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FIXATION OF ATOMIC WASTES IN INERT SOLID MATERIALS

MASTER

By

Eric B. Fowler

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Presented at the 19th Purdue Industrial Waste Conference, Lafayette, Indiana, May 5-7, 1964.

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FIXATION OF ATOMIC WASTES IN INERT SOLID MATERIALS

By

Eric B. Fowler*

INTRODUCTION:

A relatively efficient solution to many of the problems associated with the disposal of low-level radioactive wastes occurred at an early date in the history of the Atomic Energy Industry. Such wastes represent minor radiation hazards and can be treated with conventional equipment. One such treatment plant is the new \$2,000,000 facility located at the Los Alamos Scientific Laboratory, Los Alamos, New Mexico, which uses chemical precipitation for alpha removal and ion exchange for beta-gamma control. The processes are very similar to standard water treatment methods and equipment is identical to that of standard water and sewage treatment plants.

In contra-distinction, the problems associated with the disposal of high-level wastes which arise from the plutonium production industry and from the processing of spent reactor fuel elements are largely unsolved at this date. This paper will review some of the approaches to these problems and the present status of the science of fixation of high-level atomic wastes in inert, solid materials.

To be presented at the 19th Purdue Industrial Waste Conference, May 5-7, 1964, Lafayette, Indiana.

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The principal problem associated with the disposal of a high-level waste is due directly or indirectly to the intense radiation encountered. Other problems are related to the half-lives of the radionuclides present and to the corrosive nature of many of these wastes.

The magnitude of the problem is best illustrated by data relative to the volumes of wastes and associated radioactivities currently being produced. High levels of radioactivity are created when uranium, enriched uranium, or plutonium are used as fuels in nuclear reactors. A typical power reactor operating at 100 electrical megawatts for 10 days will produce about 11 pounds of fission products, or about the same amount as produced by a 100 kiloton atomic weapon.

Reactors burn fuel just as do all other types of energy-producing machines. However, in the case of a reactor the end-products are radioactive fission products from the parent element.

When the spent fuel elements are removed from the reactor, they are usually stored at the reactor site until the short-lived radioisotopes have decayed to a point where the fuel elements can be processed for the recovery of useable fuel. In the case of a 150 electrical megawatt plant, the radioactivity from the stored fuel elements of only 1/3 of the core may contain an average of 30,000,000 curies of radioactivity*. These fuel elements would generate about 100 thermal kilowatts of energy during a six month storage period.

*The curie is a measure of decay rate and is equal to 3.7×10^{10} disintegrations per second.

The radiation and thermal data indicate the problems encountered for short-term storage of these elements and for ultimate disposal of the wastes which later arise from their processing. It is significant to note that most of the man-made radioactive material produced to date has not been released to the environment, but has been generated by reactors and has been contained.

Radioactive wastes derived from spent nuclear fuels will continue to require processing and a method of ultimate disposal. The projected 35,000 electrical megawatts of installed nuclear electrical power by 1980 will require the processing of from 200,000 to 2,000,000 gallons of radioactive waste per year. Furthermore, by 1980 the stored volume of radioactive wastes may reach 1,000,000 to 10,000,000 gallons and these wastes will contain approximately ten billion curies of fission products.

NEED FOR PROCESSING:

There are a number of reasons for the processing of wastes arising from irradiated fuels - one of the more important being the isolation and containment of those radioactive materials which present radiation hazards. Radioactive decay is a random physical process; there are no known methods of changing the rate of decay. The biological-disposal approach does not apply.

Other objectives of processing irradiated fuels include the recovery of unused fuel material, the separation of new fissile material, and the isolation of fission products - some of which have industrial uses. All production or processing operations to date involve aqueous stages resulting in liquid wastes.

The chemical techniques involved in processing depend on the fuel element structure, particularly the cladding material, and on the presence of inert alloying materials in the fuel. (1-4) At present as many as eight decladding and nine solution procedures along with seven solvent extraction systems are being studied. Obviously the multiplicity in fuel element structure and fuel element reprocessing leads to variations in waste treatment and disposal.

