Problems in the Disposal of Acid Aluminum Nitrate High-Level Radioactive Waste Solutions by Injection Into Deep-Lying Permeable Formations

GEOLOGICAL SURVEY BULLETIN 1088

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PROBLEMS IN THE DISPOSAL OF ACID ALUMIMUM NITRATE HIGH-LEVEL RADIOACTIVE WASTE SOLUTION BY INJECTION INTO DEEP-LYING PERMEABLE FORMATIONS

By Edwin Roedder

ABSTRACT

The problems of injection and the possibility of chemical reactions occurring upon contact between earth materials and typical high-level acid aluminum nitrate wastes, from atomic reactor fuel processing, are discussed in connection with proposed methods of disposal of such wastes by injection into deep-lying, brine-saturated permeable beds (salaquifers). To discuss the mechanics of the interaction of moving waste with salaquifer minerals, the concept of a "zone of equilibration" is developed and the factors modifying it are considered; it is shown that the width of the zone of equilibration controls the usable storage capacity of the salaquifer, per well.

Although the known variables include physical effects, chemical effects, and rate processes, most of which cannot be calculated rigorously but can be truly evaluated only by large-scale tests, it is shown experimentally that reactions with carbonates, limonite, clays, and other typical salaquifer materials will occur. These reactions can reasonably be expected to cause the precipitation of aluminum and ferric hydroxide gels, effectively blocking further injection. Whether this stoppage will occur before the amount of waste pumped into the well is sufficient to make the procedure economically feasible depends upon various factors that cannot be evaluated precisely without a number of simplifying assumptions and further experimental work, but the procedure would appear to be feasible only under certain very special conditions.

A few extrapolations of the data to other types of wastes and salaquifers are made, remedial procedures to avoid precipitation are discussed, and suggestions are offered for future studies, based on the pertinent literature.

It is concluded from safety and technical considerations that if wastes are to be disposed by injection, the only truly realistic approach to the problem involves (a) removal of the more dangerous and heat-producing long-lived isotopes, (b) aging to remove short-lived heat-producing isotopes, (c) chemical pretreatment of the waste or salaquifer or both to improve compatibility, and (d) injection into a deep-lying salaquifer of glass-sand quality that is far below any potable waters and is very carefully selected after extensive exploration and testing. The procedure might be made somewhat safer by some process whereby a portion of the salaquifer is sealed off to form a leakproof underground reservoir, but this cannot be substituted for adequate depth of burial.

INTRODUCTION

Atomic fission results in the formation of two atoms of fission products for each atom of uranium, plutonium, or thorium (converted to

U^{233}) that undergoes fission. Most of these fission products are highly radiocative beta and gamma emitters, and some have rather long half-lives. At present the bulk of these fission products are obtained during fuel processing as a relatively small volume of 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 waste is small, the amounts of radioactivity involved are so large that disposal by dispersal into natural environments is generally not feasible.[1] 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. Some nonradioactive materials, such as nitrate or fluoride,[2] as well as certain very long half-life elements, may be biologically hazardous in the concentrations reported here for hundreds or even thousands of years.

Various proposals have been made of methods whereby these high-level wastes might be effectively stored in natural underground "containers" instead of the present technique of confinement in tanks at the surface.[3] One of the widely considered methods involves pumping of the waste through wells into porous and permeable beds or formations situated several thousand feet or deeper in the earth, below the potable water zone (Pecsok, 1954; Theis, 1956; Thurston, 1956). As these formations presumably will be saturated with saline waters, the convenient term salaquifer is used in this report. It is generally assumed, in such proposals, that the strata occurring above and below the salaquifer are perfectly impermeable. As most such confining beds are *not* truly impermeable (Theis, 1956) the direction, volume, and rate of movement of the waste are of vital concern to future generations. Unfortunately, the tracing of such underground pollution is particularly difficult (American Water Works Association, 1952).

The problem then, assuming that the waste can be delivered to the site of the well, is essentially that of injecting such wastes into a

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[1] For example, a single gram of one particular fission product (Sr^{90}) could contaminate, to twice the maximum permissible concentration (National Bureau of Standards, 1953), a quantity of drinking water equal to that consumed by the total human population of the world in a one-year period. Published estimates indicate that by 1980, 1×10^7 to 3×10^7 grams of this isotope alone will be produced *per year*. Even the oceans are not an adequate diluent for such amounts of radioactivity (Renn, 1956).

[2] Safe upper limits, for drinking water, are 10–20 ppm NO_3 (Walton, 1951) and 1.5 ppm F (Hardenbergh, 1952).

[3] Several summaries of possible methods have been published. See Wolman and Gorman, 1956; Lieberman, 1956; National Academy of Sciences, 1957.

specific zone or stratum of porous, permeable rock without having stoppage, and under such hydrologic conditions that the waste will not be reintroduced into the human environment for the necessary number of hundreds or thousands of years (Kaufman, Orcutt, and Klien, 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.

Any interaction of waste and salaquifer that impedes the flow of waste through the salaquifer by increasing the viscosity of the waste, by precipitating on the walls of the pores, or by forming 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. It will be shown in the discussion of reactions with carbonate that 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.

Each waste type and salaquifer combination will have its own particular interactions and problems. The following discussion has been limited to the disposal of a specific type of waste (high-level acid aluminum nitrate) in a specific type of salaquifer (sandstone), as this seems to be one of the most promising combinations. Many of the results are reasonably applicable, however, to other types of salaquifers (for example, porous basalts) and have some significance in connection with the disposal of other types of waste or the use of entirely different disposal methods. An outline of the factors involved in the selection and use of a salaquifer for waste disposal (p. 62–65) covers the major problems, and also many aspects not discussed in this paper.

Even if high-level waste products are never put into the ground purposely, the possibility of contamination of large areas by the explosion of a reactor (Gilbert, 1954; Dietrich, 1956; Marley and Fry, 1956) or a chemical processing plant (Ullmann, 1956; Culler, 1956), by leakage or complete failure of waste tanks during processing, transportation, or storage (Culler, 1956), or by atomic warfare

(Amphlett, 1955), makes it desirable to know what phenomena might be expected and what corrective measures, if any, might be taken.

Dorothy Carroll, John Hathaway, and Ivan Barnes of the U. S. Geological Survey helped in some of the experimental work. I wish to acknowledge in particular many stimulating discussions with C. V. Theis & R. M. Garrels of the U. S. Geological Survey, and a careful review of the manuscript by J. Wade Watkins of the U. S. Bureau of Mines. This work was done by the U. S. Geological Survey on behalf of the Division of Reactor Development of the Atomic Energy Commission. A preliminary summary of this paper was presented at the 2nd Nuclear Engineering and Science Conference, Philadelphia, Pa., March 11–14, 1957 (Roedder, 1957).

SPECIFIC PROBLEMS

COMPOSITION OF THE WASTES

Although the variety of reactor types, fuel types, and fuel-processing procedures results in a great variety of waste types, one of the most common wastes for the present and near future appears to be the type high in nitric acid and aluminum nitrate. The composition assumed throughout, except where otherwise specified, is as follows:

Constituent	Concentration per liter	Notes
HNO_3	2 moles	126 g HNO_3 = 126 ml 70 percent HNO_3 (density = 1.42 g per cm^3)
$Al(NO_3)_3$	2 moles	426 g = 750 g $Al(NO_3)_3 \cdot 9H_2O$ = 54 g Al
Mixed fission products.	0.10 g [1]	Equivalent to 20 to 100 curies activity

[1] Approximately.

Note in particular that the quantity of nonradioactive salts and acids is over 5,000 times as great as the total quantity of fission products. Such a solution, but without fission products, was used in the experiments. It was a thin syrupy liquid with a density of 1.37 $g \cdot cm^{-3}$. It contained 372 grams of NO_3 per liter and had a viscosity of approximately 5.7 centipoises at 24.3° C, which dropped rapidly to 1.2 centipoises at 99.6°C.

In some processing procedures a waste containing somewhat lower concentrations of $Al(NO_3)_3$ (1.6 moles), and of HNO_3 (0.5 mole), might be obtained.[4] As shown on page 33 this lower concentration of acid *increases* the difficulty of injection by decreasing the extent of neutralization needed before possible precipitation. Wastes from other processes may have up to 8 moles of HNO_3 per liter, or high concentrations of iron, zirconium, fluorine, or other elements. In some cases the wastes are highly alkaline sodium aluminate solutions.

[4] This waste also included 0.05 mole $Fe(NO_3)_3$, and 0.005 mole $Hg(NO_3)_2$, in order to duplicate more precisely one specific waste composition. A list of the waste types to be expected from seven solvent extraction processes is given by Culler (1956, p. 24), and by Culler and McLain (1957).

Many aspects of the atomic waste disposal problem are discussed in a 227-page review, compiled and edited by Culler and McLain (1957) as a report of the Committee on Disposal and Dispersal of Radioactive Wastes, of the National Academy of Sciences. The publication contains data on the range of compositions, concentrations, volumes, and sources of the various types of wastes, present and future, and descriptions of the current disposal practice, including discussion of the hazards and costs involved. Several extensive bibliographies are included.

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 need not be considered by the time the waste is to be disposed. In table 1 the longer half-life radionuclides (including also some radioactive daughter nuclides from the decay of fission products) are listed, along with their half-lives and the slow neutron fission yield [5] for their respective mass numbers. Note that 18 of them have half-lives of one year or longer, and that these include members from each of the eight groups in the periodic table. Of these 18, Sr^{90} and Cs^{137} are the most serious by far because they have long biological half-lives (Glasstone, 1950, p. 508), very long radioactive half-lives (28 and 33 years, respectively), and are among the highest in fission yield (5.8 and 5.9 percent, respectively, Steinberg and Glendenin, 1956), but the others certainly cannot be ignored, and unless special processing steps are used, practically the entire fission product spectrum will be present in the waste.[6] Estimates of the total accumulated activity of waste products expected in the United States have been placed at 10^{10} curies by about 1965 and 10^{11} curies by about 1985 (Zeitlin, Arnold, and Ullmann, 1956).

In addition to the fission products, however, there will be produced, by parasitic neutron capture, small amounts of a number of different isotopes of thorium, uranium, and the transuranium elements, and their various daughter products in the four actinide decay series (Culler, 1956). Many of these are strong alpha emitters of exceedingly long half-life and exceedingly high radiochemical toxicity. (See table 2.) The amounts of such elements, and of their daughter products, will vary with the reactor and processing technology used, but may become a major radiation hazard in the future (Glueckauf, 1956), particularly with the newly-proposed power reactors and with increased fuel recycling. Even at present the traces of Pu^{239} in some wastes present a serious problem in disposal due to the high radiochemical toxicity of plutonium (Brown, Parker, and Smith, 1956).

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[5] "Fission yield" represents the number of fragments of a given mass formed from 100 fissions; it is usually given in "percents," the sum of which will be 200 (that is, 200 fragments).

[6] The major exceptions will be the noble gases such as Kr and Xe, and to a lesser extent, readily volatile elements such as I.

TABLE 1.—*Half-lives and slow neutron fission yield of the longer half-life fission product nuclides from* U^{235} [a]

Nuclide [b]	Half-life		Fission yield percent [c]
	Days	Years	
Se79		6.5×10^4	0. 04
Kr85		10. 27	1. 5
Sr89	53		4. 8
Sr90		28	5. 8
Y91	61		5. 8
Zr93		1.1×10^6	6. 4
Nb93		3. 7	6. 4
Zr95	63		6. 3
Nb95	35		
Tc99		2.1×10^5	6. 1
Ru103	40		2. 9
Ru106		1	. 38
Pd107		7.5×10^6	. 2
Cd113		5. 1	. 01
Cd115	43		. 01
Sn119		245	. 01
Sn121		>1	
Sn123	136		. 014
Sb125		2. 7	. 023
Te125	58		. 023
Te127	90		. 25
Te129	33		1. 0
I129		1.72×10^7	1. 0
Cs135		3.0×10^6	6. 3
Cs137		33	5. 9
Ce141	33. 1		5. 7
Ce144	290		6. 1
Pm147		2. 6	2. 6
Sm151		73	. 5
Eu155		1. 7	. 031

[a]Data from Arnold (1956); Steinberg and Glendenin (1956); and Booth and Schweitzer (1956).
[b]Nuclides of exceedingly low fission yield (such as Rn102) or of half-life >10¹⁰ years (Rb87, In115, Nd144, and Sm147) have not been included as they are of negligible importance here.
[c]These fission yield data are not all strictly comparable with each other, as they are not all calculated on the same basis. The yields for other fissionable nuclides and for fast neutron fission are somewhat different.

Many of these thorium, uranium, and transuranium isotopes may be expected to form, in various amounts, and as their long chains of daughter products build up to amounts representing radioactive equilibrium, the total alpha activity of a given waste containing them can be expected to increase over a period of years. As U^{233} and Pu^{239} are fissionable nuclides, they will certainly be recovered from the wastes as far as possible, but 100 percent recovery is never possible. Table 2 lists the longer half-life thorium, uranium, and transuranium isotopes that can be expected to form, along with their half-lives. Arnold (1956, p. 52) shows that after a 20-year decay, starting in 1990, the biological hazard involved in the various waste products

is as follows, in order of decreasing hazard for water contamination: Sr^{90}, Cs^{137}, Am^{241}, $(Pu^{239}+Pu^{240})$, Pr^{147}, and Cm^{242}.

TABLE 2.—*Longer half-life radioactive nuclides that may be formed by parasitic neutron capture* [1]

	Actinide decay series and mass number			
	Thorium 4n+0	Neptunium 4n+1	Uranium 4n+2	Plutonium 4n+3
Nuclides and half-lives.	Cm^{244} (19 years). Pu^{240} (6,850 years). U^{236} (2.4×10^7 years). U^{232} (70 years) Th^{228} (1.9 years).	Pu^{241} (14 years). Am^{241} (470 years). Np^{237} (2×10^6 years). U^{233} (1.6×10^5 years).	Pu^{242} (5×10^5 years). Am^{242} (500 years). Cm^{242} (162 days). Pu^{238} (90 years). U^{234} (2.5×10^5 years). Th^{234} (24 days)	Am^{243} ($\sim10^4$ years). Pu^{239} (24,100 years).
Stable end product.	Pb^{208}	Bi^{209}	Pb^{206}	Pb^{207}

[1] Not necessarily all of these will form in one type of reactor, however. Data from Arnold (1956), General Electric Company (1956), and other sources.

When all of the various sources of materials present in the wastes are considered, it is evident that there are least 50 elements present, in significant amounts, in a single typical acid aluminum nitrate waste solution. Obviously, any chemical reactions involving such a complex solution will not be easy to predict or to interpret.

