referred to as the precoat. In addition, it is customary to add a small amount of diatomite to the unfiltered water entering the filter during operation. Diatomite added in this manner is deposited on the filter cake together with the removed turbidity and is called the body feed. The body feed serves to maintain a more porous filter cake, thereby, prolonging the useful filter cycle.

During this study, the coated diatomite was not used on a diatomite filter. However, the column studies indicated that the permeability of the material may increase slightly during degeneration. ξ index values were not determined for degenerated samples for comparative purposes. However, if the permeability does increase during degeneration, this would tend to result in disproportionately higher flow-through rates in areas of limiting exchange capacity. This, in turn, would accelerate the rate of degeneration in these areas.

Since the body feed is applied during the filtering operation, it tends to distribute itself over the filter in proportion to the localized filtration or flow-through rate. Thus, if, in addition to its use for the precoat, coated diatomite were used for body feed, it would tend to be deposited in the areas of limiting capacity. This would improve the filter operation in two ways. It would tend to equalize the filtration rate over the filter septa, and it would selectively increase the exchange capacity in the areas of limiting capacity. These factors would tend to provide for the maximum utilization of the available exchange capacity.

However, there is one possible disadvantage to the use of coated diatomite for body feed. Since the dissolved cations are removed from solution by an ion exchange process, it is possible that the released sodium ions might tend to regenerate underlying, degenerated material thereby releasing previously removed radiocations in the filtrate. As a result, a study was made to evaluate this possibility.

For this purpose, 20 grams of previously degenerated, coated diatomite were placed in each of two columns. Twenty grams of non-degenerated, coated diatomite were then added to each of the columns. The columns were operated in the normal manner for determining exchange capacities. The samples used for this purpose were 116-1 and 119. During the runs, the minimum hardness concentrations in the effluent from the columns were 26 mg/l and 23 mg/l as $CaCO_3$ for Samples 116-1 and 119, respectively. The average hardness of the effluent from these columns during the runs was 44 mg/l and 35 mg/l as $CaCO_3$ for Samples 116-1 and 119, respectively. (Under normal operation, the hardness of the effluent from the softening columns was generally zero until breakthrough occurred.) The runs were terminated when a sharp increase was noted in the hardness of the effluent. The resulting exchange capacities were 0.51 meq/g and 0.66 meq/g, respectively. These values were higher than the exchange capacities obtained for these samples by the normal process. These values were 0.45

meq/g and 0.57 meq/g for Samples 116-1 and 119, respectively. The higher exchange capacities obtained by the modified procedure are readily explainable since the depths of the softening beds were greater and the terminal hardness of the effluents was higher.

Due to the relatively high initial hardness concentration of the water used in this study, 341 mg/l of calcium as $CaCO_3$, and the initial complete degeneration of the lower 20-gram samples in the columns, the test conditions were probably more stringent than would normally be encountered in actual radioactive waste treatment. However, the depths of the softening columns, approximately six inches, were also greater than would normally be encountered in actual operation. Thus, the use of coated diatomite as body feed could result in the regeneration of underlying, degenerated material and the release of previously removed cations in the filtrate. Additional study is needed in this area.

Coating of Perlite

In addition to the diatomite samples, a limited study was made to determine whether perlite filter aid could also be coated with an inorganic zeolite. Several samples were prepared with perlite. The exchange capacities of most of these samples were lower than expected. This was probably due to elevated drying temperatures. However, the drying temperature of one sample, Sample 171, was kept within the range of 65°-70°C.

This sample was prepared with Dicalite perlite 4106, a product of the Great Lakes Carbon Corporation, Los Angeles, California. A similar sample, Sample 170, was prepared with diatomite, Celite 545, for comparative purposes. The coated perlite sample had an exchange capacity of 0.81 meq/g as compared to an exchange capacity of 0.75 meq/g for the coated diatomite sample.

It is, therefore, readily apparent that perlite can be coated with an inorganic zeolite. However, the exchange capacity determinations of these two samples were not made under identical conditions and, thus, a direct comparison of these results should not be made. First of all, Dicalite perlite 4106 does not have the same permeability, and hence, probably not the same size characteristics. As indicated previously, this could affect the exchange capacities of the final products to a limited extent.

However, probably the greatest variations in the exchange capacity determinations were the flow rates and the depths of beds. The depth of bed of the 20 grams of coated perlite was 4.8 inches, while the depth of bed of the 20 grams of coated diatomite was only 3.4 inches. Since an increase in the depth of the softening bed reportedly increases the apparent exchange capacity, this was an important factor (32).

Secondly, due to the higher head loss of water passing through the bed of coated perlite, the flow-through rate in this column was only 0.8 gal/ft^2-min instead of the normal 1.0 gal/ft^2-min used for the coated diatomite sample. Again, the slower flow-through rate for the column containing the coated perlite would tend to increase the apparent exchange capacity of this material.

Thus, a direct comparison cannot be made of the exchange capacities of these two samples. However, this study proves that perlite can be coated with an inorganic zeolite in the same manner as diatomite.

Economic Evaluation of Various Coating Preparations

Another factor which was studied was the cost of the various coatings or preparations in relationship to their exchange capacity. For this purpose, ten coated diatomite samples were prepared. Sixty grams of Celite 545 were used for each sample, but the amount of sodium aluminate and sodium silicate was varied. Information regarding the chemical additives for these samples, Samples 161 to 170, together with cost data is tabulated in Table 9. The samples were mixed as previously described, spread, frozen at -20°C, thawed, washed and dried. The drying temperature was 65°-70°C. All of these samples were prepared the same day and were dried at the same time in the same drying oven. Therefore, variations in sample

Table 9. Economic evaluation of several coated diatomite mixes

		Material requirements for one equivalent of exchange capacity			Analysis of mix (% by weight)				
Sample No.	Exchange capacity (meq/g)	Wt. of starting materials (gms)	Wt. of product (gms)	Yield %	Sodium silicate solution	Sodium aluminate	NaOH	Diatomite[a]	Cost of materials per equivalent of exchange capacity[b] (cents)
161	0.497	2584	2012	77.9	25.4	8.3	0.9	65.4	29.7
164	0.551	2368	1815	76.6	24.4	11.4	1.3	62.9	28.8
162	0.551	2308	1815	78.6	25.0	9.4	1.0	64.6	27.1
163	0.598	2150	1672	77.8	24.7	10.4	1.1	63.8	25.7
165	0.622	2138	1543	72.2	29.4	8.8	1.0	60.8	24.5
168	0.651	2109	1536	72.8	33.4	8.3	0.9	57.4	23.4
169	0.692	1979	1445	73.0	33.2	9.2	1.0	56.6	22.4
166	0.699	1886	1431	75.9	29.2	9.8	1.1	59.9	22.3
167	0.759	1754	1304	74.3	28.7	10.8	1.2	59.3	20.9
170	0.751	1787	1332	74.5	32.7	10.2	1.1	56.0	20.6
136E	0.790[c]	1678	1266	75.4	32.7	10.2	1.1	56.0	19.4
171[d]	0.811	1662	1233	74.2	32.7	10.2	1.1	56.0	19.1

[a] Except for Sample 136E, 60 g of diatomite (Celite 545) were used for sample preparation. Perlite was used for Sample No. 171.

[b] Chemical cost data obtained from McKesson and Robbins Chemical Co. and Thompson-Hayward Chemical Co.: 40° Baumé sodium silicate solution @ \$2.85 cwt = 6.28¢/kg, assumed 1 ml = 1.38g; sodium aluminate @ \$14.00 cwt = 30.86¢/kg; NaOH @ \$7.65 cwt = 16.87¢/kg; Diatomite and perlite, assumed @ \$100.00/ton = 11.02¢/kg.

[c] Average of nine determinations.

[d] Dicalite perlite 4106 was used in place of Celite 545.

preparation and handling were minimized. Samples were weighed prior to seiving; however, losses from this operation would be nominal. Sample 171, which was prepared at the same time and in the same manner, was prepared with Dicalite perlite 4106 filter aid instead of diatomite.

It is apparent from Table 9 that over the range tested the cost of materials per equivalent of exchange capacity tends to decrease with increasing chemical additions. Of the ten 60 gram diatomite samples prepared, the lowest cost per equivalent exchange capacity was 20.6 cents. The composition of this sample, Sample 170, was the same as that for Sample 136 and for Sample 136D, which was used for glass preparation and radioactivity removal studies. It was also the same composition as an additional large sample, Sample 136E, which was also analyzed for material costs. The cost of materials per equivalent exchange capacity for Sample 136E was 19.4 cents. The lower material cost per equivalent exchange capacity for the large sample was due to a higher yield and a higher exchange capacity. The exchange capacity of Sample 170, 0.75 meq/g, is actually slightly lower than was normally obtained for this composition. The average exchange capacity of Sample 136E, 0.79 meq/g, more nearly represents the capacity normally obtained with this composition. The higher yield obtained from the large sample was probably due to reduced percentage losses in the handling of the larger sample.