A brief review of some processes associated with production and recovery follows as background material for the problems associated with ultimate disposal.

In the Purex process where aluminum clad elements are processed, irradiated natural uranium and fission products are dissolved in nitric acid. Tributyl phosphate (T.B.P.) is used as the solvent to separate the uranium and plutonium from the fission products.

In the Darex process dilute aqua regia is used to dissolve the stainless steel cladding of the fuel elements and TBP extraction is used to recover uranium and plutonium after the chloride ion concentration has been reduced by nitric acid stripping.

The Zirconium fluoride process is used to remove zirconium or zirconium alloy cladding material from fuel elements. Hydrofluoric acid is used to dissolve the zirconium clad element. Chromate is added to oxidize the uranium to uranium-6 and aluminum is added to complex the free fluoride. Uranium is finally recovered by TBP extraction after the addition of nitric acid. In some processes mercuric nitrate is used as a catalyst; in others boiling 8 to 12 normal sulfuric acid is used to

dissolve stainless steel cladding. It is quite evident that the wastes arising from these processes are far different from those arising in a normal industrial process.

In some recovery processes about 99.9% of the radioactive material is removed in the initial aqueous fission product waste. Such high-level wastes may contain 500 to 10,000 curies per gallon; this concentration of radioactivity may be sufficiently high to generate heat through radioactive decay at a rate of 10 to 200 BTU/gallon/hour.

APPROACHES TO PROCESSING:

High-level waste disposal requires containment for periods of several thousand years. Containment may be accomplished in temporary storage tanks or by environmental storage after absolute fixation. The waste disposal concept adopted will, to a large extent, be dictated by the waste processing scheme. Hence, in a waste management system of the type being discussed, treatment and disposal form a unified effort. Ultimate storage possibilities, the temperament of the public, and an economic balance between the value of nuclear power and the reduction of hazards are factors which must be considered in developing methods for the handling and disposal of radioactive wastes. It is highly probable that if the point is attained where the probability of harmful release of radioactivity is infinitely small, then the cost of handling the waste will exceed the value of the generated electrical power.

In a program of ultimate disposal, the following possibilities exist as offering a minimum hazard to present and future generations:

1. Subsurface disposal of high-level solid and liquid waste as in salt deposits.
2. Buried tanks for storage of high-level liquid waste.
3. Separation, isolation, and recovery of the most toxic and long-lived isotopes.
4. Conversion of high-level liquid wastes into stable, solid forms and ultimate storage.

Of these possibilities, only the last is of interest here. The concept of ultimate disposal implies that the radioactive material is fixed in a non-leachable matrix for the lifetime of that radioactive material. Presumably the radioactive material will be placed in a suitable container and stored in some subsurface formation.

At present it seems desirable to use a system of intermediate containment in addition to that which might be provided by a geological formation. Underground vaults or abandoned mines seem to hold promise as sites for storage of high-level fixed radioactive waste.⁽⁵⁾ Fixation of the waste in a stable form is desirable since the amount of radioactive material that can be safely released to the environment is exceedingly small. As an illustration, the maximum permissible concentration for Sr^{90} in drinking water is equivalent to about 10^{-9} ppm by weight and the allowable arsenic concentration in water is 0.05 ppm or a factor of 50 million times greater. The requirement for absoluteness of fixation becomes obvious when one considers that if a gallon of high-level radioactive waste concentrate containing 5,000 curies of Sr^{90} were fixed in a material which yielded a total leach of only 1/10 of 1% of the waste

present, then 8×10^8 gallons of dilution water would be required to reach the allowable maximum permissible concentration of Sr^{90} for drinking water related to bone deposition and the 40-hour work week. With these restrictions the term "ultimate fixation" assumes a new meaning and requires a new technology which is still in its infancy.

The development of technology and systems for the fixation of waste into solid, inert forms has been directed along the following lines:

1. In-tank solidification.
2. Conversion of the waste into glasses and synthetic "micas".
3. Fixation in montmorillonite clay.
4. Calcination.
5. Conversion into other ceramics.
6. Entrapment in other materials.
7. Sorption of the radioactive nuclides on synthetic zeolites.

