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FEASIBILITY OF UNDERGROUND STORAGE/DISPOSAL
OF NOBLE GAS FISSION PRODUCTS

by

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R. M. Winar, L. E. Trevorow, and M. J. Steindler

ABSTRACT

The quantities of ^{85}Kr that can be released to the environment from nuclear energy production are to be limited after 1983 by Federal regulations. Although procedures for collecting the ^{85}Kr released in the nuclear fuel cycle have been developed to the point that they are commercially available, procedures for terminal disposal of the collected gas are still being examined for their feasibility. In this work, the possibilities of underground disposal of ^{85}Kr by several techniques were evaluated. It was concluded that (1) disposal of ^{85}Kr as a solution in water or other solvents in deep wells would have the major disadvantages of liquid migration and the requirement of extremely large volumes of solvent; (2) disposal as bubbles entrained in cement grout injected underground presents the uncertainty of gaseous migration through permeable solid grout; (3) disposal by injection into abandoned oil fields would be favored by solubility of krypton in residual hydrocarbons, but has the disadvantages that such fields contain numerous shafts offering avenues of escape and also that the fields may be reworked in the future for their hydrocarbon residues; (4) underground retention of ^{85}Kr injected as a gas may be promising, given the right lithology, through entrapment in interstices between fine sand grains held together by the interfacial tension of wetted surfaces.

I. INTRODUCTION

A. General

This study was undertaken to provide an initial determination of the feasibility of disposing of, or storing, noble gas fission products in sub-surface rock strata. Such gases, krypton (^{85}Kr) and stable xenon isotopes, would be released during the reprocessing of spent uranium fuel rods from nuclear energy generating plants and would be collected.

Although retrievable gas storage may be possible, the contemplated action is primarily that of "disposal" and it will be so referred to throughout this report.

B. Background

Future requirements for nuclear fuel to produce energy may necessitate that uranium and plutonium be recovered from spent fuel for reuse in nuclear power reactors. If this need arises, the reprocessing operations will release ^{85}Kr from the spent fuel at a rate of approximately 11,000 Ci of ^{85}Kr per Mg of reprocessed fuel, the quantity being dependent on fuel burnup and fuel

cooling time. This release of ^{85}Kr will occur in the head end of a reprocessing plant. In most previous U.S. reprocessing operations associated with weapons production and the short-term commercial program of the Nuclear Fuel Services reprocessing plant, no effort was made to collect the ^{85}Kr . Instead, ^{85}Kr was vented directly to the atmosphere, since it could be shown that its radiological impact on the public in the immediate environs of these plants was small and that the radiological impact on world population was negligible. It appears that if worldwide reprocessing operations are instituted in the future, the radiological impact resulting from release of all ^{85}Kr may be of significance; therefore, programs and investigations of methods of recovering, storing, transporting, and disposing of ^{85}Kr are presently under way.

The most recently designed and constructed spent fuel reprocessing plant in the U.S. is the Barnwell Nuclear Fuel Plant (BNFP) owned by Allied General Nuclear Services, Inc. This plant, which has not been operated, was designed to reprocess 1,500 Mg of spent fuel per year. If the facility were to process maximum-burnup fuel at full capacity, about 16 MCi of ^{85}Kr could be released annually from head end operations. It has been estimated that if this quantity of ^{85}Kr were vented directly to the atmosphere, it could result in an annual skin exposure to a person living at the boundary of the plant of about 12 mrem [BARNWELL]. A recent study [NEA] by a group of experts for the Nuclear Energy Agency of the Organization for Economic Cooperation and Development estimated that a hypothetical plant four times the size of the BNFP operating in the year 2000 could result in an annual exposure to the skin of the most highly exposed individual near the plant of 90 mrem, as compared with the skin dose limit of 1500 mrem recommended by the International Commission on Radiological Protection (ICRP). This hypothetical plant would expose the world population to a skin dose of 2.5 mrem. Similar estimates of skin exposure from ^{85}Kr can be obtained from a report by the National Council on Radiation Protection and Measurement [NCRP].

The various estimates of exposure to the world population in future years, if reprocessing becomes the modus operandi, have led to proposed restrictions on the venting of ^{85}Kr . The U.S. EPA, in Title 40, U.S. Code of Federal Regulations, Part 190, requires that by 1983 the release of ^{85}Kr be limited to 50,000 Ci per GWe-y produced. This requirement would limit the release of ^{85}Kr to approximately 15% of the ^{85}Kr contained in spent fuel assemblies. The Federal Republic of Germany has recommended a limitation of 1 MCi/y from a reprocessing plant, with appropriate systems to retain as close to 100% of the ^{85}Kr as possible [NEA]. A 1 MCi/y limitation would amount to releasing about 6% of the ^{85}Kr from a plant operating similarly to and at the capacity of the BNFP. Since ^{85}Kr has a 10.7-y half-life and is a relatively inert gas, it will be dispersed globally, independent of the country of origin. Accordingly, the NCRP has suggested that the International Atomic Energy Agency (IAEA) and ICRP develop policies for ^{85}Kr which will be acceptable on an international basis.

A plant that reprocesses 1500 Mg of uranium fuel per year will produce an estimated 150 m³ of krypton, 1500 m³ of xenon, and, based on 100 cfm flow rate of air into the dissolver, 1.5 x 10⁶ m³ of air (all at standard temperatures and pressures). If there is a cooling-off period of 150-180 days prior to further processing, the concentration of the longest-lived radioactive isotope of xenon (xenon-127, half-life 32 days) will have been reduced by a factor of 30-60. The major radioactive constituent will then be krypton-85 with a half-

life of 10.7 y. The ratio of krypton-85 to stable krypton present within this process stream, based on amounts at the time of discharge of fuel from the reactor [DIABLO], will be 8/90.

C. Scope and Methods

This study includes consideration of the general feasibility of disposing of noble gases underground as either a gas or as a solute in various liquids. The use of abandoned gas or oil wells as the conduit for introducing this material into the subsurface is also considered. The third possibility investigated is entrainment of noble gases in a cement grout to be injected into subsurface shale beds.

Alternative operations which would precede the injection of noble gases into a deep geologic media are illustrated in Fig. 1. Four options are listed for on-site disposal; two of these are also considered for off-site disposal. These choices essentially include: Alternative A, direct disposal of all process off-gas from the head-end system of the reprocessing plant; Alternative B, dissolution of all off-gases in liquid followed by pumping of the solution into an injection well. In alternative C, gas separation and packaging is followed by transport and then gas unloading and/or compression into the injection well. Alternative D includes separation of gases in the gas recovery system, followed by packaging and then transport to the well site where the gas is dissolved and pumped down the well. Alternatives C and D (identified as C-1 and D-1 in Fig. 1) are for off-site disposal. These indicate that for off-site disposal, gas separation must precede transport to the well site. Once the gas is there, it can be introduced into the well as gas or solution.

The method of investigation includes a review of (1) literature pertaining to the underground storage of noble gas and (2) other applicable literature related to gas storage and deep well injection. The behavior parameters of the noble gases were researched and their solubilities in various liquids considered (Appendix C). These alternatives were evaluated as to their general feasibility, and some generalized cost estimates were made.

A report by Trevorrow et al. [TREVORROW] considers deep well disposal of tritium-bearing low-level aqueous waste. Although that study pertains to liquid waste disposal, the technology is very applicable. Described in that report are the siting of injection disposal wells; design, construction, and operation of an injection well and system; legal and regulatory controls; environmental impact; costs; and examples of injection wells for radioactive effluents. Reference is made to that report throughout the present study, and a conscious effort was made to avoid duplication of portions of this earlier report.

D. Limitations

The methods of investigation for this study were limited to literature research, interviews with knowledgeable individuals, personal experience, and calculations. In those instances where predictions are made, an attempt has been made to identify the reliability of such predictions. Since the cost

On-Site Disposal

Alternative A - Systems 1, 5, 7

Alternative B - Systems 1, 4, 6, 7

Alternative C - Systems 1, 2, 3, 5, 7

Alternative D - Systems 1, 2, 3, 4, 6, 7

Off-Site Disposal

Alternative C-1 - Systems 1, 2, 3, 5, 7

Alternative D-1 - Systems 1, 2, 3, 4, 6, 7

Fig. 1. Alternative Operations Associated with Injection Disposal of Noble Gases or Noble Gases in Solution

estimates included in this study are not in all instances complete, they must be considered relative costs and not absolute estimates. They are provided primarily to allow general cost comparisons with other methods, and they pertain to the cost of gas and liquid disposal wells as wells for disposing of hazardous wastes. Special costing provisions for the handling of radioactive materials are not included, but the significance of such hazards and the need for such safeguards are identified where this is considered crucial.

Mined underground openings are not within the scope of this study of underground disposal of noble gases, nor is the concept of noble gas disposal into dissolved or excavated cavities in salt beds. The latter possibility is presently being investigated for high level wastes, and the information derived could be extremely helpful in determining the feasibility of disposing of radioactive noble gas in salt cavities. Flow of salts due to thermal loading of the radioactive wastes would be expected to be a major problem. Although natural gas is successfully being stored in such cavities at present, salt flowage has been reported to be a serious problem.

II. UNDERGROUND DISPOSAL OF RADIOACTIVE NOBLE GASES

A. History and Background

The underground storage of natural gas involves a technology which can be applied to underground disposal of ^{85}Kr . Natural gas storage was initially done in 1916 and experienced a very slow growth until the early 1950s when a total gas storage capacity of $2.86 \times 10^{10} \text{ m}^3$ of gas (one trillion cubic feet) was attained. Thereafter, its development proceeded more rapidly. By the end of 1976, 386 pools had been developed which store gas volumes about seven times that in 1950 (Fig. 2). Of these, 302 were dry gas fields, 18 were oil and gas fields, 7 were oil fields, 53 were aquifers (water-bearing), and 6 were man-made caverns [VARY, 1976]. Twenty-six states contain one or more underground gas storage fields.

The very limited amount of prior literature on the subject of underground disposal of radioactive gases has been reviewed. In point of fact, most of these are site-specific geological studies in which the problems of gas which describes the problems in general is at a rather fundamental level. Perhaps the best discussion is that by Reist [REIST-1965, 1967]. Even he, however, fails to recognize the very important differences between single-phase and two-phase flow in estimating the possible leakage of gas through cap rock. He based his estimates upon measurements related to the permeability of the cap rock to water and did not consider the decrease or elimination of effective permeability to dual-phase flow behavior within the cap rock. Consequently, his calculations of gas diffusion through the cap rock are in error. His cost estimates, discussed in section IV.E of this report are also unrealistic because he failed to identify the potential cost of unsuccessful exploration expenses. These could double or triple the final well cost. (Also, see section VI.D of this report on "Estimated Well costs.")

Fig. 2. The Growth of Underground Gas Storage Reservoir Capacity in the United States, 1920-1976. Modified from [VARY-1976].

In 1964, a series of gas injection field tests was undertaken at the National Reactor Testing Station (now Idaho National Engineering Laboratory) to collect data concerning storage capacity, migration, dilution, and injection pressures, etc. associated with underground gas injection [MUDRA]. The program included the injection of air containing a helium tracer into basaltic rocks having sedimentary interbeds. No closed structure appears to have been identified, nor was a continuous cap rock defined. Air was injected above and below the regional water table, above the water table and below a perched aquifer, and directly into the regolith.

Unfortunately, these tests are of questionable applicability to the evaluation of a gas disposal well which utilizes a closed storage structure as its disposal formation. The study correctly reports that the geologic environment was that of an "incomplete trap," but it does not emphasize this point, nor does it comment upon the potential viability of utilizing a closed structure as a disposal reservoir. Consequently, the latter concept seems to have been condemned in this report or at least has somewhat suffered by association with the negative results obtained when testing this "incomplete trap" (see Fig. 3 and Appendix G for illustrations of geological characteristics necessary for gas entrapment).

An article by Clebsch et al. [CLEBSCH] states that with underground gas disposal, "the principal disadvantages include the uncertainty of predicting directions and rates of flow and the related concentration distribution, and the difficulty in verifying predictions." Although these comments are truly applicable, they are not necessarily insurmountable. In this instance, the author appears to have drawn many of his conclusions from previous gas storage investigations carried out at the Idaho National Reactor Testing Station (INRTS) and reported upon by Mudra and Schmalz [MUDRA]. But Clebsch fails to report that the Idaho results were applicable only to an "incomplete trap" in unusual geological terrain. His conclusions are applicable only to a geologic situation similar to that at the INRTS gas storage investigation!

The underground storage of natural gas (primarily methane) is, as stated above, a fairly common practice. Helium is also stored underground on a limited scale. Tade [TADE] reported on the Cliffside helium gas storage field which had thus far successfully placed $4.375 \times 10^8 \text{ m}^3$ (15.3 BCF) of crude helium into storage. He projected that $1.43 \times 10^9 \text{ m}^3$ of gas (50 BCF) would ultimately be placed in storage. The storage field is a dome-shaped, geological structure that was previously a producing gas field.

As can be seen in the References section, most of the literature cited in this report pertains to the existing technology of underground storage of hydrocarbon gases.

B. General Geological Requirements

The general geological conditions for the underground disposal of noble gas fission products in the gas phase are identical with those required for the underground storage of natural gas, a well-developed technology. Two major elements are required: (1) a "reservoir" formation suitably permeable and porous to provide for the transmission and containment of the injected gas; and (2) an impermeable "enclosure" which restricts the injected gas to a specific portion of the subsurface environment (Fig. 3).

Fig. 3. Elements of Underground Storage Containment: Structure, Porous and Permeable Rock, Cap Rock, Depth, Water Seal. Adapted from [KATZ-1968].

1. Reservoirs

The most common reservoir lithologies are sandstones and porous carbonates (limestones and dolomites), from which connate waters have been removed either by displacement laterally and downward by the injected gas or by withdrawal to the surface. Particularly in the Appalachian region, some reservoirs consist, in part, of fractured dense rock. Other porous and permeable lithologies, such as vesicular lava, might conceivably be utilized as storage reservoirs under suitable geological conditions, but no instances of storage in such unusual lithologies are known at this time. Most sedimentary basins contain several stratigraphic units which are potentially useful as storage or disposal reservoirs.

2. Enclosures

The enclosure, which restricts the injected gas to the desired location, commonly results from a combination of geological and hydrological mechanisms (see Appendix G and Fig. 3).

a. Impermeability of Cap Rock

A major element of the enclosure in all storage or disposal projects is an impermeable or relatively impermeable rock stratum which must invariably form the superadjacent component of the enclosure. This rock stratum is important in preventing vertical upward movement, but may also restrain lateral movement, and, less commonly, vertically downward movement. In gas storage technology, their orientation with respect to the reservoir is ignored, and such units are generally known as "cap rock." They are termed "aquicludes" or "aquitards" in hydrological terminology.

Very few sedimentary lithologies are absolutely impermeable. To some extent, this is due to the presence of mechanical discontinuities within the rock, bedding planes, fractures, joints, and faults. In addition, most sedimentary rocks have a finite intrinsic permeability; the most common exception is salt. Generally, reservoir and cap rock lithologies differ only in degree. All are composed of assemblages of mineral grains or crystals, and even in the most heavily cemented or densely intergrown lithologies, some degree of intercrystalline or intergranular void space commonly persists. If these void spaces are interconnected, even in the most minimal degree and by the most tortuous path, a finite permeability exists.

On the other hand, in very dense lithologies where the diameter of interpore apertures is small, a condition of relative impermeability may exist for two-phase flow (two immiscible liquids or a liquid phase and a gas phase) as a result of interfacial tension. If a finely porous rock is water-wet, water is bound in the interpore apertures or pore throats by capillary pressure. No gas can be injected through such a rock until the pressure differential across the pore throat exceeds the displacement or threshold pressure of the water bound by capillarity within the pore throat. For common cap rock lithologies, shales and dense carbonates, this threshold pressure may range from 30 to more than 100 atm.

