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# Risk Analyses for Disposing of Nonhazardous Oil Field Wastes in Salt Caverns\*

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## ABSTRACT

Argonne National Laboratory (ANL) has completed an evaluation of the possibility that adverse human health effects (carcinogenic and noncarcinogenic) could result from exposure to contaminants released from nonhazardous oil field wastes (NOW) disposed of in domal salt caverns. In this assessment, several steps were used to evaluate potential human health risks: identifying potential contaminants of concern; determining how humans could be exposed to these contaminants; assessing the contaminants' toxicities; estimating contaminant intakes; and, finally, calculating human cancer and noncancer risks.

Potential human health risks associated with hazardous substances (arsenic, benzene, cadmium, and chromium) in NOW were assessed under four postclosure cavern release scenarios: inadvertent cavern intrusion, failure of the cavern seal, failure of the cavern through cracks or leaky interbeds, and a partial collapse of the cavern roof. To estimate potential human health risks for these scenarios, contaminant concentrations at the receptor were calculated using a one-dimensional solution to an advection/dispersion equation that included first order degradation.

Assuming a single, generic salt cavern and generic oil field wastes, the best-estimate excess cancer risks ranged from  $1.7 \times 10^{-12}$  to  $1.1 \times 10^{-8}$ , and hazard indices (referring to noncancer health effects) ranged from  $7 \times 10^{-9}$  to  $7 \times 10^{-4}$ . Under worst-case conditions in which the probability of cavern failure is 1.0, excess cancer risks ranged from  $4.9 \times 10^{-9}$  to  $1.7 \times 10^{-5}$  and hazard indices ranged from  $7.0 \times 10^{-4}$  to 0.07. Even under worst-case conditions, the risks are within the U.S. Environmental Protection Agency (EPA) target range for acceptable exposure levels. From a human health risk perspective, salt caverns can, therefore, provide an acceptable disposal method for NOW. (At the time this paper was prepared, Reference 2 was a draft; the findings are, therefore, preliminary and subject to change).

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## INTRODUCTION

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

As discussed in Reference 1, 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 caverns in salt domes. 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, 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 phrase "nonhazardous oil field waste" does not mean that oil field wastes 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. 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 never harmful. The EPA documented several cases where the "wastes from crude oil and natural gas operations have endangered human health and caused environmental damage when managed in violation of State and Federal requirements" (12).

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 (13). 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 ground water; and concentrations at which human health effects, aquatic toxicity, or resource damage start to occur (13). 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.

The contaminants of concern identified in these two EPA studies constitute the list of potential contaminants of concern for the current study. Of the potential contaminants of concern, arsenic, benzene, boron, cadmium, chromium VI, and lead, two were eliminated from further consideration. Boron was eliminated because of its high probability of forming insoluble hydroxyborate compounds; lead was eliminated because of its low solubility, large distribution coefficient, and large retardation factor (3).

## POSTCLOSURE RELEASE SCENARIOS

On the basis of several postclosure accident scenarios identified in a 1995 study of cavern failure modes for LPGs (14), the current study examines four postclosure scenarios: (1) inadvertent intrusion, which could produce a release of cavern fluid to the ground surface; (2) failure of the cavern seal, which could release contaminated fluid to the ground water at the depth of the cavern or more shallow depths; (3) failure of the cavern through cracks or leaky interbeds, which could release contaminated fluid to deep ground water; and (4) a partial collapse of the cavern roof, which could release contaminated fluid to deep or shallow ground water, depending on the condition of the cavern seal (2).

For the inadvertent intrusion scenario, an exploratory well is assumed to penetrate the disposal cavern, which has been pressurized because of salt creep and thermal effects. For postclosure conditions, in which the pressure in the liquid is about equal to the lithostatic value, a small amount of waste fluid (about 2,000 gallons) could be released (2). If the pump system in the exploratory well is not isolated from the ground surface or if the cement plug fails, contaminated liquid could move up the wellbore and spill onto the ground, forming a small pool in the vicinity of the well pad. Because of evaporation, infiltration, and the small volume of fluid released, this pond would be ephemeral and would probably last less than two weeks. This pond would not interact with any surface water features because well pads are usually not located near a stream or other surface water feature. Although ingesting this fluid is unlikely because of high turbidity and poor taste, it is included as part of this study for completeness. Because a spill of this type would be cleaned up quickly, no impacts to ground water are assumed. In the event of the absence of regulatory control (e.g., drilling many years after cavern closure), the probability of a cavern release by inadvertent intrusion can be conservatively approximated as the ratio of the planar area of the disposal cavern to the area of the top surface of the salt deposit. Based on typical cavern sizes (8) and the planar area of a typical salt dome (5), the probability of inadvertent intrusion is 0.0001 (i.e., one in ten thousand). This value was used as a best-estimate for the probability of occurrence. In this context, "best-estimate" does not mean "best-case" or the best or least risky case, but instead it refers to the probability of occurrence that is most likely in the best judgment of the authors. "Worst-case" values were assigned to produce bounding, conservative assessments. For inadvertent intrusion, the worst-case value was set equal to the best-estimate value; the probability of occurrence was assumed to be known with certainty.

