Risk Assessment of Nonhazardous Oil-Field Waste Disposal in Salt Caverns[1]

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ABSTRACT

In 1996, Argonne National Laboratory (ANL) conducted a preliminary technical and legal evaluation of disposing of nonhazardous oil-field wastes (NOW) into salt caverns. Argonne determined that if caverns are sited and designed well, operated carefully, closed properly, and monitored routinely, they could be suitable for disposing of oil-field wastes. On the basis of these findings, Argonne subsequently conducted a preliminary evaluation of the possibility that adverse human health effects (carcinogenic and noncarcinogenic) could result from exposure to contaminants released from the NOW disposed of in domal salt caverns. Steps used in this evaluation included the following: identifying potential contaminants of concern, determining how humans could be exposed to these contaminants, assessing contaminant toxicities, estimating contaminant intakes, and calculating human cancer and noncancer risk estimates.

Five postclosure cavern release scenarios were assessed. These were inadvertent cavern intrusion, failure of the cavern seal, failure of the cavern through cracks, failure of the cavern through leaky interbeds, and a partial collapse of the cavern roof. Assuming a single, generic, salt cavern and generic oil-field wastes, potential human health effects associated with constituent hazardous substances (arsenic, benzene, cadmium, and chromium) were assessed under each of these scenarios.

Preliminary results provided excess cancer risk and hazard index (referring to noncancer health effects) estimates that were well within the U.S. Environmental Protection Agency (EPA) target range for acceptable exposure risk levels. These results led to the preliminary conclusion that from a human health perspective, salt caverns can provide an acceptable disposal method for nonhazardous oil-field wastes.

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INTRODUCTION

In a 1996 study, Argonne National Laboratory (ANL) determined that if salt caverns are sited and designed well, operated carefully, closed properly, and monitored routinely, they could be suitable for disposing of nonhazardous oil-field wastes (NOW) (1). This paper presents the findings of an assessment of the potential for adverse human health effects (carcinogenic and noncarcinogenic) resulting from exposure to contaminants released from caverns used for NOW (2). The assessment addressed risks after cavern closure and did not consider potential risks resulting from surface equipment emissions, surface oil leaks, or other equipment-related spills or accidents.

As discussed in the 1996 study, surface salt deposits occur in two forms in the United States: bedded salt and salt domes. Bedded salt formations occur in layers. These layers are separated by such nonsalt sedimentary materials as anhydrite, shale, and dolomite, which are generally of low permeability (3). Salt domes, on the other hand, are large, nearly homogeneous formations of sodium chloride (4). The depth of the salt can be greater than 10,000 ft, and the top width of the domes can be up to 2.5 miles (5). Starting in the early 1900s, salt domes were mined commercially using various leaching methods. Bedded salt was first used in the 1940s (6), and salt domes were first used in about 1951 to store liquefied petroleum gas (LPG). Stored products include propane, butane, ethane, ethylene, fuel oil, gas, natural gas, and crude oil. In 1975, the U.S. Department of Energy (DOE) acquired the rights to use several existing caverns to store crude oil as part of the Strategic Petroleum Reserve (SPR) (7). Private industry operates more than 1,800 caverns for storing liquid petroleum products, petrochemicals, and natural gas in the United States. Typically, these caverns are smaller than those used in the SPR and have an average diameter of about 115 ft (8). European countries have used salt caverns as containment sites for various wastes, but the use of salt caverns for waste disposal in the United States has been limited (1).

This paper addresses potential health impacts of disposing of NOW in domal salt caverns. The NOW would be solid or sludge-like tank bottom wastes (waste material from washing tanks, heater tanks, and stock tanks) consisting of accumulated heavy hydrocarbons, paraffins, inorganic solids, and heavy emulsions (9). Physically, these wastes consist of approximately 50% water, 15% clay, 10% scale, 10% corrosion products, and 5% sand (2).

Prior to disposal, a salt cavern used for NOW disposal would be filled with brine. Wastes would then be introduced as a slurry of waste and a fluid carrier (water or brine). This slurry would be pumped down one annulus, and brine would be removed from another. Once filled with waste, the cavern would be sealed, and the borehole would be plugged with cement.

