

Atomic Waste Disposal by Injection into Aquifers¹

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Experimental proof is given that chemical reactions between earth materials and acid aluminum nitrate wastes can be expected to prevent injection of such wastes into aquifers, unless wastes or aquifers are pretreated. Conditions are described that make injection not only feasible but reasonably safe and economical.

INTRODUCTION

THE bulk of the fission products from nuclear reactors are obtained during fuel processing, as a comparatively small volume of relatively concentrated or "high-level" waste solution; smaller amounts of fission products are obtained in a much larger volume of comparatively dilute "low-level" wastes. Although the percentage concentration of actual fission products in the high-level wastes is small, the amounts of radioactivity involved are so large that disposal by dispersal into natural environments is generally not feasible. Instead, some method of confinement or storage must be used for a length of time sufficient to permit decay of the radioactivity to a safe level, except for whatever small amounts of fission products may be extracted and temporarily or permanently "stored" in applications making use of their radioactivity. For wastes containing significant quantities of the biologically more hazardous, long half-life isotopes such as Sr^{90} (28 yrs.) and Cs^{137} (33 yrs.), controlled storage for several hundred years or more may be required for safety, and some non-radioactive materials, such as nitrate,* as well as certain very long half-life elements, may be biologically hazardous in these concentrations for practically indefinite periods.

Various proposals have been made of methods whereby these high-level wastes might be effectively stored in natural underground reservoirs instead of the present technique of confinement in tanks at the surface. One of the widely considered methods involves pumping of the waste through wells into porous and permeable formations (aquifers) situated several

thousand feet or deeper in the earth, below the potable water zone (Theis, 1955).

As the pumping of waste into a given well in any such procedure would presumably take place continuously over a period of months or even years, the waste will be in intimate contact with the natural materials of the "container" for a long time, and any chemical interaction that might take place between the waste and the materials of the environment has a high probability of reaching approximate equilibrium. Consequently, it is important to look at some of the possible and expected interactions with specific minerals in terms of the effect of such interactions on the environment, and in particular their effect on the waste itself. This has been done by means of some comparatively crude but still valid calculations and experiments described below.

Each waste type and aquifer combination will have its own particular interactions and problems, but to limit the discussion a specific type of waste (acid aluminum nitrate) and a specific type of aquifer (sandstone) are considered here, as this seems to be one of the most promising combinations. Many of the results are reasonably applicable, however, to other types of aquifers, for example, porous basalts, and have some significance in connection with the disposal of other types of wastes or the use of entirely different disposal methods.

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* Walton (1951) suggests 10–20 ppm NO_3 as a safe limit in water.

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GENERAL PROBLEM

The problem, assuming that the waste can be delivered to the site of the well, is essentially that of injecting such wastes into a specific zone or stratum of porous, permeable rock without having stoppage, and under such hydrological conditions that the waste will not be reintroduced into the human environment for the necessary hundreds of years. It is generally assumed, in such proposals, that *perfectly* impermeable strata occur above and below the aquifer, but as most such confining beds are *not* truly impermeable (Theis, 1955) the direction, volume, and rate of movement of the waste are of vital concern to future generations.

It is assumed that the waste will be completely free of all suspended solids before pumping, so that there should be no stoppage from filtration at the point of injection into the aquifer. Any interaction of waste and aquifer that impedes the flow of waste through the aquifer by increasing the viscosity of the waste, by precipitating on the walls of the pores, or by resulting in suspended solids that can filter out in constrictions in the pores, can be considered to be detrimental. With an acid high-aluminum waste, the condition most likely to result in stoppage would be that of an increase in pH yielding a gelatinous aluminum hydroxide precipitate. As shown beyond, there is a large increase in viscosity upon partial neutralization, and gelatinization occurs in these concentrated solutions upon neutralization with CaCO_3 to a pH of approximately 3.

SPECIFIC PROBLEMS

Composition of the Wastes

Although the variety of reactor types and of fuel-processing procedures results in a variety of different waste types, one of the most common wastes for the present and near future seems to be the type high in nitric acid and aluminum nitrate. In the following discussion, this waste is assumed to have two moles of HNO_3 and two moles of $\text{Al}(\text{NO}_3)_3$, plus approximately 0.10 gram of mixed fission products, per liter. Such a solution, without fission products, was used in the experiments unless specified otherwise. It is a thin syrupy liquid with a density of 1.37 gm.cm^{-3} and a viscosity of approximately 5.7 centipoises at 24.3°C , which drops rapidly to 1.2 centipoises at 99.6°C .

In some cases, a waste containing somewhat lower concentrations of $\text{Al}(\text{NO}_3)_3$ (1.6 moles), and of HNO_3 (0.5 mole), might be obtained in the processing. As shown beyond, this lower concentration of acid *increases* the difficulty of injection by decreasing the amount of neutralization needed before possible precipitation. Wastes obtained by still other processes may have up to eight moles of HNO_3 per liter, or high concentrations of iron, zirconium, fluorine, etc.,

and in some cases are highly alkaline sodium aluminate solutions.

Although some 250 different radionuclides between mass numbers 70 and 164, are formed in the fission process most of these have short half-lives and hence by the time the waste is to be disposed, only the longer half-life radionuclides need be considered. These include members from each one of the eight groups in the periodic table: Kr, Xe, Rb, Cs, Sr, Ba, Ce, Pr, Nd, Pm, Sm, Y, Zr, Nb, Mo, Te, I, Tc, Ru, Rh and Pd (Zeitlin et al., 1956; Glueckauf, 1955). Of these only seven have half-lives of one year or more: Kr, Tc, Sr, Ru, Cs, Pm and Sm. In addition to the fission products, however, there may be present small amounts of various exceedingly long half-life, alpha-emitting, transuranium elements, such as Pu^{239} , Pu^{242} , Np^{237} , Am^{241} and Cm^{244} , which are formed by interaction of neutrons with fuel elements. The amount and nature of such elements will vary with the reactor technology used, amount of fuel recycling, etc., but may become a first-order radiation hazard in the future (Glueckauf, 1955). Even at present the traces of Pu^{239} in some wastes present a serious problem in disposal due to the high radiochemical toxicity of Pu (Brown et al., 1955). In addition a number of the longer-lived alpha-emitters in the actinide decay schemes may be formed, such as U^{233} and Th^{228} , and present similar problems.

Heat and Pressure

It is possible that the wastes might be warm or even hot at injection, and if not, they can be expected to become warm or hot by their own radioactivity if adequate heat flow is not permitted. Depending on the "cooling time" permitted for radioactive decay before processing and before disposal, the heat generation from these wastes may be any value less than approximately 1000–7000 calories/hour/liter.* This must be dissipated to the enclosing or adjacent rock in some manner, or the temperature, and hence pressure, will climb (Theis, 1955).