HEAT AND PRESSURE

One of the most serious problems in any injection method will be the radioactive heat. The wastes probably will be warm or even hot at injection; if they are not, and adequate heat flow is not permitted, they will become warm or hot by their own radioactivity. No single value can be set for the heat generation of the wastes, as it will be controlled by the amount of burnup of the fuel, the fuel type, the chemical process used, and particularly the length of time since fuel irradiation. The heat generation from typical fresh undiluted acid aluminum nitrate wastes will be in the range of 1,000 to 7,000 calories per hour per liter (Culler, 1956).[7] This must be dissipated to the enclosing or

[7] 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. Since about 200 curies of fission product activity is equal to only 1 watt of heat energy, utilization of this heat except for boiling off water from the waste ("self concentration") does not appear too feasible. After a few months' cooling time, the total power output from the fission products in a pile is only a few hundredths of a percent of the total power of the pile and thus would not be a serious loss of power. After 1 year of cooling, the fission product heat is only 10^{-6} that of the equivalent reactor heat. In spite of this, however, Glueckauf (1956) has proposed using separated Sr and Cs as a heat source, and Durham (1957) has suggested using wastes fused to a silicate glass as a concentrated heat source.

adjacent rock in some manner, or the temperature, and hence pressure, will climb (Theis, 1956). If for any reason the pumping is stopped with a column of waste in the well, the heat generated might be adequate to cause geysering of the fluid in the well and in the salaquifer near the well. Kaufman, Orcutt, and Klein (1955, p. 21) have calculated the length of time for injected wastes to "evaporate to dryness," but it is difficult to envisage a mechanism for releasing steam that would not blow out most of the waste.

In the present discussion, a temperature of injection in the range of 25° to 100°C is assumed. If the salaquifer chosen is about 1 kilometer deep, the normal geothermal gradient would result in a rock temperature of about 50°C with no addition of radioactive heat from the waste; this higher rock temperature would increase the temperature of the waste. In connection with the problems of heat dissipation, it should be mentioned that cation exchange phenomena fixing fission products on clays, or coprecipitation phenomena yielding high concentrations of fission products in hydroxide precipitates, might result in localized heating.

The temperatures attained may have considerable effect on the possible recrystallization of gelatinous precipitates to porous granular masses, on the chemical equillibria involved, on ion exchange phenomena, on permeability (Breston and Pearman, 1953; Greenstein and Preston, 1953), 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 salaquifer. The hydrostatic head in the well, using a liquid of a density of 1.36 g per cm³, would be 132 atmospheres (1,930 psi) per 1,000 meters (3,281 ft) of depth. Considerable additional pressure may be needed to overcome the frictional resistance involved in forcing a viscous fluid through many meters of salaquifer, and as explained below, considerable carbon dioxide pressure may be generated by reaction with salaquifer carbonates.

The expectable ranges of temperatures and pressures in the formation at the start of injection are given in figure 1. The two geothermal gradients represent high and low values; the true value for most regions will lie between, at approximately 1°C per 100 feet. The geobaric gradient is more difficult to estimate, particularly for a salaquifer isolated above and below by truly impermeable formations, although it will certainly lie somewhere between the values for the lithostatic and the hydrostatic loads. For safety, it would appear that wastes should not be maintained in the ground for any appreciable
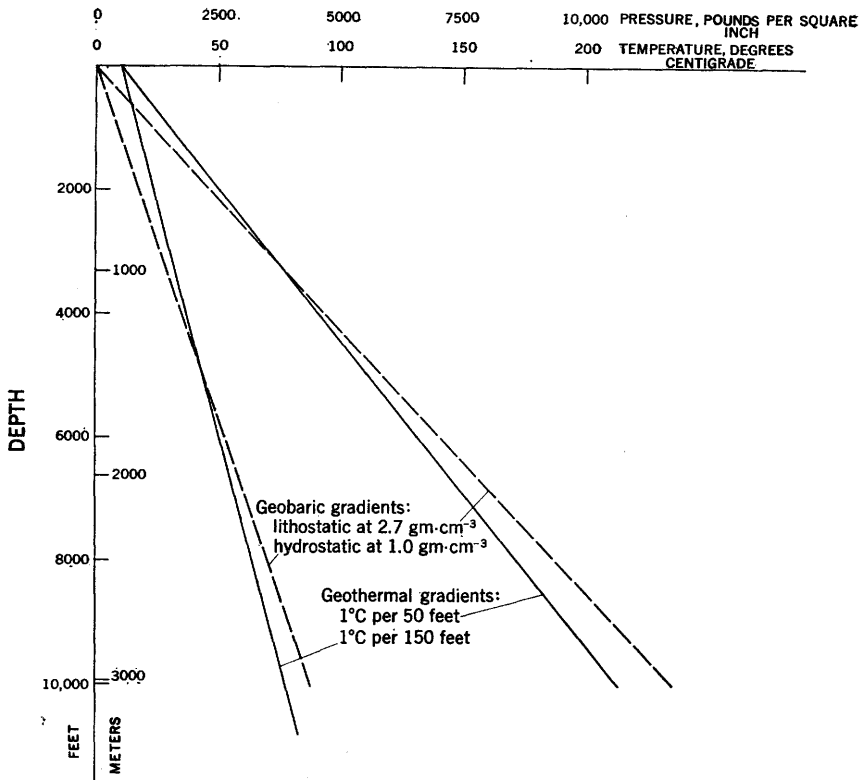
FIGURE 1.—Geothermal and geobaric gradients.

length of time at pressures greater than the normal hydrostatic pressure at that place.

The effects of the generation of heat by the radioactivity of the waste are shown in figure 2, on which the pressure-temperature diagram for pure water has been plotted from the data of Amagat (1893), Dorsey (1940), and Kennedy (1950), along with the normal geothermal gradient for a hydrostatic column. Any increase in temperature of injected wastes from radioactive heat must result either in a dramatic rise in pressure at constant volume, as along the 0.90 isodensity line, or in a slow, then fast increase in volume of the wastes, at constant pressure. At pressures below that of the critical point,[8] there would be an additional, sudden, large increase in volume if the solutions crossed the two-phase boundary, that is, they "boiled." These increases in volume must also be considered in any calculations of the mechanics of injection. Birch (1958) has shown that wastes generating heat at rates of 0.01 watts per gallon (about 2 calories per hour per liter) or less can be accommodated without undue rise

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[8] The critical temperature for these solutions will probably be considerably higher than that for pure water.
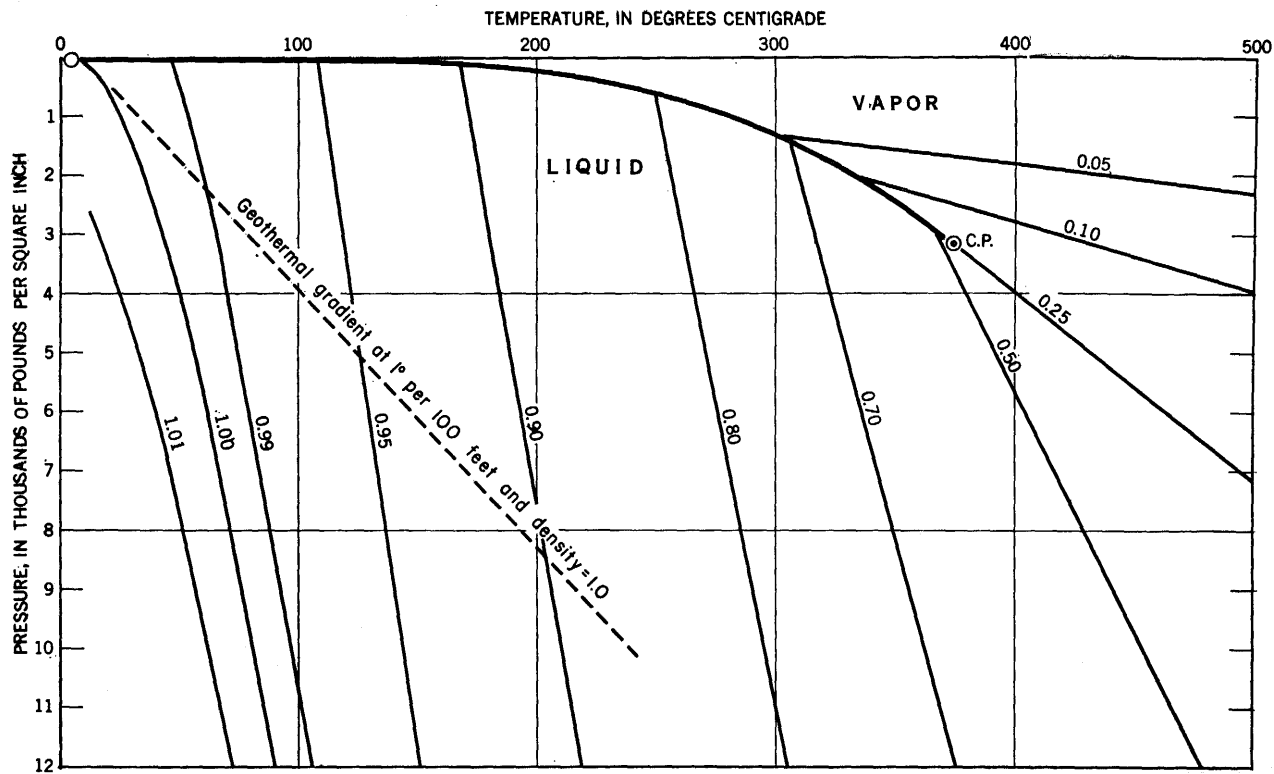
FIGURE 2.—Pressure-temperature diagram for water, showing lines of equal density. Data from Amagat (1893), Dorsey (1940), and Kennedy (1950) ; and smoothed where the data are contradictory.

of temperatures. Fresh wastes would thus require, from thermal considerations alone, dilution with 500 to 3000 volumes of water.

Under the pressures involved here, the compressibility of water itself becomes a significant factor, particularly if the permeability of the salaquifer is high. Using the value for the compressibility of water at 100°C, in the range of 100 to 200 atmospheres (46.8×10^{-6} volumes per unit volume per atmosphere, Amagat, 1893), an increase in pressure of 100 atmospheres on the water in the pores of a disk only 1,000 meters in radius and 10 meters thick, would cause a contraction of approximately 1.5×10^7 liters volume. This assumes constant reservoir volume, 10 percent porosity, zero compressibility for the rock minerals, and no interactions with the minerals. In actual practice, much larger volumes can be injected than the simple compressibility of the water can account for, because the salaquifer and adjacent strata themselves behave elastically, to an extent much greater than the water does. This compressibility of fluids in porous beds is used in the reverse direction in petroleum production. (See Muskat, 1934; Schilthuis and Hurst, 1935; and Buckley, 1951.) 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 salaquifer and present an added safety hazard.

CUMULATIVE CHEMICAL REACTIONS

It is shown (p. 22 ff.) that chemical reactions with salaquifer materials can be expected. One of the most serious problems that must be considered is the possibility of the effect on the advancing front of the waste being cumulative, as it continues to contact and react with fresh portions of the salaquifer in its travel, resulting eventually in precipitation. To consider this problem adequately, a "zone of equilibration"[9] is envisaged for each possible interaction. It could be defined as including that part of the salaquifer traversed by the uniformly moving waste solution in the time necessary for a specified process or reaction to come to equilibrium.[10] Thus, in the case of a mineral in a salaquifer 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.

This is illustrated for the general case in figure 3, where the development and movement of a leached zone, an equilibration zone, and

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[9] 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."

[10] In the case of reaction products forming an "armor" on the reactive mineral, effectively removing it from further contact, an "apparent" zone of equilibration would be obtained.
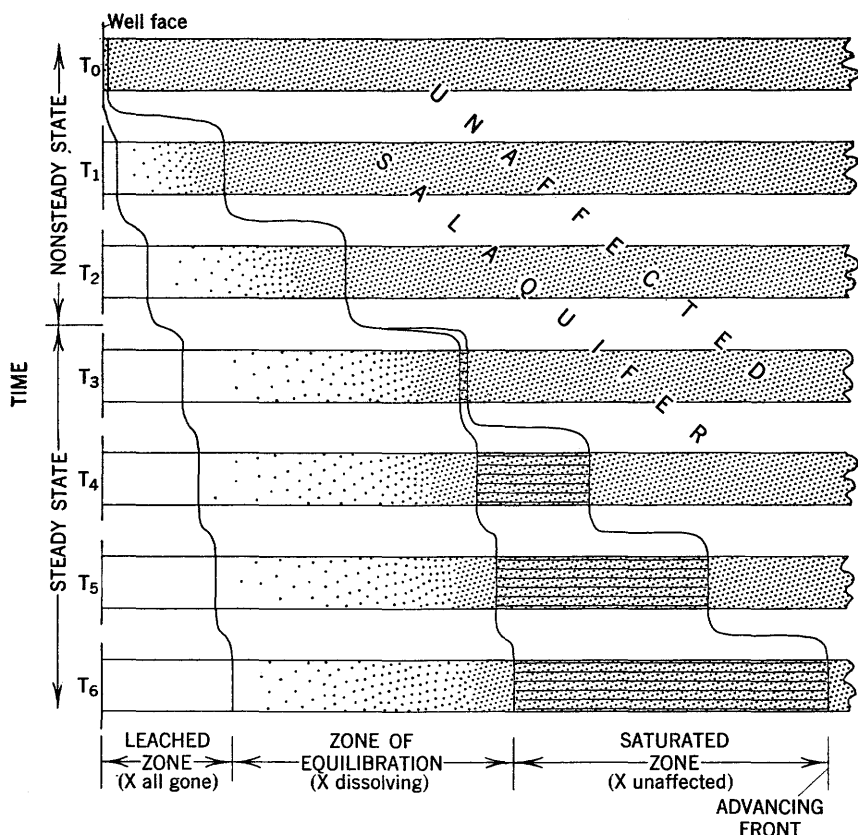
FIGURE 3.—Diagram showing the concept of the "zone of equilibration" in a salaquifer containing a slowly soluble mineral X (black dots) dissolving in a solution injected uniformly with time from the left side starting at T_0. A rate of flow that is uniform with distance is assumed.

a saturated zone are traced. At time T_1 and T_2 no saturated fluid is present, but at T_3 the front (leading) edge has just become saturated and at the trailing edge of the zone of equilibration the last remnants of the soluble mineral are just disappearing; hence a moving "steady state" is established.[11] After this the width of the equilibration zone will remain constant, other factors remaining constant, as the leached zone and the saturated zone increase in width and migrate outward from the injection well (T_3 through T_6). In actual practice, the rate of advance of the front from a single well in a permeable bed enclosed above and below by impermeable beds might decrease with distance from the injection well, as described beyond, and the width of the equilibration zone would decrease proportionately due to the longer contact times involved.

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[11] If the rate of solution and quantity of soluble mineral are high, and the solubility low, saturation may well occur before any leached zone appears.