Following closure, the pressure and temperature of the cavern would rise because of salt creep (10) and the addition of sensible heat (11). After closure, inadvertent intrusion or cavern failure could release NOW to the environment, thus potentially affecting human health. The remainder of this paper discusses the sources and probabilities of such events and their impacts on human health.

CONTAMINANTS OF CONCERN

The term "nonhazardous oil-field waste" does not mean that wastes generated during oil and gas exploration and production contain no hazardous contaminants. In 1988, the U.S. Environmental

Protection Agency (EPA) exempted oil and gas exploration and production wastes from regulation under the Resource Conservation and Recovery Act (RCRA) Subtitle C hazardous waste management program (53 FR 25446, July 6, 1988). The EPA provided this exemption because it found that other state and federal programs could protect human health and the environment more effectively; not because oil-field wastes are benign.

The EPA used its 1987 Report to Congress, "Management of Wastes from the Exploration, Development and Production of Crude Oil, Natural Gas, and Geothermal Energy" (the Report to Congress) as the basis for the above regulatory determination (12). In that report, the EPA identified contaminants of concern for produced water and drilling muds. Factors used to select these contaminants included median and maximum concentrations in waste samples; frequency of detection; mobility in groundwater; and concentrations at which human health effects, aquatic toxicity, or resource damage start to occur. Chemicals that the EPA screened as likely to dominate risk estimates included arsenic, benzene, boron, cadmium, and chromium (VI). In 1988, the EPA began evaluating the relative hazards posed by waste streams associated with exploration and production, including tank bottoms, oily debris, workover fluids, produced sand, emulsions, and others (9). It found that tank bottom wastes exceeded RCRA toxicity characteristics for benzene and lead.

Of the potential contaminants of concern identified in these two EPA studies (i.e., arsenic, benzene, boron, cadmium, chromium (VI) and lead), two were eliminated from further consideration in this study: boron because of its high probability of forming insoluble hydroxyborate compounds, and lead because of its low solubility, large distribution coefficient, and large retardation factor (3).

POSTCLOSURE RELEASE CONDITIONS AND CONCENTRATIONS

On the basis of several postclosure accident scenarios identified in a 1995 study of cavern failure modes for LPG (13), the current study examined the following five postclosure scenarios:

(1) Inadvertent intrusion by unintentionally drilling a new well into a closed cavern, which could produce a release of cavern fluid to the ground surface;

(2) Failure of the cavern seal due to increased pressure from salt creep and geothermal heating, which could release contaminated fluid to the groundwater at the depth of the cavern or at more shallow depths;

(3) Release of contaminated fluid through deep cracks to groundwater;

(4) Release of contaminated fluid through leaky interbeds or nonhomogeneous zones composed of higher-permeability material, which could contaminate deep groundwater; and

(5) A partial collapse of the cavern roof, which could release contaminated fluid to deep or shallow groundwater depending on the condition of the cavern seal (2).

Concentrations of contaminants of concern expected at the point of human exposure for each of these scenarios were calculated on the basis of (1) estimated initial concentrations at the release point, (2) hydrogeolgy of the area, (3) fate and transport mechanisms of the contaminants of concern, (4) release scenarios, and (5) probabilities that the releases would occur.

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Initial Concentrations

Conservative estimates of the initial concentrations for each contaminant (i.e., the concentrations of the contaminants leaving the cavern) for use in fate and transport modeling were made by using the maximum concentrations found in produced water (12, 14, and 15), drilling waste data using EPA's toxicity characteristic leaching procedure (TCLP) (12), and tank bottoms TCLP data (9). These estimates are 20.4 mg/L, 1.7 mg/L, 0.29 mg/L, and 0.85 mg/L for benzene, arsenic, cadmium, and chromium, respectively.

Hydrogeolgy

The analysis assumed a generic salt cavern located in the Gulf Coast of the United States. Depth to the water table was assumed to be on the order of about 20 ft (2). This shallow groundwater system is composed primarily of sands and is overlain and underlain by deposits of silt and clay. Where the silts and clays have been eroded, the shallow aquifer is unconfined; confined to semiconfined conditions exist where the clays and silt are present (16). Beneath the shallow groundwater system are other sequences of clays and silts, interspersed with beds of sand. The sandy areas constitute other potential groundwater aquifers that are predominantly confined (17). Recharge to the shallow groundwater system is derived from precipitation. The majority of recharge occurs in areas where the clay and silt are absent. Discharge of the aquifer is to surface waters and to underlying deeper aquifers.