Under the failure of the cavern seal scenario, pressurized brine and contaminants are assumed to move into the wellbore. Based on engineering judgment and the results of the 1995 study (14), the probability of this type of failure is estimated to be 0.001. This value is considered to be a best-estimate. Depending on the condition of the wellbore casing and the presence and condition of the cement plugs installed at closure, contaminated material could be released to the environment at the depth of the cavern or at shallower depths. Because the salinity of ground water increases with depth, a wellbore casing is more likely to fail at the depth of the cavern than at shallower depths because of increased corrosion in the more saline water. We estimated that failure at the depth of the cavern is ten times more likely than failure at a shallow depth. Under a worst-case scenario, the probability of occurrence would be 1.0 (i.e., failure would occur 100% of the time). Future work will attempt to reduce the uncertainty in the range of this variable for all cavern-failure scenarios.

For the third type of postclosure failure, contaminated material exits the pressurized cavern through cracks or leaky interbeds. Fluids released from the cavern under this failure scenario would affect deep ground water. Based on engineering judgment, the best-estimate probability of this type of failure is on the order of one in one million ( $1 \times 10^{-6}$ ). The worst-case probability is 1.0.

Loss of cavern integrity through a partial collapse of the cavern roof was the final postclosure release scenario considered in this study. If the cavern seal remained

intact, contaminants could be released through cracks in the salt. The probability of such a failure was estimated on the basis of engineering judgment to be on the order of one in one million. If the cavern seal fails and the casing fails at the depth of the cavern, the impacts would be the same as those described for cavern seal failure with casing failure at depth, and the best-estimate probability is also estimated at  $1 \times 10^{-6}$ . If the cavern roof collapses, the cavern seal fails, and the casing fails at a shallow depth, the results would be the same as those for a cavern seal failure with casing failure at a shallow depth. The probability of cavern roof collapse with cavern seal failure and casing failure at a shallow depth is estimated to be 10 times less than the probability of cavern seal failure and casing failure at the depth of the cavern, i.e.,  $1 \times 10^{-7}$ . Worst-case probabilities were 1.0.

## **HYDROGEOLOGY**

This analysis assumes a generic salt cavern located in the Gulf Coast of the United States. The depth to the water table is assumed to be on the order of about 20 ft (2). This shallow ground water 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 (15). Beneath the shallow ground water system are other sequences of clays and silts, interspersed with beds of sand. The sandy areas constitute other potential ground water aquifers that are predominantly confined (16). Recharge to the shallow ground water system is derived from precipitation. The majority of recharge occurs in areas where the clay and silt are absent. Discharge of this 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 ground water velocity at the depth of the cavern is estimated to be less than 10 ft/yr). At shallow depths, the ground water velocity is expected to be greater (about 100 ft/yr).

## **INITIAL CONCENTRATIONS**

Conservative estimates of the initial concentrations for each contaminant (i.e., the concentrations of the contaminants leaving the cavern) were estimated using the maximum of concentrations found in produced water (13, 17, and 18), drilling waste Toxicity Characteristic Leaching Procedure (TCLP) (40 Code of Federal Regulations [CFR] 261, Appendix II) data (13), 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.

## RISK CHARACTERIZATION

Human health risks associated with NOW contaminants inadvertently released from a waste disposal cavern may be carcinogenic or noncarcinogenic. Cancer risks were calculated for each contaminant and for each exposure route and were then summed across contaminants and exposure routes. For all failure modes, the potentially exposed population would be residents living near the salt caverns who drink the contaminated surface or ground

water. Cancer risks associated with disposal of NOW in salt caverns were estimated for the failure scenarios using the following relationship:

$$R_i = I_i x SF_i \quad (1)$$

where  $R_i$  is the risk associated with contaminant  $i$ ,  $I_i$  is the intake of contaminant  $i$ , and  $SF_i$  is its oral slope factor. Oral slope factors of 1.5 and 0.029 (L/mg/kg-day) were used for arsenic and benzene, respectively. These values were obtained from the EPA's Integrated Risk Information System (IRIS). Because oral slope factors were not found for cadmium and chromium, the total cancer risk is based on benzene and arsenic.

The intake rate for each contaminant was calculated according to the following equation:

$$I_i = \frac{C_i x ET x EF x ED x CF}{BW x AT} \quad (2)$$

where

- $I_i$  = Intake rate for contaminant  $i$
- $C_i$  = Exposure point concentration of contaminant  $i$  (g/L)
- IR = Intake rate in one/day
- ET = Exposure time (h/d)
- EF = Exposure frequency (d/yr)
- ED = Exposure duration (yr)
- CF = Conversion factor (d/24 h)
- BW = Body weight of receptor (kg), and
- AT = Averaging time (d): for carcinogens,  $AT = 25,550$  d (70 yr); for noncarcinogens,  $AT = 365$  d/yr times ED.