The cost of materials per equivalent of exchange capacity for Sample 167 was 20.9 cents. This value is only 0.3 cents more than that obtained for Sample 170. This indicates that the cost per equivalent of exchange capacity of Sample 170 may be slightly reduced with a higher sodium aluminate:sodium silicate ratio. An additional 1.2 g of sodium aluminate would be required for Sample 170 to obtain the same ratio as in 167. However, if the coated diatomite were to be transformed into glass, the higher alumina content could necessitate a higher melting temperature or the addition of more compensating chemicals.

Sample 171 was prepared with Dicalite perlite 4106 filter aid instead of diatomite. Assuming that the cost of these two filter aids is the same, $100.00 per ton, the material cost per equivalent exchange capacity for Sample 171 was only 19.1 cents. This value is considerably below the cost obtained from a similar diatomite sample, Sample 170. The decreased cost is due to an indicated higher exchange capacity. However, as mentioned previously, a direct comparison cannot be made of the exchange capacities of these two samples because of a variance in the flow-through rates and depths of beds.

The material costs of the other samples were considerably higher than those mentioned above and will not be discussed.

It should be noted that the material costs given in Table 9 do not include any cost allowance for electricity, water, equipment or labor. However, due to the relatively small size samples prepared in this study, percentage losses due to handling and washing were probably greater than would be encountered if the operation were on an industrial scale.

Final Coating Selected

Of the various samples prepared, the composition of Sample 136 appeared to be the most desirable, and, as a result, this composition was used for all subsequent studies involving radioactivity removal and glass preparation. The selection of this mixture was based upon the relatively high exchange capacity of the resulting product and the lower cost of materials per equivalent of exchange capacity. The results of the economic evaluation of various coatings indicate that the use of additional chemicals might result in the production of a coated diatomite (or perlite) having a higher exchange capacity and at a lower cost per equivalent of exchange capacity. However, with the coating materials used, this would also result in a coated medium having a higher alumina content. Since one phase of this study consisted of converting the coated material into glass, the higher alumina content was considered to be undesirable.

After the desired composition was selected, larger samples were prepared for use in the other phases of this study. The sample used for the strontium-89 removal studies and the corresponding glass specimens was Sample 136D. This sample was prepared with 1000 grams of Celite 545, 422.5 ml of 40° Baumé sodium silicate solution, 181.67 grams of sodium aluminate, and 20 grams of sodium hydroxide. The procedure used in preparing this sample was the same as outlined in the section on procedures. With the available mixing equipment, there was a tendency for gellation to occur before mixing was complete. As a result, the distilled water used in preparing the larger samples was cooled to 15°C to slow down the chemical reaction and thus permit better mixing.

The exchange capacity of Sample 136D was 0.79 meq/g shortly after removal from the drying oven. However, a check of the exchange capacity of this sample four months later indicated that the capacity had dropped to an average of only 0.69 meq/g. A study was not made to determine the reason for the reduction in exchange capacity. However, some of this variation in capacity may have been due to a variation in the moisture content or abrasion. A study to determine the cause(s) for this variation in exchange capacity would be desirable.

Radioactivity Removal Study

Since one of the proposed uses for the coated diatomite was radioactive waste treatment, one of the phases of this study involved the removal of a radionuclide, strontium-89, from solution by an exchange reaction with the coated diatomite. For this purpose, the coated diatomite was placed in the exchange columns previously used for exchange capacity determinations. Three runs were made using 20 grams of coated Sample 136D in each of the two columns. The average flow rates for these runs were 0.60, 0.75, and 1.45 gal/ft^2-min.

In each case, the strontium-89 was mixed with hard water to make 1010 ml of solution. Three 10 ml aliquots were then pipetted off and evaporated in two-inch diameter, concentric ring, stainless steel planchets for radioactivity measurements. The remaining 980 ml, which had a hardness as $CaCO_3$ of 410 mg/l, was passed through the column. Each column and accompanying equipment was rinsed with distilled water. The rinse water was added to the initial effluent. Aliquots of this effluent were then pipetted off, evaporated, and counted for radioactivity.

The measured activities were used to calculate the removal efficiency of each column for the three runs. The data and a typical calculation are given in Appendix C. The removal efficiencies are tabulated in Table 10. In all cases, the removal efficiencies were $\geq$99.9 percent. This represents a decontamination factor of $\geq$1000.

The flow rates used in this study, 0.60-1.45 gal/ft^2-min, are comparable to those used in normal diatomite filter operation. However, the depths of the beds, approximately 3.4

Table 10. Removal efficiency for ^{89}Sr

Sample[a] No.	Average flow rate gal/ft^2-min	Adjusted average activity in initial sample[b] (cpm)	Average activity in effluent sample (cpm)	Removal efficiency (%)
1	0.60	13,471	4.3	99.97
2	0.60	13,848	7.9	99.94
3a	0.75	8,394	7.9	99.90
3b	0.75	7,857	8.3	99.89
4a	1.45	11,046	4.5	99.96
4b	1.45	10,416	7.9	99.92

[a] Samples 1 and 2 were used for preliminary glass samples. Samples 3a and 3b were combined for radioactive glass Sample 3, and Samples 4a and 4b were combined for radioactive glass Sample 4.

[b] Includes sample size correction.

inches, were considerably greater than the normal thickness of diatomite filter cakes. Also, only approximately one-half of the exchange capacities of the beds were utilized. Therefore, the decontamination factors obtained in this study should be higher than would be obtained in actual filter operation. Some variations in removal efficiencies could also be expected between the various radiocations present in a waste because of the selectivity rules for ion exchangers. Since the coated diatomite is a base exchange material, anion removal would probably be negligible.

This study shows that the coated diatomite will effectively remove strontium-89 from solution. The decontamination factors obtained in this study were $\geq$1000. These values are comparable to the 99.1-99.8 percent strontium-89 removed obtained for cation exchange beds in another study (47).

Glass Preparation

If coated diatomite were to be used for treating radioactive wastes, consideration must be given to the treatment and/or disposal of the resulting concentrated radioactive material. Since the primary constituent of diatomite is silica, one possible method of treating the used material for disposal would be converting it into glass. This method of disposal was investigated in this study.

In selecting the composition to be used for this purpose, one of the main considerations was the desire to utilize the glass forming compounds present in the coated diatomite. In addition to silica, one of the compounds of interest was alumina. Alumina increases the chemical durability of glass in addition to reducing the coefficient of expansion and reducing the tendency of the glass to devitrify (37). Too much alumina increases the viscosity thereby making the glass mixture more difficult to melt. Therefore, since the alumina content of the coated diatomite was quite high, it was found to be desirable to include uncoated diatomite filter aid, Celite 545, to lower the alumina content of the resulting mix. Another reason for including uncoated diatomite filter aid was the fact that it would probably be used to some extent as body feed in normal operation and, as a result, would be present in the used material.

Since the chemical composition of the coated diatomite was unknown, it was necessary to have the material analyzed. It was also desirable to determine the chemical composition of the uncoated Celite 545. Independent analyses of these materials were made at the Analytical Services Laboratory of the Engineering Research Institute, Iowa State University, Ames, Iowa, and at The Bruce Williams Laboratories, Joplin, Missouri. These analyses are given in Table 11. It should be noted that the analyses made by the Analytical Services Laboratory were on a dry weight basis while those made by The Bruce Williams Laboratories were on an "as received" basis.

Another consideration in selecting a suitable glass composition was the necessity of obtaining a glass product at a temperature of $\leq$1100°C. This requirement was necessary due to the temperature limitations of the available oven used for melting the glass mixes. A relatively low melting temperature would also be desirable for a continuous melting process such as might be used for the proposed method of treatment.

Another factor which was considered in the selection of the glass mix was the desire to obtain a final glass product having suitable chemical durability characteristics. In this respect, an attempt was made to obtain a glass having a composition comparable to container glass. The average composition of container glasses manufactured in 1960 was as follows (34):

	% by weight
Silica	71.7
Stabilizing oxides (R_2O_3 group, 2.05%)	13.55
Fluxes	14.85

The high alumina content of the coated and uncoated diatomite made this impractical, however. Since alumina improves the chemical durability of glass, it was felt that some reduction could be made in the lime and silica content of the mix. This was necessary to obtain a suitable melt at a relatively low temperature.

In addition to the coated and uncoated diatomite and the other two main constituents, sodium and calcium compounds, various other chemicals were added as minor constituents to various glass mixes. These were added to serve as fining agents or to lower the melting point. These chemicals included barium hydroxide, boric acid, magnesium oxide, potassium sulfate, potassium hydroxide, ferric sulfate, arsenic pentoxide, and potassium phosphate. The addition of small quantities of sulfate appeared to be beneficial as a fining agent. However, there was a tendency for a thin, crystalline, water-soluble film to form on the glass during the cooling process. Through the use of X ray diffraction and microscopic refractive indices techniques, this was tentatively identified as sodium sulfate. In actual practice, this may not be serious since it could be readily removed, if desired, or perhaps the composition could be adjusted to eliminate this difficulty. However, in this study it was felt that this partial separation was undesirable and, as a result, the use of sulfates was discontinued.