With the previous review of waste types and problems associated with their disposal in mind, the remainder of this paper will review the above methods of fixation and disposal.

In-Tank Solidification. This approach to disposal offers the advantage of utilizing existing tank capacity and the possibility of recovering at a later date, should the need arise, certain potentially valuable materials such as strontium, cesium, and technetium. Typical "in-use" tanks are shown in Fig. 1. The complexity of these containers is obvious. In this approach to disposal, the non-heating wastes would be evaporated to form a salt cake within the tanks in which the wastes are presently stored.

Fig. 1

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Fig 1

Non-heating wastes are derived from aged wastes from which many of the short-lived radioactive constituents have decayed. There are tens of millions of gallons of these wastes stored at present having salt contents of about 30%. It has been calculated that salt cakes up to 16 feet thick can be formed from these wastes.

Self-heating wastes must be handled quite differently. They would be fractionated to permit the separate storage of the long-lived heat emitters in small-volume, high-integrity containers.⁽⁶⁾ After a few years storage, the residual wastes would be treated as non-heating wastes. Some of the heat generated arises from the long-lived cesium-137, strontium-90, promethium-147, cerium-144, and technetium-99. A treatment and disposal scheme would probably incorporate recovery of some or all of these isotopes for future industrial use. Such a treatment scheme might include any or all of the following techniques: (1) separation of extraneous solids by centrifugation; (2) removal of cesium, strontium, and rare earths by solvent extraction; (3) interim storage of the short-lived fission products and non-radioactive salts under self-boiling conditions; (4) absorption of cesium on clinoptilolite; and (5) absorption of cesium and strontium on certain alumino silicates.

The recovery of technetium would be accomplished on a strong anion exchange resin and disposal of residual wastes with other non-heating wastes for evaporation to a salt cake would be an integral part of this scheme. Cesium and strontium fractions would be absorbed on a crystalline zeolite; dehydrated and stored in stainless steel containers for future use. It is obvious that a

major disadvantage of this scheme lies in the fact that neither the fixation nor the disposal can be considered permanent since the tanks presently in use have a finite life and since the hazardous material remains as an inventory item requiring the strictest type of control.

Conversion Into Glasses and Micas. The conversion of wastes into glasses and synthetic "micas" is considered by many workers to be the most suitable present means of disposal of high-level wastes.⁽⁷⁾ The lower leachability of the glass formed as compared to concrete, calcined solids, evaporated solids, and other matrices offers a distinct advantage over these latter materials. Vitrification with or without an intermediate calcination step may be the answer to ultimate disposal of high-level waste.

The Canadians at Chalk River are nearing completion of their developmental work on the incorporation of waste fission products in glass. In their process the nitric acid waste is mixed with a finely divided nepheline syenite which is a naturally occurring aluminosilicate. Calcium oxide is added to this mixture. The gel which is derived can be rapidly dried, easily denitrated, and fused into a relatively leach resistant glass block. Blocks of this glass weighing up to 2 kilograms and containing up to 100 curies of mixed fission products have been successfully made by heating the feed at 1350°C for one hour.⁽⁸⁾

Scrubbers are provided for the furnace off-gases since very definite amounts of both ruthenium and cesium are volatilized. Some of the ruthenium and cesium has been found to react with the refractories in the furnace causing the furnace lining to become contaminated. Cesium losses can be reduced to less than 1% by providing a cover

of powdered nepheline syenite.⁽⁹⁾ Iron-containing ceramics have been used to trap ruthenium and cesium in the furnace off gases.⁽¹⁰⁾ The leach rate of these glasses is about 3×10^{-7} grams of glass per square centimeter per day, however at Sr^{90} concentrations of only 6×10^{-4} grams per gram of glass, the maximum allowable leach rate would be 5×10^{-12} grams of glass per square centimeter per day.⁽¹¹⁾ It is obvious that this glass per se could not be stored in the open environment. Modifications of this process are being studied at Harwell in England,⁽¹²⁾ at the Brookhaven National Laboratory, and at the Hanford Works. A typical flow diagram of the Harwell plant is presented in Fig. 2.