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 rate of flow, and the relative quantities of reactants (which are functions of the porosity and of the concentration in salaquifer and waste). The relative widths of the three zones for several possible combinations of solubility and rate of solution are shown in figure 4; all other factors are assumed to be constant in the four cases. If a reaction is very slow, as in grains "armored" 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 concept of a zone of equilibration is real only for a specified finite change in concentration, and is best applied to cases where a natural limit, such as saturation or phase change, occurs. In the case of a soluble mineral, as the grain is dissolving the fluid that passed
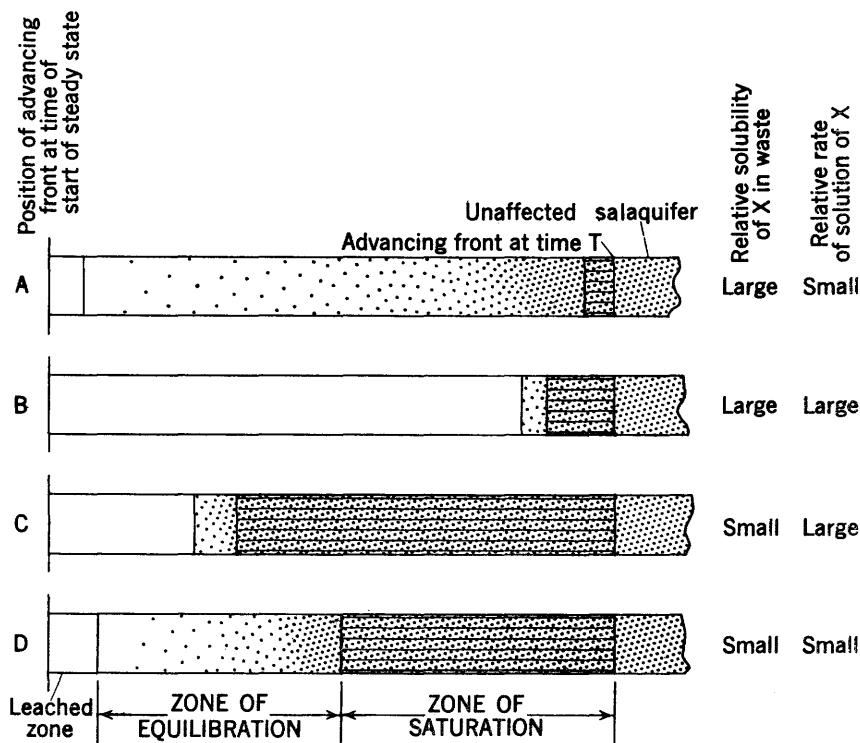

FIGURE 4.—Variations in relative widths of zones at time T after a "steady state" is established, with various combinations of total solubility of the soluble mineral X (black dots) in the waste, and rate of solution. The composition and quantity of waste and of the mineral, and the rates of injection and flow are assumed constant. Injection from the left side.

over it earlier is contacting other similar grains and gradually becoming saturated. Up to the point of first saturation, "zone of equilibration" here refers to the process of the concentration of solid soluble mineral changing from a finite to a zero value in the sediment, rather than the liquid changing from zero concentration to saturated. These two processes become equivalent, once a "steady state" is established. The specified change in concentration would then be from zero, or whatever is the concentration of the incoming waste, to saturation for the waste, and from a finite value to zero for the sediment. Once the advancing front has reached saturation, and a leached zone has been established, the zone of equilibration will be of constant width as it moves on out through the rock, barring precipitation (fig. 3). Further increases in the widths of the leached zone and the saturated zone will be functions of the porosity, solubility, quantity of mineral, flow rate, and concentration change.

If a reaction is fast relative to the rate of movement of fluid in the salaquifer, and if the quantity of soluble mineral is small or the solubility high, the zone of equilibration becomes small, as in case B, figure 4.

The major concern in any interaction between waste and salaquifer minerals is that of possible precipitation; presumably this would preclude any continuation of flow after saturation (that is, precipitation) occurred unless it formed only a lining in the pores, decreasing the permeability, or a sol, increasing the viscosity. 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 can be pumped before precipitation and plugging occurs, and hence it controls the storage capacity per well. Figure 5 illustrates this control for two cases wherein the rate of solution is varied and all other factors are assumed constant. Compared with case A, case B might represent a more finely divided reactive mineral, a more turbulent flow, a higher temperature, or any other factor which might increase the rate of reaction. The chemical compositions of the original waste, the saturated waste, and the salaquifer would be identical in the two cases. The width of the equilibration zone thus varies inversely with the rate of solution and as a consequence the storage capacity of the salaquifer (volume injected per well before precipitation blocking) will decrease with an increase in reaction rate. Taken to the extreme case, if there is a finite amount of a reactive mineral in the salaquifer, and an infinitely high reaction rate, the waste could only be pumped zero distance before precipitation and plugging. The composition of the waste, the composition of the salaquifer, and the porosity of the salaquifer control the *stoichiometry*
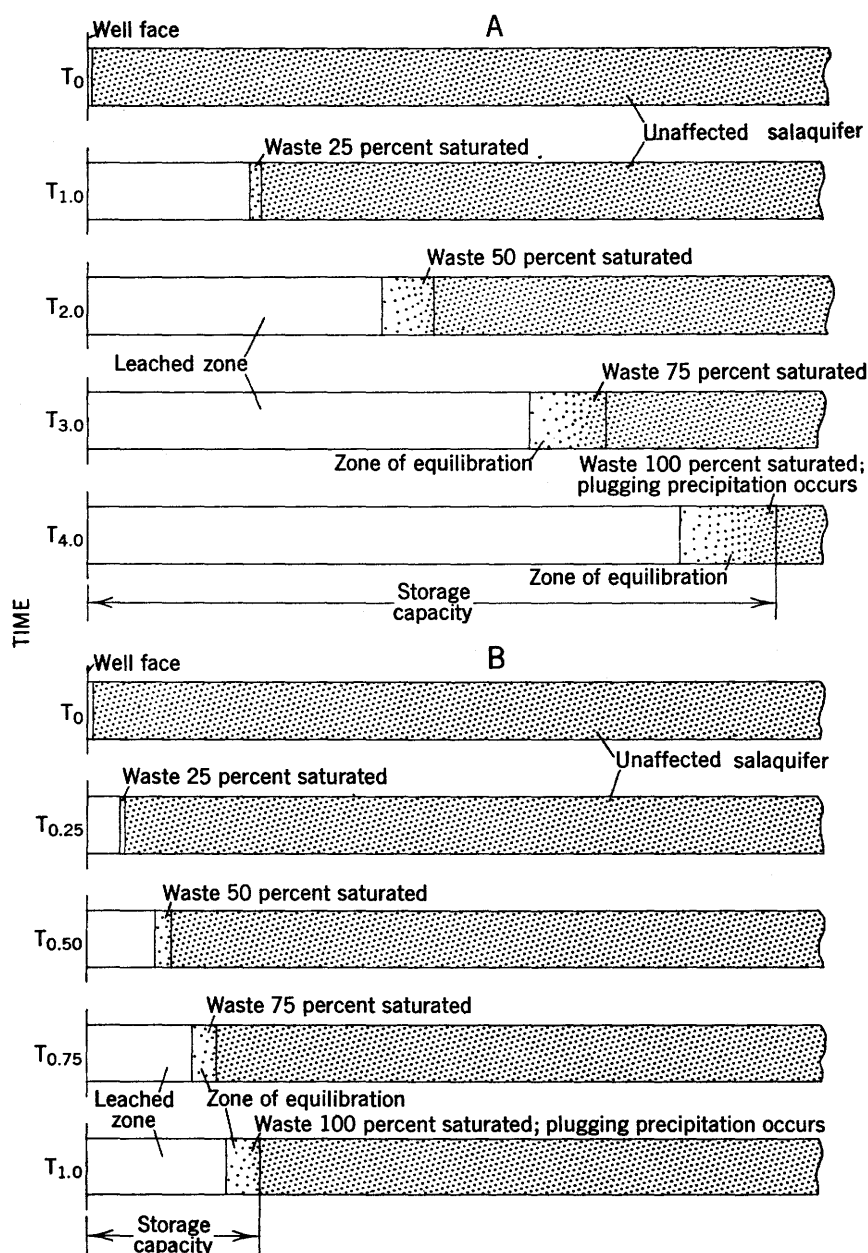
FIGURE 5.—Special cases of high rate of solution, high solubility, and small quantity of soluble mineral *X* (black dots) dissolving in waste injected from the left side starting at time *T₀*. Conditions in *B* are identical with those in *A* except that *B* has a higher rate of solution, hence a smaller zone of equilibration and storage capacity. Note that *B* became saturated and plugged at time *T₁.₀*, when the front of *A* was only 25 percent saturated.

(that is, the relative quantities involved) of any possible reaction in terms of volume of salaquifer 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 1 mm or as large as 1 km, depending upon the rate of flow and the rate of reaction of acid aluminum nitrate waste with available natural salaquifer 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 of the order of 1 or 2 cm, but it will be shown that a zone of equilibration of 10 cm or even 1 m for reactions with carbonates or clays can be expected to result in precipitation after a very short passage through the rock. In actual practice, the moving waste would be progressing through a number of different overlapping zones of equilibration simultaneously, and these may well be expected to interact by changing the reaction rates. Furthermore, it can 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." Under these conditions, the required width of the zone for a given mineral to dissolve completely becomes equal to the width of the zone for the liquid to come to saturation with respect to this same mineral. In general, the width of the zone will increase with time up to this point, as shown in figures 3 and 5.

Although it is not possible to predict accurately 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, and other processes will result in the fluid having a uniform composition throughout the zone at any given instant. Thus when precipitation occurs, the entire zone of equilibration 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; if only a small portion at the front of the zone becomes saturated, as is likely in any real situation, this precipitation can be expected to occur at a shorter distance from the injection well. Kaufman, Orcutt, and Klein (1955) have investigated the magnitude and nature of velocity variations of flow through porous media; their results indicate that the boundaries of the various zones discussed here will be diffuse.

TIME, RATE, AND VOLUME OF FLOW

To a large degree the compatability of waste with salaquifer 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 be reasonable to assume a production in the United States of 100,000 gallons of high-level waste per day within a comparatively few years.[12] If 10 processing plants are arbitrarily assumed,[13] each will thus have to dispose of 40,000 liters (about 10,000 gallons) per day. As the pumping of waste into a given well would presumably take place continuously over a period of months or even years, it is important to consider the rates of flow involved. If 40,000 liters of waste per day is introduced continuously into a salaquifer through a single well, and spreads as a uniform cylinder from the injection well, the radius of the cylinder and the rate of advance of the front after various pumping times would be that shown in table 3.

TABLE 3.—*Radius of cylinder of waste and rate of advance of waste front assuming injection at 40,000 liters per day into a static, isotropic salaquifer with 10 percent porosity by volume*

Pumping time (days)	Volume pumped (10^6 liters)	Thickness of salaquifer			
		30 meters		10 meters	
		Radius (meters)	Rate (cm per day)	Radius (meters)	Rate (cm per day)
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
1,000_____	40	65. 1	3. 26	113	5. 6
5,000_____	200	146	1. 45	251	2. 5

The data in table 3 assume a salaquifer that is uniform in thickness and that is perfectly homogeneous and hydrologically isotropic. Although many sandstone formations are remarkably uniform in many respects, few are isotropic in porosity or permeability, either horizontally or vertically (Uren, 1953; Theis, 1955). In general, porosities and permeabilities are less in deeply-buried sediments than in shallow ones (Bell, 1943), and within a given formation they will

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[12] Estimates of a world production of up to 4×10^9 gallons of high-level waste per year (1×10^7 gallons per day) by the year 2,000, have been made (Hatch, 1953; Rodger, 1956; and others). This assumes 900 tons of uranium or equivalent are burned per year. After 1 year of cooling, the fission products, from 1 year of operation alone, will have a gross activity of 4×10^{11} curies. This should be compared with the total world production of radium to date of approximately 1.4×10^3 curies (U. S. Atomic Energy Commission, 1950), and a total of only 1.3×10^5 curies of radioisotopes shipped out of Oak Ridge for scientific and engineering use (National Academy of Sciences, 1956).

[13] It is perhaps more probable that only a few large central processing plants will be in operation (Culler, 1956, p. 32), but 10 have been assumed in order to be on the conservative side concerning the disposal problem at any one plant. Culler suggests that shipping aged (5 to 10 year old) wastes as much as 1,000 miles might not be prohibitive in cost.

vary tremendously from top to bottom, and to a lesser extent, laterally. Much research has been done on these variations, their causes, and their importance in oil production; most of this research has a bearing on the problem of injection of wastes. (See, for example, Krynine, 1938; Uren, 1953; Herold, 1941; Law, 1944; and Muskat, 1950.) Permeabilities within a single formation may have a 2,000-fold range (Muskat, 1937), and loss of oil from "pocketing" due to local variations is particularly serious (Uren, 1953). In addition to the local inhomogeneities and anisotropy, permeability studies may reveal large-scale anisotropy in the plane of the bedding. Considerable work has been done on certain oil sands to determine the precise nature and cause of this directional permeability; maximum permeability vectors are not even parallel to the bedding in some cases (Griffiths, 1950; Johnson and Breston, 1951; Griffiths and Rosenfeld, 1951).

The permeability variation that is most likely to cause trouble in waste injection is that from bed to bed within a given formation. Certain layers are bound to be more permeable than others, sometimes by several orders of magnitude, causing them to carry the bulk of the waste and leading to a low storage capacity per well.[14] These variations are sufficiently troublesome that thick formations are not considered very adaptable to secondary recovery of oil by "water flooding" (van Wingen and Johnson, 1947). In the petroleum industry various procedures are used to compensate for these differences between layers and might be effective in improving the efficiency of waste injection into nonuniform sediments. Among these are controlled selective plugging of the more permeable beds at the input well face (Dickey and Andresen, 1950), and careful placement of nitroglycerine charges at the lower permeability beds ("corrective shooting," Ryder, 1939).

In any case, extensive core sampling should be done, so that the permeability and porosity measurements will be meaningful (Earlougher, 1946). Particular care should be given to the problem of evaluation of these core tests, in the light of the extensive experience in the petroleum industry. (See, for example, Earlougher and Robinson, 1949; Krueger and Vogel, 1955.)

An additional problem that might be involved is that of density. Undiluted wastes range from 1.1 to 1.4 g per cm^3, and hence would not be expected to maintain a vertical waste-ground water boundary very long (Theis, 1955; Orcutt and others, 1956), unless the displaced groundwater were a brine of equal density.

It is assumed above that the salaquifer does not have a preexisting natural flow of water through it, and hence an expanding cylinder of waste will form, pushing the ground water in front of it. Probably,

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[14] The low permeabilities perpendicular to the bedding, from thin shale partings on bedding planes, dimensional orientation of grains during sedimentation, and other phenomena, are rather effective in confining a given fluid stream to a given bed.

however, there will be some natural flow of the ground water originally in the salaquifer. The deep, relatively isolated salaquifers of interest here might have water moving as slowly as 1 mm per day. (Theis, 1955; 1956). If waste is pumped into such a salaquifer 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 (Theis, 1955). In a salaquifer 30 meters thick, with 10 percent porosity and saturated with ground water moving at 1 mm per day, an injection of 40,000 liters per day would eventually form a waste stream 13,333 meters wide, also flowing at 1 mm per day. If the rate of ground water movement were 0.3 m per day, the waste stream at equilibrium would be only 44 meters wide, also flowing at 0.3 m per day, but such flow rates are not generally found in deep salaquifers. 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 (Billings, 1955).

In the two types of hydraulic conditions described above in the salaquifer (static or flowing), either the rate of flow is very small, possibly permitting slow reactions to go to equilibrium, or else the rate of flow is fast, permitting contact of the advancing front of waste with a large area of salaquifer 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 sizes are given in table 4. The large values obtained are particularly noteworthy.