In a later portion of this report, the potential of disposing of radioactive gases dissolved in water into water-saturated porous rock is considered. It is important to note that such disposal would involve single-phase flow. Accordingly, lithologies which are treated as impermeable with respect to disposal of the gas phase may not be impermeable with respect to gas dissolved in water.

b. Hydrology

Gas, being less dense than water, is buoyant in a water-saturated rock environment. It tends to rise until stopped by a relatively impermeable cap rock or other mechanism. Accordingly, a gravitationally derived gas/water contact commonly forms the base of the enclosure for gas storage fields, as it does for most primary oil and gas fields. If there is no groundwater movement (and if the injected gas has come into equilibrium with the water), the gas/water surface will be horizontal; however, where groundwater flow exists, an additional element is added in the resulting pressure gradient. In such cases the gas/water contact tends to parallel the isopotential surface (the surface containing all points of equal hydrologic potential or "head") and may be substantially tilted with respect to the horizontal; therefore, closure should be evaluated with respect to the actual potentiometric surface rather than the horizontal plane (Appendix G).

It is, for example, theoretically possible to confine a "bubble" of injected gas under a flat-lying cap rock by drilling a ring of water injection wells at some radius around the gas injection well and thus raising the hydraulic potential around the periphery of the storage area with respect to its center [BOND]. Various proposals for manipulation of the enclosure by changes in hydrology have been proposed, but none have been extensively tested or put into operation in this country. There are reports of a Russian gas storage field which successfully stored gas in strata without a confining structure [CHARNYI]. This "flat storage" is definitely intriguing, but no additional information has been made available on the project, and it has not been duplicated by other experimenters.

c. Structure

The most common element of lateral restraint in the enclosure is the confining structural configuration of the cap rock. Most commonly, this takes the form of a domal or anticlinal structure in which the cap rock acts as both the upper and lateral elements of the enclosure, while the gas/water contact constitutes the bottom element. Faults which displace relatively impermeable cap rock material against a porous reservoir may also provide structural elements of the enclosure (see entrapment against fault, Appendix G). Clearly, the structural closure must extend below the gas/water contact if enclosure is to be maintained; commonly, a margin of at least 6 m above the spillpoint (the lowest "closed" contour of the structural closure) is maintained to ensure confinement.

d. Cap Rock Lithology

Structurally closed cap rock is the critical element of enclosure in all existing natural gas storage fields. In view of the unproven status of lateral confinement by hydrological manipulation or by the flat storage concept, this would almost certainly be the critical element in radioactive gas disposal also. The discussion of relative impermeability due to the threshold pressure effect (Appendix F) should make it clear that one requirement for a suitable cap rock is that the diameter of any flow paths existing through the rock be sufficiently small to result in a high degree of capillarity. These conditions exist most commonly in dense carbonates, evaporites, and shales.

Other characteristics are also important. Chief among these are the rheological properties. Structural discontinuities, particularly jointing, exist in almost all sedimentary rock or may be induced or reactivated by seismicity. Even cap rocks that are best in terms of intrinsic impermeability may prove unsuitable if cut by vertical joints and fractures which are unsealed. Thus, the ability of the cap rock to deform and thereby seal such potential avenues for upward migration is critically important.

At the pressures and temperatures appropriate to most existing gas storage fields and potential gas disposal operations (200-400 atm lithostatic pressure and temperatures of 26 to 42°C), carbonates generally exhibit a brittle behavior with little or no capacity for deformation. Thus, despite their generally excellent intrinsic impermeability, they are not commonly considered suitable cap rock lithologies. Salt and, to a lesser extent, anhydrite do exhibit "creep" behavior under these conditions and thus may provide the desired "self-sealing" effect. However, the creep characteristics

of evaporites are time-dependent, and the resealing of a newly opened joint or fracture requires a finite time period. In areas of low seismic activity, evaporite cap rock lithologies alone are considered satisfactory, particularly for the storage of natural gas (the localized escape of small quantities of natural gas is not considered exceptionally hazardous). Such lithologies might not be considered suitable for the containment of radioactive gases.

The most common cap rock lithology is shale, which generally deforms as a plastic medium above some limiting pressure. Unlike creep, plastic deformation is related solely to stress and is not time-dependent. Accordingly, plastic shales loaded above their pseudo-plastic limit deform immediately to seal any opening and, in fact, may prevent such openings by promoting stress dissipation.

The plasticity of shale is highly variable. Although very little work has been done on the mechanical characteristics of water-saturated, heavily loaded shales, practical experience indicates that shale containing relatively small quantities of siliceous material or carbonate in addition to the normal clay minerals has severely reduced plasticity. For practical purposes, a shale containing as much as 15 to 20% calcite or dolomite exhibits properties more like those of carbonate rocks than of shales. Geologists familiar with gas storage find little difficulty in recognizing suitable cap rock shales by visual examination of cores, particularly by observing fracture characteristics of cores when broken.

3. Limiting Considerations

Although potentially suitable combinations of reservoir and enclosure exist in most areas in North America where there is sedimentary rock, many other factors must be considered in selecting sites for underground gas storage and particularly for underground disposal of radioactive gas.

a. Competitive Use

The subsurface environment contains many important resources; their present and future value must be weighed in relation to potential contamination or increased difficulty of recovery resulting from noble gas injection. Clearly, aquifers carrying potable water are not suitable disposal reservoirs. In areas of foreseeable water shortage, it may be desirable to limit consideration to reservoirs of substantially low water quality, perhaps containing more than 10,000 mg/L total dissolved solids (T.D.S.).

Similarly, and particularly when dealing with the disposal of a hazardous substance, reservoirs should be avoided which would have to be penetrated in future drilling for oil and gas or in the sinking of shafts for the recovery of solid minerals.

The above geological considerations, together with the many demographic, sociological, and economic considerations of site selection, must be evaluated on a site-specific basis and cannot be adequately considered in a generalized regional study.

b. Seismicity

An additional limiting consideration is seismicity, although the hazards to gas storage and disposal arising from earthquake activity are less than might be expected. The most seismically active region of the continental United States, Southern California, contains a number of natural gas storage fields, together with hundreds of oil and gas producing fields. The very fact that oil and gas have been retained in subsurface traps in this area for millions of years despite a high frequency and intensity of seismic activity suggests that regions need not be eliminated from consideration as potential disposal sites solely on the bases of seismicity. Although the possibility of shearing, rending, or rupture of below-surface casing and tubing always exists, it is probable that surface and near-surface facilities, well heads, pumping stations, transportation and unloading facilities, etc. are more vulnerable to earthquake damage than are the reservoir and its enclosure.

Suitable downhole safety equipment such as flow limiters, check valves, etc. might be installed downhole in the casing of the well. Thereby, engineering could provide a means for limiting or restricting upward flow of gas that had been injected into the subsurface reservoir if disruption of surface equipment should occur.

In addition to evaluation of the frequency and intensity of seismic activity, two further seismically related geological questions should be considered. The first is the deformability or "self-sealing" characteristics of the cap rock (as discussed above) and the resulting ability of the cap rock to close any fractures induced by ground motion. The second is disruption of the hydrological regime.

Seismic effects on the hydrology of underground storage and disposal sites fall into two classifications--short-term, cyclical variations in pressure (hydroseisms) and long-term or permanent changes in hydrology. Hydroseismic activity is frequently observed in wells after major earthquakes, often at very great distances [COLDTHWAIT]. Following the 1964 Alaska earthquake, a water well at Milwaukee, Wisconsin recorded water level variations in excess of 3.65 m. Following the same earthquake, gas storage observation wells in Illinois and Iowa showed fluctuations in the water level ranging from a few centimeters to as much as 1.4 m. It should be noted that although very large water level variations are well known and anticipated in shallow wells completed in poorly consolidated sediments, all of the above wells were completed in consolidated, porous sandstones and dolomites at depths ranging from approximately 180 m to as much as 915 m. In addition to observed fluctuations in water wells, fluctuations in oil and gas producing wells are commonly reported but are difficult to verify.

Hydroseismic activity commonly persists for only a few hours or a day or two at most. With conservatively designed radioactive gas disposal well installations, it is not anticipated that hydroseismic activity would have adverse effects upon the integrity of the enclosure; however, the mechanism of hydroseisms in consolidated rock is not well understood and requires further study.

Long-term or permanent hydrologic effects of seismicity apparently depend primarily on earthquake magnitude and distance from the epicenter. Long-term effects of the 1964 Alaska earthquake upon wells completed in consolidated rock in the upper Midwest were limited to a single well, which reported a 36.5-cm increase in permanent water level. On the other hand, one can reasonably foresee a number of possible large-scale effects in the immediate vicinity of a large-magnitude earthquake. In poorly consolidated sediments such as occur at the Gulf Coast, much of Southern California, and other areas of comparatively recent deposition, it is very probable that some degree of compaction would result, resulting in reduced reservoir volume, lowered permeability, and at least temporarily increased fluid pressures. Significant compaction of aquifers may result in changes in hydraulic gradient both in magnitude and in direction, thus altering the hydrological elements of the enclosure, tilting or changing the tilt of the gas/water contact.

Although it would be expected that such effects should be well documented from oil and gas producing operations in seismically active areas in Southern California, this is not the case. Oil well pressures are measured only infrequently and rarely with precision. Production rates are commonly controlled artificially (choked), and production is generally gauged no more frequently than daily and is recorded by lease rather than by individual well. Although gas well pressures are more often recorded continuously, they are subject to many variables and their interpretation is difficult. Wells peripheral to an oil and gas accumulation, which might be useful in tracing hydrocarbon escape, are generally plugged as soon as it is found that they are nonproductive.

As in the case of hydroseisms, long-term effects of seismic activity upon the hydrology of deep reservoirs is poorly known and requires substantial further study. It is assumed that for future installations seismic risks associated with a given area would be considered and well and surface installation design modified accordingly; alternatively, high-risk areas may be avoided during the siting process.

C. General Volume Considerations

It was stated earlier that a nuclear fuel recovery plant processing 1500 Mg of uranium per year would produce 150 m^3 of krypton and 1500 m^3 of xenon and that these gases would in turn be mixed with some $1 \times 10^6 \text{ m}^3$ of air. (Appendix A lists various physical properties of noble gases, oxygen, and nitrogen.) If the entire volume were to be injected as a gas into a subsurface "gas storage structure" at an assumed depth of 1,000 m, the reservoir volume required at this depth would be approximately $1.0 \times 10^4 \text{ m}^3$ per year of operation. It should be noted that even with twenty years of gas injection at this rate, the total gas stored would be approximately $2.0 \times 10^5 \text{ m}^3$, a volume which would be roughly equivalent to that of some of the smaller gas storage fields currently operating in this country.

There has been some discussion that the air volumes presented above as being associated with krypton and xenon may be too high by an order of magnitude; also, there is some possibility that this volume might be reduced by changing the process in some other manner. No attempt has been made to change these volumes in this evaluation; instead, it was considered that these volumes are extremely conservative or represent the worst possible case. In the calculations

made, use of this larger volume did not constitute a restricting or negative effect on gas disposal; therefore, it must be assumed that using the maximum volume of purged air in the estimate does not greatly affect preliminary conclusions concerning the feasibility of noble gas disposal as a gas.

Since krypton comprises such a small amount of the yearly total of gas produced in this process, 150 m^3 out of a total of each $10,000,000 \text{ m}^3$, it is possible that cryogenic separation of the krypton might be feasible and desirable. If injection disposal of only the krypton was necessary, the daily volumes would be extremely low. They would amount to an approximate 0.4 m^3 (STP) per day. If injected into a reservoir at a depth of $1,000 \text{ m}^3$, the actual reservoir volume required would be only 1.5 m^3 per year or $4.0 \times 10^{-3} \text{ m}^3$ per day. (Appendix B describes the production and properties of ^{85}Kr .)

D. Factors Controlling Reservoir Capacity

1. Porosity and Water Saturation

The porosity of reservoir rocks used for the storage of natural gas typically ranges between 12 and 25%. However, even after gas injection, a portion of the intergranular or intercrystalline pore space is water-filled. Most of this water is retained by capillarity. Its volume is determined by grain size, degree of cementation, sorting, and other elements of internal structure, together with distance above gas/water contact. Additional water may be retained within the formation by entrapment above impermeable (or relatively impermeable) zones within the reservoir, such as shale laminations in sandstone reservoirs or "upturned" vugs in carbonate reservoirs. In typical gas storage reservoirs, the residual water saturation ranges between 15 and 35%. Both porosity and residual water saturation may be determined by geophysical logs or, with higher reliability, by the analysis of core samples.

2. Pressure

The pressure in most aquifers is approximately hydrostatic, with a typical gradient of approximately 0.1 atm per meter of depth. However, significant variations in gradient do exist, and reservoir pressure and gradient must be determined for each prospective reservoir. For purposes of approximation, in the selection of disposal structures at conventional depths (less than 2,000 m), it is customary to use the idealized gas relationships expressed in Boyle's and Charles' laws. Departures from ideality as expressed in the compressibility factor must be considered in final volumetric calculations, but for the purpose of this analysis, such corrections would constitute such a minor volume change that they are not considered in this study; also, the potential variations of the estimate of relative air volumes required could introduce errors far in excess of any correction factors introduced for departures from the gas laws.

Volumetric efficiency in the storage of gas improves with greater pressure at greater depth; however, when the costs of both surface and subsurface facilities are taken into account, the optimum depths are normally found to lie between 500 and 2,000 m, with typical pressures of from 50 to 200 atm.

3. Temperatures

In most sedimentary basins, the temperature gradient ranges between 1.5 and 3°C per hundred meters of depth, increasing downward from the mean surface temperature. Within the contiguous 48 states, mean surface temperature ranges from approximately 4°C in the vicinity of the North Dakota/Canada border to approximately 25°C in Southern Texas and Southern Florida. Similarly to subsurface pressures, subsurface temperatures may be significantly higher or lower than those estimated from these generalizations and must be confirmed for each specific reservoir.

An additional thermal element possibly requiring consideration is the heat induced by compression of the injected gas. In the event that only krypton is injected, the displacement rate will be so small that there will be little temperature elevation from this event and the gas will be substantially in thermal equilibrium by the time it reaches the reservoir formation. In the event the noble gas fission products are injected along with air diluent, there may be compressive heating and the gas may reach the reservoir at a significantly elevated temperature. The difference between gas temperature and reservoir temperature will be dependent upon the design and method of operation of the compressor facilities at the surface; the reservoir temperature; the depth, casing, and completion practices; and many other factors which must be considered on a site-specific basis. It is anticipated that compressor and well installations will be designed to minimize the differences between the temperature of the injected gas and that of the reservoir in order to reduce thermal stress on the casing string and upon the cement seal in the annulus between the casing and overlying formations.

In Appendix D are calculations and considerations of possible heat loading of an underground reservoir or associated cap rock resulting from the disposal of the krypton gas generated in 20 y from a typical nuclear fuel reprocessing plant.

If a diluent needs to be added to the krypton before it is disposed of in the well, first subjecting the effluent to cryogenic separation and later diluting it with air prior to injection into the well would not be prudent. Solution of the heat-loading problem might indicate that initial separation of noble gas from air is not advisable or that a lower air to krypton ratio might possibly be attained in the head end of the process. In either case, the gas mixture obtained might have a small enough volume that it does not cause a heat loading problem.

In some interesting research, [SKIBITZKE] considers the possibility that radioactive fluids moving through porous media would be adsorbed upon various solid surfaces in the media and that this would occur selectively, depending on the chemical and physical nature of the porous medium and the formation waters. The effect of this phenomenon would be to concentrate radioactive materials in certain select bands concentric to the well bore. Hence, the heat loading would not be evenly distributed throughout the reservoir but would be concentrated in select zones concentric to the well bore.

E. Possible Interactions with Injected Gases

1. Rock

The most probable reservoir lithologies are sandstones, limestones, and dolomites. Sandstones of sufficient porosity and permeability to be suitable for a disposal reservoir consist primarily of quartz grains, with the quartz grains consolidated by relatively small quantities of secondary silica, calcite, dolomite, or clay minerals occurring primarily as a cement consolidating the quartz grains. In addition, various metallic oxides, particularly iron oxide, may be present as a "stain" on the grain surfaces, and a wide variety of minerals may be disseminated in small quantities throughout the sandstone. Carbonate reservoirs (limestone and dolomite) typically are relatively free of other mineral species, but they may contain minor quantities of clay minerals, pyrite, or quartz grains.

Cap rock formations consist of carbonates of approximately the mineralogical composition described above or, more commonly, of shales consisting of compacted clay minerals with minor admixtures of quartz, the carbonate minerals, pyrite, or other minerals.

It is not anticipated that any of the common rock-forming minerals found in the reservoir rock will be reactive with noble gas fission products (also see Appendices A and P). If air is injected with the fission products, there may be slight oxidation of a few of the mineral components, such as iron-rich minerals. Industrial experience in the injection of air into porous rock for various applications has not resulted in any known history of a formation deteriorating from this cause, but not a great deal of information is available on this subject.