The mixture selected for radioactive glass preparation was as follows:

Coated diatomite, Sample 136D	40.00 g
Celite 545	153.12 g
Calcium carbonate	38.04 g
Sodium carbonate	51.06 g
Boric acid	1.07 g
Barium hydroxide	2.46 g

The coated diatomite used for the above glass samples was partially degenerated due to its use in the radioactivity removal study. The strontium-89 content of this material was insignificant as far as chemical composition was concerned and was ignored. The weights of the Celite 545 and the coated diatomite were on an "as is" basis rather than on a dry weight basis. The indicated weights of the calcium carbonate and sodium carbonate are the amount of chemicals added in addition to the calcium and sodium present on the diatomite.

Table 11. Chemical analyses of diatomite samples

	Celite 545		Coated Sample 136D	
	ERI[a]	BWL[b]	ERI[a]	BWL[b]
SiO_2	88.90%	86.23%	77.02%	78.08%
Al_2O_3	4.48%	5.48%	8.19%	10.20%
Fe_2O_3	1.46%	2.57%	1.14%	1.22%
CaO	0.98%	0.88%	0.70%	0.63%
Na_2O	2.64%	4.40%	4.88%	4.80%
TiO_2	0.81%	0.06%	1.60%	0.06%
Moisture	0.07%	-	2.83%	-
Loss on ignition	0.31%	0.33%	5.49%	5.01%

[a] Analysis by the Analytical Services Laboratory of the Engineering Research Institute, Iowa State University, Ames, Iowa. Values are on a dry weight basis.

[b] Analysis by The Bruce Williams Laboratories, Joplin, Missouri. Values are on an "as received" weight basis.

The analyses of the coated and uncoated diatomite from each of the laboratories were used to calculate the theoretical chemical composition of the resulting glass (see Tables 11 and 12). The average of the two calculated chemical compositions was also determined. At the time that the radioactive glass samples were prepared, a similar nonradioactive glass sample was prepared. In this case the coated diatomite had not been

Table 12. Chemical composition of glass product

	Calculated values[a]			Chemical analysis[b]
	1	2	3	
SiO_2	68.86%	67.07%	67.96%	65.95%
TiO_2	0.77%	0.05%	0.41%	0.06%
Al_2O_3	4.17%	5.12%	4.64%	5.61%
Fe_2O_3	1.11%	1.81%	1.46%	1.19%
B_2O_3	0.25%	0.25%	0.25%	0.70%
CaO	9.73%	9.59%	9.66%	9.25%
BaO	0.49%	0.49%	0.49%	0.16%
Na_2O	14.61%	15.62%	15.11%	16.70%
Loss on ignition	-	-	-	0.37%

[a] Values in Column 1 are based upon analyses by the Analytical Laboratory of the Engineering Research Institute, Iowa State University, Ames, Iowa, and chemicals added. Values in Column 2 are based upon analyses by The Bruce Williams Laboratories, Joplin, Missouri and chemicals added. Column 3 is the average values of Columns 1 and 2.

[b] Analysis of the glass product by The Bruce Williams Laboratories, Joplin, Missouri.

partially degenerated, and, as a result, the quantities of sodium and calcium carbonate were adjusted accordingly to 50.21 g and 38.85 g, respectively. This nonradioactive glass sample was analyzed by The Bruce Williams Laboratories (see Table 12).

The chemical analysis of the nonradioactive glass sample differed, somewhat, from the calculated compositions (see Table 12). Of the four major constituents, the analysis of the glass sample showed the silica content to be 1.12-2.91 percent less than the calculated values, the sodium oxide content to be 1.08-2.09 percent more than the calculated values, the calcium oxide content to be 0.34-0.48 percent less than the calculated values, and the aluminum oxide content to be 0.49-1.44 percent more than the calculated values.

For melting purposes, the glass mixtures were placed in a muffle furnace at 600°C. During the next two hours, this temperature was increased to the ultimate temperature of 1090°C. After 14 hours at this temperature, the samples were removed from the oven and air cooled.

The weights of the glass samples were determined by subtracting the weights of the empty crucibles from the combined weights of the cooled crucibles and glass. In each case, the weight of the radioactive glass sample was found to be 241.1 grams. The nonradioactive glass sample weighed 241.8 grams. Based upon the analyses of the Analytical Services Laboratory of the Engineering Research Institute, the calculated weight of each of the glass samples should have been 241.8 grams; based upon the analyses of The Bruce Williams Laboratories, this should have been 243.4 grams.

The specific gravity of the radioactive glass samples was determined by the displacement or Archimedes' method. The specific gravity of the radioactive samples was 2.53.

In summary, some adjustments were necessary in the intended composition of the radioactive glass samples. These changes were required due to the high alumina content of the glass mixture and the upper melting point limitation of 1100°C. The required time of melt, 16 hours, appears to be excessive, but this period of time could be reduced by increasing the temperature. It is possible that additional research in this area would yield a more easily melted glass having comparable chemical durability qualities.

The primary purpose of this phase of the study was to determine whether the coated diatomite could be transformed into glass for final disposal. The results indicate that this is a potential useful method of treating and disposing of the used, radioactive material.

Chemical Durability Study

If coated diatomite were used for the decontamination or treatment of radioactive wastes and were transformed into glass, the resulting radioactive product would be ready for ultimate disposal. However, in the disposal of this material, additional safeguards may be required. These safeguards would be designed to prevent the release of radionuclides to the environment in concentrations believed to be potentially harmful to man. One of the factors that must be evaluated before determining the required safeguards is the chemical durability or leaching characteristics of the product. Therefore, the final study made in this research was the determination of the chemical durability or leaching characteristics of the glass.

Tests for determining the chemical durability of glass vary depending upon the intended use of the product. In the case of the utilization of glass as a means of radioactive waste disposal, the retention of radionuclides under conditions which might be encountered in disposal areas is of prime importance. However, as mentioned previously, attempts to obtain a uniform leaching test which reflects these conditions have as yet been unsuccessful. As a result, leaching studies have been conducted under various conditions and the comparison of results is difficult, if not impossible.

It was noted, however, that at least two leaching studies were conducted using a similar method (21,41). This method uses -40+60 glass particles contained in 200 mesh stainless steel cloth bags suspended in boiling, distilled water in a reflux condenser apparatus. It was recognized that the nucleate boiling on the surface of the submerged glass probably produced an erosive effect and a somewhat greater apparent leaching rate (21). However, it was felt that this method represented a set of conditions more indicative of that expected if ground water contacted hot, stored glasses. It was also believed that the powdered glass improved the sensitivity of the test due to the increased surface area. The effective surface area may vary, however, due to agglomeration of particles, vapor locks, etc. If one assumes, however, that the surface area per unit weight of most powdered glasses is relatively constant, this method of determining leaching rates is relatively simple. The reproducibility of this leaching test was believed to be indicated by the standard errors associated with the mean corrosion rate, generally about ±5 percent.

As a result, this was the method adopted for determining the apparent corrosion rate of the glass product made in this study. Modifications which were made included (1) the use of a steel mortar and pestle in place of a hammer mill for powdering the glass, (2) the use of 250 mesh stainless steel cloth leaching bags (wire diameter = 0.0016 inch) in place of 200 mesh stainless steel cloth, and (3) the use of 0.1 N HNO_3 and distilled-demineralized water for rinsing purposes in place of 0.1 $\underline{M}$ HCl and distilled water or merely distilled water.

It was noted in one of the studies that the reflux receiver flask was rinsed with two 10 ml portions of 0.1 $\underline{M}$ HCl followed by two 10 ml aliquots of distilled water at the end of each leaching cycle, all of which were added to the leachate and evaporated to dryness (21). In the other similar study, the procedure varied (41). For beta counting, the flask and leaching bag were washed three times (apparently with distilled water) into the leachate at the end of each leaching run or cycle. The leachate was then evaporated to dryness after which the beaker was washed 5-6 times with 2-3 ml of distilled water. The wash solutions were transferred to a planchet and evaporated for counting. In this case, the indicated residual activity in the beakers, 2-3 cpm, was considered to be insignificant. For gamma counting, the same initial rinsing procedure was used. However, the leachate was only evaporated to 2-3 ml before being transferred to the test tube for counting. The beaker was then rinsed 5-6 times with dilute HNO_3. All of these rinses were added to the test tube previously mentioned.

In this study, two preliminary leaching studies were made. In the first, the reflux receiver flasks were rinsed with 0.1 N HCl in quantities ranging from two 10 ml portions to one 5 ml portion followed by two 10 ml aliquots of distilled-demineralized water—all of which were added to the leachate. The leachate, which was poured into 250 ml Pyrex beakers, was evaporated to 10-15 ml at which time it was transferred to planchets. The beaker was then rinsed with 5-10 ml of 0.1 N HCl and two 10 ml aliquots of distilled-demineralized water. Again, these rinses were added to the planchet and evaporated to dryness for counting purposes. During this study, it was noted that the dried samples absorbed moisture during the counting period due to the hydrophylic nature of the contained salts. This increased self absorption and tended to create inconsistencies in the results. Therefore, this preliminary study was stopped.