The French workers have prepared synthetic "micas" as well as glasses of a high leach resistance⁽¹³⁾ and are operating a pilot plant at a continuous flow rate of about 5 liters per hour.

The processes involving the incorporation of high-level wastes into glasses offer a number of advantages. A well prepared glass is fairly resistant to wear, decay, chemical attack, and leaching. Natural low cost material can be used; the product is dense, it can be molded and it can be produced by a continuous process. With the exception of a few elements such as uranium, iron, and aluminum, most constituents of the waste solution can be incorporated into glasses without recourse to extremely high fusion temperatures. There are certain disadvantages such as increase in cost as fusion temperatures are increased; the volatilization of alkali metals which occurs at higher fusion temperatures; and possible increased leaching which may be brought about by the addition of

Fig. 2

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Fig 2

certain fluxes. Further, since the fused mass of glass has a relatively low melting point the structural integrity of the glassy mass may be affected by the heat of radioactive decay. Volume reduction is not as great as experienced in calcination, and certain of the fusion mixtures have proved extremely corrosive.

Montmorillonite Clay Process. Some research has been directed toward the use of natural clay such as montmorillonite as a fixing medium. Some of the original work at the Los Alamos Scientific Laboratory was that of Elgin Rex.⁽¹⁴⁾ The cation exchange capacity of montmorillonite is fairly high, being 100 to 150 milliequivalents per 100 grams.⁽¹⁵⁾ Its structure can be changed by heating to form an alumino silicate lattice thereby blocking the reversibility of the exchange reaction. Fixation at 900°C is fairly complete.

At the Brookhaven National Laboratory clays have been extruded in pellet form as seen in Fig. 3.⁽¹⁶⁾ Radioactive wastes have been passed through columns of these extruded clays; after the available exchange sites have been exhausted, the clay and fission product mixture is fired at 1250°C. The process is simple and significant amounts of fission products are not released when the vitrified mass is leached with sea water. However, large amounts of stable salts in the high-level waste reduce the efficiency of any direct process based on ion exchange reactions. Furthermore, clays are quite selective toward the ions present and the wastes contain various chemical forms and many ions which may not be readily sorbed. Ruthenium again presents a problem, the system is pH sensitive and sludges in the feed can not be tolerated.

MONTMORILLONITE CLAY -"SPAGHETTI"- CONTAINED IN GLASS CYLINDER

Fig. 3

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Combinations of ion exchange and solvent extraction processes are being studied at Hanford.⁽¹⁷⁾ Alkaline Purex supernatant waste is being treated with synthetic zeolite resin and with the natural ion exchange mineral clinoptilolite in a program of purification and recovery of cesium. The scavenging of cesium with sparingly soluble metal ferro cyanides, ferri cyanides, phosphotungstates, and phosphomolybdates is under study at Savannah River as well as at the Hanford Works.⁽¹⁸⁾ The sorption of strontium and rare earths on inorganic high capacity and low selectivity zeolites is also being studied at Hanford for the treatment of high-level wastes.⁽¹⁹⁾ After loading, the synthetic zeolite bed is dehydrated prior to encapsulation to prevent pressurization from radiolytic decomposition of residual moisture.

One advantage of this modification of the clay ion exchange process is that it allows for the selective recovery of radionuclides and for the isolated storage of high-level materials. However, as in the case of in-tank storage, containment control of the separated fractions will be required over extended periods of time.

Calcination. A number of calcination processes have been developed to reduce waste to granular solids. The drying and decomposition which occurs on calcination produces a mixture of oxides. Calcination may be employed as an intermediate or as a final step in ultimate fixation. Investigations include pot calcination, spray calcination, fluidized bed calcination, and calcination in a rotary ball kiln.