The temperatures attained may have considerable effect on the possible recrystallization of gelatinous precipitates to porous granular masses, on the chemical equilibria involved, on the stability of any sols, and on the viscosity of the liquids. Bridgman (1931) has shown that the increase in viscosity of water with high pressures is slight compared with the decrease in viscosity with increasing temperature.

The pressures that may be involved are also in doubt, as they will vary with the temperature, the depth of injection, and the pressure head needed to force the waste into the aquifer. The hydrostatic head, using a liquid of a density of 1.36 gm.cm^{-3} , would be 132 atmospheres (1930 psi) per 1000 meters (3281 ft.)

* Both β and γ energy should be included here, as opposed to the frequent consideration of the β energy only, in surface installations, where the γ radiation is assumed to escape.

depth. Considerable additional pressure may be needed to overcome the frictional resistance involved in forcing a viscous fluid through many meters of aquifer, and as indicated beyond, considerable CO_2 pressure may be generated by reaction with aquifer carbonates.

Under the pressures involved here, the compressibility of water itself becomes a significant factor, particularly if the permeability of the aquifer is high. Using the compressibility of water at 100°C , in the range 100–200 atmospheres (Amagat, 1893), an increase in pressure of 100 atmospheres would cause a contraction of approximately 1.5×10^7 liters in the water in the pores of a disk only 1000 meters in radius and 10 meters thick, assuming 10% porosity and zero compressibility for the rock minerals. In actual practice, much larger volumes can be injected than

aquifer in its travel. In order to consider this problem adequately, a more or less abstract but important concept of a "zone of equilibration"* is envisaged for each possible interaction. It could be defined as including that part of the aquifer traversed by the moving waste solution in the time necessary for a specified process or reaction to come to equilibrium. Thus in the case of a mineral in an aquifer going into solution in the advancing front of the waste, the width of the zone of equilibration would be represented by the distance traversed by the moving waste during the time from the first point of contact with the soluble mineral concerned to the point where the mineral grain has completely dissolved, as illustrated in Fig. 1.

The width of the equilibration zone will obviously be a function of many variables, but of these the most important are the solubility, the rate of solution, the

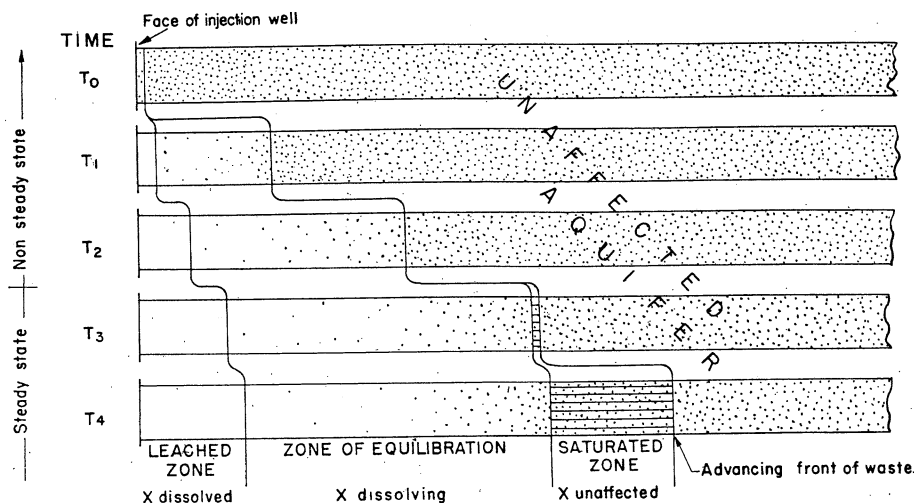


FIG. 1. Development of "zone of equilibration" for solution of mineral X in aquifer.

the simple compressibility of the water can account for, because the aquifers and adjacent strata themselves behave elastically, to an extent much greater than does the water. This compressibility of fluids in porous beds is used in the reverse direction in petroleum production. Although it would be possible to use this compressibility to provide room for injection, this would place the waste under strongly "artesian" conditions in the aquifer and present a safety hazard.

Cumulative Chemical Reactions

It is shown beyond that chemical reactions with aquifer materials can be expected. One of the most serious problems is the possibility of a cumulative effect on the advancing front of the waste as it continues to contact and react with fresh portions of the

rate of flow, and the relative quantities of reactants (which are functions of the concentration in aquifer and waste, and of the porosity). If a reaction is very slow, as by the occurrence of an "armoring" of the grains with reaction products, a leached zone may never develop, but a saturated zone could still form ahead of the ever-increasing equilibration zone. In such a case there might be, however, a very small "effective" zone of equilibration in which the bulk of the armoring takes place.

The major concern in any interaction between waste and aquifer minerals is that of possible precipitation; presumably this would preclude any continuation of flow after saturation (i.e., precipitation) occurred, unless the precipitation occurred only as a lining in the pores, decreasing the permeability. The precise mechanism of the reaction during the development of the equilibration zone up to the point of saturation is of far more than academic interest here in that it controls the distance through which waste

* Except for special cases, such as the formation of a metastable sol from a reaction, instead of a precipitate, the zone of equilibration will equal the "zone of reaction".

can be pumped before precipitation and plugging occurs, and hence it controls the storage capacity per well. The composition of the waste, the composition of the aquifer, and the porosity of the aquifer control the *stoichiometry* (i.e. the relative quantities involved) of any possible reaction in terms of volume of aquifer traversed by, and reacted with, a given volume of waste, but the *reaction rate* controls the width of the zone of equilibration, hence the depth of penetration before precipitation, and therefore controls the storage capacity. With natural materials, it is perfectly possible that this depth of penetration before precipitation might be as small as one millimeter or as large as one kilometer, depending upon the rate of flow and the rate of reaction of acid aluminum nitrate waste with available natural aquifer minerals. From available information on probable reaction rates and flow rates, it seems likely that the zone of equilibration for many of the possible reactions considered below will be in the order of one or two centimeters, but it will be shown that a zone of equilibration of 10 cm or even one meter for reactions with carbonates or clays can be expected to result in precipitation after a very short passage through the rock. In actual practice there will be a number of different overlapping zones of equilibration existing simultaneously, for separate reactions, and these may well be expected to interact on each other by changing the reaction rates. It can also be expected that the width of a given zone of equilibration may change drastically during the time prior to the establishment of a "steady state".