In the second preliminary study, the rinses used initially consisted of only 5 ml of the 0.1 N HCl for each flask and beaker plus the usual subsequent rinses with distilled-demineralized water. However, the dried samples still absorbed moisture during the counting process. As a result, the use of the 0.1 N HCl rinses was stopped and an additional rinse with the distilled-demineralized water was used. Complete reliance on the water rinses eliminated any visual absorption of moisture by the dried samples during the counting operation. However, the determined activities of the leachate samples were reduced thereby indicating that these rinses were insufficient for removing the leached strontium-89 from the receiving flasks and beakers. As a result, at the conclusion of the next weekly run, an initial rinse was made with 7.5 ml of 0.1 N HNO_3. The radioactivity determinations for this run were approximately three times those of the previous run thereby confirming that the use of water rinses by themselves was inadequate. There was no noticeable problem with adsorbed moisture for the samples rinsed with the 0.1 N HNO_3 solution. Therefore, this method was adopted.

In the final leaching study, each flask was given an initial rinse with 10 ml of 0.1 N HNO_3. This was followed by two 10 ml rinses with distilled-demineralized water. All rinses were added to the leachate in the beaker. This leachate was then evaporated to 10-15 ml prior to being transferred to a planchet. Each beaker was then rinsed in a similar manner, and all rinses were added to the planchet. The solution in the planchet was evaporated to dryness and weighed prior to making activity determinations.

At the conclusion of the leaching study, the reflux condensers, receiving flasks and beakers were rinsed with a dilute HF solution to check on the effectiveness of the rinsing procedures used during this study. Again these rinses were evaporated and transferred to planchets for activity determinations. The activity determinations for these samples ranged from -0.40 ± 0.43 cpm to $+0.53\pm0.43$ cpm. It is, therefore, apparent that the rinsing procedure used for this study was adequate.

Therefore, the three variations made for this leaching study—(1) the method of crushing the glass, (2) the use of 250 mesh stainless steel cloth leaching bags in place of similar bags made of 200 mesh stainless steel cloth, and (3) the use of 0.1 N HNO_3 for rinsing purposes—are not believed to have adversely affected the leaching rate.

Since the initial leaching rate is generally considerably higher than that of the stable state condition, it was decided to change the leaching solution after an initial 24-hour leaching period and again after an additional 48 hours. Subsequent leaching runs were for seven consecutive days. For each run the pH of the leachate and of the fresh water was determined and recorded. The pH of the fresh water varied from 6.4 to 7.1. The pH of the leachate varied from 8.4-8.5 at the end of the initial 24-hour leaching run to 8.1-8.2 at the end of the weekly leaching runs. The relatively low radioactivity content of the leachate, coupled with the relatively short half-life of the radionuclide, strontium-89, made it desirable to terminate the study after the sixth week. The results of this study are tabulated in Table 13. The data and sample calculations for this study are given in Appendix D.

As in the two similar studies previously mentioned, the mean leaching rate was calculated in terms of the apparent corrosion rate (21,41). The apparent corrosion rate used in those studies was the depth of a uniform volume increment at the surface of the product which would contain the weekly eluted activity at the initial activity concentration. The resulting equation was as follows:

$$\frac{\text{cm}}{\text{wk}} = \frac{\text{eluted activity (cpm/wk-g)}}{(\text{surface area-cm}^2/\text{g})(\text{initial activity concentration, cpm/cm}^3)}$$

Table 13. Apparent corrosion rates of glass Samples 3 and 4

	Mean values and standard errors for each weekly leaching period cm/wk		Mean values and standard errors of accumulated data[a] cm/wk	
Date	Sample No. 3	Sample No. 4	Sample No. 3	Sample No. 4
11/11/66	$(1.21 \pm 0.03)\times10^{-4}$	$(9.90 \pm 0.18)\times10^{-5}$	$(1.21 \pm 0.03)\times10^{-4}$	$(9.90 \pm 0.18)\times10^{-5}$
11/14/66	$(5.86 \pm 0.08)\times10^{-5}$	$(5.78 \pm 0.03)\times10^{-5}$	$(5.86 \pm 0.08)\times10^{-5}$	$(5.78 \pm 0.03)\times10^{-5}$
11/21/66	$(1.09 \pm 0.10)\times10^{-5}$	$(0.91 \pm 0.08)\times10^{-5}$	$(1.09 \pm 0.10)\times10^{-5}$	$(0.91 \pm 0.08)\times10^{-5}$
11/28/66	$(1.72 \pm 0.03)\times10^{-5}$	$(1.48 \pm 0.03)\times10^{-5}$	$(1.41 \pm 0.15)\times10^{-5}$	$(1.19 \pm 0.13)\times10^{-5}$
12/03/66	$(1.45 \pm 0.16)\times10^{-5}$	$(1.53 \pm 0.06)\times10^{-5}$	$(1.42 \pm 0.11)\times10^{-5}$	$(1.31 \pm 0.10)\times10^{-5}$
12/10/66	$(1.32 \pm 0.06)\times10^{-5}$	$(1.19 \pm 0.06)\times10^{-5}$	$(1.40 \pm 0.08)\times10^{-5}$	$(1.28 \pm 0.08)\times10^{-5}$
12/17/66	$(1.54 \pm 0.14)\times10^{-5}$	$(1.40 \pm 0.17)\times10^{-5}$	$(1.42 \pm 0.07)\times10^{-5}$	$(1.30 \pm 0.07)\times10^{-5}$
12/31/66	$(1.56 \pm 0.06)\times10^{-5}$	$(1.52 \pm 0.05)\times10^{-5}$	$(1.45 \pm 0.06)\times10^{-5}$	$(1.33 \pm 0.06)\times10^{-5}$

[a] Since leachate samples for dates 11/11/66 and 11/14/66 were for short initial leach periods, they were figured individually. Accumulated data were used for the period 11/21/66-12/31/66, inclusive. For example, the values for the date 12/10/66 are based upon the data for 11/21/66-12/10/66, inclusive.

However, in this study the activity concentration in the glass was adjusted for natural decay and for previously leached radioactivity. The adjustment for natural decay was desirable in this study since the tracer radionuclide, strontium-89, has a relatively short half-life, 50.5 days. As a result, the modified equation is as follows:

$$\frac{\text{cm}}{\text{wk}} = \frac{\text{eluted activity (cpm/wk-g)}}{(\text{surface area-cm}^2/\text{g})(\text{activity concentration, cpm/cm}^3)}$$

The data and calculations are given in Appendix E.

In one study, the surface area of -40+60 mesh glass particles was determined by gas adsorption techniques (21). It was found that all glass particles in this size range having a specific gravity of 2.9-3.6 had a surface area of 125 cm^2/g ±5 percent. As a result, this value was used for the surface area of the -40+60 mesh glass particles used in the similar leaching studies previously mentioned (21,41). In this study, the specific gravity of the glass was 2.53. Thus, the specific gravity of the glass used in this study was lower than those used in the gas adsorption-surface area study. As a result, the surface area of the -40+60 mesh glass particles used in this study may have been greater than this value. However, in view of the findings of the previous study, this variation in surface area would probably be quite small and would have but a limited effect upon the determined leaching rates. As a result, in this study a surface area of 125 cm^2/g was used.

The indicated errors of the leaching values were determined by the standard deviation of the mean or standard error, $\sigma_{\bar{X}}$, where

$$\sigma_{\bar{X}} \approx \sqrt{\frac{1}{n(n-1)}\sum_{1}^{n}(X_i-\bar{X})^2}$$

and

n = the accumulated number of leachate samples (3× the number of weeks of the study since three one gram specimens were used for each glass sample).

Again, this was the same approach used in the other studies (21,41).

As in the radioactivity removal study, relative activities were used for evaluating the leaching characteristics of the glass product. It was assumed that all of the strontium-89 removed by the coated diatomite during the radioactivity removal study was incorporated into the glass. It was further assumed that the strontium-89 was uniformly distributed throughout the glass sample. Thus, the strontium-89 present per gram of glass was determined by dividing the total determined activity present by the weight of the glass sample.

All leachate samples were evaporated to dryness in two inch diameter, concentric ring, stainless steel planchets. This provided a surface area of over 20 cm^2 for deposition of solids leached from the glass. The initial activity was determined from dried samples having net weights of approximately 0.0055 grams. Of the 7-day leachate samples, the average net weight of solids was 0.0244 grams. This value includes one sample which had a net weight of 0.0532 grams. This value may be in error. Excluding this sample, the average net weight of solids from the 7-day leachate samples was 0.0236 grams. Thus, regardless of which value is used, the differential in sample thickness between that of the average for the leachate samples and those of the initial activity determinations was less than 1 mg/cm^2. A check on self-absorption for strontium-89 showed that this factor was negligible at this thickness. Therefore, no correction was made for self-absorption.

The initial activity values were obtained from determinations made on September 15-16, 1966. The final activity determinations for the leaching studies were made on December 31, 1966. Since the strontium-89 sample initially contained a small percentage of strontium-90, the relative effect of this isotope and its radioactive daughter, yttrium-90, increased during the leaching study due to the shorter half-life of strontium-89. Thus, the activity present in the glass was probably higher than the calculated value. If considered, this effect, though small, would tend to reduce the apparent corrosion rate obtained from the leaching study.