2. Formation Waters

No chemical interaction between injected noble gas fission products and native formation waters is anticipated. Some gas will go into solution in these waters, however. This consideration is included in the section, "Avenues for the Escape of Gases (II.G)."

The breakdown of krypton-85 in the disposal formation will introduce rubidium-85, a daughter product, into this environment. It is anticipated that this substance will be similar to potassium in its chemical reactivity; potassium is often present in trace amounts in ground water.

3. Other Reactions and Interactions

Particularly when air is injected along with noble gas fission products, there are two potentially adverse reactions which must be considered: oxidation of down hole equipment and the promotion of bacterial growth within the reservoir formation near the well bore. Presumably, the former will be controlled by proper choice of materials; the latter may be controlled by the admixture of biocides.

F. Injection Pressures and Rates

In general, it will be desirable to hold injection pressures to the minimum required to permit injection of the desired volumes of gas. If krypton alone is injected, the required rates will be so small that pressure differentials on the order of 1 atm above normal reservoir pressure should be adequate, assuming nominal reservoir thickness and permeability ($t > 5$ m, $K > 20$ millidarcies).

At this point, the concept of relative permeability, an important consideration, is introduced. Permeability data for proposed reservoirs is normally obtained by core analysis techniques, employing single-phase flow (gas through a dry sample, water through a water-saturated sample, etc.). However, these conditions do not generally exist when gas is injected into subsurface porous rock, since almost invariably the subsurface formations are at least partially water-saturated.

Consider the injection of the first increment of gas into a water-saturated, porous sandstone under constant pressure. Initially, the rate of injection will be determined by the rate at which water can be displaced to make room for the gas, a condition of single-phase flow of water through water-saturated rock. However, by the time gas has actually been displaced into the porous structure, two-phase flow (gas through a partially water-saturated rock) begins to significantly control the rate of injection. Even though the viscosity of the gas is of the order of 1/100 that of the displaced water, by the time the water has been displaced some distance from the injection point, the rate of injection is not dominantly controlled by either the permeability of the rock to water nor the permeability of the rock to gas, but rather by the permeability of the partially water-saturated rock to gas. Depending on the pore size and pore geometry and on the degree of water saturation, this relative permeability may be only 10 to 15% of the permeability to single-phase flow. As gas injection continues and water saturation is reduced to the irreducible capillary saturation, the effective permeability may again approach the permeability to gas in a dried sample. In short, if constant injection and reservoir pressures are assumed, the greater the gas saturation in the reservoir, the higher the rate of injection. It is for this reason that natural gas storage operators customarily withdraw only a half (more or less) of the total injected gas, leaving the remainder as "cushion" gas or "base" gas.

This makes possible two modes of operation in disposing of radioactive noble gases in water-filled porous rock: (a) injection of the noble gas directly or (b) injection of air or another gas before injection of the radioactive gas.

If the noble gases are injected directly into a water-saturated rock, a greater pressure differential will be required. If, on the other hand, a nonhazardous gas is injected before the noble gases are, the pressures during injection of the radioactive gases can be minimized, and the total volume of gas stored will be increased. This choice of alternatives is probably only applicable to the injection of relatively small quantities of gas, e.g., separated krypton, since if krypton, xenon, and air diluent is injected, the total volume is sufficiently large to minimize the advantages of preinjection.

It is evident that the gas pressure at the point of entry into the reservoir formation must exceed the fluid pressure within this reservoir if injection is to proceed. The rate of injection will vary directly with this pressure differential. However, a number of factors limit the magnitude of the pressure differential which may be prudently and practically applied.

The normal lithostatic gradient is approximately 0.225 atm per meter. Injection pressures exceeding this level may "lift" the overlying rock, with consequent rupture and loss of reservoir integrity. In fact, studies of hydraulic fracturing pressures in oil wells indicate that some rock is under tensile stress and may fracture at gradients as small as 0.15 atm per meter. Since it is very difficult to determine the stress state of deeply buried rock, it is conservative practice to limit injection pressures to a figure well below this lower limit (0.15 atm). Customary practice is to use 10 to 15% above initial reservoir pressure or a gradient of 0.110 to 0.115 atm per meter and, in no case, to exceed one-half the measured cap rock threshold pressure values (see Appendix F). These arbitrary pressure limits have been exceeded in a few cases on an experimental basis, apparently without damage to the reservoir integrity [RUDD]; however, it seems unlikely that exceeding these customary limits would be considered acceptable practice in the disposal of fission products. In fact, an even more conservative limit on injection pressures might be appropriate.

Ideally, the injection and disposal pressure would be limited to the original formation pressure. However, this would be feasible only if the initial formation pressure is artificially lowered by withdrawing water prior to gas injection. This would be practical when dealing with krypton alone, but the costs of extracting and disposing of sufficient water to accommodate the mixture of noble gas fission products and air would probably be prohibitive under most circumstances. Except in the case of an isolated reservoir, such as a sand lens within relatively impermeable shales, both the degree and the period of lowered reservoir pressure are limited by the permeability of the reservoir and the rate at which inflowing water equalizes the pressure.

G. Avenues for the Escape of Gases

1. Leakage Mechanisms

There are four primary mechanisms by which gas may escape from a disposal reservoir. These are: leakage associated with the well itself; vertical or lateral migration through rock; migration through joints, fractures, or faults; and diffusion in water.

2. Leakage Associated with Wells

Unquestionably, the most frequent causes of leakage in aquifer gas storage are defects associated with the wells themselves. Defects or corrosion of casing, tubing, or items of down hole equipment may permit gas to escape directly up the well or into shallower rock formations. However, the incidence of leakage from such causes is relatively infrequent and comparatively easily remedied. A more common source of leakage at the well is imperfect cementation of the annulus between the casing and the bore hole. Such leaks may result from improper techniques at the time of cementing (such as failure to adequately clean the hole prior to cementing), from subsequent operations within the well

(such as perforating and hydraulic fractures during completion or cyclical stressing of the casing by pressure or temperature), or from age and deterioration of the cement. Such leakage at the well site is usually readily detected and can normally be repaired with comparative ease. In extreme cases the well bore might have to be abandoned because of the faulty repair techniques, but shutoff of the well would be accomplished.

3. Leakage Through Rock

As has been discussed at length in section II.B.2.a (and Appendix F), the effective impermeability of a cap rock usually is related to the threshold pressure effect, which is in turn a function of grain size and pore aperture diameter. Threshold pressures may be determined by laboratory studies of core samples. However, since core sampling frequency may be no more than one well per 65 hectares (160 acres) and is rarely more than one well per 40 hectares, very few representative samples are taken. It is unfortunately true that most sedimentary rock types are subject to considerable lateral variations; the lateral persistence of adequate cap rock may be a matter of geological interpretation.

Particularly when the cap rock formation is thin, it may tend to be absent locally due to either nondeposition or post-depositional erosion. Even where the cap rock formation itself is persistent, there may be intraformational facies changes which result in localized deterioration of cap rock integrity and as a result, upward or outward gas migration. Leakage of this nature is extremely difficult to detect until rather large volumes of gas have escaped. Remedial action other than withdrawing gas from the reservoir and abandoning the project is rarely possible.

4. Leakage Through Joints, Fractures, and Faults

Jointing and, to a lesser extent, fracturing and faulting, are commonplace in sedimentary rocks and must be anticipated in any underground disposal site. As suggested in an earlier section of this report, a desirable characteristic of a suitable cap rock is the ability to deform or seal such flaws. If such sealing does not occur, gas may escape from the reservoir at one or more points along the "crack." As in the case of leakage through the rock itself, escape of gas through joints, fractures, etc. is very difficult to detect and, unless the precise point of leakage can be established, virtually impossible to remedy.

5. Diffusion in Water

Some gas is invariably lost from all aquifer gas storage sites by diffusion. The rate of diffusion and degree of loss are controlled by the characteristics of the water-saturated rock adjacent to the gas bubble and by the rate of movement of water in these formations, as well as by temperature and pressure. The low porosity (typically less than 6%) and the tortuous interconnection of pore space characteristic of most cap rocks permit very minimal water movement and thus severely restrict diffusion of gas into the ground water at the enclosure or uppermost portion of the gas storage reservoir. However, where the bottom of the gas "bubble" is in contact with the underlying ground water (gas/water contact) in a highly porous and permeable reservoir, gas diffusion rates may be significant. This is particularly true when there is relatively rapid water movement through the reservoir.

Methane solubilities are reported to be 0.25×10^{-4} mole fraction at 25°C while krypton is credited with a solubility of 0.65×10^{-4} mole fraction at 25°C [WILHELM-1973B]. The solubilities of both are in the same order of magnitude. The gas storage industry has not been seriously concerned that a major loss or reduction of natural gas volumes within a storage reservoir would result from solution of natural gas in ground water, and to date no such loss has been reported. Since the solubilities in water of both gases are relatively similar, this suggests that no major krypton loss by solution should be expected.

H. Secondary Entrapment of Escaped Gas

The loss of some gas from the primary reservoir (not necessarily into the human environment), is commonplace in aquifer storage operations and must be anticipated if noble gas fission products are disposed of in the gaseous form. At the very least, there will be a limited loss of gas by diffusion. But even the loss of gas through incompetent cap rock or through fractures is not necessarily unacceptable in aquifer storage nor need it be in the disposal of radioactive gas.

1. Secondary Traps

It is common practice in the gas storage industry to select as a primary reservoir a formation which is overlain, above its cap rock, by another porous and permeable interval and a "secondary" cap rock. This secondary reservoir provides not only an observation zone in which leakage can be detected by pressure variations and by sampling of the reservoir fluids, but also a "gathering" zone from which any gas escaping from the primary reservoir can be scavenged and reinjected. An example of this is the well-known Hersher Storage Field in Kankakee County, Illinois, in which $1.43 \times 10^8 \text{ m}^3$, about 13% of the storage formation's total storage volume, is recycled each year [RZEPCZYNSKI].

2. Threshold Pressure and Gas Dispersion

Even in the absence of a secondary reservoir or gathering zone, minor quantities of gas escaping are dispersed and entrapped in superincumbent strata. Threshold pressures are not exclusively a phenomenon pertaining to the interface between reservoir and cap rock. To the contrary, the threshold pressure phenomenon exists at every point at which a gas tries to move through a water-filled pore aperture. Where the pore diameter is large, as in the case of coarse-grained sandstones, the threshold pressure may be only a few hundredths of an atmosphere, but even this may be sufficient to bar the entry of a small, discrete gas bubble. Thus, some gas may be retained in a stable condition--even in more porous and permeable rocks (see Appendix F).

The volume of gas not recoverable, from a natural gas storage reservoir varies greatly from one reservoir to the next. Conditions such as the rate of injection, rate of production, homogeneity of reservoir, etc. all influence the percentage of gas ultimately recoverable. "Base Gas" is defined as the volume of gas required within the storage reservoir to cause displacement of the working gas at acceptable rates. If one considers that the base gas within the storage field may amount to 40 to 60% of the total field capacity, perhaps only 40 to 60% of the base gas may be recovered. It becomes obvious

that threshold pressure could play a very important role in the ultimate disposal of noble gases and could also influence the volumes of gas that might be released if an accident were to occur.

As an additional illustration of gas entrapment by dispersion, consider that the geologic column in a sedimentary sequence invariably contains innumerable alternations of comparatively porous and comparatively dense lithologies. Each porous zone, even if only a few millimeters or centimeters thick, may be considered to be a "mini-reservoir" overlain by a "mini-cap rock." Although the volume of gas each such small reservoir will hold is limited either by the small volume of the reservoir itself or by the limitations of cap rock, the cumulative effect of many such zones permits the stable retention of rather large volumes of gas.

As a rule of thumb, one might consider that in relatively well consolidated sedimentary rocks (such as the Paleozoic rocks of the Upper Midwest), a conservative estimate of the retentive capacity of an "average" lithology is one cubic meter per thousand cubic meters of rock [RUDD]. Since the retained gas is compressed to the reservoir fluid pressure at its point of retention, the volume of retained gas at standard temperature and pressure can be estimated by multiplying the fluid pressure by one-tenth the mean depth (in meters) of the zone in which the gas is dispersed. (Thus, if gas is stored at a depth of 1500 m, and if it is assumed that the leaked gas is at a depth of 1500 m to 500 m, the mean pressure would be approximately 100 atm, and the estimated retentive capacity for gas at STP is calculated to be 10 m^3 per 1000 m^3 , or 1% of the total rock volume.)

Clearly, this calculation of the retentive capacity within the stratigraphic column is a guide or perhaps a conservative estimate of the "mini-entrapment" capabilities of a sedimentary sequence. It suggests that minor leakage may never reach the surface or that it will be ensnared before it reaches shallow fresh water aquifers. It suggests that the deeper in the section the gas is placed, the better the chance that complete entrapment will be accomplished.

3. Leakage Experience in the Gas Storage Industry

The gas storage industry is understandably reluctant to discuss leakage experience, and thus accurate estimates and documentation are all but impossible. However, it is generally known that a large proportion of gas storage fields leak, or have leaked, to some degree for one reason or another. On the other hand, whether because of the recycling of gas from gathering zones or because of the retentive capacity of superadjacent rock units, relatively few storage fields have leaked gas to the surface or near-surface environment. Those few instances in which gas has reached the surface or influenced potable water supplies have been largely due to problems with individual well completions or to improper interpretations of the geological environment surrounding the storage site. With monitoring wells being used increasingly to observe pressure changes or the occurrence of gas in up-hole formations, the incidence of gas leakage to the surface continues to decline.

4. Quantification of Leaks

No gas storage operation and certainly no gaseous fission product disposal operation would be initiated if a potential leak was known to exist. In other words, if site-specific studies revealed a leakage mechanism through which a predictable volume of gas might move at a predictable rate, consideration of that site would be cancelled. Leakage is not predictable, but in all but the most extreme cases, it is controllable if appropriate geological environments for storage and disposal are selected and fully utilized. The emphasis on project design must therefore be upon control, from initial exploration and site selection through completion of practice and operating procedures, rather than upon prediction. For example, overlying secondary reservoirs and secondary cap rocks may be considered mandatory, and such zones could be suitably equipped for observation and gas recycling if necessary.

The best case is of course zero leakage at least of the gas phase. When there is at the disposal site a limited area of stable geologic environment with appropriate conditions of enclosure, this is a realistic expectation.

The "maximum credible event" of leakage would be a well head failure or casing rupture which would allow direct venting of the reservoir, essentially a "puff" release. Between the two extremes, zero leak and total release, there is no satisfactory way of predicting probability, mechanism, or magnitude (see section VI.G, Radiological Dose Considerations, and Appendix D).

III. DISPOSAL IN ABANDONED OIL AND GAS RESERVOIRS

Apparent advantages of using abandoned oil or gas wells include: reduced exploration cost (site selection cost); more abundant geological and reservoir information; reduced cost of construction; and lower hydrostatic pressure.

Although there are these advantages, there are a number of serious difficulties to this approach to disposal or storage. First, it is important to recognize that designs of wells developed for oil and gas production and of wells developed for storage or disposal differ significantly. These differences are reflected in many ways, particularly in well completion practice. Generally speaking, a producing well is designed as a temporary facility to be used only for the anticipated productive life of the well (typically twenty to thirty years), and it is built under cost constraints imposed by the anticipated value of the commodity to be produced. The construction specifications are normally controlled by the lowest economic cost necessary to permit the recovery of the oil and gas in place. Further, production wells function primarily in the withdrawal mode, rather than the injection mode. That is to say, pressure differentials with respect to normal hydrostatic pressure at the point of injection become increasingly negative with the passage of time.

In contrast, a well designed for storage or disposal is customarily constructed with the expectation of a longer useful life and under a budget which reflects the value of the well as an integral part of the whole process and which is thus less restrictive. It is specifically designed to operate in the injection mode, at pressures at or above normal hydrostatic pressure over a prolonged useful life.