In general, water quality decreases with depth. At the depth of salt deposits suitable for disposal, water quality is expected to be poor because of high salinity. In the vicinity of the cavern, hydrological properties are unlikely to favor rapid transport of contaminants (e.g., the groundwater velocity at the depth of the cavern is estimated to be less than 10 ft/yr). At shallow depths, the groundwater velocity is expected to be greater (about 100 ft/yr).

Fate and Transport

Fate and transport of the contaminants of concern were estimated on the basis of the chemical and physical characteristics of the constituents. These characteristics included density, solubility, volatility, distribution, retardation, and bidegradation. Qualitative results are summarized below.

Benzene

Benzene is very soluble in water, and, once in a groundwater system, it is very mobile. Because of bidegradation and volatilization, however, it would have a limited range of travel in an aquifer.

Arsenic

Because of the low solubility and large distribution coefficient of arsenic, its concentration and mobility in groundwater would be very low.

Cadmium

Because of the presence of iron in the tank bottom wastes, cadmium is likely to precipitate out as a hydroxide. Given the low solubility of cadmium hydroxide and its moderate rate of sorption, the mobility of cadmium in groundwater would be low.

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Chromium

Because of low solubility and high distribution coefficients, both trivalent and hexavalent forms of chromium are expected to have low concentrations and mobilities in groundwater. The mobility of the hexavalent form, however, is expected to be greater than that of the trivalent form.

Release Scenarios

Scenarios that could lead to the release of contaminants are summarized below. Estimated contaminant concentrations in the groundwater at the location of a potential receptor at a time 1,000 years in the future, a typical time horizon for risk analyses, are shown in Table 1.

Inadvertent Intrusion

For the inadvertent intrusion scenario, contaminated fluids would move quickly to the surface where, if not contained by the drilling blowout-prevention system, the fluids would most likely form a pool on the ground surface. The fluids would not penetrate very far into the ground and could be readily cleaned up. Because the volume of released fluid for this scenario would be small, the effects would be of very short duration, the liquid would not be potable, and such a spill would be quickly remediated, this scenario was eliminated from further analysis.

Release through the Cavern Seal

After disposal is completed, the cavern would be sealed and abandoned. At the time of sealing, the cavern would be filled mostly with solids and semisolids that are not fully compacted. Brine would remain between the top of the cavern and the top of the waste mass. The well bore would have cement plugs installed during cavern closure and abandonment. With time, the well casing may deteriorate because of the presence of brine in the vicinity of the caprock, or at the top of the cavern if a caprock is not present. The well casing would be expected to corrode and fail near the top of the cavern first. With additional time, the well casing would fail at shallower depths.

For a deep casing failure, fluid moving up the well bore would move into the deep aquifer and would be transported laterally. The presence of low-permeability beds at shallower depths would prevent vertical transport of the contaminated fluid to overlying aquifers and the ground surface. The extent and magnitude of contamination would depend on the hydrological properties of the material in the vicinity of the failed casing, the volume of fluid that is released, the duration of the discharge, and the transport properties of the contaminants. In the vicinity of the cavern, hydrological properties would unlikely favor rapid transport of the contaminants.

For the second alternative considered for this release scenario, the cavern seal is again assumed to fail; however, the well bore casing at the depth of the cavern is assumed to be intact. Contaminated fluid would then flow up the well bore and exit the casing at a failure point adjacent to a shallow groundwater aquifer. For a release to shallow groundwater, the concentrations would be larger than those discussed above because of shorter travel time. The concentration of benzene, however, would remain at 0.0 mg/L because of its biological degradation.

Release of Contaminated Fluid through Cracks

As the combined effects of thermal heating and salt creep lead to increasing pressure on the cavern, cracks might develop that would release fluid into the surrounding material, thereby

reducing the pressure in the cavern. The volume of fluid released would be a function of the pressure in the cavern, the volume of the cracks, and the crack pressure.