In one study, the apparent corrosion rate was determined for four different glass mixes containing strontium-89 (21). These mixes had silica concentrations ranging from 10-50 percent, lime concentrations ranging from 25-45 percent, and Darex waste oxide concentrations ranging from 20-50 percent. The melting temperature of these glass mixes ranged from 1350°-1400°C. The apparent corrosion rates ranged from $(5.47 \pm 0.37) \times 10^{-6}$ cm/wk to $(9.00 \pm 0.63) \times 10^{-6}$ cm/wk. The compositions of these glass mixes were quite different from the one used in this study (see Table 12).

The data from this leaching study and the calculated apparent corrosion rates of the various leachate samples are given in Appendix D. The average or sample mean apparent corrosion rates of the weekly samples and the standard errors are given in Table 13. There is no apparent explanation for the lower apparent corrosion rates for the first full seven-day leaching period. Two possible factors are errors in the laboratory technique and peculiarities of the glass itself. For Sample No. 3, it would appear that it may have been due to an incomplete rinse since the apparent corrosion rate for the following week is higher than that for any subsequent weeks. However, this is not true for Sample No. 4. For the six-week leaching period, the mean apparent corrosion rates and standard errors for Samples 3 and 4 were $(1.45 \pm 0.06) \times 10^{-5}$ cm/wk and $(1.33 \pm 0.06)\times 10^{-5}$ cm/wk, respectively. These values are approximately 1.5-2.5 times those obtained for the previously mentioned leaching study.

It is interesting to note that the apparent corrosion rate of Sample No. 3 was slightly higher than that of Sample No. 4. Since Sample No. 4 was placed near the thermocouple at the back of the muffle furnace during the melting process, it is possible that the temperature of this sample was slightly higher than that of Sample No. 3. Since relatively small variations in melting temperatures may have a noticeable effect upon the solubility of the glass, it is possible that this variation in sample placement in the muffle furnace might have caused the noted variation in the apparent corrosion rate. If so, it is possible that a small increase in melting temperature might have substantially lowered the apparent corrosion rate of the glass used in this study.

At the conclusion of the leaching study, the glass samples were dried and weighed. For Sample No. 3, the average final weight was 0.9684 grams. This represents an average loss in weight of 0.0316 grams or 3.16 percent. For Sample No. 4, the average final weight was 0.9685 grams. This represents an average loss in weight of 0.0315 grams or 3.15 percent. Based upon the determined apparent corrosion rates—which were adjusted to the actual period of leaching for the initial leaching runs, a specific weight of 2.53 g/cm^3, and a surface area of 125 cm^2/g, the calculated weight losses of Samples 3 and 4 were 0.0383 g and 0.0349 g, respectively.

In summary, the results of this study indicate that coated diatomite can be mixed with other glass forming ingredients and be converted to a glass. The apparent corrosion rate of the glass made during this study was approximately 1.4×10^{-5} cm/wk. Since this was a limited study, additional research in this area could be expected to result in further improvements in the glass product. However, the present results indicate that this might be a feasible means of disposing of coated diatomite used for radioactive waste treatment.

SUMMARY AND CONCLUSIONS

This study was devoted to the development of a new medium for decontaminating radioactive wastes that could lead to the modification of two existing waste treatment methods. The new medium consists of diatomite (or perlite) filter aid coated with an inorganic base exchange material. When used as a filter aid, this material will remove particulate matter by the filtration process and dissolved cations by the base exchange process. Separate units are normally used for the filtration and exchange processes—only one unit, a filter, would be needed with the new medium. The new medium was evaluated by removing radioactivity, strontium-89, from solution. In addition, the depleted material was converted into glass and a chemical durability study was made on the glass product.

Many variations of composition and preparatory techniques were tried to arrive at a near optimal medium in terms of its exchange capacity and hydraulic characteristics. The basic constituents used in preparing the coated material included diatomite (or perlite) filter aid, 40° Baumé sodium silicate solution, sodium aluminate, and caustic soda. The caustic soda was added to the sodium aluminate solution to stabilize this solution. It also served to increase the exchange capacity of the final product. For convenience, distilled water was used in preparing the samples, but soft water prepared by sodium base exchange could have been used. After gellation, the samples were dewatered by freezing at -20°C. They were then thawed and washed with distilled water. The medium was then dried in a drying oven and sieved prior to being used. The recommended procedure for preparing the medium is given in the Procedures section. The ion exchange capacity of this material should be 0.75-0.80 meq/g. The cost of the materials used in preparing the medium was approximately \$0.20 per equivalent of exchange capacity. The ξ index of the medium should be approximately 409 ft/lb.

A medium of this kind was evaluated in the laboratory for decontaminating a strontium-89 solution. The indicated decontamination factor for the method used in the laboratory was $\geq$1000.

One possible method of ultimate disposal of the depleted medium was evaluated in the laboratory. This involved admixing the coated material or medium with uncoated diatomite filter aid, calcium carbonate, sodium carbonate, boric acid, and barium hydroxide. The resulting mixture had a composition approximating that of container glass and melted at 1090°C. A sample of this glass and its contained radionuclides was subjected to an accelerated leaching test. The eluted radioactivity was used to determine the apparent corrosion rate. The results indicate that for the intended purpose, the glass had reasonably good chemical durability characteristics.

Several conclusions can be drawn from this study regarding the development of a base exchange coating for diatomite filter aid and its possible use for treating radioactive waste:

1. Diatomite and perlite filter aids can be coated with an inorganic, base exchange material.
2. Based upon current prices, the cost of materials for coated diatomite or perlite having base exchange capacities of 0.75-0.80 meq/g is approximately $0.20 per equivalent of exchange capacity.
3. The filter aid resistance or ξ index of coated diatomite is less than that of similar uncoated diatomite. For non-degraded or abraded samples, the filter aid resistance of the coated diatomite is much less than that of the uncoated diatomite. For degraded, coated diatomite, there is a large initial increase in the filter aid resistance of coated diatomite. However, the final filter aid resistance is still less than that of similarly degraded uncoated diatomite filter aid.
4. Coated diatomite is effective in removing strontium-89 from solution. Removal efficiencies of $\geq$99.9 percent are obtainable at flow rates of 0.60-1.45 gal/ft^2-min through filter beds 3.3-3.4 inches deep.
5. The use of coated diatomite for body feed may result in the regeneration of underlying degenerated material with the accompanying release of previously

removed cations.

6. Coated diatomite can be transformed into glass. Therefore, coated diatomite which had been used for radioactive waste treatment could be transformed into glass for final disposal.

RECOMMENDATIONS

Since this preliminary study of the proposed process indicated that it may be feasible, it is recommended that this study be expanded to a pilot plant basis and that actual radioactive wastes be used to evaluate the medium.

In this study, an inorganic zeolite coating was developed for a filter aid. An organic coating could possibly provide a higher exchange capacity and a wider pH operating range. It is, therefore, recommended that the possibility of coating filter aids with an organic ion exchange material be investigated. Ultimate disposal of the depleted material might be provided by admixing with a cementing substance.

In this study, the prepared medium was not actually used as a body feed in a filter for removing particulate matter and dissolved solids from a waste. This should be done on a pilot plant scale using a low-level radioactive waste. It will be important to determine whether the use of coated diatomite as a body feed would result in the regeneration of the underlying material and the release of previously removed radionuclides.

The results of this study show that coated diatomite can be transformed into glass as a means of disposing of removed radionuclides. However, it is recommended that additional developmental work be done to improve the chemical durability and melting characteristics of the glass without, if possible, increasing the required melting temperature. If glass were used for disposal, it is possible that an impervious coating on the glass would be beneficial in reducing the leaching rate.

It is further recommended that studies be made to determine the feasibility of other methods of ultimate disposal for depleted, radioactive, coated diatomite or perlite. Some possible methods include admixing with cementing materials such as cement, asphalt, or plastic resins.

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APPENDIX A

Table 14. Coated diatomite sample data

	Materials			NaOH[a]		Temperature[b]			
Sample No. (1)	Diat. (gms) (2)	Sod. Sil. Soln.(ml) (3)	Sod.Alum. Soln.(ml) (4)	(gms) (5)	(gms) (6)	°C (7)	°C (8)	Exch. cap.[c] meq/g (9)	Remarks (10)
89-1	60	16.9	40	0.8	0	-5	100;85	0.48	Split sample
89-2						60;-5	100;85	0.46	
89-3						60;100	100;85	0.42	
90-1	80	16.9	40	0.8	0	-5	100;85	0.36	Split sample
90-2						60;-5	100;85	0.34	
90-3						60;100	100;85	0.36	
91-1	100	16.9	40	0.8	0	-5	100;85	0.28	Split sample
91-2						60;-5	100;85	0.26	
91-3						60;100	100;85	0.25	
92-1	80	25.3	40	0.8	0	-5	100;85	0.45	Split sample
92-2						60;-5	100;85	0.47	
92-3						60;100	100;85	0.42	

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[a] Values in Column 5 are for the NaOH added to the sodium aluminate solution. Those in Column 6 are additional quantities.