These differences in construction philosophy are reflected in differences in casing strength, casing diameter, the use of protective casing strings, corrosion protection, cementing program, and many other ways. Thus, it is not normally desirable to contemplate the use of old oil or gas producing wells for injection for either storage or disposal. This is particularly true because, by definition, a depleted oil or gas well will be near the end of its designed useful life and may be expected to be in poor mechanical condition. At best, extensive remedial work will be necessary that may prove more costly than drilling and completing a new well of appropriate design. Further, oil or gas wells are rarely isolated, i.e., with only a single well in a given reservoir. If a reservoir is to be used for storage or disposal, every well penetrating that reservoir must be reconditioned or plugged. Since reconditioning or plugging of old wells has not always proved to be fully reliable, each old well must be considered a potential avenue of gas leakage.

A further problem in the use of depleted oil or gas wells may lie in the unpredictable effects of stimulative treatments. The majority of oil and gas wells are acidized, shot, or hydrofractured one or more times in their productive lives. The spatial orientation and the magnitude of the effects of such treatments are largely conjectural. Although frequently unimportant during operation in the withdrawal mode (while flow is from the formation towards the well bore), such treatments can later result in great uncertainty about the actual location of injected fluids or gases into a reservoir.

Perhaps the greatest objection to the use of abandoned oil and gas wells may lie in conservation considerations. Most oil wells that are now abandoned have had no more than 40 to 50% of their total oil content produced. The pre-abandonment production of gas wells is generally somewhat higher--perhaps 60 to 70% of the gas being recovered. In both cases, however, a very significant quantity of hydrocarbons remains in place. A variety of advanced technology production methods seem to be regularly developed which, with increasing prices for oil and gas, may prove to be economically feasible. In view of the well-recognized probable shortages of both oil and gas, it seems generally unwise to use depleted fields for purposes which might prevent their reactivation and the recovery of additional hydrocarbon resources. However, since the volumetric requirements for the disposal of noble gas fission products are small, there may be individual cases of geologically isolated reservoirs penetrated by only a very few wells in which the future value of residual hydrocarbons may be judged to be less than the value of their use as disposal sites. The identification of such depleted reservoirs will require very detailed studies on a case-by-case basis and is not considered to be within the scope of this report. Such studies might well be included in regional site exploration programs. The history and present condition of a former gas-producing area, the Pasco Basin in the Hanford Reservation, is described in Appendix E together with a brief evaluation of its suitability for krypton disposal.

Historically, aquifer storage fields have provided very large reservoirs for natural gas. In Illinois, many have total capacities of $2.86^3 \times 10^9 \text{ m}^3$ of gas. It should be recognized that this might be somewhat related to the economics of exploration. Those gas storage reservoirs that formerly contained hydrocarbons are generally smaller (less volume), and they come in a wider variety of capacities. As an example, the old hydrocarbon reservoirs now being used for storage fall into the following numbers and categories: five

pools have a maximum capacity of 1.43×10^6 to 6.86×10^6 m³, three have a maximum capacity of 1.86×10^7 to 4.0×10^7 m³, three are from 1.0×10^8 to 2.0×10^8 m³, and the largest is 1.32×10^9 m³ [BUSCHBACH-1974]. The above example suggests that the volumes needed for the subsurface disposal of radioactive noble gases may be in the range of those offered by abandoned oil or gas fields.

IV. UNDERGROUND DISPOSAL OF NOBLE GASES IN SOLUTION

A. Introduction

In an effort to consider ways radioactive noble gases could be withheld from release to the atmosphere, this study included consideration of disposal of these nuclear fission products into a deep geologic environment. Previous sections herein discuss the potential for such disposal into aquifers and into abandoned oil and/or gas fields. This section considers the solubility of these gases in various liquids and the general feasibility of subsequent disposal by injecting the solutions into underground formations. It should be realized that the concept of subsurface gas disposal has not been adequately considered in the past, but at least in the United States, injection-disposal of liquids has become a fairly common practice. Probably more than 300 injection wells are presently disposing of industrial effluents in this manner [WARNER-1972].

It follows that once it has been determined that a noble gas can be dissolved in a suitable solvent, the "fairly common practice" of injection-disposal of liquid effluents becomes applicable in determining the feasibility of noble gas disposal in a solution.

B. History and Background of Injection Disposal Wells in the United States

The underground disposal of liquid waste has been a common practice associated with the production of petroleum and natural gas since early in this century. Large volumes of waste liquids, specifically brine, have been received by many thousands of disposal wells. These have been in common use at oil and gas fields throughout the United States. Still later, the practice of water flooding (injecting water into an abandoned field to flush unrecovered oil from a porous reservoir) added additional proof that porous subsurface strata could safely accept large volumes of liquids at modest pressures.

The underground injection of industrial effluents produced at processing or manufacturing facilities was not widely used prior to the early 1950's. By then, six wells were in operation. This number grew to 150 by 1969 and to over 246 by the mid-1970's [CLEARY, WARNER-1972]. Presently, there are one or more wells in at least 22 states. Texas alone has more than 70 wells.

The compositions and volumes, as well as the chemical and physical properties, of the effluents being handled by injection-disposal wells vary greatly. They include highly toxic substances, strong acids or bases, and weak brines. Organic materials such as ketones, cyanides, and numerous hydrocarbons are also injected.

Previously, deep-well injection of both high-level waste and low-level waste were discussed by Trevorrow, Warner and Steindler [TREVORROW]. They report that interest in deep well disposal of high-level wastes has generally diminished because too many serious problems are associated with this method, i.e., gas formation, heat loading, and the potentially dangerous impact if the waste escaped into the surface or certain subsurface environments. Disposal of low-level wastes by deep well injection would generally not be subject to the above disadvantages.

The referenced report discusses in detail several injection wells that dispose of radioactive wastes. One in Oklahoma was proposed to dispose of a major effluent from a uranium ore processing plant (Kerr-McGee Sequoyah facility).

Another well disposes of radioactive wastes associated with the Idaho Chemical Reprocessing plant. It is only 590 ft deep and disposes into the top of the 1,000 to 10,000-ft Snake River Plain aquifer. The effluent's principal radioactive component is tritium. Radioactivity averages 430 pCi/mL. This well does not conform to the generally accepted characteristics of a typical injection disposal well. It is very shallow, 590 ft deep, injects into a fresh water aquifer, uses a disposal horizon which is not hydrologically restricted by a confining stratum, was not subjected to normal licensing procedures, and utilizes a very heterogeneous disposal reservoir.

C. Potential Solvents

The literature was extensively searched for information concerning the solubility of krypton and xenon in various liquids, but the data was given for only a very limited range of conditions. The information obtained is listed in Appendix C (more specifically, in Table C-1).

In summary, the only information obtainable for xenon is its solubility in water, 0.78×10^{-4} mole fraction, a value fairly similar to that of krypton, 0.65×10^{-4} mole fraction (Table C-1).

By use of this solubility factor, the total annual krypton production of a 1500 Mg/y plant is calculated to be soluble in 42 m³ of water at 50°C and 200 atm (Table C-2). At atmospheric pressure, dissolution of this volume of krypton would require approximately 8500 m³ of water. Since some discrepancies are associated with the solubility relationships of krypton at high temperatures and pressures, it is quite possible that future experimental data will indicate these projections to be somewhat in error.

Since very little data was available concerning the solubility of xenon at high pressure, solubility calculations required that pressure relationships be assumed to be similar to those for krypton. Based on these assumptions and considering only the total annual xenon production, this volume could be dissolved in approximately 560 m³ of water at 200 atm and 50°C.

No calculations were made to determine the volumes of water needed to dissolve the entire volume of noble gases and air produced. The water volumes that would be required, estimated to be between 1 to 2×10^7 m³, are believed to be too great to justify consideration for injection-disposal.

The table of solubility of krypton in various organic liquids (Table C-1) covers a range of 23.0×10^{-4} to 111.2×10^{-4} mole fractions and generally suggests that the solubility becomes greater as the complexity of the organic liquid becomes greater.

If the liquid with the highest solubility, perfluorotributylamine (a complex fluorocarbon), were used as the solvent for the krypton, a volume of only 287 m^3 would be needed at one atmosphere (Table C-3), compared with that required for water solution (8500 m^3 at one atmosphere). Note that the solubilities in the hydrocarbons (the most common constituents of petroleum) are grouped in a range near 70×10^{-4} mole fractions, while an alcohol (2-methyl-1-propanol) is approximately 50 times more effective than water, dissolving 25×10^{-4} mole fractions (Table C-1).

It was not possible to determine solubility in brine or in fluids more nearly like formation waters. In these calculations, solubility in water has been assumed to approximate the solution capabilities of formation waters. However, it was stated earlier in this report that the waters in a disposal formation would most likely have a dissolved solids content in excess of 10,000 mg/L (T.D.S.). This assumption is reasonable and suggests that solubilities in fresh water may not be appropriately used.

D. General Geologic Requirements

The general geologic requirements for liquid disposal in injection-disposal wells are much the same as those required for underground gas storage. Reservoir, cap rock, and compatibility with formation chemistry are among the requirements, but an enclosing structure (a major requirement for underground gas storage) is not generally considered to be a prerequisite for liquid disposal wells. A detailed description of the geologic requirements is covered in [TREVORROW].

Upon injection into a disposal reservoir of gas dissolved in a liquid which is miscible with water, the threshold pressure effect no longer controls movement of the injected liquid, and all constraints are related to density and permeability.

On the other hand, if the gas is dissolved in a liquid immiscible in water, the threshold pressure effect continues to influence liquid movement, although its magnitude changes in proportion to the interfacial tension of the liquid with respect to water. Obviously, if the liquid in which the gas is dissolved is denser than water, the fluid will move downward and superadjacent cap rock will no longer be a factor. Instead, the configuration of a sub-adjacent formation may be the control.

The behavior parameters under reservoir conditions with regard to temperature and pressure and to injection pressures and rates are substantially the same as those for gas-phase disposal. The possible mechanisms of escape from the disposal reservoir are also much like those described for potential leakage mechanisms for underground gas disposal. Perhaps the principal difference might be that a gas leak has the potential of reaching the atmosphere, whereas a fluid waste leak would be expected to stay in the soils or the uppermost strata. Nevertheless, a fluid saturated with gas would tend to lose gas from

solution as it migrated towards the surface and moved into environments of lower pressure; thus, the impact of leaks from waste disposed of as gas or liquid would apparently be much the same.

V. DISPOSAL OF NOBLE GAS FISSION PRODUCTS ENTRAINED IN CEMENT GROUT

A. Introduction

No literature was found pertaining to mechanical entrainment of gases in cement grout. There are, however, numerous references about air entrainment in concrete. The latter condition is primarily accomplished by chemical means rather than mechanical methods.

B. Air-Entrained Concrete

Concrete consists of cement, sand, gravel, and water, whereas grout is essentially a neat cement that might contain minor additives as required. Grouts are used for a variety of purposes. Examples of these uses are: to stabilize foundations, to fill cracks and joints in concrete work or bedrock, and to seal oil well casings. An interesting comment pertaining to the entrainment of gas or air within grout states that, "While drying, hardened concretes or grout made with a gas-forming material decrease in volume an amount equal to or greater than for normal concrete or grout" [PORTLAND].

Air-entrained concrete, discovered in the mid-1930's, enhances the physical and chemical properties of concrete in several ways that relate to its use and "weatherability." Usually, the entrained gas in concrete, intended to be in the range of 3 to 7% is in the form of minute air voids of high specific surface area. Some cement mixtures may have air entrainments on the order of 10 to 30%, primarily for weight reduction, but these high-porosity concretes are suspected of having high permeability.

Air is apparently entrained only in the mortar fraction of the concrete; therefore, the ability of a concrete to hold air increases with greater mortar volumes. This ability also increases with decreasing aggregate size below 3.8 cm. Prolonged vibration of concrete should be avoided if air entrainment is to be preserved. Tests indicate that initial air entrainments of 4 to 5% can decrease to 3% after 15 s of vibration and to 2% after 2 min of vibration.

The watertightness of non-air-entrained cements increases as the ratio of the original water to cement decreases. Hence, we assume that higher water/cement ratios produce more permeable cements.

The above comments generally refer to air-entrained cement rather than grout, but no other related information appears to be available. It is anticipated that this data is the best basis for interim conclusions and estimates concerning the properties of cement grout in which noble gas fission products are entrained.

As air is entrained in cement grout, void percentage per unit volume increases and hence porosity increases, but there is no experimental evidence that permeability increases, although theory suggests that it would.

The technique involved in emplacing grout containing a radioactive admixture into hydraulically induced fractures in underground shales has been adequately described in numerous articles [DELAGUNA-1968A, DELAGUNA-1971, MCCLAIN]. This method has been used for the disposal of intermediate-level liquid wastes (ILW) at the Oak Ridge National Laboratory for about 8 y but has never been applied to gases. The designated references are but a few of those available, but none deal with the entrainment of noble gases within such grouts, and so this concept appears to be entirely new to the literature.

C. Radioactive Grout Emplacement

In a safety analysis report based in part on developmental studies and on actual waste injection experience, it was concluded that the injection of grout having radioactive material entrained in it is a safe procedure and not hazardous to the public [DELAGUNA-1971]. It follows that radioactive gas adequately entrained in a grout might also be safely disposed in this manner if:

1. The radioactive gas does not separate from the grout during hydraulic injection into the receiving formation.
2. The group does not have an inherent permeability or develop one as it ages, which would cause it to release entrained gases.
3. Radioactive gas which escapes from the grout does not migrate into regions that might adversely affect public health and safety.

It must be concluded from the description of the method of grout injection that the process of manipulating the grout through various pumps, hoses, pipes, and eventually into the formation would subject the grout to a major vibratory motion. Thus, it appears that gas entrainment could be substantially reduced by vibration inherent in the mechanics of the procedure. Presumably, such disentrained gas could be captured and recycled.

It has been mentioned in the related literature, and would be readily confirmed by individuals knowledgeable about hydrofracturing (or hydraulic fracturing), that although the desired mode for storage is to create horizontal fractures within a shale, vertical fractures ultimately form and there is virtually no method or course of action that can completely control fracture orientation. Since the very process of hydraulic fracturing can create vertical avenues for gas migration and since that gas has a low specific gravity, gas might have a ready avenue to migrate to where it is not wanted--into the human environment.

As indicated above, the ILW at Oak Ridge is mixed into a cement grout; it is pumped into hydraulically induced fractures in the Conasauga formation shales. Various admixtures (fly ash, attapulgite, illite, sugar, and a few others) are added and mixed into the grout. Some regulate the properties of the grout, while others are included for their high capacity to adsorb or otherwise retain various radioactive constituents introduced into the grout [MOORE].

Recent studies performed on the leach behavior of hydrofracture grout containing radioactive wastes [MOORE] indicate that grout can have low leach rates (comparable to those obtained for wastes incorporated into borosilicate glass) but that leach rates increase markedly as leachants are replaced more frequently. The latter suggests that actively moving groundwater in contact with a cement grout would greatly increase leach rates. Since various additives are specifically placed in the grout to retain certain radioactive constituents, it must be assumed that separation of radioactive materials and grout would commonly occur or at least would occur more frequently if these additives were not included.

D. Additional Considerations for Disposal of Gas-Entrained Grout Disposal

Presumably, any effort to dispose of gas in cement grout would need to be conducted in thick shales where the configuration and orientation of the grout sheet might be controlled by bedding. Also, because it is anticipated that gas retention within the grout will not be permanent, the geological setting should also provide for additional entrapment of escaping gas phase and for restraining groundwater so that flow does not leach the injected grout.

If gas entrainment in cement grout is found to be possible, it is assumed from the information obtained on air-entrained concrete that the gas-entrained grout would contain gas volumes of 4 to 6%. If the entire volume of noble gas and air were entrained in grout, the gas-entrained grout volumes would approach $2 \times 10^8 \text{ m}^3$. These volumes would be large compared with those for liquid disposal where wastes are mixed into grout in a 40 to 50% ratio [DELAGUNA-1968].

The annual krypton production postulated amounts to only 40 m^3 ; thus with a 5% entrainment, this quantity could be contained in 800 m^3 of grout.

The method of disposal by means of an injection well figuratively makes its own reservoir volume. Essentially, it forces grout between bedding planes and isolates it there. Often, it causes corresponding uplifts in the surface elevation of the land; thus, it seems to simply move storage space from the surface to the subsurface.

VI. DISPOSAL WELL DESIGN, OPERATIONS, AND RELATED CONSIDERATIONS

A. Introduction

All three methods considered for achieving deep well disposal of radioactive noble gas (i.e., as a gas, a liquid, or entrainment in a grout) would be subject to the laws and/or rulings which pertain to injection disposal wells, although disposal in a grout does not conform to the generally accepted prerequisites for classification as a disposal well. In the following discussion, these types of disposal wells are generally considered in relation to regulations, design, costs, suitable areas, and several other common topics. It will become obvious that the well itself is generally very similar for all modes of disposal.