Release of Contaminated Fluid through Leaky Interbeds or Nonhomogeneous Zones

In this scenario, the cavern is assumed to have a leaky interbed or heterogeneity that allows communication with the outside environment. As the cavern pressure rises because of thermal effects and salt creep, fluid would be discharged into the interbed where it would be transported laterally under existing gradients. Eventually, the entire fluid volume of the cavern would be discharged into the surrounding material. The leaking brine would mix with in-situ water and would be transported downgradient. Because of this mixing, the contaminant concentrations would be reduced by dilution.

Concentration Estimates

Maximum exposure point concentrations for each of these scenarios were calculated using a one-dimensional analytical solution to an advection/dispersion transport equation that included adsorption, first-order degradation, and dilution (18). Contaminants were assumed to exit the cavern for a period of 250 years. The contaminant retardation factors for transport were derived from (a) their respective distribution coefficients (K_d) that were obtained from the literature — benzene - 0.62 mL/g (19), arsenic - 10 mL/g (20), cadmium - 3 mL/g (20), and chromium - 30 mL/g (20); (b) a bulk density of 1.7 g/cm³; and (c) a porosity of 0.10 (3). The duration of the source used in the calculations is expected to be conservative because of the self-healing ability of any cracks in the salt matrix and the small volumes of fluid that would be released. Table 1 summarizes the maximum contaminant concentrations associated with the specified release scenarios at a point 1,000 years in the future.

Release Probabilities

To assess human health risks the expected exposure-point concentrations and the probability that a given scenario would occur are required. Because there is no operational history for disposing of NOW in salt caverns, the probabilities of occurrence for the release scenarios described above are uncertain. Under the most optimistic conditions, no releases would occur, and the associated probabilities of occurrence would be 0.0. For the most pessimistic conditions, releases would always occur and the probabilities of occurrence would be 1.0.

To reduce the uncertainty in the range of the probabilities of occurrence, a questionnaire was distributed to experts in the field of salt caverns. The experts were asked to provide both a "best-" and a "worst-case" estimate of the probability of occurrence for each release scenario. In the context of this questionnaire and study, best case referred to the most likely probability of occurrence in the best judgment of the expert; worst case referred to the least likely probability of occurrence in the best judgment of the expert.

Responses from the expert panel were aggregated to form consensus values for each of the probabilities of occurrence using an arithmetic average to represent the aggregate value for the probabilities of occurrence.

Table 1 presents best- and worst-case aggregated probabilities of occurrence for each release scenario. The highest probabilities of occurrence were for a partial fall of the roof (0.10 and 0.29, respectively). The smallest probabilities of occurrence were for a partial roof fall with a cavern seal failure and release to a shallow aquifer (0.006 and 0.051, respectively), and a cavern seal failure with subsequent release to a shallow aquifer (0.012 and 0.040, respectively).

Exposure point concentrations for use in the risk assessment were calculated through multiplying the calculated exposure point concentrations (assuming the release scenario occurs) by the associated probabilities of occurrence. The results are shown in Table 1.

RISK ASSESSMENT

Human health risks associated with NOW contaminants released from a waste disposal cavern may be carcinogenic or noncarcinogenic. Carcinogens are believed to act via a "nonthreshold" mechanism of action; that is, a risk would be associated with any exposure level, no matter how small. Noncarcinogens are believed to act via a "threshold" mechanism of action; that is, there is some level of exposure (the threshold) below which the contaminant is unlikely to have an effect.

Human Health Hazards of NOW Constituents

Human health hazards associated with arsenic, benzene, cadmium, and chromium are summarized below. For all release scenarios, the potentially exposed population would be residents living near the salt caverns who drink the contaminated groundwater.

Arsenic

Arsenic exposure comes from ingesting contaminated water or soil or breathing contaminated air. High levels (60 ppm [mg/L]) in food or water can be fatal; lower levels can cause nausea, decreased production of blood cells, and abnormal heart rhythms. Arsenic is a known carcinogen; ingesting inorganic arsenic increases the risk of skin cancer and tumors of the bladder, kidney, liver, and lung. The EPA has set a maximum contaminant limit (MCL) of 0.05 ppm for arsenic in drinking water.