[b] Temperatures in Column 7 are for after the initial set at room temperature. Those in Column 8 are drying temperatures. For Samples 89-93 the 100°C drying temperature was due to an initial, partial drying step on a steam table. For Samples 115-2 and 115-3, the 122°C drying temperature was unintentional and of short duration—no adverse effects were noted.

[c] For Samples 89-127, a $CaCl_2$ solution was used for exchange capacity determinations. A $CaCl_2$-$MgSO_4$ solution was used for the other samples. The indicated exchange capacity values for Samples 89-127 are the adjusted values. Adjustments were made by multiplying the exchange capacity obtained using the $CaCl_2$ solution by a laboratory-determined correction factor, 0.864. This reflects a variance in the exchange capacity of the material due to the variation in hard water composition.

Table 14. (continued)

Sample No. (1)	Materials			NaOH[a]		Temperature[b]		Exch. cap.[c] meq/g (9)	Remarks (10)
	Diat. (gms) (2)	Sod. Sil. Soln. (ml) (3)	Sod. Alum. Soln. (ml) (4)	(gms) (5)	(gms) (6)	°C (7)	°C (8)		
93-1	80	25.3	60	1.2	0	-5	100;85	0.50	Split sample
93-2						60;-5	100;85	0.51	
93-3						60;100	100;85	0.46	
94-1	60	16.9	40	1.2	0	-6	85	0.48	Split sample
94-2						-6	85	0.41	Dewatered prior to freezing
95	60	16.9	40	1.2	0	-6	85	0.53	Used thick sodium silicate suspension
96	60	33.8	40	1.2	0	-6	85	0.59	
97	60	33.8	40	1.2	0	-6	85	0.50	Used thick sodium silicate suspension
98	60	16.9	40	1.2	0	-6	85	0.46	Mixed diatomite w/sodium aluminate solution first
99-1	60	16.9	40	1.2	5	-6	85	0.37	Split sample
99-2						-6	85	0.38	Dewatered prior to freezing
100	60	16.9	80	2.4	0	-6	85	0.45	Mixed diatomite w/sodium aluminate solution first
101	60	33.8	80	2.4	0	-6	85	0.73	
102	60	0	40	1.2	0	Var.	85	Neg.	Heated for four hours at 60-70° prior to freezing at -6°

Table 14. (continued)

	Materials			NaOH[a]		Temperature[b]			
Sample No. (1)	Diat. (gms) (2)	Sod. Sil. Soln.(ml) (3)	Sod.Alum. Soln.(ml) (4)	(gms) (5)	(gms) (6)	°C (7)	°C (8)	Exch. cap.[c] meq/g (9)	Remarks (10)
103-1	60	16.9	56	1.7	0	-6	85	0.49	Split sample
103-2						-6	85	0.53	Washed prior to freezing
104-1	90	25.4	60	1.44	0	-20	85	0.56	Split sample
104-2						-6	85	0.57	
105-1	90	38.0	60	1.44	0	-20	85	0.61	Split sample
105-2						-6	85	0.56	
115-1	90	25.4	60	1.44	0	-20	90	0.60	Split sample
115-2						-20	90;122	0.59	Dewatered prior to freezing
115-3						-20	90;122	0.57	Unwashed sample
116-1	90	25.4	40	0.96	0	-20	90	0.45	Split sample
116-2						-20	90	0.48	Dewatered prior to freezing
116-3						-20	90	0.38	Unwashed
117	60	16.9	40	0.96	0	-20	90	0.62	
118	60	16.9	40	0.96	2	-20	90	0.58	
119	60	16.9	40	0.96	0	-20	90	0.58	Frozen in beaker
120	60	25.4	40	0.96	0	-20	90	0.66	
121	60	25.4	40	0.96	0	-20	90	0.63	Frozen in beaker
122-1	60	25.4	40	0.96	2	-20	90	0.65	Split sample, frozen in beaker
122-2						-20	90	0.52	Unwashed sample

Table 14. (continued)

	Materials			NaOH[a]		Temperature[b]		Exch. cap.[c]	
Sample No. (1)	Diat. (gms) (2)	Sod. Sil. Soln.(ml) (3)	Sod.Alum. Soln.(ml) (4)	(gms) (5)	(gms) (6)	°C (7)	°C (8)	meq/g (9)	Remarks (10)
123-1	60	12.7	30	0.72	0	-20	90	0.47	Split sample, frozen in beaker
123-2						-20	90	0.41	Unwashed sample
124	60	16.9	20	0.48	0	-20	90	0.34	Frozen in beaker
125	60	16.9	20	0.48	2	-20	90	0.34	Frozen in beaker
126	60	16.9	40	0.96	0	25	90	0.58	Washed after setting only 3 hours
127	60	16.9	40	0.96	0	35	90	0.24	
128	60	25.4	40	0.48	0	-20	76	0.62	
129	60	21.1	40	0.48	0	-20	76	0.62	
130	60	16.9	35	0.42	0	-20	76	0.58	
131	60	16.9	40	0.96	0	-20	76	0.62	
132	60	25.4	40	0.96	0	-20	76	0.68	
133	60	21.1	40	0.96	0	-20	76	0.68	
134	60	16.9	35	0.84	0	-20	76	0.62	
135	60	16.9	40	0.96	0	25	76	0.23	
136	60	25.4	50	1.2	0	-20	76	0.78	
136A	600	253.5	109	12		-20	70	0.74	Low capacity probably due to inadequate mixing due to rapid set
136B	600	253.5	109	12		-20	70	0.77	

Table 14. (continued)

	Materials			NaOH[a]		Temperature[b]		Exch. cap.[c]	
Sample No. (1)	Diat. (gms) (2)	Sod. Sil. Soln. (ml) (3)	Sod. Alum. Soln. (ml) (4)	(gms) (5)	(gms) (6)	°C (7)	°C (8)	meq/g (9)	Remarks (10)
136C	960	405.6	174.4	19.2		-20	70-85	0.72	Low capacity probably due to inadequate mixing due to rapid set
136D	1000	422.5	181.7	20		-20	70	0.78	
136E	1000	422.5	181.7	20		-20	80	0.79	
137	60[d]	16.9	40	0.96	0	-20	76	0.64	
138	60[d]	25.4	50	1.2	0	-20	76	0.79	
139	60[d]	16.9	40	0.96	0	-20	76	0.68	Used zeolite softened water for preparation & washing of sample
140	60	33.8	40	0.96	0	-20	25;80	0.58	Later exchange cap. value = 0.56
141	60	25.3	40	0.96	0	-20	25;80	0.63	Later exchange cap. value = 0.70
142	60	20.9	40	0.96	0	-20	25;80	0.63	
143	60	16.9	40	0.96	0	-20	25;80	0.55	
144	60	14.4	40	0.96	0	-20	25;80	0.49	
145	60	33.8	40	0.96	0	-20	80	0.58	Later exchange cap. values = 0.66;0.69

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[d] Johns-Manville Celite 535.

Table 14. (continued)

	Materials			NaOH[a]		Temperature[b]		Exch. cap.[c]	
Sample No. (1)	Diat. (gms) (2)	Sod. Sil. Soln.(ml) (3)	Sod.Alum. Soln.(ml) (4)	(gms) (5)	(gms) (6)	°C (7)	°C (8)	meq/g (9)	Remarks (10)
146	60	25.3	40	0.96	0	-20	80	0.62	Later exchange cap. values = 0.68;0.69
147	60	20.9	40	0.96	0	-20	80	0.68	Later exchange cap. values = 0.69;0.72
148	60	16.9	40	0.96	0	-20	80	0.66	Later exchange cap. values = 0.67;0.67
149	60	14.4	40	0.96	0	-20	80	0.51	Later exchange cap. values = 0.61;0.62
150-160							85-105		Discarded,erratic exchange capacity; probably due to elevated drying temperature
161	60	16.9	35	0.84	0	-20	65-70	0.50	
162	60	16.9	40	0.96	0	-20	65-70	0.55	
163	60	16.9	45	1.08	0	-20	65-70	0.60	
164	60	16.9	50	1.20	0	-20	65-70	0.55	
165	60	21.1	40	0.96	0	-20	65-70	0.62	
166	60	21.1	45	1.08	0	-20	65-70	0.70	
167	60	21.1	50	1.20	0	-20	65-70	0.76	
168	60	25.4	40	0.96	0	-20	65-70	0.65	

Table 14. (continued)

	Materials			NaOH[a]		Temperature[b]			
Sample No. (1)	Diat. (gms) (2)	Sod. Sil. Soln.(ml) (3)	Sod.Alum. Soln.(ml) (4)	(gms) (5)	(gms) (6)	°C (7)	°C (8)	Exch. cap.[c] meq/g (9)	Remarks (10)
169	60	25.4	45	1.08	0	-20	65-70	0.70	
170	60	25.4	50	1.20	0	-20	65-70	0.75	
171	60[e]	25.4	50	1.20	0	-20	65-70	0.81	

[e] Dicalite perlite 4106.