TABLE 4.—*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 percent) | Average grain size (mm diam) | Sediment contacted per liter [1] | | |
		Surface area [2] (10^8cm²)	Bulk volume (m³)	Weight [3] (kg)
5_____	1. 0	1. 14	2. 0	4, 750
	. 4	2. 85		
	. 2	5. 73		
	. 1	11. 40		
10_____	1. 0	. 54	1. 0	2, 250
	. 4	1. 34		
	. 2	2. 71		
	. 1	5. 39		
20_____	1. 0	. 24	0. 5	1, 000
	. 4	. 60		
	. 2	1. 21		
	. 1	2. 40		

[1] 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.
[2] 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.
[3] This assumes a mineral density of 2.5 g per cm³.

Such problems as pumping, well-casing corrosion, and leakage around the outside of the well casing, although they are quite pertinent here and frequently encountered in the petroleum industry, are not within the writer's experience and are not discussed. An additional problem brought about by the intense radioactivity of these wastes is the difficulty of shielding; all above-ground pumps and piping would require shielding equivalent to 5 to 10 inches of lead, and would require facilities for remote operation and servicing.

PLUGGING AT THE FACE OF THE INJECTION WELL

Up to now it has been tacitly assumed that the waste will be *completely* free of all suspended solids before pumping. If this is not so, one of the most serious operational problems will be that caused by plugging of the pores of the salaquifer at the face of the injection well. This is a critical zone that can be expected to contribute a major part of the total pressure drop in the system, even in a new well, as it may represent the smallest effective cross-sectional area in the system. Away from the face of the well the effective injection area increases as a function of the radius from the well and hence will have considerably less effect on the pressure drop.

Injection of liquids (and gases) into salaquifers is common practice in the petroleum industry for aiding the recovery of petroleum ("water flooding"), and to a lesser extent in the chemical industry; a fairly extensive technology has been developed concerning it. (See, for example, Lee, 1950; Elliott, 1946; Cecil, 1950a; Dickey and Andresen, 1950; Henkel, 1953.) Under very favorable conditions, up to 20,000 barrels per day (2×10^6 liters) of *water* have been injected by gravity alone into single wells, the flow from the injection well to the pumping well being an elliptical area in plan (Herold, 1941; Jones, 1945; Theis, 1955). In many cases strong brines obtained with the petroleum are recharged into wells either to aid in the production of petroleum, or as a convenient way to dispose of an unwanted waste product (Schoeneck, 1946; Morris, 1946).

As high-level waste disposal requires essentially 100 percent confinement for 100 years, and nearly 100 percent confinement for centuries thereafter, the control over the injection would have to be far better than is normally the case in water flooding as a break-through into other formations would be intolerable.

There is an almost universal trouble in water injection, however, due to exceeding minute amounts of solid matter in the water filtering out within a fraction of an inch of the face of the injection well, causing high pressure loss and small injection rates.[15] For example,

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[15] Additional trouble is frequently encountered wherein particles from the drilling fluid seriously affect the permeability (Krueger and Vogel, 1955).

trouble has arisen from scale from corrosion of piping (Clarke, 1934), iron hydroxide precipitates from oxidation of ferrous iron (even 0.2 part per million of ferrous iron in natural waters is serious, Cecil, 1950b), and from oxidation of manganese (Ellenberger, 1950). Other substances causing blocking include calcium carbonate (Cerini, Battles, and Jones, 1946; Plummer and Walling, 1946), dust and algae from exposure to air (Herold, 1941), and bacteria and their precipitated metabolic products including hydroxide, metal sulfides, sulfur, or $CaCO_3$ (Plummer, and others, 1944). Presumably corrosion-resistant metal, plastic, glass or cement linings (Theis, 1941; Lee, 1950; McRae, 1951), would have to be used for all pipes, pumps, and well casings, for corrosion is a frequent source of trouble in the use of water injection in the petroleum industry (Trube and Dewitt, 1950; Watkins, 1950). Blocking may also take place at the contact of two different waters upon water injection, yielding precipitates of $SrSO_4$ or $BaSO_4$ (Heck, 1940; Sudbury, 1952), $CaSO_4$ (Stiff and Davis, 1952a), $CaCO_3$ (Stiff and Davis, 1952b), and silica gel (Kennedy, 1936; Uren, 1953), although this idea has been challenged by Bernard (1955). Other cases of trouble may include expansion of clay minerals in the formation upon contact with new waters, and solution and redeposition of gypsum ($CaSO_4 \cdot 2H_2O$) (Yuster, 1939), calcite, and limonite (Krynine, 1938). Even filtered, completely clear solutions may precipitate and block injection where they have not been "stabilized" (Plummer and Walling, 1946), that is, they were supersaturated during filtration.

A large portion of the technology of water injection or water flooding deals with the methods of avoiding or curing this plugging at the face of the injection well. Many different methods are used (Breston, 1951). Reverse pumping at intervals (back flowing or "swabbing") is sometimes used in attempts to remove blocking, but is not wholly satisfactory and would not be very feasible in atomic waste disposal operations, where the well would be thoroughly contaminated with radioactivity. Far more stringent clean-out practices often must be used (Bossler and Taylor, 1950). Water jetting, supplemented by concentrated doses of chlorine or other biocides (amazingly hardy microorganisms are one of the most frequent causes of plugging), detergents, alkalies, or acids—including even hydrofluoric (Pfister, 1946)—are used. For relatively insoluble substances, such as barium sulfate, it may be necessary to scratch the walls of the bore hole (J. Wade Wakins, U. S. Bureau of Mines, personnel communication, 1956). In practically all water flooding procedures, elaborate precautions must be taken to pretreat the water before injection to reduce, as far as possible, the amounts of solids in suspension in the injection waters (Watkins, 1955). It is apparently impossible to

prevent such blocking completely, and any waste injection operation must be prepared to cope with it. Many high-level wastes are saturated with respect to one or more precipitating solid phases; simple filtering then would not be adequate pretreatment, as small changes in conditions after filtration might yield more precipitate in a saturated fluid of this type.

In the oil industry high pressure hydraulic fracturing ("hydrofracing", Clark 1949), is 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 common problem of clogging from the inevitable suspended solid matter. This procedure would be very desirable in waste disposal, and apparently it can be controlled to the extent that there is no danger of damage to the enclosing impermeable beds. (See, for example, Harrison, Kieschnick, and McGuire, 1954.) The actual nature of the fractures formed may be determined with cameras lowered into the well (Hurst, Moore, and Ramsey, 1955). Other methods of increasing the effective area at the well face include acidizing (in carbonate rocks) and high explosives.

Obviously, the essential problem involved here in waste disposal is that of preventing blocking from occurring at the well face. As the waste is a concentrated fluid containing many different elements, some of which are changing concentration appreciably with time, because of their radioactive decay, the research problems in physical chemistry and chemical engineering that must be studied to insure freedom from precipitation before injection, even to the extent of a single part per million, loom rather large. Preparations must be made for remedial steps appropriate to the particular precipitation occurring. For example, it might be necessary to use modifications of the existing procedures now used for perforating well casings, such as gun perforation (Allen and Atterbury, 1954) or shaped charge perforation (Caldwell and Owen, 1954), to permit continued injection, rather than the use of chemical agents alone.

REACTIONS WITH SALAQUIFER MINERALS

GROSS FEATURES OF SALAQUIFER COMPOSITION

Most natural salaquifers that might be considered for waste disposal sites consist almost entirely of a small number of minerals. The following list of minerals and mineral groups would probably include at least 95 percent of the mass of most sedimentary salaquifers; the figures are the percentages for average sandstones in the earth's crust (Clarke 1924):

Quartz group of minerals (including chert, flint, jasper, and others) _____ 66. 8
Feldspar group of minerals (particularly orthoclase, and the plagioclase
 series) _____ 11. 5
Mica group of minerals (mainly muscovite and biotite) _____ ⎫
Clay group of minerals (including kaolin, montmorillonite, "illite", and ⎬ 6. 6
 others) _____ ⎭
Limonite group of iron oxides, plus hematite_____ 1. 8
Carbonate group of minerals (mainly calcite and dolomite)_____ 11. 1
Miscellaneous _____ 2. 2

   Total _____ 100. 0

The composition of individual sandstone strata or formations will deviate rather widely from this average, so obviously there is no one truly "typical" composition for salaquifers. To simplify the following discussion, however, a specific salaquifer is assumed—one that has a 10 percent porosity and 0.4 mm grain size, and contains about 90 percent quartz, 10 percent feldspar, and 0.1 percent each of mica, clay, limonite, and carbonates. It is admittedly a rather optimistic estimate, in terms of the known data on salaquifer sandstones, but it will be shown that even this rather "pure," hypothetical salaquifer can probably be expected to become plugged with precipitate when acid aluminum nitrate waste is injected into it. Possible deviations from this composition are discussed under the individual minerals, and other possible constituents are discussed beyond. In each case the effects of the individual mineral alone are considered; the results of their joint effects are considered at the end of this section.

The porosity is assumed to be 10 percent by volume, and the grains of quartz and feldspar are assumed to be 0.4 mm diameter spheres.[16] If a larger average grain size were to be assumed, the permeability might be considerably higher, and the surface area per unit volume considerably smaller than the above case, but most of the very "clean" sands that might be of sufficient purity to use for disposal sites are of rather small grain size. A very coarse sand might also be expected to have a considerably higher rate of natural ground water flow than a fine one. A finer grained sand than the case chosen might be just as porous, but would probably be much less permeable, and might be expected to contain more clay minerals.

SPECIFIC MINERALS AND MATERIALS

QUARTZ

Although by far the most abundant mineral in most salaquifers, quartz is the least reactive. At the temperatures involved here, its solubility is in the parts per million range, even in moderately alkaline

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[16] The average porosity in the Bradford oil field (where water flooding or injection was used so successfully) is 11.5 percent, and the grains average 0.2 mm diameter. This, with the clay content, yields a uniform permeability of 5 to 10 millidarcys, but water drive has been profitable at permeabilities as low as 1 millidarcy (Torrey, 1940).

waters (Krauskopf, 1956), so it can be considered inert in most waste solutions, except insofar as its surface acts in ion adsorption. The sandstone assumed above would be classed as of "medium" grain size (0.4 mm grain), and 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) and Goates and Anderson (1956), would be about 10^{-11} moles per cm², 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 appears to be of little concern. Highly alkaline solutions, such as those containing sodium aluminate, can be expected to react with quartz, however, and experimental work with such solutions is now in progress in the U. S. Geological Survey.

FELDSPAR

Sandstones containing practically no feldspar are rare; average sandstones contain 11 to 12 percent (Pettijohn, 1957) and few contain less than 2 percent. For this reason it is important to consider the possibility of reactions occurring between the feldspar minerals and wastes.

The effect of feldspar is somewhat difficult to predict. It is known that feldspar (mainly $KAlSi_3O_8$ and $NaAlSi_3O_8$) 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 salaquifer (containing 10 percent feldspar, as is not uncommon) a waste solution moving through the rock will come in contact with unexpectedly large areas of feldspar surface. This would amount to an apparent area of 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 amount of feldspar surface actually available may be much greater than this apparent area. Brody (1953), in a study of the effects of etching on quartz oscillator plates, using a combination of sensitive oscillation frequency response and X-ray diffraction methods, determined that surfaces ground with abrasive of 0.1 mm (100μ) grain size had a distorted surface layer 105,000 A $(10\mu$ or 0.01 mm) thick. Plates ground with abrasive of 0.0035 mm (3.5μ) grain size had a distorted surface layer 4,400 A (0.44μ) thick. This layer is shown to have a structure distorted from that of the underlying crystal, as indicated by a very appreciable broadening of X-ray diffraction peaks, and to be much more soluble, as is indicated by curves showing amount of etching with time. The exact nature of this distorted layer is unknown, but it can certainly be expected that natural mineral grains such as quartz and feldspar, abraded by

natural processes to the extent that they usually have visibly pitted or frosted surfaces, probably have effective surface areas considerably larger than their apparent area, obtained assuming smooth, physically perfect surfaces. In feldspar, which is easily altered during weathering, and has two good cleavages so that it characteristically has a frosted surface in sediments, the amount of feldspar surface contacted would be at least 10^8 cm^2 per l. 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, although they point out (page 32 of their paper) that their experimental method of grinding in water might yield results other than those obtained from simple contact of water with the mineral surface. The interpretation of these values is complicated by a variety of factors, such as local high temperatures and pressures during the grinding, release of fluid from fluid-filled inclusions within the mineral grains, purity of the water, and absorption of atmospheric CO_2, but it is clear that pH values greater than 7 can be expected.

R. M. Garrels (oral 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:

$$\text{Orthoclase (solid)} + \text{H}^+ \longrightarrow \text{Mica (solid)} + \text{K}^+$$
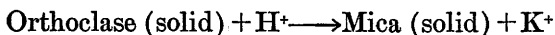
these values require that a layer approximately 30 angstroms thick on the surface of the orthoclase grains must have contributed its K$^+$ to the solution (that is, exchanged its K$^+$ for H$^+$). While it is not known how much feldspar might be involved in any reaction with waste due to the likelihood of insulating coatings forming on the grains and the high concentrations of ions in the waste, it would appear that if the above amount of reaction can occur with pure water in seconds or minutes, highly acid wastes might be expected to react with considerably thicker layers of the feldspar in the many months, or even years, during which the waste would be injected into a given well. This is particularly true in view of the increased reactivity of the distorted layer found on abraded surfaces. (See discussion of work of Brody above.) At 10^8 cm^2 of surface contacted per liter of solution, if a layer only 100 angstroms thick on the surface of the grains of potassium feldspar in the salaquifer were involved, it could yield one

mole of potassium to the 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.

If the pH of the waste were increased by removal of a large portion of the HNO_3, the rate of attack would presumably be less, but the amount of attack necessary to cause precipitation would also be less. In any case, it is unlikely that waste will be injected for a length of time adequate to establish a leached zone for feldspar. It is not impossible that a "saturated" zone might develop, however, "saturation" referring here to a pH of 3 and hence precipitation of some $Al(OH)_3$, but not necessarily saturation with respect to feldspar. Preliminary short-time experiments putting waste through short feldspar columns have yielded first effluents with a pH of 2.

MICA

Included here are muscovite and its fine-grained variety sericite, and biotite. 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_3^+). That this can take place is evident from the fact that potassium mica will yield appreciable K^+ to water upon electrodialysis, and with some micas it is possible to remove most of the large cations, leaving behind a silica-rich residue that yields a vaguely mica-like X-ray pattern (Roy, 1949). A similar process, due to leaching alone, takes place naturally during the weathering of micas to clays. Because the average sandstone contains very little mica and its possible effects would be expected to be subordinate to those of the feldspar and particularly those of the clay minerals present, it is not discussed further.