Pot calcination in its simplest form is a batch operation, shown schematically in Fig. 4. The high-level waste is slowly fed into a heated pot where the waste is concentrated, dried and calcined. The pot is then sealed and becomes the fission product containment vessel. Both Hanford⁽²⁰⁾ and Oak Ridge⁽²¹⁾ have contributed to the development of this process. Several waste types have been investigated. Nitrate wastes are converted to refractory oxides at 900°C without difficulty. Phosphate and borophosphate glasses can be prepared from TBP-25 solvent extraction wastes, Darex waste and Purex waste. Hanford Works plans to have a full sized prototype calciner in operation by 1965.

Problems common to all high temperature processes require further investigation. The presence of mercury causes some difficulty since mercury forms no compounds stable at high temperatures. Sodium nitrate, which is not calcined at the temperatures of the pot, is unstable to radiation. The volatility of ruthenium remains a problem and sulfate in excess amounts causes the formation of the less stable sulfates of iron, nickel, and chromium. Decomposition products of the sulfates are extremely corrosive. Excesses of magnesium and calcium have been used to minify the sulfate problem.⁽²²⁾

The group at Oak Ridge is investigating a process in which the calcined material is mixed with additives and then converted to a glass.⁽²³⁾ The magnitude of the off-gas problem varies with the type of waste. Condensers, caustic scrubbers, electrostatic scrubbers, silica gel beds, and absolute filters have been installed in an attempt to solve these problems. The possibility of a

Fig. 4

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Fig 4

chemical explosion occurring when nitrates and organic raffinates are heated to dryness must be realized.

Spray Calcination. Spray calcination has been investigated at the Hanford Works where it was first used to process high-level radioactive wastes on larger than laboratory scale, Fig. 5. Liquid waste is injected through a pneumatic atomizing nozzle and the calcine is collected in pots below the calciner where a melt can be produced thus offering a continuous flow process. Where the volume of waste from the processing of one ton of uranium fuel was 40 gallons, a waste volume reduction of 13 was experienced.⁽²⁴⁾ Extreme volume reductions are not desirable since at higher concentrations the heat of radioactive decay becomes a problem during ultimate storage.⁽²⁵⁾ Obviously as wastes age, higher concentrations, that is, higher volume reductions may be employed.

In the spray calciner, off-gas problems are multiplied and special scrubbers and filters must be employed to reduce the volume of ejected radionuclides. Sugar has been admixed with the waste and thus used as a reducing agent to decrease the volatility of ruthenium. Furthermore, sugar promotes the destruction of nitrate and provides a "thermal spike" thereby aiding in the calcination of refractory type wastes. Although the spray calciner does offer a simple unit operation, major disadvantages are associated with the off-gas problems and the controlling of particulate matter. The variety of units involved in the spray calciner requires close supervision and maintenance.

Fig. 5

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Fig 5

Fluidized Bed Calcination. The fluidized bed calciner provides a continuous conversion process and has been under study at the Idaho Chemical Processing Plant over the past several years.⁽²⁶⁾ A simple schematic (Fig. 6) illustrates the heart of the process. In this process the waste is injected into a heated bed of granular solids which is fluidized with air. As thermal decomposition proceeds, layers of solids build up on the bed particles. Bed temperatures are maintained between 300 and 600°C. Heat may be introduced into the bed through the use of circulating NaK, the use of sheathed electrical resistance heaters, or by the use of direct-fired tubes.

Particle size may be controlled by varying the atomizing rate. Several factors control the structural type alumina produced and its porosity.⁽²⁷⁾ The average bed particle size decreases and particle elutriation rate increases with increasing alpha alumina content.⁽²⁸⁾ However, particle attrition also increases with alpha alumina content and with high alpha alumina content in the bed virtually the entire theoretical feed rate is removed from the calciner as entrained solid. As would be expected, off-gases constitute a major problem due to the entrained material. An air-cooled product storage facility is a necessary part of this system since the calcined wastes have a relatively high leachability. However, this process might also be used as an intermediate step toward ultimate fixation.