Although it is not possible to predict accurately what will be the distribution of concentrations within the zone of equilibration, particularly before a "steady state" is achieved,* a maximum limiting value for possible movement of fluid before precipitation occurs is obtained by assuming that mixing, diffusion, etc., will result in the fluid having a uniform composition throughout the zone at any given instant. Thus when precipitation occurs, the entire zone is assumed to precipitate simultaneously; by this artifice the chemical calculations are put on a more rational basis, but it must be remembered that it represents the optimum conditions.

Time, Rate, and Volume of Flow

To a large degree the compatibility of waste with aquifer minerals will be based on rate processes, and hence a realistic approach to the problem of disposal involves the time and rate of flow. For this reason an estimate of the volumes to be dealt with must be made. According to various published estimates, it would not seem unreasonable to assume a production in the United States of 100,000 gallons of high-level waste

per day with a comparatively few years. If 10 processing plants are arbitrarily assumed, each one will thus have to dispose of 40,000 liters (approximately 10,000 gallons) per day. This would yield flow rates as shown in Table 1, for a static aquifer. Probably,

Table 1

Radius of cylinder of waste and rate of advance of waste front assuming injection at 40,000 liters per day into a static isotropic aquifer with 10% porosity by volume

Days pumped	Volume pumped (10 ⁶ liters)	Thickness of Aquifers			
		30 meters		10 meters	
		Radius (meters)	Rate (cm. day ⁻¹)	Radius (meters)	Rate (cm. day ⁻¹)
10	0.4	6.51	32.6	11.3	56.4
50	2.0	14.6	14.5	25.1	25.2
100	4.0	20.6	10.3	35.8	17.9
200	8.0	29.1	8.28	50.1	12.6
600	24.	50.5	4.21	87.7	7.3
1000	40.	65.1	3.26	113.	5.6
5000	200.	146.	1.45	251.	2.5

however, there will be some natural flow of the ground water originally in the aquifer. The deep relatively isolated aquifers of interest here might have water moving as slowly as 1 mm. day⁻¹ (Theis, 1955). If waste is pumped into such an aquifer it will displace the ground water and spread out as a stream moving with the ground water, at the same flow rate, with an area of cross section of the stream controlled by the volume injected. In any case the flow patterns and rate would be considerably altered if ground water is pumped out of another well simultaneously to "make room" for the waste.

It should be noted that if the rate of flow is small, slow reactions may possibly go to completion, but if the rate is large, the advancing front of waste will contact a large area of aquifer mineral surfaces for possible reaction. In this connection, approximate data on the surface areas, volumes, and weights of sediments contacted, for several different porosities and apparent average grain size are given in Table 2. The large values obtained are particularly noteworthy.

Injection of liquids (and gases) into aquifers is common practice in the petroleum industry for aiding the recovery of petroleum ("water driving"), and a fairly extensive technology has been developed concerning it. Under very favourable conditions, up to 10,000 barrels per day (10⁶ liters) of water have been injected into single wells, the flow from the injection well to the pumping well being an elliptical area in plan. It should be noted, however, that much trouble has occurred due to minute amounts of solid matter in the water filtering out at the face of the injection well, causing high pressure loss and small injection rate. Trouble has arisen from scale from corrosion of

* This will be indicated by an ever-widening leached zone, a uniform-width zone of equilibration, and an ever-widening saturated zone; it assumes a completely uniform rate of flow.

pipings, from various precipitates,* from expansion of clay minerals in the formation upon contact with new waters, and from solution and redeposition of gypsum, calcite, and limonite. Reverse pumping at intervals ("swabbing") is frequently resorted to, for the purpose of removing blocking, but is not wholly satisfactory and would not be very feasible in atomic waste disposal operations. Even filtered, completely clear solutions may precipitate and block injection where they have not been "stabilized", i.e. they were super-saturated during filtration.

In the oil industry, high pressures or explosives are used to increase the area of injection surface and thus to decrease the serious pressure drop that occurs normally at that surface, as well as to minimize the problem of clogging from the inevitable suspended solid matter. This procedure would be very desirable in waste disposal, but might not be done without the possibility of serious damage to the enclosing impermeable beds.

There are numerous other technical problems in pumping highly radioactive wastes into wells, such as the pump design, possible leakage around the outside of the well casing, and the corrosion of well casing. All of these are quite pertinent here and although frequently met in the petroleum industry,† are not within the writer's experience and will not be discussed further.

Composition of Aquifers

Gross Features

Most natural aquifers that might be considered for waste disposal sites consist almost completely of a comparatively small number of minerals. The following list of five minerals and mineral groups would probably account for at least 95% of the mass of most sedimentary aquifers; the figures are the percentages for average sandstones in the earth's crust, according to Clarke (1924):

Quartz group of minerals (including chert, flint, jasper, etc.)	66.8
Feldspar group of minerals (particularly orthoclase, and the plagioclase series)	11.5
Mica group of minerals (mainly muscovite and biotite)	6.6
Clay group of minerals (kaolin, montmorillonite, "illite", etc.)	
Limonite group of iron oxides, plus hematite	1.8

* Even one part per million of ferrous iron in natural waters is serious.

† An additional problem, not involved in "water drives", is the need for shielding equivalent to 5 to 10 in. of lead on all above-ground pumps and piping, as well as operation and maintenance by remote control.

Carbonate group of minerals (mainly calcite and dolomite)	11.1
Miscellaneous	2.2

100.0

Individual sandstone strata or formations will deviate rather widely from this average, so there obviously is no one truly "typical" composition for aquifers. In order to simplify the discussion below, however, a specific aquifer is assumed, with 10% porosity and 0.4-mm grain size, containing $90 \pm$ % quartz, 10% feldspar, and 0.1% each of mica, clay, limonite, and carbonates. It is admittedly a rather optimistic estimate, in terms of the known data on aquifer sandstones, but it will be shown below that even this rather "pure", hypothetical aquifer can probably be expected to plug with precipitate upon injecting acid aluminum nitrate waste into it.

Specific Minerals and Materials

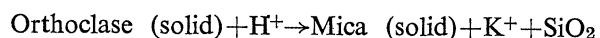
Quartz. Although by far the most abundant mineral in most aquifers, quartz is the least reactive. It can be considered inert in most waste solutions other than the highly alkaline ones, except insofar as its surface acts in ion exchange. The sandstone assumed above would have about 1.3×10^8 cm² of quartz surface per cubic meter. An approximation of the adsorption of sodium ions on quartz under these conditions, extrapolated from the results of Gaudin, Spedden, and Laxen (1952), would be about 10^{-11} moles.cm⁻², indicating that only a small fraction of a gram of solids at best could be adsorbed per cubic meter. Unless this adsorption strongly favors the radioactive ions over the much more concentrated Al⁺⁺⁺ ion, the quartz seems to be of little concern.