B. Legal and Regulatory Aspects of Noble Gas Disposal

It may appear that the legal and regulatory aspects have been relegated to a brief section of this report, and thus it might be inferred that this topic is unimportant. This is definitely not the case. Legal status is all-important, for only with legal endorsement can underground disposal of radioactive noble gases be accomplished.

The radiological impact associated with future releases of radioactive noble gases from reprocessing plants will be of national or even international concern. The control of such releases and/or the storage of such materials logically falls into the hands of a national agency. Giving control of radioactive materials to the individual states would not be consistent with past events. Recently, numerous bills have been introduced proposing state control. Possibly another federal agency (i.e., EPA, HEW, etc.) may subsequently be handed the reins controlling this problem, but if this happens, the NRC or its successor in any subsequent agency reorganization would undoubtedly continue to contribute a major input to future decisions.

At present, the NRC has no formal guidelines for injection disposal of radioactive wastes, and all such considerations are handled on an individual basis [WARNER-1977]. Various state regulations and the opinions of state agencies and officials will, no doubt, influence decisions on specific radioactive disposal wells. Each well will be judged on its own merits.

It is believed that a radioactive gas disposal well design generally paralleling the various industrial disposal wells and specifically similar to those for disposing of hazardous wastes, would stand the best chance for approval by the NRC--that is, if any well is approved. It is time for a generic impact study for this method to be undertaken and for decisions to be made.

C. Conceptualized Disposal Well

A very generalized well design is depicted in Fig. 4. It is basically the design used for a gas storage well and also not at all unlike that used for a liquid injection disposal well. The chapter on design, construction, and operation of an injection disposal system in the report by [TREVORROW] describes these concepts in detail.

Several modifications or additions to this design might be advisable. The present arrangement depicting the well head above the ground surface might be changed to place it below ground surface for safety. Also, surrounding the well head, some additional protection against exposure to radioactivity might be designated. It was earlier suggested that some form of containment should surround the well head and other surface installations to restrict and collect any noble gases that might escape during the surface pumping operations; this is definitely recommended.

The equipment required for an underground natural gas storage compressor station is considered to generally meet the needs of a noble gas disposal well injection station. An associated control room operates monitor wells at various crucial positions along the natural gas storage structure. This same

NOTES: NOT TO SCALE.

CASING SPECS AND SIZES DEPENDENT
UPON SPECIFIC PROJECT DESIGN.

Fig. 4. Generalized Injection Well Design

function would be provided for the noble gas disposal station but the monitoring program would most probably be far more sophisticated and would provide a higher degree of protection for the public. In several ways, monitoring for radioactive gases would be somewhat easier than monitoring for methane.

Deciding to locate an acceptable subsurface disposal reservoir near a reprocessing plant or, alternatively, to site a reprocessing plant so that it has direct access to a suitable gas disposal well site would have two direct advantages: (1) the entire volume of krypton, xenon, and air off-gas mixture might be disposed of directly with a pipeline designed to carry this gas from the plant to the injection disposal well site; and (2) off-site transportation would not be necessary.

An off-site disposal well would require some unloading and storage facilities, security, and a variety of surface equipment associated with the transfer of gas from its container to the injection well. It is futile to dwell further on such design needs since they are greatly affected by many other associated variables: pressure of the gas container, composition of the gases, radioactive level of the container, volume of the container, injection pressures needed at the well head, pretreatment needed, etc. In each instance, the well design must satisfy the requirements of a certain site.

Design of the surface installation for disposal wells is by far the most complicated portion of the effort. The well bore is merely the pipeline that delivers the effluent to the storage reservoir. The function of the surface installation is to preheat the injected material to a specified temperature and to deliver this material to the bottom of the well bore at the desired temperature and pressure. Also, the operations end of the surface installation, the storage reservoir, must be monitored to ascertain if leakage is occurring and if leakage is controlled.

The conceptualized grout injection well has been thoroughly described in numerous articles describing the operations at Oak Ridge National Laboratory. It is evident [DELAGUNA, 1968A] that the design of the treatment and injection portions of the surface plant is a major effort in the program.

D. Cost Estimates for Underground Gas Disposal

Although Reist [REIST-1965, REIST-1967] generally outlined the basic potential for underground gas disposal, his cost estimates are greatly in error. Most of this error is not related to the cost of basic drilling and completion of such wells, but rather is related to the entire philosophy of exploration and development.

Reist recognized that the basic practices of underground gas storage would provide the technology needed for the underground disposal of radioactive gases, but apparently he did not adequately understand the concepts of exploration and development associated with underground gas storage. In fairness, it should be stated that Reist's work is generally good, and that it would be very difficult to acquire an understanding of exploration philosophy from the literature because little is written about it; however, knowledge of these concepts would have indicated that: (1) exploration costs must include the cost of all searching undertaken, and it must include even those developmental costs associated with testing of potential storage structures that do not

prove to be viable. In addition to subsurface geology, an exploration effort may include: a shallow well program, aerial photography, remote sensing, gravity and seismograph surveys, etc. (2) Developmental costs include all wells drilled to determine the size, volume, and integrity of the structure; these wells must also provide the means for a variety of testing and logging procedures. It is very roughly estimated that four wells would be required for a small gas storage field, but ten wells could easily be more appropriate. Some of the development wells would later be utilized for pump testing and subsequently for monitoring purposes.

Costs associated with the conversion of an abandoned oil or gas field would require a major overhaul of all wells drilled into the structure, and a major capital investment would be associated with the purchase of the structure and the hydrocarbon reserves in the ground.

In the following direct quotation from his study, [REIST-1965] indicates that he recognizes the basic principles of underground gas storage, but he also reveals that he has, perhaps inadvertently, forsaken these in his cost estimates of deep well disposal.

"In the cost analysis of a waste gas disposal field, . . . exploration and development costs must be included in the overall cost, at least for the first injection well. Hence, they are included in this estimate. However, for the deep disposal wells, an extensive testing procedure . . . would probably not be necessary because injection is into a saline aquifer with no nearby outcropping, and there are many impermeable barriers between the injection stratum and the ground surface."

His subsequent estimate did not include appropriate costs for exploration and development; yet without these steps, there can be no assurance that disposed gas would be contained in the disposal reservoir; therefore, such gas might be free to migrate laterally within the disposal reservoir.

In his later article [REIST-1967], Reist included more realistic cost estimates for exploration. These might be acceptable, but they are extremely low. The total estimates developed include only one well, the surface equipment, and again inadequately considers the total developmental costs required. Since exploration and development costs could easily exceed the cost of one well by a factor of ten or twenty, it is obvious that these earlier cost estimates are not reliable.

E. Disposal Well Costs

Most decisions involving a major course of action generally involve careful consideration of the associated economics. It is therefore essential to develop generalized costs covering the various possible options for deep well disposal of noble gas. Previous publications include detailed cost estimates for liquid disposal wells [TREVORROW] and grout injection wells [DELAGUNA-1968]; it was decided that only relative costs should be developed to avoid presenting misleading information.

Each alternative method of deep well disposal was found to have several major variables associated with it. Since the costs of these variables could

constitute over one-half of the total cost, it quickly became evident that inclusion or omission of one or more variables could cause a major change in the cost estimate.

Before the total estimated costs in Table 1 are compared, it should be emphasized that these costs do not consider all possible major variables. Drilling costs depend on depths, the specific area where the well is drilled, the distance from active drilling areas, etc. Any or all of these factors could double the figure presented or reduce it. In like manner, each factor listed can change. However, this table presents some general costs.

An aquifer field for gas storage would be expensive to find. Exploration costs would thus be high and development costs would also be high. However, such fields are generally quite large and might be expected to provide vast volumes of storage space for disposal wells. Numerous input wells drilled into such a structure might also mean that the volume injected into each well could be limited to a certain maximum. Such a practice might lower the effects of the major credible accident for a storage field.

Apparently, it is not possible to compare the cost of disposal in an aquifer with that in an abandoned oil or gas field since the cost of the latter cannot be determined. It is suspected that storage in an abandoned oil or gas field would be more economical, but this can only be proven by an active effort to purchase such a field. A field may have to satisfy the following criteria:

1. Field in low seismic risk region.
2. No active gas or oil production within the disposal reservoir or within the formations above or below this zone.
3. Low population count in the region.
4. Close to nuclear fuel reprocessing plants or near good transportation facilities.
5. Geologic structure known to be simple and favorable.
6. No history of drilling in the area before 1965.
7. A minimum number of wells per unit area.
8. Good atmospheric diffusion in the region.
9. Sufficient volume available for storage.
10. A relatively small surface area overlying the reservoir.

If such a field could be found, it would provide ideal containment. Several aquifer storage fields have been partially developed or have undergone extensive exploration expenses and then were ultimately abandoned.

Placement in a contained structure of gas dissolved in a liquid offers as a chief advantage that the maximum credible accident would release a much smaller volume of gas into the atmosphere although copious quantities of radioactive liquid might flow. Costs would be much the same as for gas disposal. Disposing of a gas dissolved in liquid in an unconfined aquifer, beneath an aquiclude, appears to offer the lowest-cost disposal. This method is not recommended for gases, but might be used for solutions of gases in water, oil, or fluorocarbons. Solvents for the gas which are immiscible in water and have a density similar to that of water would be best.

Grout costs (Table 1) are gross estimates based on costs for Oak Ridge grout disposal wells. Estimates do not attempt to reflect the mechanics and expenses of gas entrainment but only to present some basis of comparison with the other options.

F. Suitable Areas for Disposal of Noble Gas Fission Products

Synclinal sedimentary basins, as well as both the Atlantic and Gulf Basins (Coastal Plains), are reported to be particularly favorable areas for waste injection wells [TREVORROW]. Numerous reports on the specific capacities of selected basins and their potentials for accepting injected radioactive wastes were completed in the early and mid-1960 period. It would be inadvisable to summarize them all, since they have a wide range of conclusions and since the range of time, experience, and expertise devoted to them also varies greatly. Suffice it to say that the regional studies reported are very general. Although they can provide a general idea of the potential of an area, individual well studies truly answer the question of feasibility.

1. Areas for Liquid and Gas Disposal Wells

A review of the regional geology of the United States was performed to identify areas that appeared to be generally suitable for underground disposal of liquids or gas. Areas where extensive, thick sequences of salt water-bearing sedimentary rock are present in regional basins were considered the most favorable, and these are shown in Fig. 5. Not all of the known sedimentary basins within the United States are depicted, since disposal in many of the smaller basins may be found to be feasible only after detailed studies are made. Additional portions of the country that are not underlain by major sedimentary basins, but are adjacent to one, may be found to be suitable for disposal if the potential injection zones are (1) geologically suited, (2) hydrologically confined from fresh-water-bearing aquifers, and (3) at sufficient depth.

The Atlantic Coastal Plain and the Gulf Coastal Plain are a complex of numerous basins and platforms, some onshore, some extending beneath the ocean (Fig. 5). The generalized nature of this map is emphasized.

2. Areas for Disposal by Grout Injection

Generally, sites suitable for this method of disposal include the same sedimentary basins designated for the other forms of injection disposal (Fig. 5) except that more specifically, grout injection disposal requires that thick shale sequences be present. The suitable basins include, among others, the Appalachian, Illinois, and Michigan basins, much of the Gulf Coast,

Table 1. Relative Costs of Disposal Wells for Radioactive Noble Gases.
Costs do not reflect engineered safeguards necessary for control
of radiological hazards. Data from [TREVORROW, DELAGUNA-1968A].

Option	Site Adjacent to Reprocessing Plant or Nearby	Exploration Cost Per Site, Dollars	Drilling Cost Per Well, Dollars	Surface Equipment Cost Per Site, Dollars	Monitor Wells and Development Cost Per Site, Dollars	Minimum Estimated Cost, Dollars
<u>Gases</u>						
Into aquifer with a containing ^a structure	low probability	100,000 to 3,000,000 (Major)	150,000	150,000	600,000 to 1,500,000	1,000,000 to 6,000,000
Into abandoned oil or gas field	moderately possible	cost of field	150,000	150,000	450,000	750,000 plus cost of field
<u>Gas in Solution</u>						
Into aquifer with a containing ^a structure	low probability	100,000 to 3,000,000 (Major)	150,000	150,000	600,000 to 1,500,000	1,000,000 to 6,000,000
Into abandoned oil or gas field	moderately possible	cost of field	150,000	150,000	450,000	750,000 plus cost of field
Into aquifer with confining ^b aquicludes	highly possible	150,000 (Minor)	150,000	150,000	150,000	600,000
<u>Grout Disposal Well</u>						
Into shale beds	highly possible	50,000 (Minor)	100,000	500,000	500,000	1,150,000

^aContainment: Placement of waste material that precludes major movement.

^bConfinement: Placement of waste material such that essentially horizontal movement takes place beneath aquiclude.

Fig. 5. Major Sedimentary Basins of the United States

the Pierre and Mancos shale of Colorado and adjacent areas, much of the southern California coast (although the latter area may be eliminated due to seismic considerations), and many additional areas.

G. Radiological Dose Considerations

Any consideration of a repository for radioactive wastes requires analyses of the potential construction, thermal, radiological, and post-operational impacts to define the limitations imposed by these impacts on site selection and reservoir design. A preliminary analysis of the radiological limitations is presented below.

Appendix D presents information on the maximum radiological dose from routine and accidental releases of ^{85}Kr to a receptor 1300 m from the facility. The maximum continuous release corresponding to 15 mrem per year dose to the skin of the receptor is estimated to be 0.35 MCi of ^{85}Kr per year. The maximum accidental release corresponding to a lifetime emergency dose of 75 rem to the skin of the receptor is estimated to be 2.8 MCi of ^{85}Kr for an accident of less than 8 h duration and 17.9 MCi of ^{85}Kr for an accident of 8 h to 24 h duration.

The annual release limitation of 0.35 MCi of ^{85}Kr implies that the design of the reservoir must ensure that no more than this amount is released annually from all potential sources of ^{85}Kr within the facility.

The maximum accidental release limitations also impose constraints on the design of the facility. In this study, it is assumed that the maximum credible accident is a complete failure of the well head. The following are two calculations for estimating the maximum potential radioactive release from a well head failure and their implications.

1. Case 1

The following assumptions are made with regard to the reservoir in this case:

1. The reservoir is a right circular cylinder; height 10 m, radius 100 m.
2. The reservoir is located at a depth of 1000 m and has a pressure of 100 atm.
3. It has an effective porosity of 25% (taking into account water saturation).
4. It has a permeability varying from 50 millidarcy to 1 darcy.
5. The well has an inner diameter of 4 in.

Using these assumptions yields a reservoir volume (at STP) of about $7.85 \times 10^6 \text{ m}^3$, and a flow rate varying from 6.3 to $9.0 \text{ m}^3/\text{s}$ (at STP) if a well head failure should occur (see Appendix H). And if:

6. The reservoir contains 190 MCi of ^{85}Kr (the decay-corrected total radioactivity stored from a 1500 Mg per year processing facility between the years 1980 and 2000),

we obtain radioactivity release rates ranging from 153 to 218 Ci/s, using the previously determined volume and flow rates.

Therefore, for an accident that releases material at a flow rate of $9.0 \text{ m}^3/\text{s}$ (at STP), the duration of time the accident can last without exceeding the limit of the lifetime emergency dose of 75 rem to the skin is 3.56 hours, i.e.,

$$2.8 \times 10^6 \text{ Ci} / (218 \text{ Ci/s} \times 3600 \text{ s/h}) = 3.56 \text{ h.}$$

The corresponding figure for a release rate of $6.3 \text{ m}^3/\text{s}$ is 5.1 h.

2. Case 2

The following assumptions are made with regard to the reservoir in this case:

1. The reservoir is a right circular cylinder; height 5 m, radius 30 m.
2. The reservoir is located at a depth of 680 m and is at a pressure of 68 atm.
3. The reservoir has an effective porosity of 25% (taking into account water saturation).
4. The reservoir has a permeability varying from 50 millidarcies to 1 darcy.
5. The well has an inner diameter of 6 in.