CLAYS

The clay minerals are ubiquitous, no sedimentary rock being free from them. Reactions between acid aluminum nitrate waste and the clay group of minerals are likely to be of more importance than reactions with the feldspars or micas, mainly because clays have a far smaller grain size and hence a much greater surface area. As some clays may average less than 0.2 μ in grain size, their surface area may run over 10^6 cm^2 per g. All slow-moving water in deep permeable sandstones thus 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. Such would be true, for example, in sand containing volcanic debris and feldspars or other minerals partly altered to clay on their surfaces. In ordinary screen analysis the bulk of such clay would probably not be reported as

clay, but rather as part of the grain-size range of the parent materials. This is true also of many clay coatings on inert grains such as quartz, which will not be reported as "clay" unless special methods are used to disaggregate the sediment. Sandstones, containing in bulk analysis less than 0.1 percent actual clay minerals, may not exist anywhere in the United States, except possibly in small deposits of exceedingly pure commercial glass sand. High-grade glass sands are not abundant, and where they occur in large deposits are of considerable value for glass manufacture. 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, and other minerals. Before washing, many have a composition about as follows (Bownocker, 1926):

	Weight percent		Weight percent
SiO_2	97.5	MgO	0.1
Al_2O_3	1.0	H_2O	.4
Fe_2O_3	.5	Misc.	.4
CaO	.1		

The Al_2O_3 here represents feldspars and clays, the CaO and MgO represent carbonates, and the Fe_2O_3 is probably present as limonite (hydrated ferric oxide). The H_2O occurs in limonite and clays. 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. In most cases, the bulk of the clay in a sediment will be well distributed as coatings or cement, and hence easily available for contact with waste (Krynine, 1938, 1940; Andresen and Heck, 1950).

Even if the salaquifer has only the assumed 0.1 percent of clay, the amount of clay surface contacted by the advancing front of waste is very large. With a 10-cm zone of equilibration, waste in such a sal-aquifer would contact 2.25×10^9 cm^2 of clay surface 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.

Possible trouble from reactions between clays and acid wastes might result from three phenomena: cation exchange, destruction of physical bonding of clay particles, and 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 the normal clay minerals kaolinite, montmorillonite, halloysite, and the mixed-layer mica-montmorillonite mineral "illite," and also the other similar sheet structure silicate minerals such as glauconite,

chlorite, and chamosite. This latter group of minerals, as they occur in sediments, behave much like the true clay minerals.

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. Thus, by cation exchange alone it would be expected that some H^+ or Al^{+++} from the waste might be exchanged for exchangeable bases such as K^+ and Na^+ from the clays, possibly resulting in an increase in pH of the waste and precipitation of some $Fe(OH)_3$ or $Al(OH)_3$. This exchange could occur in a very short distance (a short zone of equilibration) due to the large surface area of the clays.

It has been shown that, in general, the fission products are not removed from acid aluminum nitrate waste by cation exchange. 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.[17]   In the presence of rather high concentrations ($0.2\ M$) of $NaNO_3$, however, Ginell, Martin, and Hatch (1954) were able to remove fission products at $10^{-5}M$ concentrations. In the absence of Al^{+++} and H^+, fission products such as Sr^{++} and Cs^+ can be adsorbed rather effectively by some clays and soils, with decontamination factors as high as 10^5 under good conditions (Amphlett and Warren, 1956; Amphlett and McDonald, 1956; Hatch and others, 1956; McHenry, Rhodes, and Rowe, 1956). Recent work by Brockett and Placak (1954), and by Straub and Krieger (1954) has shown, however, that the cation exchange rating is not necessarily a good index of the ability of a soil to remove a radioelement. This process, using natural "soils" (unconsolidated sediments) to adsorb radioactive nuclides by ion exchange before the discharged waste reaches the ground water, has been used for several million gallons of relatively low-level scavenged wastes at Hanford (Burns and Stedwell, 1957).

The *lowest* cation-exchange capacity obtained thus far on natural materials from Atomic Energy Commission sites was on a glacial material at Brookhaven, Long Island. Its cation-exchange capacity was only 0.5 milliequivalent per hundred grams. Even this low value is equivalent to approximately 0.5 percent 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 percent porosity and a 10-cm zone of equilibration. The actual exchange would depend upon the cations present in the waste and those in the exchange sites from natural ground water,

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[17] Ivan Barnes (oral communication 1956) has suggested that ion exchange substances, such as zeolites, might be found that are sufficiently preferential to the adsorption of specific *sizes* of ions that the larger Sr and Cs might be preferred to the more abundant aluminum.

but cation exchange would certainly have a major effect on the composition of any waste moving through rocks. 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. In the absence of aluminum, most fission products, other than ruthenium as $RuO_4^=$, are adsorbed by ion exchange rather well on many clays in soils at intermediate pH's, and in particular on montmorillonite (Amphlett, 1955). Apparently only Zr will adsorb well on clays from acid solutions. The ions exchange behavior of a given formation will be a function of a number of variables, of which the following are probably the most significant: specific minerals involved, their amounts and grain sizes, and the concentration of all ions and complexes in the waste, in particular Al^{+++}, pH and Eh. A general review of the factors involved in cation exchange in clays and soils is given by Kelley (1948) and Grim (1953). The problem is complicated by the existence of two different exchange sites on at least some clays (Garrels and Christ, 1956), and considerable variation among different radioisotopes (Brockett and Placak, 1954).

It was expected, however, that acid aluminum nitrate wastes would seriously affect the exchange capacity of clay minerals. A series of preliminary experiments by Dorothy Carroll of the U. S. Geological Survey, using known clay minerals in contact with acid aluminum nitrate waste for periods of 12 to 48 hours at temperatures of 25° to 48°C, showed that up to 30 percent of the clay mineral dissolved in the waste, and the cation exchange capacity of the remaining material, using the colorimetric manganese method of Bower and Truog (1940), decreased from 20 to 50 percent. As might be expected, the mineral kaolinite, having a well-crystallized structure and containing no alkali or alkaline earth cations, showed the least effects.

These changes in cation-exchange capacity, although large, are of minor importance when compared with the problem of physical effects on the clay minerals due to decomposition. Such decomposition may result in various detrimental effects that would be difficult to evaluate (Torrey, 1955). In many salaquifers clays act as a cement between the grains of other minerals; if small grains of quartz and felspar, normally held in place by the clay, were released by its decomposition, they might contribute to the blocking of the pores of the salaquifers. Geometrical factors (Pettijohn, 1957), show that in a hexagonal close-packed aggregate of uniform spherical sand grains of diameter d, grains of diameter $0.154\ d$ will just pass through the holes. Grains slightly larger than this, if free to be moved by the fluid flow, would effectively block the holes. This would be particularly true in the vicinity of the injection well where the flow would be fast and the pH low. In addition to this, considerable difficulty has been encoun-

tered on some water-flooding projects for petroleum production where bentonite (that is, montmorillonitic clay) in the sandstone swelled upon injection of new waters and caused blocking (Torrey, 1955). This swelling would probably not take place with acid high aluminum wastes, which might actually be expected to cause partial dehydration of swollen bentonite (Andresen and Heck, 1950; Grim, 1953). In general it has been found that injection into clay-bearing formations is easier with acid brines than with neutral fresh water (Hughes and Pfister, 1947).

Another problem involves the possible dispersion of clay-mineral grains themselves into the moving waste. Certainly some clay grains will be dislodged, and in part converted to an aluminum silicate gel. Whether these converted grains will stay dispersed in these concentrated solutions, raising the viscosity and perhaps filtering out in the smaller pores, or flocculate into clumps which will clog even the larger pores, cannot be predicted at this time—in either case the effects would be detrimental. In general, any solution that causes swelling of clays also causes dispersion of clays (Torrey, 1951).

In addition to the effects on the clays described above, another important factor must be evaluated; this 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, 1943, 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; Osthaus, 1954), cannot be predicted very well. As many sedimentary clays contain 5 to 10 percent 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, particularly in view of the large amounts of clay dissolved in the short-duration experiments described above. A typical "sedimentary clay" composition might be approximately as follows:

	Weight percent		Weight percent
SiO_2	56.0	K_2O	2.8
Al_2O_3	15.0	Na_2O	1.2
MgO	2.5	CO_2	3.0
Fe_2O_3	5.0	H_2O	7.0
FeO	1.0	Misc	2.0
CaO	4.5		
			100.0

This analysis, although in the range usually reported for "sedimentary clay," actually includes minerals other than true clay minerals, as finely divided grains or precipitates. Thus the iron oxides are probably present as separate iron oxide minerals and will not be considered

as a part of the clay, and the CO_2 indicates the presence of approximately 6.8 percent $CaCO_3$, so only 0.7 percent CaO is presumed to be present in the clay itself.

Using the estimated minimum of 2.25 kilograms of true clay contacted per liter of waste, the following amounts of alkali plus alkaline earths would presumably be available from the clay minerals alone:

Moles per liter

Mg^{++} _____ 1.39	
Ca^{++} _____ 0.28	5.5 equivalents per liter
K^+ _____ 1.34	
Na^+ _____ 0.86	

It is not likely that all of the clay containing these ions will be decomposed by a single liter of waste containing only 2 moles of HNO_3, as the decomposition would stop once the bulk of the acid is consumed, but the reaction with carbonate (below) shows that the "effective" H^+ content is 5.6 moles per liter in this waste, and 3.4 moles per liter in the more dilute waste containing 0.5 mole HNO_3 and 1.6 moles $Al(NO_3)_3$. Presumably the amount of destruction of clay minerals would be less with the lower amount of HNO_3, but Nutting (1943) has shown that even dilute acids dissolve appreciable material from some clays, and Osthaus (1954) has shown that montmorillonite loses most of its Mg, Fe, and Al when exposed to 10 percent HCl for 10 to 20 hours. Similar work has been done on chlorites (Brindley and Youell, 1951), and on micas (Foster, 1959).

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 pII still further to the point of precipitation.

LIMONITE

This term refers to a group of hydrated ferric oxide minerals which are as ubiquitous as clay, and frequently as abundant; the most common is goethite ($Fe_2O_3 \cdot H_2O$). Most buff, yellow, brown, and reddish-brown rocks owe their color to these iron minerals, frequently as very thin films on grain surfaces, or as the cementing material. Red and purplish-red sediments may contain hematite (anhydrous Fe_2O_3) as well. It was expected that any acid waste moving through a rock containing limonite would have its hydrogen ion content effectively reduced to a level aproaching 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 27 grams of hematite (Fe_2O_3) or 30 grams of goethite ($Fe_2O_3 \cdot H_2O$) for neutralization; at the assumed 10 percent porosity and 0.1 percent limonite, each liter of waste will be in contact with 22 grams of

limonite, with no movement of the fluid, and of course will contact more with movement. With a 10-cm zone of equilibration, each liter of waste will contact 2,250 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. This precipitate might be expected to scavenge a considerable part of the Nb, Ru, and Zr radionuclides from the waste, as this precipitation has been proposed as an effective means of separating these elements from wastes (Higgins and Wymer, 1955; Blanco, Higgins, and Kibbey, 1956), and thus might result in excessive heating locally. Under some conditions in the laboratory work iron hydroxide sols were formed rather than precipitates, but these are known to be unstable and cannot be relied upon to delay the onset of precipitation very long. Actually, the value of 0.1 percent limonite is very low; there are some good commercial glass sands that have bulk analyses below this, but they are rare indeed. As noted above, average sandstones contain 1.8 percent limonite (Clarke, 1924).

To verify the magnitude of the effect of limonite, acid aluminum nitrate waste was stirred continuously with powdered crystalline goethite for eight days at 35°C. The amount of goethite dissolved amounted to only 0.14 percent by weight, far below the amount which would be expected to dissolve in a solution as acid as this. Nitric acid itself, even boiling, is a poor solvent for goethite. It is thus apparent that the *rate* of solution of limonite is low in these fluids, but this cannot be extrapolated to other waste compositions, as limonite (including goethite) is readily soluble in other acids. Even this amount of iron would be significant in forming $Fe(OH)_3$ precipitate upon further neutralization. Under field conditions more iron oxide can be expected to dissolve than this experiment indicates, however, as a consequence of higher temperatures, longer times for equilibration, considerably greater amount of contact surface, and a lesser degree of crystallinity, as much limonite in sediments occurs as thin films of very fine-grained to nearly amorphous hydrates.

<div align="center">CARBONATE</div>

Of all the possible interactions between sedimentary salaquifers and acid aluminum nitrate wastes, probably the most important are those involving carbonates. Carbonates are exceedingly widespread, and the hypothetical 0.1 percent carbonates assumed here is very conservative. Only the highest-grade glass sands contain <0.2 percent

CaO+MgO, which may or may not be present as carbonates. Clarke (1924) lists average sandstones as having 11.1 percent carbonates, but it is presumably possible to obtain sediments containing very little carbonate, either by lack of deposition originally, or through solution by moving waters after deposition. If natural CO_2-bearing waters have moved through a sandstone, it might be thoroughly leached of all free carbonates. 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 solution need not be confined to near-surface sediments.

If carbonate is present in the salaquifer, 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 carbonate with the evolution of CO_2.[18] 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 280 to 310 grams of $CaCO_3$ has been added per liter of waste, depending upon the technique used, 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 1:1 dilution of the waste with water before reaction with carbonate results in a similar stiff gel forming after the addition of an equivalent amount of $CaCO_3$ (140–150 g per l).[19] 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 when the pH has increased to 3.4, after which the solution will not dissolve further $CaCO_3$. Turbulence in this gel is arrested suddenly throughout the fluid as the rate of movement decreases after stirring.

As the two moles of HNO_3 per liter of waste require only 1 mole (100 grams) of $CaCO_3$ for neutralization, it is obvious that a considerable part of the hydrogen ion reacting with solid $CaCO_3$ here is that formed by the 2 moles of $Al(NO_3)_3$ present. As a check, 2 molar $Al(NO_3)_3$ was "titrated" with solid $CaCO_3$. It reacted with effervescence, dissolving the equivalent of approximately 180 grams $CaCO_3$ per liter of solution, changing from a pH of 0.6 to a pH of 3.2, at which pH it turned into a stiff gel like the others that contained HNO_3. A solution containing 1.6 moles $Al(NO_3)_3$ and 0.5 mole HNO_3 per liter required approximately 200 grams of $CaCO_3$ per

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[18] Wastes of the sulfuric acid type will also react thus, but in addition will precipitate the slightly soluble compound $CaSO_4$, or a hydrated $CaSO_4$.

[19] Several of these gel samples were put aside and examined one year later. In several instances, involving both the concentrated and the 1:1 dilution samples, the stiff gel had liquefied completely, to a thin fluid, with no change in pH. A small addition of NH_4OH to these fluids caused immediate precipitation.

liter to gelatinize. The actual "end points" are not precise, as the high viscosities make mixing difficult and the $CaCO_3$ powder tends to become lumped together in an armor of gel.

If the above reactions are assumed to represent the behavior of such wastes in a natural salaquifer containing 0.1 percent $CaCO_3$, the waste would be expected to precipitate as a gel in a rather short distance. A zone of equilibration of 10 cm is not unlikely for the solution of carbonate films, in which case the solution would go only 120 cm before precipitation. Even if the zone of equilibration is 1 meter, the waste can travel only 12 meters before precipitating as a gel.

However, a number of other factors enter into the process above, in particular the buildup of CO_2 gas pressure. Morrison (1950) has shown that the rate of solution of $CaCO_3$ in HCl decreases considerably as the pressure increases up to 400 psi (pounds per square inch)—further increases in pressure cause less decrease in the rate. It is not known whether these results may be extrapolated to $CaCO_3$ plus waste.