Feldspars. There are sandstones containing practically no feldspars but they are rare, and seldom do they contain less than 2% (Pettijohn, 1949). Their effect is somewhat difficult to predict. It is known that feldspar (mainly KAlSi₃O₈ and NaAlSi₃O₈) will react slowly with water to yield solid hydrated silicates (micas or clays) and an alkaline solution containing potassium or sodium if given adequate contact surface or time. In the assumed aquifer a waste solution moving through the rock will come in contact with 1.3×10^7 cm² of feldspar surface per liter of waste on moving through 10 meters with a 10-cm zone of equilibration. The effective surface area may be much greater than this, however, as a consequence of the greater solubility of the distorted surface layer on abraded surfaces (Brody, 1953). It is thus apparent that if the waste and the surface of the feldspar can react together at all, there is considerable surface available for reaction.

The problem is to decide how much reaction might take place between feldspar and the waste in the available time. There are some data on the action of water

on feldspars, for example the "abrasion pH" determinations of Stevens and Carron (1948). This is the pH that results from grinding a mineral in water, and hence might be an indication of the pH to be expected from contact of water with the mineral. They obtained pH values of 8 to 10 for various feldspars. The interpretation of these values is complicated by a variety of factors, but it is clear that pH values greater than 7 can be expected.

R. M. Garrels (personal communication) has shown that in the absence of air, 200 mg of dry-ground minus 100-mesh potassium feldspar (orthoclase) will react rapidly with 3 ml of pure water to yield a pH of 11.5. If the equation for this reaction can be written:



these values require that a layer approximately 30 Ångströms thick on the surface of the orthoclase grains must have contributed its K^+ to the solution (i.e., exchanged its K^+ for H^+). At 10^8 cm^2 of surface contacted per liter of solution, if a layer only 100 Ångströms thick on the surface of the grains of potassium feldspar in the aquifer were involved, it could yield one mole of potassium per liter of waste. The physical effect on the feldspar would be negligible, but this much potassium in effect exchanged for hydrogen, could have a major effect on the pH of the solution. It is expected, however, that the rate of reaction with feldspar would decrease rapidly with increase in pH. Preliminary short-term experiments putting waste through feldspar columns have yielded first effluents with a pH of 2.

Micas. As with the feldspar, the possible effects of mica lie in the ease with which the potassium or other large cation can be removed and replaced with H^+ (or OH_2^+). As the average sandstone contains very little mica, however, and as its possible effects would be expected to be subordinate to those of the feldspar and particularly those of the clay minerals present, it will not be discussed further here.

Clays. Reactions with the clay group of minerals are likely to be of major importance because clays have a very large surface area, up to $10^6 \text{ cm}^2 \text{ gm}^{-1}$. The clay minerals are ubiquitous and no sedimentary rock is free of them; all slow-moving water in deep permeable sandstones can be presumed to be in chemical equilibrium with some clay, at least with respect to surface phenomena. Furthermore, much clay can be present in a sand without any "clay" showing up in an ordinary screen analysis. Sandstones, containing in bulk analysis less than 0.1% clay minerals, may not exist anywhere in the United States, with the possible exception of the highest purity commercial glass sand formations of very limited occurrence. Even these "pure" glass sands usually have to be washed or even scrubbed to free them from several percent of interstitial or adhering finely divided clays, iron oxides,

etc. Most geologists dealing with sedimentary mineralogy would assume that even a "clean" sand has at least several tenths of a percent clay minerals unless proved otherwise.

Even if we assume that an aquifer has only 0.1% of clay, and 10% porosity, the amount of clay surface contacted by the advancing front of waste with a 10-cm zone of equilibration is $2 \times 10^9 \text{ cm}^2$ per liter, in 10 m of travel. In this case each liter of waste would have been in contact with, and possibly reacted with, 2.25 kilograms of clay. It is possible that the zone of equilibration for interactions with clay minerals might be only a few centimeters wide, as a result of the large surface area exposed and the slow rates of flow involved.

Table 2

*Surface areas, volumes, and weights of sediment contacted, per liter of waste, in 10 meters of travel with a 10-centimeter zone of equilibration**

(Porosity volume%)	Average grain size (mm diam.)	Sediment contacted per liter*		
		Surface area† (10^8 cm^2)	Bulk volume (m^3)	Weight‡ (kg)
5	1.0	1.14	2.0	4,750
	0.4	2.85		
	0.2	5.73		
	0.1	11.40		
10	1.0	0.54	1.0	2,250
	0.4	1.34		
	0.2	2.71		
	0.1	5.39		
20	1.0	0.24	0.5	1,000
	0.4	0.60		
	0.2	1.21		
	0.1	2.40		

Possible trouble from reactions between clays and acid wastes might result from three phenomena: (1) cation exchange, (2) destruction of physical bonding of clay particles, and (3) chemical solution of part of the clay. The possible reactions involved are complex, owing to the wide range in chemical and mineralogical composition of clays, including here both the normal clay minerals and other similar sheet structure silicates.

Clays are well known for their ability to participate in cation exchange (base exchange) with fluids, to the extent of up to 100 or more milliequivalents per 100 grams of pure clay. The lowest cation-exchange

* If the zone of equilibration is smaller than 10 cm, the values for surface area, volume, and weight of sediment contacted must be increased proportionately. Thus for a 1-cm zone, multiply these values by 10.

† For simplicity this assumes uniform spherical grains. These cannot give the actual porosities assumed, but the data are compatible if there is some mixing of different grain sizes and shapes.

‡ This assumes a mineral density of 2.5 gm.cm^{-3} .

capacity obtained thus far on natural materials from AEC sites was only 0.5 milliequivalent per hundred grams. Even this low value is equivalent to approximately 0.5% clay minerals, but whether this represents actual clay minerals or the exchange capacity of the large surface is of little consequence; this material theoretically could exchange *all* cations from the 10-cm front of waste moving 7 meters through it, assuming 10% porosity and a 10-cm zone of equilibration. It is logical to expect, however, that H^+ from the waste would be exchanged for Na^+ or Ca^{++} from the clays only until the increase in pH caused precipitation of iron and aluminum hydroxides.

Much attention has been given to the behavior of fission products in ion exchange on clay minerals; with aluminum nitrate wastes it seems that the aluminum ion, which has a high charge and is present in amounts (atomic percent) at least 2×10^4 times that of the most abundant fission product, dominates in the occupation of exchange sites. The actual exchange would depend upon the cations present in waste and those in the exchange sites from natural ground water, but cation exchange can certainly be expected to be a major factor in affecting the composition of any waste moving through rocks.