Benzene

The most common exposure route for benzene is inhalation, but it can also be ingested. Benzene is a known human carcinogen and is associated with leukemia. EPA has set a maximum permissible level of benzene in drinking water of five parts per billion (ppb) (5×10^{-9}) per day for a lifetime of exposure. The EPA has set a maximum contaminant limit goal (MCLG) of 0 ppb for drinking water and rivers and lakes.

Cadmium

Cadmium can accumulate in the human body from many years of low-level exposure. Exposure comes from eating foods that contain cadmium and from drinking contaminated water. On the basis of weak evidence of lung cancer in humans from breathing cadmium and strong evidence from animal studies, cadmium and cadmium compounds may be reasonably anticipated to cause cancer in humans. It is not known whether cadmium causes cancer from eating or drinking contaminated food or water. The EPA has set an MCL of 5 ppb for cadmium in drinking water.

Chromium

Human exposure to chromium comes from ingestion or inhalation. At high levels, all forms of chromium can be toxic, but chromium VI is more toxic than chromium III. Long-term exposure to high or moderate levels of chromium VI can damage the nose and lungs. Ingesting large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and death. Certain chromium VI compounds are known carcinogens. The Agency for Toxic Substances and Disease Registry (ATSDR) has insufficient data to determine if chromium VI or chromium III are carcinogens. The EPA has set an MCL for total chromium of 0.1 mg/L.

Characterization of Cancer Risks

To estimate the amount of contaminant actually received from drinking contaminated water, assumptions regarding intake rate, exposure time, exposure frequency, and duration of exposure to the water were made. Unless otherwise indicated, standard EPA default exposure factors are used in the assumptions (21). Using these assumptions and the exposure-point concentrations presented in Table 1, an intake rate for each contaminant of concern was calculated using the following equation:

$$I_i = \frac{C_i \times IR \times ET \times EF \times ED \times CF}{BW \times AT} \tag{1}$$

where

I_i = Intake of contaminant I;

C_i = Exposure point concentration of contaminant I, in g/L;

IR = Intake rate in L/d (assumed to be 2 L/d);

ET = Exposure time, in h/d (assumed to be 24 h/d);

EF = Exposure frequency, in d/yr (assumed to be 350 d/y);

ED = Exposure duration, in yr (assumed to be 30 y);

CF = Conversion factor of 1 d/24 h;

BW = Body weight of the receptor, in kg, (assumed to be 70 kg); and

AT = Averaging time, in d (for carcinogens, AT = 25,550 d (70 years); for noncarcinogens, AT = 365 d/y × ED)

Cancer risks were calculated for each contaminant and were then summed over all contaminants. Because the only exposure pathway for potential contaminant releases from a disposal cavern would be groundwater, the only exposure route is ingestion.

Human cancer risks associated with disposal of NOW in salt caverns were estimated for the release scenarios using the following equation:

$$R_i = I_i \times SF_i \qquad (2)$$

where

R_i = Risk from contaminant I;

I_i = Intake of contaminant I; and

SF_i = Slope factor for contaminant I.

Slope factors are used to estimate the toxicities of carcinogens; a slope factor is defined as a plausible upper-bound estimate of the probability of a response per unit intake of a chemical over a lifetime. Oral slope factors of 1.5 and 0.029 (1/mg/kg-day) were used for arsenic and benzene, respectively. These values were obtained from the EPA's Integrated Risk Information System (IRIS).

The total cancer risk for each release scenario is the sum of the individual cancer risks for all contaminants of concern. Because there are no slope factors available for cadmium and chromium, and the exposure-point concentration of benzene would be 0.0 for all of the release scenarios, the total cancer risk is equal to the risk estimate for arsenic. Total estimated cancer risks for each release scenario under best- and worst-case probability assumptions are presented in Table 2.