The process is extremely sensitive due to the large number of complex variables which must be controlled in order to maintain fluidization. However, a 59 gallon per hour treatment plant has been operated successfully at the

Fig. 6

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Fig 6

Idaho Chemical Processing Plant since December 3, 1963. It is the only production scale plant of any type presently in operation in the United States. The operation of the fixation plant is manned by the same crew that operates the fuel reprocessing plant. The bed temperature is maintained at 400°C with NaK. Boric acid is added to the waste to prevent the formation of alpha alumina. The waste treated is five years old, contains 15 curies per gallon, and is 1.7 molar in aluminum nitrate. A volume reduction of 10.2 is obtained, and the product solids can be incorporated into lead borate glass. Costs are comparable with tank storage.

Rotary Ball Kiln Calciner. In the rotary calciner (Fig. 7) waste is fed into the upper section of an inclined rotating ball mill which is heated electrically to a temperature of about 700°C. Hatch and coworkers⁽²⁹⁾ have heroically developed the techniques and equipment in use and have processed synthetic wastes.

Off-gas and particulate entrainment problems are not as great as encountered with the spray calciner, however this process does not produce a material which is ready for ultimate disposal, and a number of wearing surfaces require continuous maintenance. It appears that the development of the more promising phosphate glass process will replace the rotary ball kiln.

Entrapment In Other Materials. Materials such as concrete, tar, sulfur, and synthetic zeolites have been considered as media for the entrapment of wastes generated in the Atomic Energy industry. The French have used concrete extensively for the fixation of low-level and intermediate-level wastes. The Belgians and the English

Fig. 7

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Fig 7

have considered the use of tar for the disposal of non-heating radioactive wastes. However, in neither case is fixation complete.

At the Savannah River Laboratory⁽³⁰⁾ wastes have been mixed with molten sulfur. After evaporation of the liquid and solidification of the block, the final volume is somewhat less than that of the original waste solution.

Leaching tests indicate a stable sulfur waste matrix of relatively low leachability. Ruthenium volatility may be reduced in this system since the temperatures encountered are lower than those employed in calcination.⁽³¹⁾ Sulfur is relatively inexpensive and is not as susceptible to radiation damage as are other media employed in ultimate fixation. However, melting of the sulfur mass by fission product heat could occur with subsequent settling of the fission products, hence local concentration and enhanced heating problems.

Conversion Into Other Ceramics. As has been intimated, the ideal medium for ultimate fixation of high-level materials would have the following characteristics: (1) the medium should be essentially non-leachable; (2) it should be resistant to corrosion by all chemical entities encountered; (3) it must be resistant to the effects of radioactivity; and (4) it should be of such a nature as to readily allow for the dissipation of locally generated heat. A ceramic body can be prepared to satisfy these requirements to a high degree.

In theory, a ceramic might be employed as a sponge in which the wastes are sorbed. A sponge composition having proper fusion characteristics can be fired after the sorption cycle thus fixing the radionuclides within the ceramic matrix.

Early in 1958, an investigation was initiated at the Los Alamos Scientific Laboratory on the various types of ceramics produced by Coors Porcelain Company.⁽³²⁾ Ceramics of high porosity were prepared which could be used to sorb liquid wastes through several soaking and drying cycles. Ceramics have been produced which have porosities of about 50%. The spherical shapes formed were found to sorb about 10 gallons of waste per packed cubic foot when five soaking and drying cycles were employed.

After the fifth soaking and drying cycle the clay body was fired and fused at about 1300°C. Leaching rates from the fused body were extremely low. Recent changes in technology indicate that waste volumes may be decreased by a factor of 10 or more and burnup in reactors may be increased such that the specific activity of the waste will be much higher than wastes previously treated. As a result multiple soakings and dryings may not be necessary and work is progressing on the investigation of a single soaking and drying cycle of the ceramic spheres.

The single cycle approach leads to more flexibility in the selection of the ceramic sponge composition since the body strength required for multiple soaking and drying is no longer necessary. A number of factors must be controlled to produce a porous ceramic in which the internal voids are connected by a network of capillaries.