It was expected, however, that acid aluminum nitrate wastes would seriously affect the exchange capacity of clay minerals. A series of preliminary experiments with known clay minerals in contact with acid aluminum nitrate waste for periods of 12 to 48 hours at temperatures of 25–48°C, showed that up to 30% of the clay mineral dissolved in the waste, and the cation-exchange capacity of the remaining material decreased 20 to 30%.

These changes in cation-exchange capacity, although large, are of relatively minor importance compared with the more serious problem of physical effects on the clay minerals due to decomposition. Such decomposition may result in a variety of detrimental effects that would be difficult to evaluate, particularly in the vicinity of the injection well where the flow would be fast and the pH low.

Another important factor that must be evaluated is the effect on the waste of the partial destruction of the clay structure in acid solutions, with release of the cations K^+ , Na^+ , Mg^+ , and Ca^{++} . It is well known that many clays react readily with acids, giving either "gelatinous" silica or "insoluble" silica precipitates (Murata, 1946) and cations in solution, but the specific reaction mechanism is not known, and the results, except in a few cases where a careful study has been made (Nutting, 1943), cannot be predicted very well. Since many sedimentary clays contain 5 to 10% or more of alkali plus alkaline earth oxides, the possibility of a gross change in composition of the waste solution, and resultant precipitation, is evident. At a minimum of 2.25 kilograms of true clay contacted

per liter of waste, in 10 meters of travel through 10% porosity sandstone containing 0.1% such clay, with a 10-cm zone of equilibration, 5.5 equivalents of Na^+ , K^+ , Ca^{++} , and Mg^{++} would presumably be available for solution, per liter of waste, from the clay minerals alone.

If the flow were not interrupted by the physical effects of the waste on the clays, it is reasonable to expect that the clays in the first portions of sediment traversed would be decomposed, raising the pH, and later portions would act in cation exchange, presumably raising the pH still further to be point of precipitation.

Limonite. This term refers to a group of hydrated ferric oxide minerals that are as ubiquitous as clay, and frequently as abundant; the most common is goethite ($Fe_2O_3 \cdot H_2O$). It was expected that any acid waste moving through a rock containing limonite would have its hydrogen ion content effectively reduced to a level approaching the equilibrium value for $Fe(OH)_3$, estimated at a pH of 2 or 3. Each mole of available hydrogen ion in the waste needs only 30 grams of goethite for neutralization; at 10% porosity and 0.1% limonite, each liter of waste will be in contact with 22 grams of limonite, with no movement of the fluid, and with a 10-cm zone of equilibration, each liter of waste will contact 2250 grams of iron oxide minerals in 10 meters of travel.

It is thus apparent that these iron oxide minerals could play a major role in any increase in pH of the solution as it traverses normal rocks, and the dissolved iron (plus traces of manganese) might well contribute to any hydroxide precipitate formed beyond as a result of further increase in pH from other causes; in fact the iron would be expected to precipitate before any $Al(OH)_3$ can form. Laboratory experiments have shown that the *rate* of solution of limonite is low in these fluids, but extrapolation from these results to field conditions indicates that $Fe(OH)_3$ precipitation can be very important.

Carbonates. Of all the possible interactions between sedimentary aquifers and acid aluminum nitrate wastes, probably the most important are those involving carbonates. Carbonates are exceedingly widespread, and the hypothetical 0.1% carbonates assumed here is very conservative. Only the highest grade glass sands contain less than 0.2% $CaO + MgO$, mostly as carbonates. The most likely place for low-carbonate sandstones to occur would be in those beds that might have been subjected to intrastratal solution by natural CO_2 -bearing waters. This CO_2 does not have to originate in the atmosphere, but may be derived from decomposing organic matter in the sediment (Foster, 1950); hence such intrastratal solution need not be confined to near-surface sediments.

If carbonate is present in the aquifer, the problem in evaluating interactions with it is the lack of experimental data under the conditions of rather high pressure and high concentrations involved. At atmospheric

pressure the waste reacts rapidly with solid calcium carbonates with the evolution of CO_2 . As small additions of CaCO_3 are made the reaction becomes slower and eventually the viscosity of the clear liquid increases. When the equivalent of approximately 300 grams of CaCO_3 has been added per liter of waste, the pH is about 3.3 and the waste is so thick that it will pour only with difficulty. It will not react appreciably with more CaCO_3 . The waste at this stage is presumably a sol, as it eventually becomes a stiff transparent gel that can be broken into pieces. A one-to-one dilution of the waste with water before reaction with carbonate results in a similar stiff gel forming after an equivalent addition of CaCO_3 . A 20-to-1 dilution results in a thin gel, although it does not become solid, and even a 50-to-1 dilution yields a faintly gelatinous liquid. A solution containing 1.6 moles $\text{Al}(\text{NO}_3)_3$ and 0.5 mole HNO_3 per liter required approximately 200 grams of CaCO_3 per liter to gelatinize.

From stoichiometry, it is obvious that a considerable part of the hydrogen ion reacting with solid CaCO_3 in these experiments is that formed by dissociation and hydrolysis of the two moles of $\text{Al}(\text{NO}_3)_3$ present. If the above reactions are assumed to represent the behavior of such wastes in a natural aquifer containing 10% porosity and 0.1% CaCO_3 , the waste would be expected to precipitate as a gel in 120 cm of movement. This assumes a zone of equilibration of 10 cm, as is not unlikely; even if the zone of equilibration is 1 meter, the waste can travel only 12 meters before precipitating as a gel.

The behavior of the CO_2 evolved is not known. Some will dissolve in the waste solution, but the actual amounts involved are controlled by several reactions whose equilibria under such conditions are unknown and cannot be determined accurately by calculation. Wiebe (1941) shows that a liter of pure water at 50°C will dissolve a mole of CO_2 at about 75 atm CO_2 pressure, and over 700 atm CO_2 pressure is needed to dissolve 2 moles at 50°C , but it is possible that the solubility of CO_2 in these solutions might be very different. It is impossible to calculate rigorously the CO_2 pressures that might develop, but they might be expected to rise to the range of hundreds of atmospheres. Pumping pressures would have to overcome this CO_2 pressure or the waste would be blown back to the surface. The specific effects on pH are not known under these conditions, but it appears that a pH of 3 could be reached by reaction with CaCO_3 alone, with no release of CO_2 .