Use of these assumptions would yield a reservoir volume (at STP) of $2.4 \times 10^5 \text{ m}^3$, and a flow rate varying from 3.4 to $19.0 \text{ m}^3/\text{s}$ (at STP) if a well head failure should occur. And if:

6. The reservoir contains 190 MCi of ^{85}Kr , we calculate that radioactivity release rates would range from 2.7×10^3 to $1.5 \times 10^4 \text{ Ci/s}$, using the previously determined volume and flow rates. Therefore, for an accident that releases material at a flow rate of $19.0 \text{ m}^3/\text{s}$ under these conditions, the duration of time an accident can last without exceeding the limit of the lifetime emergency dose of 75 rem to the skin is about 3 min. The corresponding figure for a release rate of $3.4 \text{ m}^3/\text{s}$ is 17 min.

An "initial stable flow rate" is taken to mean that rate of flow established after release of gas which has been compressed in the casing and equilibrium flow pressures have been established within the reservoir. The initial stable flow rate would, of course, decline with time. For example, it is estimated that a reservoir with an effective volume of $7.85 \times 10^6 \text{ m}^3$

(STP), and having a permeability of 1 darcy would blow down to a very minimal flow within less than two weeks if it experienced a complete well head failure, whereas if the initial stable flow rate were maintained throughout flow, this volume would be discharged in approximately 3.5 days.

In the discussion of potential leakage as a result of seismic activity (see section II.B.3.b), it is indicated that techniques and equipment common to natural gas production can be designed into the downhole casing program of the well so as to restrict gas flow if surface accidents should occur.

H. Transportation of Noble Gases

Several processes are available or at various stages of development which could be used to remove and collect ^{85}Kr from the off-gas of a nuclear fuel reprocessing plant. The two processes that appear most suitable for use at this time are cryogenic distillation and selective adsorption by liquid fluorocarbons. Other processes such as cryogenic adsorption on charcoal, adsorption on molecular sieves, absorption by liquid carbon dioxide, and precipitation as a clathrate have been considered. Either the cryogenic distillation or the selective adsorption process would recover at least 98% of the krypton and xenon released from processed spent fuel assemblies.

If required, transport of ^{85}Kr to the disposal site can be accomplished in appropriately designed shipping containers. A current shipping container design [NEILSON] has an outer diameter of 30 in. and is 84 in. long. This container weighs 5200 lb, and shielding is provided by about 2 in. of lead around its circumference and 4 in. of lead on its ends. The inner containment vessel has a capacity of about 1.9 ft³ and would hold about 75,000 Ci of ^{85}Kr in a mixture of radioactive and stable krypton gases, that is, six moles of ^{85}Kr at a pressure of 500 psig.

An alternative method of shipping or storing krypton in gas cylinders is under investigation. This alternative [ERDA] would utilize encapsulation of krypton in zeolite crystals. The encapsulation would be accomplished by diffusing krypton into the pore structure of a zeolite-type crystal at high temperature and pressure and then reducing the temperature and pressure. At the lower temperature, the entrapped krypton in the crystal would have insufficient energy to diffuse out of the crystal structure at an appreciable rate. A zeolite-filled container of the same volume as a 500-psig gas cylinder would hold a quantity of encapsulated krypton comparable to, but slightly less than, the quantity of compressed krypton in a gas cylinder.

All processing, storage, transport, and handling systems for ^{85}Kr should be designed to ensure leak-free operation, to contain and recover ^{85}Kr if leaks do occur, and to remove decay heat. Aside from capital and operating cost considerations, it is clear that substantial advantages would accrue to those alternatives which minimize the potential for leakage.

VII. CONCLUSIONS AND RECOMMENDATIONS

An article discussing underground disposal wells [DRESCHER] defines containment as placement of waste material that precludes movement, and confinement as placement of waste material such that movement takes place under restricted conditions.

Noble gases within a secure, porous reservoir which has the added feature of being a closed geologic structure and is overlain with an impervious cap rock might be defined as being in containment. Monitor wells for checking for gas escaping at the spill point of the structure and additional monitors guarding against radioactive materials finding pathways into the public environment would be added safeguards to this containment.

A fluid consisting of a noble gas in solution and injected into a saline aquifer (which is confined beneath an aquiclude and is perhaps overlain with several additional porous zones and additional cap rocks higher in the section) might be termed fluid in confinement. Monitor wells within the disposal reservoir and in several formations between the reservoir and fresh water aquifers, as well as within the aquifer, might be established to safeguard confinement. It is further assumed that this salaquifer would be one that characteristically displays a very low rate of groundwater movement.

It is concluded from this study that radioactive noble gases would be contained as gas in closed structures or confined within porous salaquifers below suitable cap rock. It is uncertain whether radioactive noble gas can be successfully entrained in grout and remain entrained during the injection phase. Related information suggests that entrainment may not be possible and that the volumes created by a grout injection method are too large to be handled in this manner. Experimentation should be carried out to determine directly whether the gas can be entrained in grout and can withstand injection pressures, and also whether the permeability of the hardened grout so formed would allow gas to escape from it.

The technology developed for the underground storage of natural gas and for injection disposal wells can provide adequate methodology for the underground disposal of radioactive noble gases.

A literature review revealed virtually no general investigations related to the disposal of noble gases in a gaseous state. Various publications written on such disposal pertained to research projects conducted at specific locations. A review of the costs predicted for such undertakings has uncovered errors of varied importance. Most cost estimates did not consider that a complete exploration and development program might be necessary--a program that could make the cost 10 to 20 times the cost of one completed well.

In some studies of the volumes necessary for containment of the gas and hence the various temperature rises and associated effects, it was not recognized that there would be two-phase flow within the reservoir and that only a portion of the rock porosity would be available for the storage of an introduced gas.

Several articles pertaining to the disposal of a liquid-containing radioactive material were very complete and presented a true description of the problem. Although numerous articles describe the disposal of radioactive fluids entrained in cement grout and injected into the bedded shales beneath a portion of the Oak Ridge National Laboratory grounds, very little information was applicable to any analysis of the problems that might be associated with entrainment of a radioactive gas in the cement grout and the subsequent injection of such grout into hydrofractured partings of a dense shale bed.

Underground gas disposal would require a closed capable structure, which is uncommon. In addition, abandoned oil or gas fields capable of being converted to receive radioactive noble gases are not readily available. It would be rare to find a suitable gas disposal structure under or immediately adjacent to a reprocessing plant since reprocessing plant sites have many specialized requirements; however, the most economical and probably the safest arrangement would be a gas disposal structure immediately adjacent to a nuclear fuel recovery plant.

It is generally concluded that if transportation of the noble gas to the well site is required, this can best be done by separating the noble gases from the air with which it was mixed at the fuel reprocessing plant. Yet estimations of heat loading in the disposal reservoir and dose rates for the maximum accident both suggest that some diluent--perhaps air or xenon--might be required to mitigate excessive heat loading and excessive dose rates.

Of the 386 pools being utilized for underground natural gas storage, 302 were dry gas fields, 18 were oil and gas fields, and 7 were oil fields. In addition to these, several former gas fields are now being used for the storage of helium; thus, it seems that the gas industry is making major use of abandoned gas fields for storing gas and of abandoned oil fields, to a lesser degree.

Pools which formerly contained commercial deposits of hydrocarbons have several distinct advantages: (1) their size, locations, and geology are fairly well known; (2) there would be virtually no exploration expense; (3) the potential disposal formation is probably at a reduced pressure (reservoir volumes would probably approximate those needed); (4) krypton has a relatively high solubility in oil; and (5) oil is immiscible with water and a pocket might be created within the formational water in which to inject the gas. The disadvantages include: (1) the possibility of many old and unrecorded wells in the area, and (2) radioactive noble gases would interfere with secondary recovery of petroleum products.

More work is needed on this subject to obtain more exact data on the solubility of krypton in petroleum, as well as the economics of dissolving krypton gas in fluorocarbons in which krypton is highly soluble. Further studies may show that krypton disposed of in an abandoned oil field may dissolve in residual oil in the reservoir.

The gas placed in a disposal formation would tend to become totally contained by other features besides the closed geologic structure. Such features entrapping a portion of the gas volume include the threshold effect, solution of gas in nonrecoverable water, migration to other storage zones beneath other cap rocks, solution within residual oil or gas saturations, diffusion, etc. After each has absorbed a portion of the "stored" gas, it is possible that a small fraction of the original volume would be capable of migrating.

Based on natural gas storage experience, it is anticipated that the retrievability of krypton from an underground storage site would not exceed approximately 50% of the total volume injected and, since small volumes are involved, might be substantially less. In part, retrievability would depend upon the values and the volumes of concurrent water production gas withdrawal.

Because the probability that the geological conditions can be interpreted is reduced drastically as a function of distance from the well bore, the safest disposal site is one involving the smallest volume of rock. This speaks strongly in favor of separating krypton from other gases and injecting krypton alone. Also, there are apparently great potential benefits in keeping the surface facilities small and simple. If it should be necessary to inject the gaseous fission products along with their air diluent, the site would almost certainly require a sizeable compressor station, after-cooler, etc., all of which are subject to breakdown and which might be exceedingly difficult to maintain and repair while observing radiation safeguards. In contrast, injection of krypton only could be accomplished with a laboratory-size high-pressure pump. The cost of the injection facilities as well as the energy costs, would be minimized by injecting only krypton.

When considering the underground disposal of radioactive noble gases, it is often concluded that only the krypton need be disposed of in this manner, and that perhaps cryogenic separation would be used to isolate the gases. Air would subsequently be released, and xenon would be released after it had been stored for a sufficient decay period.

Transport of krypton to a disposal well may be required, and this would appear to be a much simpler operation if only small volumes of krypton were handled. Yet consideration of the maximum possible accident (i.e., total well head failure) indicates that the volumes of ^{85}Kr released could be far in excess of the maximum dose allowed. Therefore, an engineered safeguard will be required to mitigate this problem. Such actions may include a small-diameter well, a containment for the well housing, down-hole valves for the injection well, the drilling of a new well, and plugging of the old injection well when a crucial volume is reached, etc. It is believed that a credible design can be conceived that would solve this potential problem.

From the consideration of liquid disposal (dissolution of noble gases in a solvent and subsequent injection disposal of this solution), some feasible ideas were obtained. Also, some previous options were found to be impractical. Because of very low solubilities of the gases, it would be unwise to attempt to dissolve the entire volume of noble gases and air; therefore, separation of the gases and solution of the krypton alone is the logical choice for the initial step. No attempt was made to estimate heat loading for liquid disposal since solubilities at elevated temperatures and pressures are somewhat doubtful. The possibility that krypton can be successfully dissolved in oil or one of the petroleum-related hydrocarbons and then injected into either a contained or confined disposal reservoir appears to be an especially fruitful idea. There is an excellent possibility that such an immiscible fluid might stay intact as a cylindrical area of invasion in a deep salaquifer. If this would be possible or if the solution were placed in an abandoned oil field, it is believed that good containment could be achieved. Several techniques could be used to lower the required injection pressures. Air could be pumped into the reservoir as a cushion to pump against, or water could be removed from the reservoir first to reduce pressure.

Relative costs of the various methods of liquid or gas disposal are difficult to compare. Great care should be taken when making cost estimates because the costs of exploration might amount to 20 or more times the cost of

a drilled and completed well. In like manner, the cost of surface installation and treatment and related equipment may be 20 times well costs. Therefore, it will be difficult to confidently discuss the cost of such installations until the other factors are being considered also.

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APPENDIX A.

PROPERTIES OF Kr, Xe, N₂, AND O₂ [GUERECA]

Property	Unit	Kr	Xe	O ₂	N ₂
Molecular Weight	AWU	83.8	131.3	32.0	28.0
Specific volume, 1 atm, 0°C	cm ³ /g	266.7	169.6	699.3	799.6
Expansion ratio, liquid to gas	vol/vol	643.6	518.9	777.0	666.4
Boiling temperature, 1 atm	°C	-153.3	-108.1	-183.0	-195.8
Melting temperature, 1 atm	°C	-157.0	-112.0	-218.4	-210.0
Critical properties, T _c	°C	-63.8	16.6	-118.4	-147.1
P _c	atm	54.3	58.0	50.1	33.5
d _c	g/cm ³	0.908	1.105	0.419	0.311
V _c	cm ³ /mol	92.24	118.8	76.4	90.08
Gas density, @ 1 atm, 0°C	g/L	3.75	5.90	1.43	1.25
@ 1 atm, 20°C	g/L	3.49	5.48	1.33	1.16
Viscosity, @ 1 atm, 25°C	micropoise	-	-	206.0	177.0
@ 200 atm, 25°C	micropoise	-	-	-	230.0
Dielectric constant (E) @ 25°C	(E-1) × 10 ⁴	7.68	12.38	-	-
@ 20°C, 1 atm	(E-1) × 10 ⁴	-	-	5.5	4.95
@ 16.5°C, 1 atm	(E-1) × 10 ⁴	-	-	929.0	-

APPENDIX B.

PRODUCTION AND PROPERTIES OF ^{85}Kr AND ^{85}Rb 1. Properties of Krypton

Krypton-85 is produced from the fission of uranium and/or plutonium. The yield of ^{85}Kr per fission event ranges from 0.0014 for ^{239}Pu fission to 0.0058 for ^{235}U fission. Krypton-85 is radioactive and has a half life of 10.73 y. Its two modes of decay are: 99.57% of the time to ^{85}Rb by emission of a 0.687-MeV electron, and 0.43% of the time to ^{85}Rb by emission of a 0.173-MeV electron and a 0.514-MeV gamma ray (ORNL-4923).

Krypton is a noble gas; it is colorless, tasteless, and in general, chemically inert. However, in recent years, it has been shown to enter into ionic or covalent bonding with highly reactive elements such as fluorine or oxygen. Considerable development has been directed towards processes for the removal of ^{85}Kr from the off-gas streams at reprocessing plants. The major processes include fluorocarbon extraction, cryogenic distillation, low-temperature adsorption on charcoal or silica beds, and the use of selective membranes and precipitation as a clathrate.

2. Properties of Rubidium

The daughter of krypton-85 is rubidium-85 (nonradioactive). The Encyclopedia of the Chemical Elements [HAMPEL] gives the following values for physical constants of rubidium:

Atomic number	37
Atomic weight (naturally occurring)	85.47
Crystal form	Body-centered cubic
Atomic radius	2.43 Å
Ionic radius	1.48 Å
Density:	
Solid	1.532 @ 20°C
Liquid	1.475 @ 39°C
Melting point	39°C
Boiling point	688°C
Latent heat of fusion	6.1 cal/g
Latent heat of vaporization	212 cal/g
Ionization potential of gaseous atoms	4.16 V
Electron work function	2.09 eV

Next to cesium, rubidium has the lowest ionization potential of all the elements. This property coupled with its low melting point and its low boiling point, high vapor pressure, large ionic radius, low density, and low electron work function makes the element useful for diverse applications. It is the second most electropositive element and the second most alkaline. The element

is widely distributed in the earth's crust and is more abundant than lead, copper, or zinc.

Rubidium is a very reactive metal with a silvery-metallic surface. Its properties are similar to those of the other alkali metals. Rubidium reacts vigorously with air and water, and this reactivity necessitates that special techniques be used to prepare and handle the metal. Rubidium forms four oxides-- Rb_2O , Rb_2O_2 , Rb_2O_3 , and Rb_2O_4 . The metal reacts with hydrogen and nitrogen to form rubidium hydride and nitride, respectively. Rubidium hydroxide can be formed by the reaction of the metal with water. Rubidium hydroxide is a very strong base.

The halides of rubidium can form double halide complexes with other metals, such as antimony, nickel, cobalt, thorium, bismuth, cadmium, manganese, mercury, etc. Polyhalides can also be formed. Many of the more common salts, such as the hydroxide, fluoride, and carbonate, are extremely hygroscopic and corrosive and must be handled in an appropriate fashion. A number of organic rubidium compounds are known. Rubidium will alloy with the other alkali metals, alkaline earths, bismuth, gold, antimony, mercury, and lead.

3. Monitoring for Krypton-85

Krypton-85 decays with a maximum beta energy of 0.687 MeV (whose range in air is about 5 ft) and with an average beta energy of 0.25 MeV whose range in air is about 20 in. (the rest of the energy is absorbed by the recoil nucleus). Instruments used for typical counting include liquid scintillation counters, thin window gas proportional counters, thin window Gieger Müller counters, and silicon surface barrier detectors. The choice of instrument is dependent on the needs of the investigator. Currently, for extremely low-activity environmental sample measurements, the gas flow proportional counter is the optimum choice.