Noncancer Risks

The risk associated with a noncarcinogen is expressed as a hazard quotient, which is the intake of a particular contaminant divided by its reference dose (RfD). The RfD is the estimated "safe" dose for humans; when a hazard quotient exceeds 1, there is a potential for adverse noncarcinogenic effects. Hazard quotients are summed over contaminants and exposure routes to obtain an overall hazard index. However, for salt caverns, the only exposure route would be the oral pathway (ingestion of groundwater). For a single contaminant, I, the hazard quotient is calculated according to the equation,

$$HQ_i = \frac{I_i}{RfD_i} \qquad (3)$$

where

HQ_i = Hazard quotient from contaminant I,

I_i = Intake of contaminant I, and

RfD_i = Reference dose for contaminant I.

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Noncancer risks were estimated for each of the individual contaminants for the release scenarios assuming both best- and worst-case probabilities of occurrence. The results are shown in Table 2. All of the contaminants of concern have calculated hazard quotients much less than one. Even when the hazard quotients are summed for all contaminants in a given release scenario, the greatest hazard index under worst-case probability assumptions would be 6×10^{-5}. For best-estimate conditions, the largest total hazard index would be less (1.4×10^{-5}).

CONCLUSIONS

On the basis of assumptions that were developed for a generic cavern and generic oil-field wastes, the estimated human health risks for worst-case probability estimates are very low (excess cancer risks of between 1.1×10^{-8} and 2.0×10^{-17}), and hazard indices (referring to noncancer health effects) are between 6×10^{-5} and 1.0×10^{-7}. Normally, risk managers consider risks of 1×10^{-6} and less and hazard indices of less than 1 to be acceptable. For best-case probability estimates, the estimated excess cancer risks and hazard indices are lower.

These results should be viewed in the context of several considerations. First, this assessment did not address risks to workers at the cavern disposal site. Such risks would be comparable to or less than worker risks associated with hydrocarbon cavern storage operations. (For example, explosions are possible at hydrocarbon storage operations.) Also, the assessment did not determine whether any health effects would occur in the future; it only estimated potential cancer risks and noncarcinogenic effects. Third, risks were estimated only for contaminants for which toxicity values were available; the absence of a toxicity value does not indicate zero risk. Finally, the assessment was limited to human health effects produced by nonradioactive contamination; it did not address the possible ecological risks associated with salt cavern disposal, nor did it estimate risks associated with naturally occurring radioactive materials that may be included in oil-field wastes.

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REFERENCES

1. Veil, J., Elcock, D., Raivel, M., Caudle, D., Ayers, R.C., Jr., and Grunewald, B., 1996, "Preliminary Technical and Legal Evaluation of Disposing of Nonhazardous Oil Field Waste into Salt Caverns," prepared for the U.S. Department of Energy, Office of Fossil Energy by Argonne National Laboratory, Washington, DC, June .

2. Tomasko, D., Elcock, D., Veil, J., and Caudle, D., 1997, "Risk Analysis for Disposing of Nonhazardous Oil Field Wastes in Salt Caverns," prepared for the U.S. Department of Energy, Office of Fossil Energy by Argonne National Laboratory, Argonne, IL, May.

3. Freeze, R.A. and J.A. Cherry, 1979, Groundwater, Prentice-Hall, Inc., Englewood Cliffs, NJ, 604p.

4. Pfeifle, T.W., Vogt, T.J., and Brekken, G.A., 1995, "Correlation of Chemical, Mineralogic, and Physical Characteristics of Gulf Coast Dome Salt to Deformation and Strength Properties," Solution Mining Research Institute Project Report 94-0004-S, January.

5. Chilingarian, G.V., Robertson, J.O., Jr., and Kumar, S., 1989, Surface Operations in Petroleum Production, II, Elsevier, New York, NY, 562p.

6. Querio, C.W., 1980, "Design and Construction of Solution-Mined Caverns for LPG Storage," presented at the Solution Mining Research Institute's Fall Meeting, Minneapolis, MN, October.

7. Testa, S.A., 1990, Geological Aspects of Hazardous Waste Management, CRC Press, Boca Raton, FL, 537p

8. Hickerson, R., 1995, "Oilfield Waste Disposal in a Salt Cavern," in Proceedings of the Annual Underground Injection Control and Ground Water Protection Forum, Kansas City, MO, October.