There are a number of other factors involving particularly this build-up of CO_2 gas pressure. Morrison (1950) has shown that the rate of solution of CaCO_3 in HCl decreases considerably as the CO_2 pressure increases. If, after saturation of the waste solution, the "excess" CO_2 separates as a new gas phase it should improve mixing in the water phase but

would partially insulate carbonate grains from further reaction and probably would decrease the permeability of the aquifer, as it is more difficult to pump a mixture of gas and liquid through an aquifer than either separately (the "Jamin effect"). Some work has been done on the behavior of liquid CO_2 and carbonated waters and brines in porous rock (Breston and MacFarlane 1952). The density of this separate CO_2 phase would be a function of the temperature and pressure, but might well be close to that of a normal "liquid"—for example, at 60°C and 300 atmospheres pressure ($\approx 10,000$ feet head of water), its density would be 0.83 gm.cm^{-3} , and it would be 0.29 gm.cm^{-3} at 100 atmospheres (Kennedy, 1954). The effects of this CO_2 pressure on the viscosity of the waste, and in particular on the viscosity of any partly gelatinized sol, are not known.

The physical nature of the occurrence of calcium carbonate in the aquifer, for example, films vs. grains, can be expected to have a considerable effect on its behavior, as such differences will affect the reaction rates. If the carbonate is readily available as thin films, etc., the reaction to form a gel may occur in seconds. If it is present as discrete grains, for example, as fragments of calcite or as fossils, experiments show that once the effervescence slows down the grains may become coated with a layer of precipitated gel, through which further reaction by diffusion is slow. This would increase the width of the "zone of equilibration" and might permit continuous injection of waste for an indefinite period.

Miscellaneous materials. There are a number of materials that can be found in aquifers in small amounts, perhaps 0.1% or so of each, but not all occur in any given formation, and the amounts may be considerably greater than this in specific cases. The following are the most common minor constituents.

Pyrite is the most abundant sulfide in sedimentary rocks, and although not as abundant as limonite, it is practically as ubiquitous. It decomposes concentrated nitric acid with evolution of nitrogen oxides and some free sulfur, yielding an iron nitrate solution in which the bulk of the iron is present as Fe^{+++} .

Gypsum is very abundant in some sandstones, as a cement. Its main significance here lies in the fact that it is appreciably soluble in water; it has given trouble in "water drives" by dissolving and reprecipitating.

Volcanic glass and other volcanic debris (volcanic ash) is very common in some sandstones. Its importance here lies in the possibility of leaching of various cations from such glasses. As normally occurring in nature, they have a large surface area and alter rather readily to clay minerals, yielding considerable alkalis and alkaline earths to the solution. Only one experiment was made, using basaltic volcanic ash and waste. It showed a very sizable decrease in H^+ concentration, as would be expected. The magnitude of the

reaction would certainly vary with the possible range of composition and texture of the glasses, but any reaction that does occur can be expected to be in the direction of increasing the pH of the waste.

Organic matter is abundant in some sandstones as natural gas, various petroliferous materials, and as partly coalified plant matter. It might be of considerable help in removing the nitrate ion which is perhaps the most biologically hazardous non-radioactive material in the waste. Natural organic matter can certainly be expected to affect the oxidation potential of the waste in contact with it, as shown by the work of Pommer (1956), and all variable-valence elements present in the waste should be viewed in this light, for example iron from stainless-steel fuel-element cladding.

"Heavy minerals": this is a general term to cover a variety of minerals usually found in aquifers in amounts less than 1%. Their occurrence in sediments is a consequence of their chemical and physical stability during weathering at the surface of the earth and hence they are, comparatively speaking, rather inert in comparison with the other minerals discussed, and are not expected to have any significant effects on the waste.

Natural brines. Depending upon a variety of factors that will not be discussed here, the natural ground water occupying the pores of any aquifer before injection of waste may vary from practically pure water to a strong brine containing over 25% dissolved solids of variable composition. As these waters are frequently alkaline, consideration must be given to the possibility of precipitation occurring at the advancing front of waste due to dilution with such waters. A number of experiments on the dilution of waste solutions with various amounts of synthetic carbonate and bicarbonate waters were made, from which it was evident that some precipitation can be expected at the advancing front of waste in contact with many natural waters.

Joint Effects of all Aquifer Materials

From the above discussion it is fairly clear, in a qualitative way, what can be expected during the pumping of acid aluminum nitrate waste into a hypothetical aquifer of the composition assumed. Most of the possible interactions, if they occur at all, will be in the direction of an increase in pH, and several different reactions may augment as well as succeed each other. If pumping could be continued after a pH of 2 or more is reached, base exchange in the clays, rather than solution of clays and other minerals, might take over as a mechanism for further removal of H^+ from the waste in exchange for K^+ , Na^+ , Ca^{++} , and Mg^{++} from the clays. Presumably precipitation of a part of the iron and aluminum as hydroxide gels

would occur when the reactions have increased the pH to about 3.5.

One very important question concerns the behavior of this waste plug *after* stoppage. After the well has become sufficiently plugged by precipitation at the front so that further injection is impractical due to the high pressures needed, presumably some non-radioactive water would be pumped in to flush the well casing, and this would be followed by cement to prevent blowback to the surface or leakage into higher strata. The liquid waste would thus be completely enclosed by impermeable beds above and below, and by a wall of aquifer cemented with a slowly hardening gelatinous precipitate on all sides. It is to be expected that pressures would then rise, from two causes; first, any delayed reaction with precipitate-coated carbonate grains within the interior of the mass would slowly yield more carbon dioxide, and second, any increase in temperature from radioactive heat must result in either expansion or higher pressures.

The results of a temperature increase can be of considerable magnitude. Assuming that the data for water (Kennedy, 1950) may be used as a crude approximation, a rise in temperature from 100°C, at 150 atmospheres, to 200°C, will result in either a 10% volume expansion of the liquid at constant pressure, or an increase in pressure to approximately 2000 atmospheres, at constant volume. This pressure is equivalent to the confining pressure from a layer of rock 25,000 feet thick, and thus could not be contained at lesser depths as it would lift the overlying rocks. The problem here lies in the thermal capacity and conductivity of the surrounding rocks, as compared with the heat generation of the waste. If the increase in temperature is too great, the obvious answer is to resort to thinner aquifers or longer cooling before injection, but either of these would increase the cost of disposal proportionately.

An entirely separate problem involves the degree to which the original precipitate wall formed from waste represents a complete enclosure and immobilization of all of the materials. Some fission products will undoubtedly escape by various processes; the probable fate of most of these released materials lies in ion exchange on mineral surfaces downstream, except anions such as NO_3^- , which apparently is not adsorbed appreciably by ion exchange (Brown *et al.*, 1955; Amphlett, 1955).