A typical method for concentrating the gas and counting the subsequent betas is the one used by the Las Vegas National Environmental Research Center and is quoted herein: "Samples are collected using a compressor to pump air into a steel tank during a 20-minute period. The pressure attained in the tank is about 400 psi which results in about one cubic meter of air at STP. The mass of air is determined gravimetrically with an analytical balance which has an accuracy of ± 0.5 g. Samples are analyzed in the laboratory within 48 hours of collection. The analytical procedures . . . consist of collecting the krypton on a charcoal trap at liquid nitrogen temperature. Oxygen and nitrogen are purged off the trap with helium. The krypton, along with methane, argon, and traces of oxygen and nitrogen, is transferred to a six-foot molecular sieve column at liquid nitrogen temperature. The temperature is raised to -37°C and the gases are selectively eluted from the column. This process is repeated for better separation and the krypton is then transferred to a liquid scintillation vial. The krypton is dissolved in a toluene-based liquid scintillation solution . . . and counted for four 50-minute periods."

According to the IAEA, this technique has a minimum detection limit (MDL) of 1×10^{-12} $\mu\text{Ci/mL}$ or approximately 10^{-5} below the maximum permissible concentration (MPC).

APPENDIX C.

SOLUBILITY OF KRYPTON AND XENON IN WATER AND ORGANIC LIQUIDS

The solubility of krypton has been measured at near standard conditions for a remarkably wide range of liquid solvents. Our literature search, which was extensive although probably not complete, identified 28 different liquid solvents (including water) for krypton, but the only solvent data found for xenon was for water. These solubilities at one atmosphere and 25°C are listed in Table C-1 in the order of increasing mole fraction of gas dissolved.

Two different units of solubility are standard in current literature: one is the Ostwald coefficient, L , which is defined as the volume of gas per volume of solution; the other is the mole fraction, X_2 , of gas dissolved in the solvent. These terms and their interrelationship are defined below:

$$L = V_2/V_1$$

where:

V_2 = volume of gas dissolved

V_1 = volume of saturated solution (usually considered to equal the volume of the pure solvent)

The mole fraction solubility is related to L by:

$$X_2 = \left[\frac{RT}{LP_2V_1^0} + 1 \right]^{-1}$$

where:

V_1^0 = solvent molar volume

P_2 = vapor pressure

Mole fraction is defined as:

$$X_i = \frac{n_i}{n_T}$$

where:

n_i = number of moles of component i

n_T = total number of moles of all i components

In standard terminology and in this report, the solvent is given the subscript 1 and the solute (gas) is given the subscript 2:

X_1 = mole fraction of solvent

Table C-1. Solubility of Krypton and Xenon in Liquids

Solvent	Solvent Specific Gravity	Solubility at 25°C and 1 atm $X_2 \times 10^4$		Reference
		Krypton	Xenon	
water	1.0	0.65	0.78	[WILHELM-1977]
benzene	0.879	23.0		[EVANS]
2-methyl-1-propanol	0.801	25.7		[BATTINO]
toluene	0.867	33.5		[FIELD]
o-xylene	0.880	33.8		[BYRNE-1975]
cyclooctane		34.4		[WILCOCK]
m-xylene	0.864	36.2		[BYRNE-1975]
p-xylene	0.861	37.8		[BYRNE-1975]
cyclohexane	0.779	46.7		[WILHELM-1973]
c-1,2-dimethylcyclohexane		54.5		[WILHELM-1973]
hexafluorobenzene		56.0		[EVANS]
methylcyclohexane		57.3		[FIELD]
perfluorobenzene		59.0		[FIELD]
t-1,2-dimethylcyclohexane	0.764	59.7		[GELLER]
c-1,4-dimethylcyclohexane	0.767	60.0		[GELLER]
n-hexane	0.660	69.6		[WILHELM-1973]
n-octane		70.7		[WILHELM-1973]
2,3-dimethylhexane	0.724	70.8		[WILHELM-1973]
3-methylheptane	0.716	71.1		[WILHELM-1973]
n-heptane	0.684	71.2		[WILHELM-1973]
n-nonane	0.718	71.2		[WILHELM-1973]
n-decane	0.730	71.9		[WILHELM-1973]
2,4-dimethylhexane	0.708	73.4		[WILHELM-1973]
n-dodecane	0.766	75.5		[WILHELM-1973]
2,2,4-trimethylpentane	0.692	79.3		[WILHELM-1973]
n-tetradecane	0.765	80.1		[WILHELM-1973]
perfluoromethylcyclohexane		84.8		[WILHELM-1973]
perfluorotributylamine		111.2		[WILHELM-1973]

X_2 = mole fraction of gas dissolved in the solvent

n_1 = number of moles of solvent

n_2 = number of moles of gas dissolved in the solvent

$n_T = n_1 + n_2$

$$X_2 = \frac{n_2}{n_T}; \quad X_1 = \frac{n_1}{n_T}$$

$n_1 = n_T - n_2$

These relationships were used in this report to estimate the volumes of solvent required to accommodate the volumes of gas produced as wastes in a reprocessing facility. We chose to standardize on the use of mole fraction X_2 rather than L in this study.

In estimating reservoir conditions, a typical temperature of 50°C and a pressure of 200 atm were considered representative. These conditions were used when the appropriate data were available to make calculations at these nonstandard conditions. They represent a reservoir at a depth of approximately 2000 m (10 m depth per atmosphere of pressure, which is probably at the extreme end of the range of potential depths). Unfortunately, very little high-pressure data was found.

1. Solubility of Krypton and Xenon in Water

An excellent review of gas solubilities in water at low pressure was published in Chemical Reviews by Wilhelm [WILHELM-1977]. The temperature dependence of the solubility of krypton and xenon at one atmosphere, taken from that paper, is shown in Fig. C-1. The temperature dependence of solubility in terms of the Ostwald coefficient is also shown in Fig. C-2. In general terms, they indicate a decrease in solubility with increasing temperature. The solubility is reduced by about 30 to 40% when the temperature is increased from 25°C to 50°C.

Conversely, as the gaseous pressure (or partial pressure) increases, the solubility increases in direct proportion, in accordance with Henry's law:

$$X_2 = KP$$

where:

P = partial pressure,

K = Henry's law constant, mole fraction/atm

The Henry's law constant for krypton varies linearly with temperature over a wide range of temperatures [ANDERSON], but in the range from 25 to 50°C, it can be considered to be approximately:

$$K_{Kr} = 1.4 \times 10^{-5} \text{ mole fraction/atm}$$

Fig. C-1. Temperature Dependence of the Solubility of Kr and Xe in H_2O at 1 atm Partial Pressure. Source: [WILHELM-1977].

No Henry's law data for xenon and for the nonaqueous solvents were found; this may constitute an area for fruitful research.

2. Water Volume Required to Dissolve Annual Krypton Gas Production

If it is assumed that the total annual krypton production is 150 m^3 (at STP), the volume of water required to dissolve this volume of gas at 50°C and 200 atm can be calculated as shown in Table C-2.

This volume is an imprecise estimate due to a lack of knowledge of exact temperature effects but is a minimum quantity. If the temperature increases to 50° at the reservoir conditions and if this temperature increase

Fig. C-2. Temperature Dependence of the Ostwald Solubility of Krypton in H₂O

is not accounted for in the Henry's law constant used above, the required volume of water could increase by 30% from 42 m³ to approximately 55 m³.

At atmospheric pressure, the required water volume would be approximately 8500 m³, if the same Henry's law constant were applied. Considerable discrepancy is found between the Henry's law calculation at 1-atm pressure and the reported atmospheric solubility of krypton. This discrepancy was not resolved in this general evaluation.

Table C-2. Calculation of Water Volume to Dissolve Annual Krypton Production

Assumption

Production rate of Kr	= (90 L stable Kr + 8 L ^{85}Kr)/Mg
	= 98 L total Kr/Mg
Annual Kr production	= 147 m ³ @ STP (1500 Mg)
Henry's law constant for Kr	= 1.4×10^{-5} mole fraction/atm at temperatures of 25-50°C and pressures to 200 atm
V_1° , molar volume of H ₂ O	= 1.8×10^{-5} m ³
Mole fraction, X_i	= $\frac{n_i}{n_T}$,

where

$$n_i = \text{number of moles of } i$$

$$n_T = \sum n_i$$

and

$$n_T = \frac{n_2}{X_2}$$

Calculations

Component 1 is the solvent (water) and component 2 is the solute gas (krypton); at STP,

$$n_2 = \frac{(98 \text{ L/Mg}) (1500 \text{ Mg})}{22.4 \text{ L/mole}}$$

$$= 6562 \text{ moles Kr per year}$$

$$X_2 = KP$$

$$= (1.4 \times 10^{-5} \text{ mole fraction/atm}) 200 \text{ atm}$$

$$= 2.8 \times 10^{-3} \text{ mole fraction}$$

$$n_T = \frac{n_2}{X_2}$$

$$= \frac{6562}{2.8 \times 10^{-3}}$$

$$= 2.34 \times 10^6$$

(Contd.)

Table C-2. (contd.)

$$\begin{aligned}
 n_1 &= n_T - n_2 \\
 &= (2.34 \times 10^6) - 6562 \\
 &= 2.33 \times 10^6 \text{ moles}
 \end{aligned}$$

The volume of water required to dissolve the annual production of krypton at a pressure of 200 atm is:

$$\begin{aligned}
 V_{\text{H}_2\text{O}} &= n_1 V_1^\circ \\
 &= (2.33 \times 10^6 \text{ moles}) (1.8 \times 10^{-5} \text{ m}^3/\text{mole}) \\
 &= 42 \text{ m}^3
 \end{aligned}$$

Certainly, the calculations for high-pressure dissolution shown in Table C-2 are subject to considerable variation and should be considered approximations. The calculations are done with the assumptions of infinite dilution (fugacity = 1) and at the neglect of compressibility of both liquid and gas phases.

3. Water Volume Required to Dissolve Annual Xenon Production

No high-pressure data were found for xenon. However, the solubility parameters are similar to those for krypton, and if a similar pressure relationship is assumed, the total annual xenon gas production of 1500 m^3 could be dissolved in approximately 615 m^3 of water at 200 atm and 50°C .

These estimates are critically dependent upon the value used for Henry's law constant for each gas component.

4. Solubility of Krypton in Organic Liquids

The solubility of krypton in various organic liquids is shown in Table C-1, along with references. The values of X_2 probably are not as precise as the reported values indicate. One obvious indication of this is that both hexafluorobenzene and perfluorobenzene are entered although they are the same compound. The two entries represent experimental results by two investigators and there is a 5% difference in the reported values of X_2 .

More importantly, the solubilities of krypton in organic compounds are significantly greater than in water, by at least one order of magnitude. For alkanes, X_2 appears to increase with increasing molecular weight, up to a value of 8×10^{-3} mole fraction for tetradecane. Also, X_2 is apparently higher for a fluorinated compound than for its hydrocarbon homologue; for example, X_2 for hexafluorobenzene is 56×10^{-4} and for benzene, it is 23×10^{-4} . The highest X_2 found in the literature we surveyed was that of perfluorotributyl amine, $(\text{C}_4\text{F}_9)_3\text{N}$. Krypton is 171 times more soluble in this compound than in water.

Calculations similar to those for water may be performed for these organic liquids to estimate the required volumes for disposal of the annual krypton gas production. However, such estimates would be crude and perhaps misleading without some experimental data on pressure and temperature effects.

The fluorinated amine mentioned above, with X_2 equal to 111.2×10^{-4} at STP, is an example of compounds that might be considered for disposal solvents. At atmospheric pressure, approximately 300 m^3 of $(\text{C}_4\text{F}_4)_3\text{N}$ would dissolve the annual production of krypton (150 m^3). The calculations are shown in Table C-3.

Most of these potential organic solvents have a specific gravity lower than that of water and would tend to disperse upward in the reservoir if the appropriate conditions were available; however, most are also immiscible with water, and if injected into a "pocket" surrounded with water might tend to remain in this pocket rather than displacing the water surrounding it. This consideration may be worth additional investigation; yet it is also recognized that using halogenated organics would most likely cause increased environmental concern.

Table C-3. Calculation of Volume of Perfluorotributylamine
Required to Dissolve Annual Krypton Production

$$X_2 = 111.2 \times 10^{-4} \text{ (at } 25^\circ\text{C and 1 atm; see Table C-1)}$$

$$n_2 = 6696 \text{ mol of Kr}$$

$$n_T = \frac{n_2}{X_2}$$

$$n_T = 6.022 \times 10^5 \text{ mol (solvent + solute)}$$

$$n_1 = 5.95 \times 10^5 \text{ mol } (\text{C}_4\text{F}_9)_3\text{N}$$

$$\text{molecular wt of } (\text{C}_4\text{F}_9)_3\text{N} = 386$$

$$\text{wt}(\text{C}_4\text{F}_9)_3\text{N} = n_1 \text{ (m wt)}$$

$$= 2.3 \times 10^8 \text{ g}$$

If a liquid density of approximately 0.8 g/mL is assumed

$$V_1, \text{ volume of } (\text{C}_4\text{F}_9)_3\text{N} = \text{wt} \times \frac{1}{d}$$

$$= 2.87 \times 10^8 \text{ mL}$$

$$V_1 = 287 \text{ m}^3$$

APPENDIX D.

RADIOLOGICAL IMPACT

This section discusses two radiologically related issues. It considers the radiological dose which could result from (1) routine or (2) accidental release of ^{85}Kr to the atmosphere from operations associated with the deep geologic disposal of ^{85}Kr .

1. Meteorological Diffusion Factors

To calculate the meteorological diffusion factor (χ/Q) for routine releases applicable to a given site, the distance from the source to the receptor and the annual average wind speed and wind frequency distributions by stability classes have to be known. With these data, an "annually averaged χ/Q " can be calculated. Annually averaged χ/Q 's have been calculated for a ground level release for various distances in [GESMO]. See Fig. D-1 for geometry used in release calculations. Also given in GESMO is χ/Q for a distance of 1300 m from the source to the unrestricted area for a model reprocessing plant. The GESMO χ/Q of 1×10^{-6} s/m³ for 1300 m has been utilized in our calculations since no specific site has been designated at this time.

The meteorological diffusion factors for accidental releases have been calculated as a function of release height and the distance of the receptor from a reactor in NRC Regulatory Guides 1.3 and 1.4. These χ/Q 's have been utilized in our calculations for a ground-level release and a distance of 1300 m from the source point. For accidental releases lasting 0 to 8 h, the value is:

$$(\chi/Q) = 6.2 \times 10^{-4} \text{ (s/m}^3\text{)}$$

and for releases lasting 8 to 24 h, the value is:

$$(\chi/Q) = 9.7 \times 10^{-5} \text{ (s/m}^3\text{)}.$$

2. Radiological Doses

The "as low as reasonably achievable" dose limits from routine releases, which are applicable to the design of a reactor facility as given in Appendix I, 10 CFR 50 [USNRC-1976A], are 5 mrem/y to the whole body and 15 mrem/y to the skin of a person located at the site boundary. The ICRP-recommended maximum annual doses to the whole body and the skin of a person are 500 mrem/y and 1500 mrem/y, respectively. The guidance provided by 10 CFR 100 for the siting and design of a reactor facility in the event of an accident is that the lifetime accidental or emergency dose be limited to 25 rem to the whole body. In line with these limits, an emergency or lifetime accidental dose of 75 rem to the skin can be assumed. It turns out that the limits for the skin dose are more restrictive limitations than those for the whole body dose for krypton-85. Accordingly, doses of 15 mrem/y to the skin for routine releases and 75 rem to the skin for accidental releases have been assumed to be applicable to the releases associated with the deep geologic disposal of ^{85}Kr .

Fig. D-1. Geometry Associated with Release Calculations

Utilizing these skin dose limitations, the above-given meteorological diffusion factors, and the skin dose conversion factor for ^{85}Kr of $43.1 \text{ (mrem-m}^3\text{)/(Ci-s)}$ given by USNRC Regulatory Guide 1.109, maximum permissible releases can be calculated. This calculation yields 0.35 MCi as the maximum annual release which results in a skin dose of 15 mrem, 2.8 MCi as the maximum release in an accident of duration less than 8 h, and 17.9 MCi as the maximum release in an accident of duration more than 8 h but less than 24 h.