Ten compositions known to yield ceramics with desirable sponge characteristics were investigated. The sponge finally selected had a composition of 20% diatomaceous earth, 20% silica, 45% feldspar, and 15% ball clay. This composition yielded a sponge having desirable firing and fired properties. It is worthy of note that the production of a desirable sponge presents as many problems as does the sorbing of the waste

and the firing of the ceramic shape.

Spherical sponges offer the advantage of providing a definite void volume among adjacent spheres, both in the soaking and in the drying process; this void volume is also desirable if air circulation for cooling during a storage period is required. Furthermore, the spherical sponges do not chip readily, and dry and fuse more uniformly than some other shapes.

Much of the original experimental work was conducted in a laboratory apparatus where variables could be more readily controlled, and where small volumes of waste could be tested.⁽³³⁾ The apparatus used is shown in Fig. 8.

The time required to dry a ceramic sponge to constant weight varies with the sorbed material. For example, a shape soaked in water can be dried in 30 minutes at 180°C but a similar shape soaked in waste* used in this study required 3-1/2 hours at a temperature of 180°C. Data from typical runs at varying temperatures, but with constant air flow, are shown in Fig. 9. These data were obtained with 1-inch spheres, however in one experiment 2-1/2 inch spheres were used. In these runs the time required to reach constant weight was the same for both sizes. It was found that waste sorption decreased rapidly after the initial one or two cycles. That this may be due to a filling or clogging of the interstitial capillaries is shown in Fig. 10.

Condensate from the drying cycle was found to contain only a small percentage of the radionuclide sorbed by the sponge; this condensate can be treated in a low-level waste treatment plant.

* The synthetic waste used in these experiments had the following composition: 1.5M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.0M HNO_3 , and 3.33 gms/liter Fe as $\text{Fe}(\text{NO}_3)_3$.

Fig. 8

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Fig. 8

Fig. 9

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Fig. 10

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After the final cycling, spheres are transferred to the cars of the tunnel kiln (Fig. 11) and fired in the kiln at about 1200°C. In experiments conducted thus far, cesium-137 was not volatilized in either the soaking and drying cycling or in the tunnel kiln. However, ruthenium-106 presents a problem since it was found to volatilize in the drying cycle at 300°C and in the tunnel kiln.

A very recent investigation in Group H-7 of the Los Alamos Scientific Laboratory may hold some promise for a partial solution to the ruthenium volatility problem. In laboratory prepared mixtures of clay and waste spiked with ruthenium and containing an admixture of finely divided aluminum, a 90% retention of ruthenium was experienced when the mixed mass was first treated with sodium hydroxide. This effort was based on an older analytical method for the determination of nitrate in water supplies. In the present case it is probable that a reduction of both ruthenium oxide and nitrates occurs. As a result the ruthenium metal, if indeed this is produced, is largely retained by the clay-waste-mass even at temperatures of 1000°C.

A pilot plant for the extended study of these techniques was placed in operation at Los Alamos early in 1962. Initial studies indicate that the method has merit and developmental work is continuing.

Advantages of the ceramic sponge concept for the disposal of high-level waste are well defined. Off-gas problems in the soaking and drying stages are readily controlled since airflows are within a closed system. The entrainment of particulate matter is at a minimum

Fig. 11

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Fig 11

since dusting from the solid body is almost negligible; the sorption of liquid further reduces the amount of dust encountered. The tunnel kiln can be operated under reduced pressure with condensers, silica gel, and absolute filters in the exhaust line. These have proved efficient in the removal of minor traces of activity escaping from the spheres as fusing temperatures are reached.

In a "hot operation" with high-level waste, shielding and remote manipulation would be required. The mechanics necessary are well known and have been worked out for other systems. However, the volatilization of ruthenium oxides continues to present a problem and until methods are developed to restrain its volatility, ruthenium-106 will require removal through the application of scrubbers and filters.

The above methods indicate the problems and approaches to the fixation of high-level radioactive wastes in solid materials. All methods offer some advantages and some disadvantages. Until the major problems have been solved, there is no alternative other than a continued storage of these wastes and a continuing search for the method of ultimate fixation.

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