The behavior of the CO_2 evolved is not known. Each 100 grams of $CaCO_3$ dissolved releases one mole (22.4 liters) of CO_2; some of this will enter into the waste solution to saturate it, but the actual amounts involved are controlled by several reactions whose equilibria under such conditions are unknown and can neither be determined accurately nor calculated rigorously. Wiebe (1941) shows that a liter of pure water at 50° will dissolve a mole of CO_2 at about 75 atmospheres CO_2 pressure, and over 700 atmospheres CO_2 pressure is needed to dissolve 2 moles, but it is possible that the solubility of CO_2 in these strong solutions might be very different (Quinn and Jones, 1936; Seidell, 1940; Headlee, 1950; Johnson, MacFarlane and Breston, 1952). Part of this dissolved CO_2 will go to form HCO_3^- ion by reacting with additional $CaCO_3$ or Fe_2O_3, if the temperatures are not high. Miller (1952) has shown that the solubility of $CaCO_3$ in water under CO_2 pressures increases in the presence of NaCl, but this cannot be extrapolated to high nitrate concentrations. It is thus impossible to calculate rigorously the CO_2 pressures that may develop, but they might 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. The specific effects of high CO_2 pressures on pH are listed by Headlee (1950), as well as the solubility of CO_2 in strong NaCl brines, and the solubilities of various bicarbonates up to CO_2 pressures of 1,000 psi.

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 it would partly insulate carbonate grains from further reaction, and would probably decrease the permeability of the salaquifer, as it is more difficult to pump a mixture of gas and liquid through a salaquifer than either separately (the "Jamin effect" [20]). Some experimental work has been done on the behavior of liquid CO_2 and carbonated waters and brines in porous rocks (MacFarlane, Breston, and Neil, 1952; Breston and MacFarlane, 1952), but it is difficult to predict how the evolution of CO_2 would affect the flow patterns.

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 (=10,000 feet head of water), its density would be 0.83 g per cm^3, and it would be 0.29 $g \cdot cm^3$ at 100 atmospheres (Kennedy, 1954). In any case it would probably carry some activity from volatile elements such as I^{129}. Any slow reaction using up CO_2 in the water phase, as by reaction with readily leachable alkalies from clays or volcanic glass, or by the migration of the CO_2 to new areas where it can react with $CaCO_3$ or Fe_2O_3 to form more bicarbonate, would permit more CO_2 to dissolve from the CO_2-rich phase, until it disappears altogether (Garrels and Richter, 1955). 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. Any release of CO_2 pressure can certainly be expected to cause precipitation of $CaCO_3$ or $Fe(OH)_2$ (Jessen, 1949; Stiff and Davis, 1952b). The possible permeability of the overlying formations to any gas phase such as CO_2 should also be considered. Natural gas has been stored in underground reservoirs on occasion, and in some cases inexplicable leaks have occurred in what was considered a "tight" formation (Kohl, Newacheck, and Anderson, 1955).

The physical nature of the occurrence of calcium carbonate in the salaquifer can be expected to have a considerable effect on its behavior with respect to the waste and hence on the width of the zone of equilibration. If $CaCO_3$ is in excess, stoichiometrically, and readily available, for example as thin films, the reaction to form a gel may occur in seconds. If the carbonate 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 $Al(OH)_3$ gel, through which further reaction by diffusion is slow. This would increase the width of the zone of equilibration and hence increase the storage capacity per well, but as the layer of gel may have a thickness many times that of the solid calcium carbonate, this might well cause a stoppage even before the

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[20] The nature of this increase in effective viscosity with two phases is somewhat in question, but the magnitude seems to be very large. See Beecher (1929), Tickell (1929), and Gardescu (1930).

bulk of the waste had been neutralized to the point of gelation. At room temperature, gel layers a millimeter or more in thickness form within hours on calcite surfaces in contact with partially neutralized waste.

The bulk of the carbonate needed for an increase in pH up to the point of gelation is dissolved with sufficient effervescence, in an open system, to prevent formation of a film of gel; presumably a sol is formed at the reaction surface that is sufficiently stable to permit the entire quantity of waste to come in contact with the carbonate before it all sets up as a gel, both near and far from the carbonate grains. However, in a salaquifer, with slow rates of flow and high confining pressures, gel films might form instead. It is also possible that the carbonate particles in a salaquifer might be distributed in such a manner that the formation of a gel layer on each particle would not seriously affect the flow, and thus permit continuous injection of waste for an indefinite period, leaving behind the advancing front an amount of waste, immobilized as a gel, stoichiometrically equivalent to the amount of carbonate that has reacted.

MISCELLANEOUS MATERIALS

A number of minor constituents can be found in salaquifers in small amounts, perhaps 0.1 percent or so of each, but not all occur in any one 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 also is practically ubiquitous. It decomposes 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^{+++} Pyrite dissolves easily in these aluminum nitrate wastes, with effervescence, leaving a residue of free sulfur.

Gypsum is very abundant in some sandstones, as a cement. It is significant here mainly because it is appreciably soluble in water; it has given trouble in water flooding by dissolving and reprecipitating (Krynine, 1938). Yuster (1939) has shown that the mixing of waters of different salinities, obtained during water flooding through formations containing gypsum and having a widely variable permeability, causes troublesome precipitation of gypsum as a result of the common ion effect. Sodium hexametaphosphate (Calgon) has been used to prevent this precipitation (Kleber, 1954).

Volcanic ash, including volcanic glass and other debris 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, volcanic glasses have a large surface area and

alter rather readily to clay minerals, yielding considerable alkalies and alkaline earths to the solution. Only one experiment, using basaltic volcanic ash and waste was made. It showed considerable 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 and using up available free CO_2.

Organic matter is very abundant in some sandstones in the form of natural gas, various petroliferous materials, and partly coalified plant fragments. Organic matter might, in some cases, have helped previous ground water flow to eliminate $CaCO_3$ from the sediment, by acting as a source for CO_2. It might also be of considerable help in removing the nitrate ion from the wastes, which is perhaps the most biologically hazardous nonradioactive material in the waste. Natural organic matter can certainly be expected to affect the oxidation potential of the waste in contact with it,[21] and the behavior of all variable-valence elements present in the waste (for example iron from stainless steel fuel element cladding) should be viewed in this light. Uranium and the transuranium elements in the waste might be expected to be precipitated by this organic matter (Breger and Deul, 1956).

HEAVY MINERALS

The general term "heavy minerals" includes various heavy, hard detrital minerals usually occurring in amounts of less than 1 percent in salaquifers. It includes magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), garnet (complex silicate), zircon ($ZrSiO_4$), sphene ($CaTiSiO_5$), pyroxene and amphibole (silicates of magnesium, calcium, and iron), and others. 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 inert as compared with the other minerals discussed, and therefore not expected to have any significant effects on the waste. Barite ($BaSO_4$) is a heavy, but soft, mineral occurring in some sediments. It is highly insoluble in ordinary water (2–4 ppm), but in spite of this, changes in the solubility with changing conditions cause sufficient precipitation of $BaSo_4$ in some water injection wells to result in serious blocking that is very difficult to remove.

NATURAL BRINES

Depending upon various geologic factors that are not discussed here, the natural ground waters occupying the pores of any salaquifer before injection of waste are brines containing up to 25 percent dis-

solved solids (DeSitter, 1947), and in rare instances, over 40 percent (Schmidt and Wilhelm, 1939). Many oil fields have brines containing 10 to 15 percent dissolved solids, and a crude generalization has been made that waters in deep salaquifers have higher salt contents than their shallower counterparts (McGrain, 1953). The composition of these salts is as varied as the amount, but many are alkaline (Crawford, 1940). Chlorides of sodium, magnesium, and calcium are generally the most abundant (DeSitter, 1947; Meents and others, 1952), although high bicarbonate (800 to 1,500 ppm HCO_3^-) waters are not rare (Foster, 1950), and concentrations up to 10,000 ppm are known (Crawford, 1940). Other waters may have high sulfate concentrations, up to 1,000 ppm $CO_3^=$, and lesser amounts of H_2S, or even free CO_2 and free H_2S.[22] In some areas, the subsurface brines are slightly acidic from the dissolved CO_2 and H_2S. Where these waters are alkaline, and even in some cases where they are acid, consideration must be given to the possibility of precipitation occurring at the advancing front of waste, due to dilution. A thorough review of this problem in the petroleum industry is given by Headlee (1950). The advancing waste will not sweep *all* existing water out of the pores, but will gradually become diluted with it over a considerable distance back from the true front,[23] depending on the ease of flushing (Kaufman, Orcutt, and Klein, 1955). On the basis of small-scale laboratory experiments with fluids moving in cores, Bernard (1955) concluded that the amount of mixing is slight in water flooding, and incompatibility of the injected water with the formation water will not result in serious precipitation blocking. This conclusion was not supported, however, in recent experimental and theoretical studies (Kaufman, Orcutt, and Klein, 1955; Day, 1956) which showed that considerable mixing does actually occur. It is certain, however, that any attempt to inject aluminum-bearing wastes into a salaquifer containing alkaline waters will definitely result in at least some precipitation. That the *amount* of precipitation occurring in this highly diluted front solution would be sufficient to cause serious pumping difficulties cannot be determined without tests on specific combinations of water, waste, and salaquifer, but it is a factor which definitely must be considered. One possible procedure to avert this precipitation involves the use of a plug of nonreactive water to separate the original water from the injected water (Adinoff, 1954; Lansing and Hewitt, 1955), but it can be expected that these wastes will precipitate from the increase in pH upon dilution with pure water alone.

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[22] Headlee (1950) lists also bromide, iodide, phosphate, silicate, and cations of Sr, Ba, Fe, Mn, Al, Li, and NH_3; the Sr content may be surprisingly high (Sudbury, 1952).

[23] This longitudinal dilution is not the same as the dilution problem frequently discussed in connection with flow lines in ground water hydrology; there it is usually the occurrence of dilution at right angles (lateral) to the flow lines that is under consideration.

A number of experiments on the dilution of waste solutions with various amounts of synthetic carbonate and bicarbonate waters were made to check on the calculated behavior. These are summarized in table 5, from which it is evident that some precipitation can indeed be expected at the advancing front of waste in contact with many natural waters. As might be expected from ionic equilibria, all mixtures that showed precipitation had a pH between 4 and 10. One must be careful, however, in the interpretation of such data, as very minor differences between "synthetic" and actual ground waters have been found to make the difference between compatibility and incompatibility with a given waste (Lansing and Hewitt, 1955).

TABLE 5.—*Effect of dilution of waste solutions with carbonate and bicarbonate waters*

Type of waste [1]	Concentration in water in ppm [2]		Visible precipitate (P) obtained at dilutions of waste indicated [3]				
	HCO$_3^-$	CO$_3^-$	50	100	500	1,000	5,000
Al		114					P
Al		1,000		P	P		
Al	146						P
Al	730					P	P
Al	10,000		P	P	P	P	P
Al-Fe		1,000	P	P	P		
Al-Fe	10,000		P	P	P	P	P

[1] Al=2 moles Al(NO$_3$)$_3$ + 2 moles HNO$_3$ per liter; Al-Fe=1.6 moles Al(NO$_3$)$_3$, 0.5 mole HNO$_3$, 0.05 mole Fe(NO$_3$)$_3$, and 0.005 mole Hg(NO$_3$)$_2$ per liter.
[2] Added as NaHCO$_3$ and Na$_2$CO$_3$, respectively.
[3] Volume of waste to volume of carbonate or bicarbonate water.

JOINT EFFECTS OF ALL AQUIFER MATERIALS

The above discussion shows, qualitatively, what may happen during the pumping of acid aluminum nitrate waste into a hypothetical salaquifer of the composition assumed. Most of the possible interactions, if they occur at all, will increase the pH,[24] and several different reactions may augment as well as succeed each other. Thus clay minerals, carbonates, iron oxides, and small amounts of feldspar, would probably dissolve where there is still a high concentration of HNO$_3$, and as the pH increases only carbonates would dissolve. The zone of equilibration for solution of feldspar would probably extend from the well to the waste front; zones for solution of carbonates and clays would be shorter and superimposed on the feldspar zone.

These reactions would increase the pH and hence the viscosity of the waste, and might also cause a stoppage by forming a physical suspension of decomposition products from salaquifer minerals. If pumping could be continued after a pH of 2 or more is reached, cation

[24] Some experimental work by Bouyoucos (1921) showed surprisingly high solubilities and rates of solution for a number of common minerals; all the solutions were alkaline to phenophthalein.

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. In addition, the dilution of the wastes at the advancing front by ground water would also decrease the concentration of H^+. Part of the iron and aluminum would precipitate, as hydroxide gels[25] from the undiluted waste when the reactions have increased the pH to about 3.5, causing a complete stoppage.

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 nonradioactive 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 salaquifer 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 under high pressure, and second, any increase in temperature from radioactive heat must result in either expansion or higher pressures.

It is possible that slow reactions between the CO_2 and salaquifer minerals, either with silicates or volcanic glass to form soluble carbonates and silica, or with $CaCO_3$ or Fe_2O_3 to form soluble bicarbonates, would consume CO_2, and tend to decrease the pressure, but whether this consumption of CO_2 will be greater or less than the evolution of new CO_2 cannot be predicted.

The possible results of an increase in temperature can be of considerable magnitude. Assuming that the data for water (Amagat, 1893; Kennedy, 1950) may be used as a crude approximation, a rise in temperature from $100°C$, at 150 atmospheres (2,205 psi), to $200°C$, will result either in a 10–percent volume expansion of the liquid at constant pressure, or in an increase in pressure to approximately 1,950 atmospheres (28,700 psi), at constant volume (fig. 2). 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 either force waste through the gelatinized precipitate, lift the overlying rocks, or break through in other ways. The problem here lies in the thermal capacity and conductivity of the surrounding rocks, in relation to the rate of heat generation of the waste. If the increase in temperature is too large, the obvious answer is to resort to removal

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[25] Although usually spoken of as an "Al(OH)₃ gel" or an "Fe(OH)₃ gel," the crystalline phases present in these gels vary with the process used for precipitation and with time (Weiser, 1935).

of heat-producing isotopes, thinner salaquifers, dilution of the waste, or longer cooling before injection, but these would increase the cost of disposal proportionately. Pecsok (1954) found that 30-day-old wastes would have to be diluted many thousand fold to avoid boiling when injected continuously at 4,000 feet depth, but it can be shown from ionic equilibria that dilution with pure water may raise the pH sufficiently to cause precipitation of some aluminum hydroxide.

If, as a result of an increase in pressure, or faulting (earth movement), or any other cause, the fluid waste broke through the wall of gelatinous precipitate into new areas of salaquifer, presumably the same phenomena would occur as in the original stoppage, yielding a new wall of precipitate. However, it has been tacitly assumed throughout this discussion that the enclosing beds, above and below the salaquifer, were *perfectly* impervious. Neglecting here the geologic propriety of this assumption, let it be assumed that the overlying impermeable strata are breached by the increase in pressure, or by other factors, or that they were not impermeable in the first place. Above these impermeable beds would lie permeable ones and, once the waste leaks into the bottom of the overlying salaquifer, it can be assumed that it will reach the top rapidly, as a result of thermal convection cells established there by the generation of radioactive heat. Obviously then, the most desirable situation would involve injection into the lowest permeable bed of a series of alternate permeable and impermeable beds.

The geologic factors involved in the selection of suitable salaquifers, favorably situated, are such that a rather elaborate exploration program would be needed to locate them. In addition to the problem of adequate permeability and compatibility of the salaquifer, the possibility of sedimentary inhomogeneities of various types, joints and minor faults, and old unrecorded oil, water, or gas wells in the "impermeable" enclosing beds will make the selection very difficult, even after intensive study of the area. The specific problems will vary widely with the formation and area chosen and hence cannot be detailed here.