APPENDIX B

ξ Index Calculations

$$\xi = \frac{Hpg}{qw\nu} = \xi \text{ index}$$

where

Hp = head loss or pressure differential across the filter

g = gravity constant

q = flow rate per unit of septum area

ν = kinematic viscosity = $\frac{\mu g}{\gamma_w}$

μ = dynamic or absolute viscosity

γ_w = density of water

w = weight of precoat per unit of septum area

Bromoform, $CHBr_3$, which has a density of 2.85 grams per cc at 25°C, was used as the manometer fluid. Therefore, the observed head loss, hp, is related to Hp in the following manner:

$$Hp = hp(2.85-1.00)\left(\frac{0.0328 \text{ ft}}{1 \text{ cm}}\right) = 0.0607 \text{ hp ft}$$

The filter septum had a diameter of 2.1 inch or an area of 0.0238 ft^2. Using this value, the observed flow rate, q_0, is related to q in the following manner:

$$q = q_0\left(\frac{0.0002642 \text{ gal}}{1 \text{ cc}}\right)\left(\frac{0.1337 \text{ ft}^3}{1 \text{ gal}}\right)\left(\frac{60 \text{ sec}}{1 \text{ min}}\right)\left(\frac{1}{0.0238 \text{ ft}^2}\right)$$

$$q = .089q_0 \text{ ft/min}$$

The weight of diatomite, w_0, is related to w in the following manner:

$$w = w_0\left(\frac{1\ \text{lb}}{453.6\text{g}}\right)\left(\frac{1}{0.0238\ \text{ft}^2}\right)$$

$$w = 0.0927w_0\ \text{lb/ft}^2$$

Substitution of these values into the equation for ξ index yields the following:

$$\xi = \frac{0.738hpg}{q_0 \nu w_0}$$

for

hp readings in centimeters

q_0 readings in cc/sec

w_0 readings in grams

$$g = 32.2\ \text{ft/sec}^2$$

$$\nu = \frac{\mu g}{\gamma_w} = \frac{\left(\frac{0.3482\ \text{lb-min}}{\text{ft}^2}\right)\left(32.2\ \text{ft/sec}^2\right)}{62.4\ \text{lb/ft}^3}$$

at 20.3°C.

$$\therefore \quad \xi = \frac{132\ hp}{q_0 w_0}\ \text{ft/lb at } 20.3°\text{C}$$

Using data for Sample 136D, two runs were made for this sample. Since the test conditions and results were similar, average values will be used.

Graphs were made of flow rate versus head loss for flow rates ranging from 1.43 cc/sec to 5.48 cc/sec. In this manner, a uniform slope of headloss versus flow rate was obtained, thereby, minimizing possible variations. From the graphs, a headloss of 9.25 cm was obtained at a flow rate of 5 cc/sec. Six grams of the sample were used for each run. The average temperature of the effluent during the runs was 20.4°C. Therefore, a viscosity correction of 0.998 will be required. Thus:

$$\xi = \frac{132(9.25)}{5(6)(.998)} \text{ ft/lb}$$

$$\xi = 409 \text{ ft/lb}$$

APPENDIX C

Table 15. Strontium-89 removal study data

Sample No.[a] (1)	Date (2)	Recorded total counts (3)	Time (min) (4)	Recorded activity (cpm) (5)	Recorded activity corr. for coincidence (cpm) (6)	Average true activity[b] cpm ±σ (7)
Back-	9/9/66	410	30	13.7	13.7	13.2±0.46
ground		383	30	12.8	12.8	
1-1	9/9/66	125,743	9	13,972	14,125	
1-2		124,406	9	13,823	13,972	13,746±458[c]
1-3		137,902	9	15,323	15,506	
2-1	9/9/66	133,688	9	14,854	15,026	
2-2		134,716	9	14,968	15,142	14,131±139[c]
2-3		130,415	9	14,490	14,654	
Back-	9/13/66	413	30	13.8	13.8	14.4±0.49
ground		446	30	14.9	14.9	
1-4	9/13/66	842	45	18.7	18.7	
1-5		842	45	18.7	18.7	4.3±0.49
1-6		844	45	18.8	18.8	
2-4	9/13/66	956	45	21.2	21.2	
2-5		1,051	45	23.4	23.4	7.9±0.82
2-6		999	45	22.2	22.2	

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[a] For samples, the first number refers to the large sample; the second number refers to the various aliquots of which numbers 1-3 refer to the initial sample; and numbers 4-6 refer to the filter effluent.

[b] For samples, the reported activity includes correction for background and coincidence. Standard deviations of the samples were determined from the usual equation $\sigma_{R_s} = (\sigma^2_{R_{s+b}} + \sigma^2_{R_b})^{1/2}$ where $\sigma^2_{R_{s+b}}$ was determined from the equation for the standard deviation of the mean,

$$\sigma_{R_{s+b}} \simeq \sqrt{\frac{1}{n(n-1)}\sum_{1}^{n}(X_i-\bar{X})^2}$$

[c] Includes decay correction to 9/13/66.

Table 15. (continued)

Sample No.[a] (1)	Date (2)	Recorded total counts (3)	Time (min) (4)	Recorded activity (cpm) (5)	Recorded activity corr. for coincidence (cpm) (6)	Average true activity[b] cpm ±σ (7)
Background	9/15/66	387	30	12.9	12.9	13.2±0.38
		397	30	13.2	13.2	
		401	30	13.4	13.4	
3a-1	9/15/66	25,082	3	8,360	8,414	8,565±104
3a-2		25,481	3	8,494	8,550	
3a-3		26,137	3	8,712	8,771	
3a-4	9/15/66	961	45	21.4	21.4	7.9±0.41
3a-5		938	45	20.8	20.8	
3a-6		946	45	21.0	21.0	
3b-1	9/15/66	23,277	45	7,759	7,806	8,017±114
3b-2		24,178	45	8,059	8,109	
3b-3		24,372	45	8,124	8,175	
3b-4	9/15/66	973	45	21.6	21.6	8.3±49
3b-5		990	45	22.0	22.0	
3b-6		942	45	20.9	20.9	
Background	9/16/66	413	30	13.8	13.8	13.8±0.40
		398	30	13.3	13.3	
		429	30	14.3	14.3	
4a-1	9/16/66	33,665	3	11,222	11,320	11,271±22
4a-2		33,561	3	11,187	11,284	
4a-3		33,466	3	11,155	11,252	
4a-4	9/16/66	855	45	19.0	19.0	4.5±0.60
4a-5		820	45	18.2	18.2	
4a-6		793	45	17.6	17.6	
4b-1	9/16/66	30,342	3	10,114	10,193	10,629±271
4b-2		33,104	3	11,035	11,130	
4b-3		31,557	3	10,519	10,605	
4b-4	9/16/66	967	45	21.5	21.5	7.9±0.60
4b-5		948	45	21.1	21.1	
4b-6		1,016	45	22.6	22.6	

Typical Calculations for Strontium-89 Removal Study

Sample 4a

^{89}Sr sample was diluted to 1010 ml with usual $CaCl_2$-$MgSO_4$ hardness solution. Three 10 ml samples were pipetted into planchets and evaporated to dryness for activity determinations—10 ml/planchet. The remaining 980 ml of radioactive solution were passed through the exchange column. The apparatus was rinsed and the effluent was diluted to 2000 ml with distilled water. Two 10 ml portions of the effluent were pipetted to each of three planchets and evaporated to dryness for activity determinations. Samples were counted on the same date; therefore, no decay corrections were required. Likewise, the net weights of the samples were approximately equal, and therefore, no correction was made for self-absorption. The net weight of evaporated, initial 10 ml portions ranged from 0.0049-0.0058 gms, while those for the final 20 ml portions ranged from .0043-0.0055 gms.

Coincidence corrections

General equation

$$R = \frac{R_0}{1-R_0\tau}$$

where

R = true rate

R_0 = recorded activity

Table 16. Activity determination

Sample	Net weight (gms)	Total counts	Time (min)	Counts/min
4a-1	0.0058	33,665	3	11,222
4a-2	0.0051	33,561	3	11,187
4a-3	0.0049	33,466	3	11,155
4a-4	0.0050	855	45	19.0
4a-5	0.0048	820	45	18.2
4a-6	0.0055	793	45	17.6
Background		413	30	13.8
Background		398	30	13.3
Background		429	30	14.3

τ = resolving time = 0.77 μ minutes by previous determination

Sample 4a-1

$$R = \frac{R_0}{1-R_0\tau} = \frac{11{,}222 \text{ cpm}}{1-(11{,}222 \text{ cpm})(0.77\times10^{-6} \text{ min})}$$

$$= 11{,}320 \text{ cpm}$$

Sample 4a-2

$$R = \frac{R_0}{1-R_0\tau} = \frac{11{,}187 \text{ cpm}}{1-(11{,}187 \text{ cpm})(0.77\times10^{-6} \text{ min})}$$

$$= 11{,}284 \text{ cpm}$$

Sample 4a-3

$$R = \frac{R_0}{1-R_0\tau} = \frac{11{,}155 \text{ cpm}}{1-(11{,}155 \text{ cpm})(0.77\times10^{-6} \text{ min})}$$

$$= 11{,}252 \text{ cpm}$$

∴ Average determined activity in initial 10 ml samples

= 11,285 cpm - 13.8 cpm background

= <u>11,271 cpm</u>

Samples 4a-4, 4a-5 and 4a-6

No coincidence correction is required.