These limits imply that the disposal facility design would have to ensure that no more than 0.35 MCi ^{85}Kr is released annually under routine conditions, and that not more than 2.8 and 17.9 MCi of ^{85}Kr are released in the event of an upper limit accident of duration either (1) less than 8 h or (2) more than 8 h but less than 24 h, respectively.

If a ^{85}Kr disposal facility handled 16 MCi of ^{85}Kr per year (equivalent to the processing of 1500 Mg of fuel) starting in 1980, by the end of the year 2000, a total of 190 MCi of ^{85}Kr (including radioactive decay) would have been injected into the geologic media. If disposal were stopped at the end of the year 2000, the contained radioactivity would have to be isolated from the biosphere for at least ~ 100 y before it would decay below 0.35 MCi, the quantity which if released continuously during one year would result in a 15-mrem skin dose under the assumed conditions.

3. Thermal Consideration of Krypton-85 Disposal

Assuming that 16 MCi per year of krypton-85 are disposed of starting in the year 1980 with an inert krypton to krypton-85 volume ratio of 90 to 8, the heat generation rate per unit volume at STP and the cumulative volume disposed of at STP (including radioactive decay) are given in Table D-1 as a function of time. At year 2000, a total volume of about 2700 m^3 at STP (about 40 m^3 at 68 atm) of krypton generating about 800 kW would have been disposed of.

Depending on the shape and areal extent of the reservoir, this heat generation rate would imply a certain areal heat loading. For example, if the reservoir was a right circular cylinder of height 10 m and radius 100 m (See Case 1, Radiological Dose Considerations), then the heat loading would be 103 kW/acre.

Heat loading of a geologic formation may cause effects such as plastic or brittle deformation of the medium or alteration of the groundwater flow patterns. These effects and the ensuing consequences on the disposal reservoir cannot be predicted from the data currently available. However, it is likely that an upper limit of permissible heat loading exists for each of the geologic media being considered for the reservoir design; this limit should be determined. This limitation would have to be considered in site selection, in reservoir design, and in the determination of the ^{85}Kr dilution ratio with air (if any) to ensure that the disposal reservoir is not affected significantly by the resultant heat loading.

For example, if the heat loading limitation is estimated to be about 1000 kW per acre, then at the end of the year 2000, the area of the reservoir acceptable with respect to heat loading would have to be about 0.8 acre, which corresponds to a circle with a radius of about 32 m. The assumption that the reservoir is a right circular cylinder with a diameter of 32 m, height of 10 m, and an effective porosity of 25% implies a total reservoir volume of about 8040 m^3 . If reservoir pressure was about 68 atm, the total volume of ^{85}Kr injected by the year 2000 would be about 40 m^3 at this pressure. This implies that 40 m^3 of ^{85}Kr could be diluted with about 8000 m^3 of air at reservoir conditions.

Table D-1. Total Disposed Volume and Heat Density at STP for Krypton

Year	Cumulative Volume, m^3	Heat Density, kW/m^3
1980	130	0.49
1981	263	0.48
1982	394	0.47
1983	524	0.45
1984	653	0.44
1985	782	0.43
1986	911	0.42
1987	1039	0.40
1988	1167	0.39
1989	1294	0.38
1990	1421	0.37
1991	1547	0.36
1992	1674	0.35
1993	1800	0.34
1994	1925	0.34
1995	2050	0.33
1996	2175	0.32
1997	2300	0.31
1998	2425	0.30
1999	2549	0.30
2000	2673	0.29

APPENDIX E.

EVALUATION OF THE HANFORD (WASHINGTON) RESERVATION FOR
STORAGE/DISPOSAL OF RADIOACTIVE NOBLE GASES

In the course of this study, we were asked to make a specific evaluation of a former natural gas-producing area in the Pasco Basin, which lies within the Hanford Reservation.

1. History of the Rattlesnake Hills Gas Field

The first recorded gas production in this area was in 1913, when a well drilled to obtain artesian water encountered flowing gas at approximately 220 m depth. The gas was not immediately identified as natural gas, and the well flowed until 1919 when the Walla Walla Oil, Gas, and Pipeline Company was organized to develop the field. Approximately 18 wells were drilled to depths of over 1100 m [CULVER, HAMMER, GLOVER, BROWN-1969].

By 1936, an estimated $6.49 \times 10^7 \text{ m}^3$ of gas had been produced, of which approximately $2.86 \times 10^7 \text{ m}^3$ had been used commercially. At this time the low initial well pressures (typically 0.068-0.136 atm) had declined to zero and the wells were being pumped. By 1941, the field was essentially depleted, and in 1943 the field was abandoned upon takeover by the Manhattan Engineer Project.

Other gas shows are common in the area. In 1957, a well drilled in Sec. 34-11N-26E found gas at 190 m. The Wiltard Campbell well (Sec. 22-8N-29E) also encountered gas, as did many wells in the Cold Creek Artesian Field.

2. Character of Gas and Occurrence

As may be inferred from the fact that the gas was not immediately identified from its odor, its composition is essentially methane with associated atmospheric constituents (nitrogen, methane, carbon dioxide). It is clearly of biogenic origin. This is substantially confirmed by the presence of thin coal beds observed in drilling the Standard Oil Company Rattlesnake No. 1 well in 1957-58.

The geologic section is dominated by more than 100 identified basaltic lava flows within the 3200 m section which has been penetrated to date. The gas-containing reservoirs appear to be fractured lava flow beds.

Brown [BROWN-1969] observes:

"The presence of gas and coal demonstrate that (1) the Pasco Basin was sufficiently flat for shallow lakes, ponds and swamps to form, (2) significant periods of time elapsed between the emission of some flows to permit enough vegetation to accumulate to ultimately form coal, (3) the basalt flows in fact were emitted above sea level even in the upfolded Rattlesnake Hills."

The Rattlesnake Hills anticline from which the gas was produced has limited closure on the west flank, and the apparent cap rock, the clay-rich Mabton Bed, outcrops in that direction. It has been postulated [GLOVER] that

the entrapped gas had migrated up a fault; however, no faulting is evident from data currently available and a finite level of permeability in rocks underlying the Mabton cap rock must be considered probable.

3. Suitability for Disposal of Radioactive Noble Gases

The limited subsurface data for the Rattlesnake Hills area suggests that reservoir conditions are erratic and discontinuous and of generally unpredictable configuration. Further, the very low (less than 0.136 atm) original natural gas pressures, together with the apparent mechanism of gas accumulation, suggest the presence of some vertical permeability and/or lateral migration. Although it can be argued that the production of over 5.7×10^7 m³ of gas indicates that the reservoir has the capacity to accept a like amount of gaseous fission products, it might equally well be argued that this reservoir has leaked persistently and that the gas produced is only that portion of the gas "in transit" which was temporarily pooled beneath the Mabton. There is no prima facie case for integrity of the enclosure. In fact, the low pressure, limited closure, and outcrop of the cap rock on the west flank of the structure all raise questions about the permanence of gas entrapment.

Finally, the low pressure of the original gas accumulation implies that compression of injected gas can be only minimal, limiting the injection rates and requiring the use of large reservoir volumes.

Given these considerations, the existing gas reservoirs on the Hanford Reservation are considered to be of very questionable value for radioactive gas disposal. Further, during a visit to Battelle Northwest at Hanford, we were informed by Mr. P. A. Eddy of Rockwell International that another, potentially competitive, hazardous-waste underground disposal project is planned. For this project, substantial underground excavation would be done. The risk of placing injected gas in poorly defined underground reservoirs which may subsequently be penetrated by other workings seems unacceptably high.

Whether cased wells on the Hanford property should be used on an experimental basis as disposal receptacles for receiving pressurized containers of radioactive gas is under question. From our research on this field, it has been assumed that all known gas-producing wells were plugged and abandoned upon the takeover of the field by the Manhattan Engineer project in 1943. Subsequent drilling has been of an exploratory nature only, and although some surface or intermediate casing may remain in such wells, it is not believed that these wells would be accessible.

More important than the condition of the casing in pre-existing wells is the general conclusion that this area would not be suitable for disposal of radioactive noble gases. The absence of effective aquitards or aquicludes suggests that this would be a high-risk area for such subsurface disposal--unless pressurized containers are sealed below a "cap rock," any future break in the casing could result in leakage of gas to the surface.

APPENDIX F.

RETENTION OF GAS BY INTERFACIAL TENSION
(Threshold Pressure)

In the text are discussions of gas leakage, entrapment of gas beneath a cap rock or in various units of a stratigraphic column, and secondary entrapment of gas in a porous reservoir overlying a gas storage zone (see sections II.H.1 and II.H.2 "Secondary Traps" and "Threshold Pressure and Gas Dispersion"). All of these situations are related to threshold pressures and how they influence the retention of gas. The following example, Case A, considers the mechanism of interfacial tension between the reservoir and the cap rock. Case B discusses how threshold pressures can exist within a reservoir and can cause minor or "mine" entrapments.

CASE A AT THE CAP ROCK INTERFACE

where

p_c = capillary pressure

σ = interfacial tension

θ = contact angle

r_t = throat radius

Assume

$$d_t = 0.0002 \text{ cm}$$

$$r_t = 1 \times 10^{-4} \text{ cm}$$

$$p_c = \frac{2\sigma \cos\theta}{r_t}$$

Interfacial tension of water (σ) vs. gas ≈ 72 dynes/cm

Contact angle of water vs. silica ≈ 0

Therefore, $\cos \theta \approx 1$

$$\begin{aligned} \text{Simplifying } P_c &= \frac{144}{r_t} \\ &= \frac{144}{1 \times 10^{-4}} \\ &= 1.44 \times 10^6 \text{ dynes/cm}^2 \end{aligned}$$

$$1 \text{ atm} = 1.013 \times 10^6 \text{ dynes/cm}^2$$

$$\begin{aligned} \text{Therefore, threshold pressure (atm)} &= \frac{1.44 \times 10^6}{1.013 \times 10^6} \\ &= 1.42 \end{aligned}$$

In order to enter the pore throat in the cap rock, a pressure differential of >1.42 atm must exist across the aperture. This is to say that the "buoyancy" of the gas plus any pressure differential above hydrostatic should not exceed 1.42 atm if the gas is to be confined.

As a close approximation, gas column buoyancy in brine is 0.1 atm per meter of height. Therefore, a cap rock with pore apertures <0.001 mm in radius would confine a gas column of 14.2 m thick.

CASE B DISPERSED GAS (Minor Leakage)

When gas bubbles are discrete and discontinuous (insular saturation), the following (after [BERG]) applies.

For well-sorted, uniformly packed sands,

$$r_p = 1/2 (0.414 D_e)$$

$$r_t = 1/2 (0.154 D_e)$$

where

r_p = pore radius

r_t = throat radius

D_e = effective grain diameter

In the following equations,

p_w = density of water

p_g = density of gas

Z_o = maximum vertical height of bubble retained

$$\text{Capillarity : } \Delta P_c = 2\theta \left(\frac{1}{r_t} - \frac{1}{r_p} \right)$$

$$\text{Buoyancy : } \Delta P_b = Z_o (p_w - p_g)$$

$$Z_o (p_w - p_g) = 2\theta \left(\frac{1}{r_t} - \frac{1}{r_p} \right)$$

$$\text{Equilibrium: } Z_o = \frac{2\theta \left(\frac{1}{r_t} - \frac{1}{r_p} \right)}{g (p_w - p_g)}$$

where

Z_o = maximum vertical height of bubble retained

$$(p_w - p_g) \approx 1$$

$$\text{Simplifying } Z_o = \frac{144 \left(\frac{1}{r_t} - \frac{1}{r_p} \right)}{980}$$

Example: Case B(1)

Smaller grain size = 0.1 mm = 1×10^{-2} cm

Larger grain size = 0.2 mm = 2×10^{-2} cm

$$r_t \text{ (smaller grains)} = 0.5 \times 0.154 \times 1 \times 10^{-2} = 7.70 \times 10^{-4}$$

$$r_p \text{ (larger grains)} = 0.5 \times 0.414 \times 2 \times 10^{-2} = 4.14 \times 10^{-3}$$

$$Z_o = 144 \left[\left(\frac{1}{7.70 \times 10^{-4}} - \frac{1}{4.14} \right) \right] / 980$$

$$= 144 \left(\frac{1299 - 242}{980} \right) = \frac{1.52 \times 10^5}{980} = 155 \text{ cm} = 1.5 \text{ m}^*$$

* Note that these theoretical calculations assume perfect sphericity and sorting and no cementation. In actual rock, the Z_o may be significantly less.

Therefore, the finer grained "mini-cap rock" could retain a gas bubble 1.5 m thick.

The following calculations support the conclusions involving entrapment of dispersed gas as discussed within the section entitled, "Threshold Pressures and Gas Dispersion."

Example: Case B(2)

Grain size = 0.2 mm

$$= 2 \times 10^{-2} \text{ cm}$$

$$r_t = 0.5 \times 0.154 \times 2 \times 10^{-2}$$

$$= 1.54 \times 10^{-3}$$

$$r_p \text{ (prev. determined)} = 4.14 \times 10^{-3}$$

$$Z_o = 144 \frac{\left(\frac{1}{1.54 \times 10^{-3}} \right) - \left(\frac{1}{4.14 \times 10^{-3}} \right)}{980}$$

$$= 144 \frac{649 - 242}{980}$$

$$= 59.8 \text{ cm}$$

$$= 0.6 \text{ m}^*$$

Therefore, even without a cap of any sort, a fine sand can retain internally a gas pocket thicker than 1/2 m.

Note: For coarse sand ($D_e \approx 2 \text{ mm}$), the critical thickness is reduced to 0.6 cm.*

* Note that these theoretical calculations assume perfect sphericity and sorting and no cementation. In actual rock, Z_o may be significantly smaller.

APPENDIX G.

ILLUSTRATIONS OF GAS ENTRAPMENT

1) ELEMENTS OF ENCLOSURE

2) EFFECT OF TILTED ISOPOTENTIAL SURFACE

3) ENTRAPMENT AGAINST FAULT

APPENDIX H.

CALCULATIONS OF FLOW RATE OF FAILED WELL HEAD

The geometry and the parameters of the problem are shown in Fig. H-1. There are two applicable equations for the volumetric flow rates. The first equation gives the volume of flow from the reservoir into the well:

$$q_A = \pi \cdot k \cdot h \frac{p_e^2 - p_w^2}{\mu \cdot p_a \cdot \ln(r_e/r_w)} \times 10^{-4} \quad (H-1)$$

where

- q_A = flow rate at pressure (p_a), m^3/s
- k = permeability, darcies
- h = height of the reservoir, m
- p_e = reservoir pressure, atm
- p_w = pressure at the well at depth, atm
- μ = viscosity, cP
- r_e = outer radius of the reservoir, m
- r_w = well radius, m

The second equation (Weymouth formula) gives the relation of the flow rate to the pressure drop between the reservoir and the surface:

$$q_A = 28.0 \cdot d^{2.667} \sqrt{\frac{p_w^2 - p_a^2}{G - L_m} \cdot \frac{520}{T'}} \quad (H-2)$$

where

- q_A = flow rate, ft^3/h at STP
- d = diameter of the pipe, in.
- p_w = pressure at depth, psia
- p_a = pressure at surface, psia
- G = specific gravity of the gas with respect to air
- L_m = length of pipe, miles
- T' = temperature of the gas in absolute $^{\circ}F$

The flow rates obtained from these two equations must be equal. Therefore, the pressure (p_w) that gives this equality is the pressure at depth under transient conditions. Once this pressure is calculated, the flow rate can be calculated. For example (Case 1), it can be assumed that

$k = 0.05$ darcy	$r_e = 100$ m
$h = 10$ m	$r_w = 2$ in.
$p_e = 100$ atm	$G = 2.91$
$\mu = 0.0175$ cP	$L_m = (1000/1609)$ miles
$p_a = 1$ atm	$T' = 580^\circ\text{F}$

This yields a p_w of 68.44 atm, from which a flow rate of $6.3 \text{ m}^3/\text{s}$ can be calculated. The case of $k = 1$ darcy, with other parameters remaining the same, yields a p_w of 98.08 atm, corresponding to a flow rate of $9.0 \text{ m}^3/\text{sec}$.

Fig. H-1. Geometry and Parameters for Calculation of Flow Rates

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