An entirely distinct problem involves the degree to which the original precipitate wall formed from the waste represents a complete enclosure and immobilization of all of the materials of the waste. As a consequence of mixing and dilution of the advancing front of the waste, some of the fission products would undoubtedly move off from the main mass with the ground water flow. In addition, various workers have found that ionic diffusion through gels occurs at a rate not much less than that through a liquid solution. If the precipitate wall is thin, and thus the concentration gradient is high, various ions may continue to diffuse through the precipitated gel and be flushed away by moving ground water; if the surrounding water is stagnant,

these ions cannot move far by diffusion alone, as the rate of diffusion transport will decrease rapidly as the concentration gradient is decreased. The probable fate of most of these released materials lies in ion exchange on minerals downstream, if they are of a type that can be exchanged (Amphlett, 1955; Kaufman, Orcutt, and Klein, 1955), and the pH is correct (Nishita and others, 1956). Large anionic complexes, such as $RuO_4^=$ and NO_3^-, which do not enter into ion exchange readily (Brockett and Placak, 1954; Amphlett, 1955; Brown, Parker, and Smith, 1956)[26], are also the slowest to diffuse, due to their size.

The actinide elements would probably be present as nitrate complexes; this might be expected to have serious effects on their ion exchange properties, but Goldsztaub and Wey (1955) and Nuss and Wey (1956), have shown that uranium in nitrate solutions will adsorb on clays. Apparently all the transuranium elements form linear O-X-O groups, like the uranyl group (Zachariasen, 1954) and can be expected to form similar complexes. Plutonium is held very efficiently by some soils (Brown, Parker, and Smith, 1955), even at low pH (McHenry, Rhodes, and Rowe, 1956).

Various radioactive tracers have been used in the petroleum industry to determine injection profiles, flowpaths, and velocities; but in general, it can be said that practically all adsorb on the formation to some extent and hence move more slowly than the water carrying them (Preston and Calhoun, 1952; Kaufman, Orcutt, and Klein, 1955; Flag and others, 1955). Anions such as iodide with I^{131} (Watkins and Mardock, 1954), or inert gases such as A^{41} (Kohl, Newacheck and Anderson, 1955) are used in some cases as they exhibit a minimum amount of adsorption on sediments. In addition some nonradioactive materials have been used, including fluorescein, boron compounds (Carpenter, Morgan, and Parsons, 1952) and helium (Frost, 1950).

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 SOLUTIONS TO THE MAJOR PROBLEM

Many different individual problems have been discussed in the foregoing sections, and for some, such as the filtration of solids at the face of the well, the solution was implicit in the statement of the problem. The major unanswered problem, however, is to obtain a salaquifer into which the injection of waste is not only *technically*

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[26] Brockett and Placak (1954), found that Ru^{106}, presumably as ruthenate, moved more than 80 feet through a shale at Oak Ridge, although ruthenium chloride adsorbed satisfactorily on the same shale in laboratory experiments.

possible, but also *economically feasible* and *completely safe*.   There is a possibility of finding salaquifers that contain lesser amounts of any one of the precipitating agents listed above, but the possibility of finding even one salaquifer that will fall within all of the compositional specifications listed for the "assumed salaquifer" is rather remote, and there is practically no possibility of finding a salaquifer better than these specifications.   A search for the most 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 compositionally suitable salaquifers in areas where (a) it would otherwise be economical to process fuel (Gorman, 1955); (b) transportation from the processing plant to the disposal site is inexpensive [27]; (c) no further production of water, oil, gas, brines, or other natural resources is likely in the area; (d) truly impermeable beds occur above and below the salaquifer; and (e) 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.[28]

There are several possible ways to avoid the problems of rapid precipitation and stoppage, if the waste is to be pumped into salaquifers at all.   These include:

1. Rapid injection, to decrease contact time, possibly through the use of salaquifers containing the *faster* naturally flowing waters, although these are generally potable; by this method it is possible to obtain rates of flow far faster than those obtained by pumping into a nearly static salaquifer [29]

2. Dilution to whatever is discovered to be the optimum between increasing volume of waste to be pumped and decreasing reactivity of the diluted waste; this might have to be followed by filtering to remove precipitated hydroxides, which would introduce a new problem of disposal of the radioactivity carried by the precipitate

3. Careful selection of glass-sand-quality salaquifers to avoid as far as possible the more readily reactive compounds such as carbon-

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[27] Herrington, Shaver, and Sorenson (1953) list transportation to the site as the bulk of the probable cost of disposal into the ground, and this problem is also discussed by Zeitlin and Ullman (1955) and Zeitlin, Arnold, and Ullman (1957).

[28] The increasing importance of the long-lived transuranium elements in wastes, mentioned near the beginning of this paper, would seem to indicate that storage for thousands of years might be necessary.

[29] Presumably the injection rates should be kept below the "critical input pressure" for the particular well (Grandone and Holleyman, 1949). If this pressure is exceeded, pressure parting will take place (Yuster and Calhoun, 1945) and might result in a lack of control of the direction of movement of the injected waste (Grandone and Holleyman, 1949), although very rapid high-pressure injection to cause "hydrofracing" might actually become necessary to open up a clogged well face.

ates and, possibly, clays—and yet obtain maximum porosity and
permeability

4. Chemical pretreatment of the waste to retard or eliminate precipi-
   tation, for example, by removal of part or all of the aluminum
   (Hatch and others, 1956), or by the formation of "diban" (di-
   basic aluminum nitrate, $Al(OH)_2NO_3$) by distillation (Higgins
   and Wymer, 1955)[30]

5. Pretreatment of the salaquifer with acids or other solutions, to
   improve compatibility

How these 5 factors, and others not mentioned, may interact to
control the amount of waste that can be injected per well, before stop-
page occurs, cannot be determined at this time, particularly in view
of the difficulties mentioned above concerning salaquifer location.

It is possible that under certain circumstances reasonably stable
sols may form, instead of gels or flocculent precipitates. Laboratory
experiments with waste and calcium carbonate frequently yield clear
viscous aluminum hydroxide sols, or thin red iron hydroxide sols when
only iron is present. An extensive literature has developed on the
preparation and properties of aluminum hydroxide sols, gels, and
precipitates. (See, for example, Weiser, 1935). As yet, no condi-
tions have been discovered wherein the aluminum hydroxide sols are
stable, that is, do not gelatinize within days; these experiments, un-
fortunately, were not under the conditions of high external pressure,
high CO_2 pressure, and high temperature that would characterize
wastes in natural environments. However, the rather capricious be-
havior of any "equilibrium" between sols, and their equivalent gels
and crystalline precipitates (as functions of temperature, agitation,
area of surface in contact, pressure, concentration and nature of
electrolytes, and pH) makes it difficult to place reliance on the
stability of any sols formed in rocks.

The thermal problem may be one of the most difficult to solve
safely, as overlying rocks will provide an excellent thermal insula-
tion, permitting temperatures, and hence pressures, to rise drastically.
There are a number of possible procedures, any one or combination
of which can be expected to provide a technically adequate solution,

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[30] It is not known how stable a solution of diban, containing $Al(OH)_2^+$ 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
would avoid the excessively large NaOH requirements needed (Higgins and Wymer, 1955)
to convert the raw waste to stable aluminates. Very little information is 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. Anion exchange, for example $(OH)^-$ in the waste for Cl^- in the
minerals, might eventually cause precipitation by *lowering* the pH, but in general anion
exchange capacities in clays are low (Amphlett, 1955). In the use of highly alkaline
drilling muds, some difficulties have arisen from silicates formed by the solution of silica
(Watkins, 1954).

but these all will cost money. The most obvious solutions to the heat problem involve decreasing the heat generation by (a) adequate cooling time (ageing) to eliminate the short-lived heat-producing nuclides, (b) removal of the major long-lived heat-producing nuclides Sr and Cs (also the most dangerous), (c) dilution with very large volumes of acidified water (acid to prevent precipitation on dilution), or (d) the use of thinner salaquifers. It would appear from the data on figure 2 and the calculations of Pecsok (1954), Kaufman, Orcutt, and Klein (1955), and H. E. Skibitzke (U. S. Geological Survey, personal communication, 1957), that the low thermal conductivity and low specific heat of rocks practically preclude injection of anything but very low activity wastes into deep-lying formations, and then only into rather thin beds.

CONTAINMENT WALLS WITHIN THE SALAQUIFER

A remedial method that should have serious consideration, as it might avoid many of the dangers normally inherent in the method of disposal by pumping into salaquifers, and certainly would act as an additional factor of safety, involves the construction of truly impervious underground reservoirs by a cementing procedure, prior to injection of the waste into the salaquifer. One such method would involve drilling a circular ring of wells into a reasonably unreactive salaquifer, enclosed above and below by truly impermeable beds, and injecting a cementing material into each, to form an impermeable "wall" surrounding a central cylinder of salaquifer, as shown in figure 6.
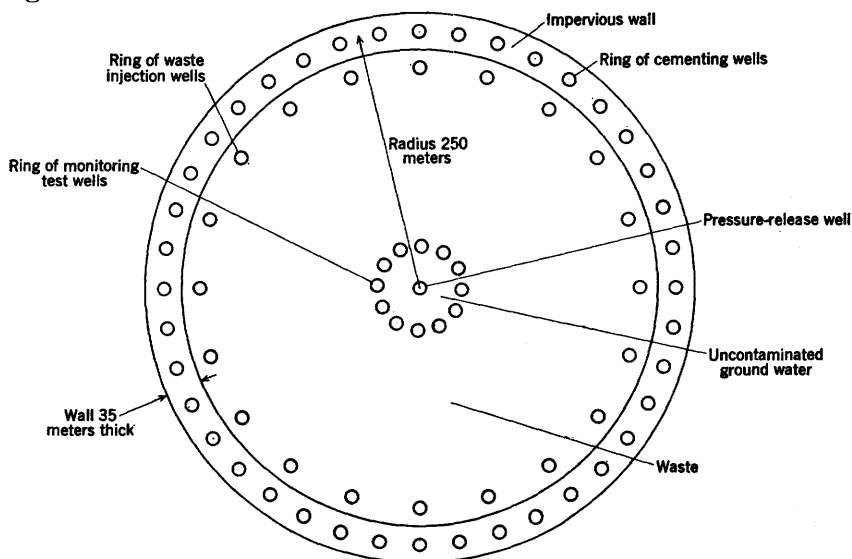
FIGURE 6.—Possible pattern of wells, using an impervious cemented wall to enclose the waste.

Just inside the wall of precipitated cement 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 figure 6. The impermeable wall would be carefully checked for leaks by pressure tests of the whole unit before any waste is injected, but it would be difficult to distinguish between a leaky wall and a leaky confining bed. During the injection of waste, the natural waters in the salaquifer would be pumped out through the central pressure-release well to provide space for the waste, until the waste front reached the ring of test wells, as determined by monitoring of samples pumped from them (Theis, 1955, p. 275), at which time pumping of waste would be discontinued in this unit. 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 nonradioactive ground water. Inequalities of flow due to anisotropy and heterogeneity of the salaquifer would have been determined in advance during the testing, and corrected for by control of the volumes injected into each of the injection wells.

Injection of waste into the peripheral wells individually in sequence might result in a very inefficient use of the available storage volume. If compatibility tests proved that the greater time of contact during injection would not cause difficulty, waste should be injected into all waste-injection wells simultaneously. This would also simplify the heat dissipation problem. Another possible procedure, using the same set of wells as illustrated in figure 6, would involve injection of waste into the inner wells labelled "monitoring test wells," and withdrawal of ground water through the outer ring labelled "waste injection wells." The withdrawn ground water would be monitored at each well. In order to maintain the central plug of uncontaminated ground water as a pressure-release mechanism, a slight flow of nonradioactive water would be maintained into this central well during the waste injection. This procedure might result in lower costs, from the decrease in stainless steel casing needed, and, if hydrofracing of the injection wells is needed, might be safer.

Once the unit was full, the pressure-release well would serve as a valuable control; pressure buildup due to heating of the waste would be relieved by withdrawing nonradioactive ground water from the pressure-release well as necessary. The possibility of leakage through the "wall" into the surrounding salaquifer, or through the underlying or overlying impervious beds, could be minimized by maintaining, throughout pumping and afterwards, a slightly lower pressure at the pressure-release well.[31] Any small leakage would thus be of ground water into the unit, rather than of waste out of the unit. This pump-

[31] This should be effective except for a section of wall immediately adjacent to the one injection well into which waste is being pumped, during the pumping.

ing should be sufficient to move ground water in at a rate greater than the outward diffusion of fission products.

G. E. Manger of the U. S. Geological Survey (written communication, July 11, 1958) has suggested an alternative method of attack on this problem that has considerable merit. This involves the establishment of a double cement wall around the reservoir area, instead of the single wall described here. Both these walls would be pressure tested by the injection of an alkaline medium, containing some tracer, into wells drilled between the walls, before waste injection. The observation wells used to detect leakage to the outside or inside of this double ring during pressure-testing would be useful later as monitoring and waste-injection wells respectively. This alkaline medium between the walls would be maintained at a pressure greater than that established by the waste inside the wall during actual waste injection; in addition, any leakage of waste might be expected to result in immediate self-plugging upon contact with the alkaline fluid.

One of the major problems in this operation would be the choice of a cementing material. Various substances have been proposed and used in the petroleum industry for the blocking or plugging of permeable formations (American Petroleum Institute, 1954).[32] 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. Even a cement grout will penetrate very porous formations under some circumstances (Parson, 1936). Presumably a material should be used that has no solid particles, however, and Lawton (1946) describes the use of silicic acid gels for such operations. Patents have been taken out on the use of napththalene and of sodium silicate or carbonate, which react with oil field water to form a precipitate. Kennedy (1936) mentions the use of superfatted soaps and colloidal solutions that precipitate on contact with salt water, and describes operations using the hydrolysis of $SbCl_3$ or $SiCl_4$ upon contact with water to develop precipitates in the pores. Considerable use has also been made of various plastics (Hefley and Cardwell, 1943).

Of all the possible materials that have been used for plugging permeable formations, probably the cheapest would be gelatinous silica. The behavior of silica gels is the subject of a fairly extensive literature. In particular the setting time can be controlled by the choice of acid used (Davis and Hay, 1939), the temperature, and the concentrations

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[32] Well cementing is performed in the petroleum industry for a variety of reasons, including (a) concentration of injection water into specific horizons, (b) "shutting out" oil-free waters from aquifers penetrated by the well, and (c) preventing entry of oil or brines into strata containing potable waters. The techniques developed should be of considerable help here, not only in the formation of the "wall", but also in protecting potable waters by sealing off *all* horizons in the disposal area other than the specific one chosen for injection.

and ratios of sodium silicate to acid (Hurd and Sheffer, 1941; Lawton, 1946) or to NH_4HCO_3 (Lehnhard and Reimers, 1939). The main problem in petroleum plugging practice is to shut off unwanted water from porous beds, and hence a great depth of penetration is neither desired nor achieved. In making an underground reservoir wall for waste disposal, however, maximum penetration would be desirable, and exceedingly slow-setting mixtures would have to be developed.