9. EPA, 1994, "Associated Waste Report: Crude Oil Tank Bottoms and Oily Debris," U.S. Environmental Protection Agency, Office of Solid Waste, Special Waste Branch, Washington, DC, March.

10. Bishop, W.M., 1986, "Long-Term Disposition of SPR Caverns Not Used for Petroleum Storage, A Draft Plan," unpublished report, October.

11. Tomasko, D., 1985, "A Numerical Model for Predicting the Thermal Behavior of Caverns in the Strategic Petroleum Reserve," dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, the University of New Mexico, Albuquerque, New Mexico.

12. EPA, 1987, "Report to Congress Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy," Volume 1 of 3, EPA/530-SW-88-003, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, December.

13. Radian Corporation, 1995, "Risk Assessment of Converting Salt Caverns to Natural Gas Storage Final Report," GRI-95/0307, prepared for the Gas Research Institute, Austin, TX, October.

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14. EPA, 1993, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Subcategory of the Oil and Gas Extraction Point Source Category," U.S. Environmental Protection Agency, Office of Water, Washington, DC, EPA 821-R-93-003, January.

15. SAIC, 1994, "Statistical Analysis of Effluent from Coastal Oil and Gas Extraction Facilities," prepared by Science Applications International Corporation, Falls Church, VA, for the U.S. Environmental Protection Agency, Office of Science and Technology, September 30.

16. Hanor, J.S., 1993, "Effective Hydraulic Conductivity of Fractured Clay Beds at a Hazardous Waste Landfill, Louisiana Gulf Coast," Water Resources Research, 29(11): 3691-3698.

17. Capuano, R.M. and Jan, R.Z., 1996, "In-Situ Hydraulic Conductivity of Clay and Silt-Clay Fluvial-Deltaic Sediments," Texas Gulf Coast, Ground Water, 34(3):545-551.

18. Tomasko, D., 1997, "An Analytical Model for Predicting Transport in a Coupled Vadose/Phreatic System," Argonne National Laboratory, Argonne, IL, ANL/EAD/TM-68, May.

19. Lyman, W.J., Reidy, P.J., and Levy, B., 1992, Mobility and Degradation of Organic Contaminants in Subsurface Environments, C.K. Smoley, Inc., Chelsea, MI, 697p.

20. Baes, C.F. and Sharp, R.D., 1983, A Proposal for Estimation of Soil Leaching and Leaching Constants for Use in Assessment Models," Journal of Environmental Quality, 12(1):17-28.

21. U.S. EPA, 1991, "Human Health Evaluation Manual, Supplemental Guidance: Standard Default Exposure Factors," OSWER Directive 9285.6-03, Office of Solid Waste and Emergency Response, Washington, D.C., March 25.