One further possibility concerns the relative diffusion rates of different ions; if H^+ diffuses appreciably faster through the gel wall than other cations, as is expected, there is a real possibility of a sufficient decrease in pH of the gel, at some distance from the front of the liquid, to cause re-solution of part of the wall and consequent remobilization of the waste.

POSSIBLE EXCEPTIONS AND REMEDICAL PROCEDURES

There is a possibility of finding aquifers that contain lesser amounts of any one of the precipitating agents listed above, but the possibility of finding even one aquifer that will fall within all of the specifications listed for the "assumed aquifer" is rather remote, and the possibility of finding an aquifer better than these specifications is practically nil. A search for suitable beds would necessitate an intensive study of the geological factors involved in the origin of such beds and an extensive drilling program. In addition, there is the serious difficulty of finding any such aquifers in areas where (1) it would otherwise be economical to process fuel; (2) transportation from the processing plant to the disposal site is inexpensive; (3) no future production of water, oil, gas, brines, or other natural resources is likely; (4) a truly impermeable bed, or beds, occurs above and below the aquifer; and (5) it is known that the existing hydrologic flow patterns, or new ones established as a result of the waste injection, will not reintroduce toxic wastes into the human environment for the necessary period of hundreds of years.

There are several possible ways to avoid the problem of rapid precipitation and stoppage, if the waste is to be pumped into aquifers at all. These include (1) rapid injection, to decrease contact time, possibly through the use of aquifers containing the *faster* naturally flowing waters, although this generally signifies potable waters; by this method it is possible to obtain rates of flow far faster than those obtained by pumping into a static aquifer. (2) Dilution to whatever is discovered to be the optimum between increasing volume of waste to be pumped and decreasing reactivity of diluted waste. (3) Careful selection of glass-sand-quality aquifers to avoid as far as possible the more readily reactive compounds such as carbonates and possibly clays, and yet obtain maximum porosity and permeability. (4) Chemical pretreatment of the waste to retard or eliminate precipitation, for example, by removal of part or all of the aluminum, or by the formation of "diban" [dibasic aluminum nitrate, $\text{Al}(\text{OH})_2\text{NO}_3$] by distillation (Higgins and Wymer, 1955).^{*} (5) Pretreatment of the aquifer with acids or other solutions. How these five factors, and

^{*} It is not known how stable a solution of diban, containing $\text{Al}(\text{OH})_2^+$ ions, would be in natural environments, but it certainly should be more compatible than one containing Al^{+++} ions. Another possibility that is also being investigated involves the removal and recovery of the bulk of the "available" HNO_3 by distillation, followed by conversion of the aluminum to an alkaline solution of aluminate ion by addition of sodium hydroxide. This avoids the excessively large NaOH requirements needed to convert the raw waste to stable aluminate. There is very little information available on the probable behavior of strongly alkaline solutions in natural environments, but from preliminary work it seems that they will not present as serious compatibility problems as the acid solutions.

others not mentioned, may interact to control the amount of waste that can be injected per well, before stoppage, cannot be determined at this time, particularly in view of the five difficulties mentioned in the preceding paragraph concerning aquifer locations.

Containment Walls Within the Aquifer

A remedial method that might bear serious consideration, as it avoids many of the dangers inherent in the method of disposal by pumping into aquifers, involves the construction of truly impervious underground reservoirs by a cementing procedure, prior to injection of the waste into the aquifer. One such method would involve drilling a circular ring of wells into a reasonably unreactive aquifer, and by injection of a cementing material into each, form an impermeable "wall" surrounding a central cylinder of aquifer, as shown in Fig. 2. Various substances have been proposed and used in the petroleum industry for the blocking or plugging of permeable formations (American Petroleum Institute, 1954). Most of these probably do not penetrate very far into the formation, but it would not seem impossible to develop a similar procedure that would plug a formation for a greater distance from the injection well, so that injection into a series of such wells would form a continuous wall.[†]

Just within the wall another circular array of wells would be drilled for the actual waste injection; an inner ring of test wells, and a centrally located pressure-release well would also be drilled, as shown in Fig. 2. The impermeable wall would be carefully checked for leaks by pressure tests before any waste is injected. During the injection of waste, the natural waters in the aquifer would be pumped out through the central pressure-release well to provide space for the waste, until the waste reached the ring of test wells, as determined by samples pumped from them, at which time pumping of waste would be discontinued in this unit. If compatibility tests proved that the greater time of contact during injection would not cause difficulty, waste should be injected into all wells simultaneously. This would also simplify the heat dissipation problem. When the unit was full, the circular zone between the injection wells and the test wells would contain waste, and there would be a central "plug" of original non-radioactive ground water. Inequalities of flow due to anisotropy and heterogeneity of the aquifer would have been determined in advance during the testing, and corrected for by control of the volumes injected in each of the injection wells. The pressure-release well would then serve as a valuable control; pressure build-up in the waste could be relieved by withdrawing

[†] It might even be possible to process a portion of the waste to remove the more dangerous long-lived radionuclides, and use this to form an $\text{Al}(\text{OH})_3$ "wall" for enclosing the bulk of the waste which still contains these radionuclides.

non-radioactive groundwater from the pressure-release well as necessary. The possibility of leakage through the "wall" into the surrounding aquifer, or through the underlying or overlying impervious beds, could be minimized by maintaining a slightly reduced pressure at the pressure-release well. This should be effective except for a section of wall immediately adjacent to the one injection well into which waste is being pumped. Any small leakage would thus be of ground water *into* the unit, rather than of waste out of the unit. This pumping should be sufficient to move ground water in at a rate greater than that of the diffusion of fission products out.