Another possibility, which is apparent from the experimental work on aluminum nitrate solutions described above is that of using either an aluminum hydroxide sol, if it can be shown that it will gelatinize upon continued contact with rocks, or else an acid aluminum solution, which will gelatinize on continued contact with salaquifer minerals.[33] Presumably the cheapest soluble aluminum salt could be used, but care must be exercised as it is well known that the nature of the anion present influences the formation and behavior of aluminum hydroxide gels (Weiser, 1935). It might even be possible to process a portion of the waste to remove the more dangerous long-lived radionuclides, and use this partially purified waste to form an $Al(OH)_3$ "wall" for enclosing the bulk of the waste which still contains these radionuclides. Considerable work has been done on the removal of Sr and Cs (Blanco, Higgins, and Kibbey, 1956; Schultz and McKenzie, 1956; Rimshaw, 1956; Glueckauf and Healy, 1956).

If the pressure-release well is to function, the distance and time of flow of waste within the unit from injection wells to the test wells should be such that no complete stoppage with precipitate occurs. Unless the salaquifer 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 (Plummer and Newcome, 1936). 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 by the highly concentrated HCl used (up to 28 percent, Morrison, 1950), from solution of cementing materials in the formation, and by the clogging of pores by insoluble residues and organic matter from the sediment, particularly if the pores are less than 0.01 mm (Plummer and Newcome, 1936). Another problem has been encountered in petroleum acidizing is that of gelatinization of silicates, such as clays, with the acid (Morrison, 1950); this gel may swell to large volumes (How-

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[33] Before this is attempted, the unexpained liquifaction of these gels, with time (footnote 19, p. 33), must be studied carefully.

ard, 1936). Acid treatment of a salaquifer would have to be done under carefully controlled pressures, as new $CaCO_3$ may precipitate and clog pores upon pressure release (Howard, 1936). This pretreatment would not only dissolve troublesome minerals such as calcite, but would also replace most cations in ion exchange sites with hydrogen, thus avoiding trouble from this source.

Although the large number of wells involved would seem at first to make this procedure too expensive,[34] 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 equal to the cost of plugging
2. The salaquifer is at a depth of 2,000 feet and drill holes cost $20,000 each ($10.00 per foot)
3. The salaquifer is 20 meters thick and has a 10-percent porosity
4. Sodium silicate ($62.50 per ton) is used for plugging (other plugging agents are more expensive per liter of storage volume)
5. The salaquifer within the well is pretreated with HCl ($28 per ton) to dissolve 1 percent by volume $CaCO_3$ or equivalent, to improve compatibility
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 theoretical capacity of over 3×10^8 liters of waste, and would cost, for drilling and chemicals, $10,500,000, or $0.03 per liter; eighty percent of this expense is for the HCl treatment. This low figure would thus permit ample funds for other costs, such as exploration, land, well surveys, special casing, piping, pumping, testing, maintenance, monitoring, and the inevitable contingencies of such an operation.[35]

In terms of the possible volume of waste that could be injected into such a unit, compared with the volume of waste that is expected to be produced, the procedure is completely adequate, one 500-meter diameter unit such as is shown in figure 6 being capable of taking the projected total production of high-level waste in the United States for two years, if injected without dilution. If uses are ever developed for the radioactive elements in the waste, for example, Sr, Cs, Ru, Rh, Pd, Am, Np, Xe, and Tc, to the extent that recovery is profitable

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[34] Some have suggested the use of abandoned oil wells for atomic waste disposal, but this might be uneconomical in view of the possibility of later improvements in secondary recovery permitting further oil production, other unexplored oil structures in the same area, and the high cost of recompletion of old wells (Wilson, Brown, and Sheppard, 1952). In addition, it is likely that old, unrecorded, wells might be present, making the operation unsafe (Schmidt and Wilhelm, 1939).

[35] For comparison, water flooding operations, in petroleum production, have been operated at a cost of $< $0.01 per barrel (119 liters) of injected waters (Theis, 1941).

(Glueckauf, 1956), this procedure of disposal also has the advantage of keeping the waste in one fixed position, from which it may be reclaimed.[36]

This procedure would involve a large amount of 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 salaquifers than are being considered for uncontrolled storage. As this would be an entirely new procedure, a number of factors must be investigated *thoroughly*. One of the most important is the anisotropy and heterogeneity of the salaquifer, in both the cementing and the waste-injection steps. Pollution of fresh water wells via unsuspected faults has caused the discontinuance of at least one chemical (nonradioactive) waste disposal operation (Lee, 1950). Other factors that must be investigated, before any such injection could be considered to be *safe*, are listed on page 62).

CONCLUSIONS

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

The most likely solution to the problem of *incompatibility*, if high aluminum nitrate wastes are to be pumped into salaquifers at all, seems to lie either in chemical pretreatment of the waste to a form that will not readily precipitate upon injection into salaquifers, or in the use

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[36] Glueckauf (1956) feels that the value of some of the fission products such as Sr and Cs might more than equal the cost of extracting them. Although many have expressed doubt concerning the economic feasibility of such an approach, separating the waste into a series of useful materials is much to be preferred to mere "disposal." The stable end members of fission-product radioactivity alone represent a storehouse of potentially useful elements, as they will be produced in amounts of hundreds of tons per year. Using data from Appendices A and B in Coryell and Sugarman (1951), and Steinberg and Freedman (1951), the following stable end members of fission product decay would be present in the wastes after a comparatively few years of cooling, the amounts representing the approximate number of atoms from an original 100 atoms of U^{235} fissioned: 2–3 atoms of Sm; 4–6 atoms each of La, Ce, Pr, Rh, Cs, and Y; 12 atoms each of Mo, Xe, and Nd; 17 atoms of Zr; and about 6 atoms each of 10^6 year half-life Tc^{99} and Cs^{135}. Much larger amounts of alloying or cladding metals such as Bi, Zr, Mo, Al, Cr, Ni, or Fe, and catalysts such as Hg will probably be present, as well as still larger amounts of "salting agents" such as Al.

of an acid pretreatment of the salaquifer to improve compatibility. If the waste is pretreated, 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 any case, acid pretreatment of the salaquifer, before injection, although costly, may be necessary, and the filtering out of minute amounts of insoluble materials on the face of the wall during waste injection can probably be expected to cause serious difficulties.

Even though the injection be far below any potable waters, one solution to the problem of *safety* seems to lie in the construction of a reasonably leakproof walled underground reservoir.   This would use the porosity of a portion of the salaquifer as the storage volume, to be surrounded by a "wall" made by filling the pores of the salaquifer with an impervious cement, and sealed above and below by impermeable beds such as shale.   The cost of construction of such a unit may be as low as a few cents per gallon of storage capacity.   The location of a suitable salaquifer, of glass-sand quality, sandwiched between truly impermeable beds, will require extensive study, however, and there are numerous safety problems that must be solved.   An outline of the factors involved in the selection of a salaquifer suitable for waste disposal, based on evidence available at this time, is given on pages 62–65.

A significant part of the problem of safety is the radioactive heat problem, as this heat may provide the energy to force wastes up into potable waters or to the surface.   This can be avoided by long cooling times before injection, chemical processing, drastic dilution, and injection into a very thin bed, but as with all waste disposal procedures, such safety measures all increase costs.

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 salaquifer assumed here.   If the waste is an acid aluminum nitrate waste, a number of the more significant points that need 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 salaquifer type.   There must be some simplifying assumptions made, either as to kind of waste or kind of salaquifer, 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 method used; it may be modified by subsequent chemical or physical treatment prior to disposal.   The kind of salaquifer available is a function of the disposal site selected and the depth of drilling.   Except for very unusual conditions, geo-

graphic 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 the 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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FACTORS INVOLVED IN THE SELECTION AND USE OF A SALAQUIFER FOR WASTE DISPOSAL

I. Safety considerations
    A. Before injection
        1. Transportation, from reactor(s) to processing plant(s) to disposal site(s)
        2. Temporary surface storage for cooling or efficiency of operation.
        3. Complete testing of site—mineralogical, chemical, geophysical, and hydrological
    B. During injection
        1. Leaks or bursts in pipes or pumps
        2. Leaks in or around well casing into other strata
        3. Geysering of waste column from well as a result of an unexpected cessation of injection following pipe or pump failure, or a sudden clogging of salaquifer
        4. Leaks into old unrecorded water, oil, or gas wells
        5. Unexpected nonuniform flow pattern of waste in salaquifer
            a. Sedimentary inhomogeneities in permeability or porosity-shale partings, conglomerate lenses, amount of cement, grain size distribution variations, in salaquifer and in surrounding rocks
            b. Compositional inhomogeneities—calcareous or argillaceous zones causing local precipitation, or evolution of CO_2
            c. Joints and minor faults in salaquifer or surrounding "impermeable" beds
        6. Unexpected flow rates
            a. Permeability lower than expected hence higher injection pressures needed
            b. Porosity lower than expected hence movement of front faster than expected, for a given volume injected
        7. Unexpected pressure development from heating or CO_2 evolution
    C. After injection
        1. Unexpected flow patterns or rate of movement of natural ground water carrying activity
        2. Pressure increase from heating or CO_2 causing break through impermeable beds above
        3. Earth movements resulting in sudden release of waste under pressure
        4. Break through $Al(OH)_3$ gel wall by more rapid diffusion of H^+ than other cations
        5. Possible presence of toxic materials after the bulk of Sr^{90} and Cs^{137} activity is gone
            a. Stable end members of fission product decay
            b. Long-lived fission products such as Zr^{93}, Tc^{99}, Pd^{107}, I^{129}, and Cs^{135}
            c. Long-lived actinide elements and their daughter products
            d. Nitrate, fluoride, and other toxic anions

I. Safety considerations—Continued
  D. Monitoring problems within and outside dedicated volume
      1. Monitor wells, pumped versus unpumped
      2. Probable first arrival at monitor wells, cation versus nitrate anion
      3. Spacing of wells to detect highly irregular flow patterns
  E. Procedure in case of accidents or unexpected movement
      1. Listing of all possible situations
      2. Probable consequences of each
      3. Corrective measures for each
          a. Emergency wells, for injection of flooding water or for pumping, drilled in advance
          b. Possibility of injection of gel-forming fluids as an emergency containment measure
II. Technical feasibility considerations
  A. Geological features
      1. Storage volume available in strata
          a. Thickness and its variations—lensing of sands in shales
          b. Permeability and its variations—variation in grain size and cement
          c. Porosity and its variations—variation in grain size range, and cement
          d. "Compressibility" of existing ground water and rock
      2. Impermeability of overlying and underlying beds
          a. Possible movement and break-through from pressure of injection, pressure of evolved CO_2, or thermal expansion
          b. Joints, faults, sand lenses, and other possible avenues of escape
          c. Possible effects of "kneading" from crustal tides
      3. Ground water; flow rate, flow direction, and distance to edge of dedicated volume
  B. Chemical and physical features
      1. Waste
          a. Composition and Eh and pH
          b. Viscosity, and its change with time, temperature, pH, CO_2, and dilution
          c. Density, compared with that of the ground water displaced
          d. Heat generation, and its change with time
          e. Complete freedom from filterable solids, at least until beyond well face
      2. Salaquifer
          a. Mineralogical composition and its variation
          b. Physical size and spatial distribution of reactive minerals
          c. Surface areas available for reaction or ion exchange
              (1) True versus effective surface area; effect of joints and other irregularities
              (2) Nature of ions present in exchange sites from ground water
          d. Physical nature of pores for fluid movement; average size, shape, and minimum cross section
          e. Composition, concentration, and pH of natural ground water

II. Technical feasibility considerations—Continued
    B. Chemical and physical features—Continued
        3. Interactions with salaquifer materials
            a. Possibilities permitting continued injection
                (1) Slow, hot, reactions forming reasonably stable sols of Al $(OH)_3$ or Fe $(OH)_3$; nature of such sols; flocculants and peptizers; stability in contact with large amounts of various mineral surfaces; increase in viscosity with sol formation and partial gelation
                (2) Formation of an insulating armor of gel on all reactive mineral grains, preventing further reaction; rates of diffusion of various ions through such gels; gel thickness; gel recrystallization to porous crystalline mass
                (3) Precipitation on or near reactive minerals being so distributed or so small in volume to permit continued flow; stoichiometric relationships of waste versus salaquifer
                (4) Cation exchange adequate to preclude precipitation; possible chromatographic phenomena giving local heating; competition between fission products and inert salting agent cations; heat formed by chemical interactions.
            b. Possibilities of partial or complete stoppage
                (1) From partial decomposition of salaquifer minerals yielding solid matter in suspension
                (2) From large increase in viscosity of waste with increase in pH
                (3) From filtration of flocculent precipitates or other materials present at injection
                (4) From coalescence of gel films at constrictions in pores
                (5) From complete gelation of entire advancing front of waste
                    (a) Reaction rates versus flow rates
                    (b) Width of zone of equilibration versus storage capacity
III. Economic considerations
    A. Geographic location
        1. Distance from disposal site to other units it serves
            a. Power consumer(s)
            b. Power reactor(s)
            c. Processing plant(s)
            d. Centralized disposal site(s) versus centralized processing site(s)
        2. Nature of dedicated surface area
            a. Original cost or value
            b. Cost of patrolling and monitoring
            c. Possibility of multiple use; test site or surface disposal of other wastes, such as solids

III. Economic considerations—Continued
  A. Geographic location—Continued
      3. Nature of dedicated underground volume
          a. Value of known natural resources forfeited—water, oil, gas, brines, salt, coal, glass sand, etc.
          b. Possibility of lateral movement increasing volume to be dedicated
          c. Depth, cost of drilling per foot, and amount of drilling
  B. Possible transportation problems
      1. Electricity from reactor to consumer
      2. Irradiated and reprocessed fuel elements between reactor and processing plants
      3. Waste from processing plants to disposal site
  C. Effect of reactor type
      1. On processing procedure
      2. On geographic location of installations
      3. On transportation methods
      4. On waste type
  D. Volume injected per well, before plugging
      1. Cost of drilling wells, including monitoring and test wells; depth and diameter
      2. Treatment to avoid slightest trace of suspended solids; possibility of precipitation at injection face from clear solutions
      3. Feasibility of hydrofracing, explosives, or other methods of enlargement of injection surface without damage to impermeable enclosing beds
      4. Probable need for stainless steel or other corrosion resistant well casing; cementing of casing in place
      5. Compatibility of waste with salaquifer
      6. Optimum dilution (volume increase versus time and volume of pumping), and nature and availability of diluent
      7. Optimum pressure and rate of injection
  E. Pretreatment of waste
      1. To remove valuable fission products or useful chemicals such as HNO_3
      2. To improve compatibility, for example, production of diban
      3. To remove longer-lived or more dangerous nuclides (Cs^{137}, Sr^{90}, U^{233}, Th^{228}, Pu^{239}, Pu^{242}, Np^{237}, Am^{241}, Cm^{244})
  F. Cost of pretreatment of salaquifer
      1. Removal of reactive ground water
      2. Acid leaching to remove reactive minerals; disposal of leaching liquid
  G. Cost of locating site
      1. Geologic exploration
      2. Test boring for representative cores
      3. Hydrological, mineralogical, and chemical tests on cores
      4. Hydrological tests of salaquifer
      5. Tests of salaquifer compatibility, in place, with simulated wastes.