Average determined activity in final effluent

20 ml samples = 18.3 cpm - 13.8 cpm background

= <u>4.5 cpm</u>

$$\text{Removal Efficiency} = \frac{100(\text{Initial Activity} - \text{Final Activity})}{\text{Initial Activity}} \text{ percent}$$

Since the 980 ml passed through the filter was diluted to 2000 ml and 20 ml were used for each final sample, the dilution correction factor = 0.980 for adjusting the initial activity per 10 ml sample to the equivalent volume of effluent.

∴ Corrected initial activity = (Initial Activity)(0.980)

= 11,271 cpm (0.980)

= 11,046 cpm

$$\therefore \text{Removal Efficiency} = \frac{(11{,}046\text{ cpm} - 4.5\text{ cpm})100}{11{,}046\text{ cpm}}$$

= <u>99.96%</u>

APPENDIX D

Calculations for Chemical Durability Study

Glass Sample No. 3

Initial activity equals sum of activity removed in Samples 3a and 3b. Average activity removed per 10 ml of sample for 3a was 8557 cpm. Average activity removed per 10 ml of Sample 3b was 8009 cpm. Specific weight of glass was 2.53 g/cm^3.

$$\therefore \sum \text{Activity} = \frac{980 \text{ ml}}{10 \text{ ml}}(8557 \text{ cpm}) + \frac{980 \text{ ml}}{10 \text{ ml}}(8009 \text{ cpm})$$

$$= 1{,}623{,}468 \text{ cpm}$$

Weight of Glass Sample = 241.1 grams

$$\therefore \text{Initial activity per gram of glass} = \frac{1{,}623{,}468}{241.1\text{g}}\text{cpm}$$

$$= 6{,}734 \text{ cpm/g}$$

$$\text{Initial activity per cm}^3 \text{ of glass} = 6{,}734 \text{ cpm} \times 2.53 \text{ g/cm}^3$$

$$= 17{,}037 \text{ cpm/cm}^3$$

Decay corrections

Radioactive decay corrections were made using the standard equation:

$$A = A_0 e^{-\lambda t}$$

where

A_0 = activity at some original time

A = activity remaining after a time interval, t

λ = decay constant = 0.01372 day^{-1} for strontium-89

e = base of natural logarithms

t = elapsed time, days

Table 17. Sample No. 3

Date	A_0 (cpm/g)	t (days)	$e^{-\lambda t}$	A (cpm/g)	Average activity leached (cpm)	Corrected activity (cpm/g)	Percent leached
<u>1966</u>							
11/11	6734	57	0.4575	3081	17	3064	0.55
11/14	3064	3	0.9501	2911	15	2896	0.52
11/21	2896	7	0.9085	2631	9	2622	0.34
11/28	2622	7	0.9085	2382	13	2369	0.55
12/3	2369	5	0.9337	2212	10	2202	0.45
12/10	2202	7	0.9085	2001	8	1993	0.40
12/17	1993	7	0.9085	1811	9	1802	0.50
12/31	1802	14	0.8252	1487	7	1480	0.47

<u>Glass Sample No. 4</u>

Initial activity equals the sum of activity removed in Samples 4a and 4b. Average activity removed per 10 ml of Sample 4a was 11,267 cpm. Average activity removed per 10 ml of Sample 4b was 10,621 cpm. Specific weight of glass was 2.53 g/cm^3.

$$\therefore \sum \text{Activity} = \frac{980 \text{ ml}}{10 \text{ ml}}(11{,}267 \text{ cpm}) + \frac{980 \text{ ml}}{10 \text{ ml}}(10{,}621 \text{ cpm})$$

$$= 2{,}145{,}024 \text{ cpm}$$

Weight of glass sample = 241.1 grams

$\therefore$ Initial activity per gram of glass $= \dfrac{2{,}145{,}024 \text{ cpm}}{241.1\text{g}}$

$= 8{,}897$ cpm/g

Initial activity per cm^3 of glass $= 8{,}897 \text{ cpm} \times 2.53 \text{ g/cm}^3$

$= 22{,}509 \text{ cpm/cm}^3$

Table 18. Sample No. 4

Date	A_0 (cpm/g)	t (days)	$e^{-\lambda t}$	A (cpm/g)	Average activity leached (cpm)	Corrected activity (cpm/g)	Percent leached
1966							
11/11	8897	56	0.4638	4126	18	4108	0.44
11/14	4108	3	0.9501	3903	20	3883	0.51
11/21	3893	7	0.9085	3528	10	3518	0.28
11/28	3518	7	0.9085	3196	15	3181	0.47
12/3	3181	5	0.9337	2970	14	2956	0.47
12/10	2956	7	0.9085	2686	10	2676	0.37
12/17	2676	7	0.9085	2431	11	2427	0.45
12/31	2420	14	0.8252	1997	10	1987	0.50

Equations Used for Apparent Corrosion Rate Determinations

The equation used for the determination of the apparent corrosion rate was as follows:

$$\frac{\text{cm}}{\text{wk}} = \frac{\text{eluted activity (cpm/wk-g)}}{\text{(surface area, cm}^2\text{/g)(activity concentrations, cpm/cm}^3\text{)}}$$

where

eluted activity = activity leached per week per sample since each sample was 1 gram

surface area = 125 cm^2/g (assumed value)

activity concentrations = activity per sample corrected for decay and leaching

weight per cm^3 = 2.53 gram, average of Samples 3 and 4.

$\therefore$ Multiply activity per gram by 2.53 to obtain activity per cm^3.

The indicated error of the leaching values or apparent corrosion rates were determined by the standard deviation of the mean or standard error, $\sigma_{\bar{\chi}}$, where

$$\sigma_{\bar{\chi}} \approx \sqrt{\frac{1}{n(n-1)} \sum_{1}^{n} (\chi_i - \bar{\chi})^2}$$

and

n = 3 × the number of weeks since three one-gram samples were used from each glass sample. Due to the short initial leaching periods, separate n values were used for the initial runs and for the 7-day runs

χ_i = individual apparent corrosion rates

$\bar{\chi}$ = mean apparent corrosion rates

Table 19. Chemical durability study

Date	Obs. No.	Eluted activity		Activity concentration		Apparent corrosion rate	
		Sample No. 3 cpm	Sample No. 4 cpm	Sample No. 3 cpm/cm^3	Sample No. 4 cpm/cm^3	Sample No. 3 cm/wk	Sample No. 4 cm/wk
1966							
11/11	1	113.4[a]	125.3[a]	7794	10440	1.16×10^{-4}	9.60×10^{-5}
	2	119.7[a]	128.8[a]	7794	10440	1.23×10^{-4}	9.87×10^{-5}
	3	120.4[a]	133.7[a]	7794	10440	1.24×10^{-4}	10.24×10^{-5}
11/14	1	56.7[b]	70.7[b]	7364	9875	6.16×10^{-5}	5.73×10^{-5}
	2	49.4[b]	71.4[b]	7364	9875	5.37×10^{-5}	5.78×10^{-5}
	3	55.6[b]	72.1[b]	7364	9875	6.04×10^{-5}	5.84×10^{-5}
11/21	1	9.6	11.1	6656	8925	1.15×10^{-5}	9.95×10^{-6}
	2	10.2	10.9	6656	8925	1.23×10^{-5}	9.77×10^{-6}
	3	7.5	8.4	6656	8925	9.01×10^{-6}	7.53×10^{-6}
11/28	1	12.6	15.4	6026	8086	1.67×10^{-5}	1.52×10^{-5}
	2	13.3	15.3	6026	8086	1.77×10^{-5}	1.51×10^{-5}
	3	13.0	14.3	6026	8086	1.73×10^{-5}	1.41×10^{-5}
12/3	1	12.3	13.1	5596	7514	1.76×10^{-5}	1.39×10^{-5}
	2	9.0	15.4	5596	7514	1.29×10^{-5}	1.64×10^{-5}
	3	9.0	14.7	5596	7514	1.29×10^{-5}	1.56×10^{-5}
12/10	1	8.3	11.1	5061	6795	1.31×10^{-5}	1.31×10^{-5}
	2	7.8	9.4	5061	6795	1.23×10^{-5}	1.11×10^{-5}
	3	9.0	9.8	5061	6795	1.42×10^{-5}	1.15×10^{-5}
12/17	1	8.4	10.3	4580	6151	1.47×10^{-5}	1.34×10^{-5}
	2	7.7	13.2	4580	6151	1.34×10^{-5}	1.72×10^{-5}
	3	10.4	8.7	4580	6151	1.82×10^{-5}	1.13×10^{-5}
12/31	1	7.4	9.9	3760	5053	1.57×10^{-5}	1.57×10^{-5}
	2	7.8	12.1[c]	3760	5053	1.66×10^{-5}	1.92×10^{-5}
	3	6.8	9.3	3760	5053	1.45×10^{-5}	1.47×10^{-5}

[a] Given values are based upon 7-day run, obtained by multiplying actual value by 7.

[b] Given values are based upon 7-day run, obtained by multiplying actual value by 7/2.

[c] Doubtful value due to spillage of previously counted sample into planchet. Value was not used in final calculations.