Table 1. Estimated Contaminant Concentrations

Scenario	Contam-inant	Initial Conc.	1,000-Year Conc.	Probability of Scenario Occurrence		Exposure-Point Concentration	
				Best Case	Worst Case	Best Case	Worst Case
Cavern seal fails, releases fluid at depth	Benzene	20.4	0.0	0.031	0.12	0.0	0.0
	Cadmium	0.3	4.1×10^{-8}	0.031	0.12	1.3×10^{-9}	$.9 \times 10^{-9}$
	Arsenic	1.7	9.5×10^{-15}	0.031	0.12	3.0×10^{-16}	1.1×10^{-15}
	Chromium	0.9	7.7×10^{-15}	0.031	0.12	2.4×10^{-16}	9.2×10^{-16}
Cavern seal fails, releases to shallow aquifer	Benzene	20.4	0.0	0.012	0.040	0.0	0.0
	Cadmium	0.3	1.0×10^{-6}	0.012	0.040	1.2×10^{-8}	4.0×10^{-8}
	Arsenic	1.7	1.2×10^{-5}	0.012	0.040	1.4×10^{-7}	4.8×10^{-7}
	Chromium	0.9	1.2×10^{-8}	0.012	0.040	1.4×10^{-10}	4.8×10^{-10}
Release from crack	Benzene	20.4	0.0	0.022	0.120	0.0	0.0
	Cadmium	0.3	4.1×10^{-8}	0.022	0.120	9.0×10^{-10}	4.9×10^{-9}
	Arsenic	1.7	9.5×10^{-15}	0.022	0.120	2.1×10^{-16}	1.1×10^{-15}
	Chromium	0.9	7.7×10^{-15}	0.022	0.120	1.7×10^{-16}	9.2×10^{-16}
Release from leaky interbed	Benzene	20.4	0.0	0.022	0.120	0.0	0.0
	Cadmium	0.3	1.6×10^{-8}	0.022	0.120	3.5×10^{-10}	1.9×10^{-9}
	Arsenic	1.7	6.1×10^{-13}	0.022	0.120	1.3×10^{-14}	7.3×10^{-14}
	Chromium	0.9	5.2×10^{-13}	0.022	0.120	1.1×10^{-14}	6.2×10^{-14}
Roof fall, release at depth	Benzene	20.4	0.0	0.100	0.290	0.0	0.0
	Cadmium	0.3	4.1×10^{-8}	0.100	0.290	4.1×10^{-9}	1.2×10^{-8}
	Arsenic	1.7	9.5×10^{-15}	0.100	0.290	9.5×10^{-16}	2.8×10^{-15}
	Chromium	0.9	7.7×10^{-15}	0.100	0.290	7.7×10^{-16}	2.2×10^{-15}
Roof fall, cavern seal failure, release at depth	Benzene	20.4	0.0	0.062	0.163	0.0	0.0
	Cadmium	0.3	4.1×10^{-8}	0.062	0.163	2.5×10^{-9}	6.7×10^{-9}
	Arsenic	1.7	9.5×10^{-15}	0.062	0.163	5.9×10^{-16}	1.6×10^{-15}
	Chromium	0.9	7.7×10^{-15}	0.062	0.163	4.8×10^{-16}	1.3×10^{-15}
Roof fall, cavern seal failure, release at shallow depth	Benzene	20.4	0.0	0.006	0.051	0.0	0.0
	Cadmium	0.3	1.0×10^{-6}	0.006	0.051	6.0×10^{-9}	5.1×10^{-8}
	Arsenic	1.7	1.2×10^{-5}	0.006	0.051	7.2×10^{-8}	6.1×10^{-7}
	Chromium	0.9	1.2×10^{-8}	0.006	0.051	7.2×10^{-11}	6.1×10^{-10}
Roof fall, release through leaky interbed	Benzene	20.4	0.0	0.062	0.163	0.0	0.0
	Cadmium	0.3	1.6×10^{-8}	0.062	0.163	9.9×10^{-10}	2.6×10^{-9}
	Arsenic	1.7	6.1×10^{-13}	0.062	0.163	3.8×10^{-14}	9.9×10^{-14}
	Chromium	0.9	5.2×10^{-13}	0.062	0.163	3.2×10^{-14}	8.5×10^{-14}

Table 2. Estimated Cancer and Noncancer Risks

Scenario	Cancer Risks		Noncancer Risks	
	Best Case	Worst Case	Best Case	Worst Case
Cavern seal fails, releases fluid at depth	5.4×10^{-18}	2.0×10^{-17}	7.0×10^{-8}	2.6×10^{-7}
Cavern seal fails, releases to shallow aquifer	2.6×10^{-9}	8.7×10^{-9}	1.4×10^{-5}	4.5×10^{-5}
Release from crack	3.8×10^{-18}	2.0×10^{-17}	4.8×10^{-8}	2.6×10^{-7}
Release from leaky interbed	2.4×10^{-16}	1.3×10^{-15}	1.9×10^{-8}	1.0×10^{-7}
Roof fall, release at depth	1.7×10^{-17}	5.1×10^{-17}	2.2×10^{-7}	6.4×10^{-7}
Roof fall, cavern seal failure, release at depth	1.1×10^{-17}	2.9×10^{-17}	1.4×10^{-7}	3.6×10^{-7}
Roof fall, cavern seal failure, release to shallow depth	1.3×10^{-9}	1.1×10^{-8}	6.6×10^{-6}	6.0×10^{-5}
Roof fall, release through leaky interbed	6.9×10^{-16}	1.8×10^{-15}	5.4×10^{-8}	1.4×10^{-7}