The distance and time of flow from injection wells to the test wells should be such that no complete stoppage with precipitate occurs, if the pressure-release

drilling and a very expensive cementing and acidizing operation. However, the possibility of adequate hydraulic testing of the unit before any waste injection (if necessary for considerable periods of time) and the added safety factor of a pressure-release well which could also control minor leakage, are favorable features, but these extra safeguards are not adequate to make feasible the use of shallower aquifers than are being considered for uncontrolled storage. As this would be an entirely new procedure, however, there are a number of factors that must be investigated thoroughly. One of the most important is the anisotropy of the aquifer, in both the cementing and waste-injection steps. In terms of possible volumes injected, the procedure is completely adequate, as a unit 1 kilometer in diameter in a 20-meter bed could contain over a billion

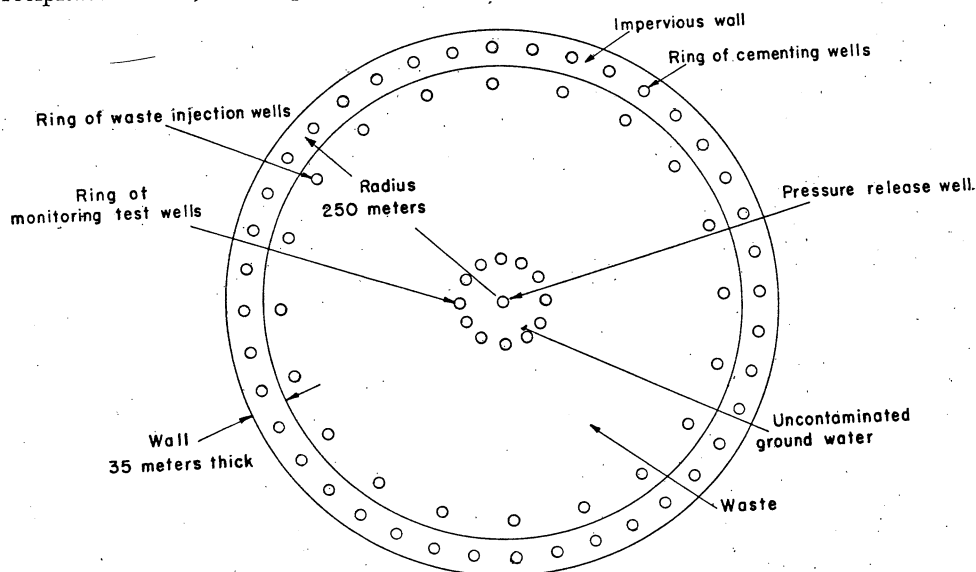


FIG. 2. Plan of wells for use of containment wall.

well is to function. Unless the aquifer is perfect, it would be desirable to pretreat it carefully with acid within the "wall" to make it accept waste readily and with no precipitation. There is an extensive literature on the use of hydrochloric acid for acid treatment of "oil sands". This operation is usually performed on carbonate-rich rocks such as limestones, to increase the permeability, particularly in the critical region near the well. The acid is injected, and then, by alternations in pumping, the insoluble debris and excess acid are "swabbed out". The operation can be troublesome, however, from corrosion of piping, solution of cementing materials, and clogging of pores by insoluble residues, colloidal gelatinized silica, and insoluble organic matter from the sediment. Acid treatment of an aquifer would have to be done under carefully controlled pressures, as new CaCO_3 may precipitate and clog pores upon pressure release.

This procedure would involve a large amount of

liters of waste. If uses are ever developed for the elements in the waste, for example Ru, Rh, Pd, Am, Np, Xe, and Tc, to the extent that recovery is profitable (Glueckauf, 1955) this procedure of disposal also has the advantage of keeping the waste in one fixed position, from which it may be reclaimed.

Although the large number of wells involved would seem at first to make this procedure too expensive, rough calculations using reasonable assumptions prove it to be economically feasible. For this calculation, the following assumptions were made: (1) the most economical operation has the cost of drilling wells for the wall plugging equal to the cost of the plugging; (2) the aquifer is at a depth of 2,000 feet and drill holes cost \$20,000 each (\$10.00 per foot); (3) the aquifer is 20 meters thick and has a 10% porosity; (4) sodium silicate (\$62.50/ton) is used for plugging (other plugging agents are more expensive per liter of storage volume); (5) the aquifer within the well is

pretreated with HCl (\$28/ton) to dissolve 1% by volume CaCO_3 or equivalent, to improve compatibility; and (6) the diameter of unit from center of wall to center of wall is 500 meters. This unit would have a wall thickness of 35 meters and a capacity of over 3×10^8 liters of waste, and would cost, for drilling and chemicals, \$10,500,000, or \$0.03 per liter (80% of this expense is for the HCl treatment). This low figure would thus permit ample room for other costs, such as exploration, piping, pumping, testing, maintenance, monitoring, and the inevitable contingencies of such an operation.

CONCLUSIONS

From a consideration of the mineralogical composition of natural aquifers presented above, it would seem that raw acid aluminum nitrate wastes cannot be injected into ordinary aquifers without causing the precipitation of aluminum hydroxide gels, effectively blocking further injection. By an exceedingly careful exploration, testing, and selection of aquifers, and pumping procedures, it might be feasible to inject wastes through wells into deep aquifers under certain conditions, but there are numerous possible or probable technical difficulties inherent to the process, as well as the ever-present problem of high costs.

The most likely solution to the problem of compatibility, if high aluminum nitrate wastes are to be pumped into aquifers at all, seems to lie either in chemical processing of the waste to a form that will not readily precipitate upon injection into aquifers, or in the use of an acid pretreatment of the aquifer to improve compatibility. In the first case, depending upon how and when the processing is done, a number of valuable products might be obtained to help pay for the processing and to make the disposal operation simpler, cheaper, or safer. In the second case, it seems that there are definite possibilities of making a reasonably leakproof walled underground reservoir at a cost of a few cents per gallon of storage capacity, assuming that a suitable aquifer of glass-sand-quality, sandwiched between truly impermeable beds, can be found.

SUGGESTIONS FOR FUTURE STUDIES

From the foregoing discussion it is evident that there are many unanswered questions, even in connection with the one combination of waste and aquifer assumed here. If the waste to be disposed is an acid aluminum nitrate waste, a number of the more significant points that need further study are implicit in the discussion, but obviously it would not be economically possible to explore experimentally all possible facets of all possible combinations of waste type and aquifer type. There must be some simplifying assumptions made, either as to kind of waste or kind of aquifer,

in order to set up a realistic approach. The composition of the waste obtained in any process is a function of the reactor type and the fuel processing methods used; it may be modified by subsequent chemical or physical treatment prior to disposal. The kind of aquifer available is a function of the disposal site selected and the depth of drilling. Except for very unusual conditions, geographic factors will be of prime importance here, as transportation for unspecified distances is involved in the distribution of electrical power from the reactor to the consumer, the movement of spent and reprocessed fuel elements between the reactor and chemical processing plant, and the movement of waste from the processing plant to the ultimate disposal site. Obviously all of these factors are interrelated by virtue of their effects on the cost of power and must be investigated simultaneously. The selection of a suitable waste-disposal method may dictate disposal site and fuel-processing procedure (or at least waste pretreatment) rather rigorously, and hence may well be a significant factor in the selection of the most suitable reactor type for a given application, in the selection of sites for both the reactor and the processing plant, and in the cost of atomic power.

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