Maximum exposure point concentrations at 1,000 ft from the point of release were obtained for the release scenarios using a one-dimensional analytical solution to the transport equation that incorporates advection, dispersion, adsorption, first-order degradation, and dilution (19). Contaminants were assumed to exit the cavern for a period of 250 years, and the contaminant retardation factors for transport were derived from their respective distribution coefficients ( $K_d$ ) which were obtained from the

literature (0.62 mL/g [20], 10 mL/g [21], 3 mL/g [21], and 30 mL/g [21] for benzene, arsenic, cadmium, and chromium, respectively), a bulk density of 1.7 g/cm<sup>3</sup>, and 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. For risk calculations, the contaminant concentration at the exposure point was adjusted to account for the probability of occurrence (2). Best-estimate and worst-case probabilities are also listed in Table 1.

Equations 1 and 2, the maximum contaminant concentrations at the receptor location (Table 1), and the associated probabilities of occurrence were used to calculate excess cancer risk estimates. The total calculated excess cancer risks ranged from a high of  $1.1 \times 10^{-8}$  for cavern seal failure with casing failure at depth, to  $1.7 \times 10^{-12}$  for cavern roof collapse with cavern seal failure and casing failure at a shallow depth. Under worst-case conditions, excess cancer risks would range from  $4.9 \times 10^{-9}$  to  $1.7 \times 10^{-5}$ . Even under worst-case conditions, the excess cancer risks lie within the target risk range ( $1 \times 10^{-4}$  to  $1 \times 10^{-6}$ ) of the EPA, which was established for remedial action goals for National Priority List (NPL) sites (22).

Risks associated with noncarcinogens are expressed as hazard quotients (2). For a single contaminant, *i*, the hazard quotient is calculated according to the following equation:

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

where  $HQ_i$  is the reference hazard quotient from contaminant *i*,  $I_i$  is the intake of contaminant *i*, and  $RfD_i$  is the reference dose. A hazard quotient greater than 1.0 denotes an unacceptable level of risk. For the present study, the oral reference doses for arsenic, cadmium, chromium III and chromium VI are 0.0003, 0.0005, 1.0, and 0.005 mg/kg/day, respectively. These values were obtained from the IRIS database mentioned previously.

Using the previously discussed exposure point concentrations, best-estimate probabilities of occurrence, reference doses, and Equation 3, noncancer risks were calculated for the proposed release scenarios. The hazard quotients range from a high of 0.0007 for inadvertent intrusion with a release to the surface, to  $7.2 \times 10^{-9}$  for cavern roof collapse with cavern seal failure and casing failure at a shallow depth (2). None of the contaminants of concern would produce a hazard quotient greater than 1.0; therefore, each contaminant has a very low potential for producing noncarcinogenic effects. Even when the quotients are summed, the greatest result, approximately 0.0007, is significantly less than 1.0. Under worst-case conditions, the hazard indices ranged from 0.0007 to 0.07.

## SUMMARY

This paper investigated the potential for human health risks associated with the use of salt caverns in domal formations for NOW disposal. Based on the assumptions that were developed for a generic cavern and generic oil-field wastes, the best-estimate human health risks are very low (excess cancer risks of  $1.7 \times 10^{-12}$  to  $1.1 \times 10^{-8}$ ) and hazard indices (referring to noncancer health effects) are much less than 1.0 ( $7.0 \times 10^{-9}$  to  $7.0 \times 10^{-4}$ ). Under worst-case conditions, excess cancer risks ranged from  $4.9 \times 10^{-9}$  to  $1.7 \times 10^{-5}$ , and hazard indices ranged from  $7.0 \times 10^{-4}$  to 0.07. Even under worst-case conditions, the cancer risk values lie within the EPA acceptable target risk range and the hazard indices are much less than 1.0. The potential for human health risks associated with using salt caverns for

NOW disposal is, therefore, considered to be low. (At the time this paper was submitted, Reference 2 was still a draft; the findings are, therefore, preliminary and subject to change).

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**Table 1.** Summary Table of Failure Calculations

| Scenario                   | Best-Estimate Probability of Occurrence                | Worst-Case Probability of Occurrence | Contaminant | Maximum Concentration (mg/L) | Comments              |
|----------------------------|--|--------------------------------------|-------------|------------------------------|-----------------------|
| Release to surface         | 0.0001   | 0.0001                               | Benzene     | 20.4                         | Ponded                |
|                            |  |                                      | Arsenic     | 1.7                          | Ponded                |
|                            |  |                                      | Cadmium     | 0.29                         | Ponded                |
|                            |  |                                      | Chromium    | 0.85                         | Ponded                |
| Release to shallow aquifer | 0.0001 <sup>a</sup><br>$1 \times 10^{-7}$ <sup>b</sup> | 1.0 <sup>a</sup><br>1.0 <sup>b</sup> | Benzene     | 0.02                         | 1,000 ft from casing  |
|                            |  |                                      | Arsenic     | 0.0006                       | 1,000 ft from casing  |
|                            |  |                                      | Cadmium     | 0.0003                       | 1,000 ft from casing  |
|                            |  |                                      | Chromium    | 0.0001                       | 1,000 ft from casing  |
| Release to deep aquifer    | 0.001 <sup>c</sup><br>$1 \times 10^{-6}$ <sup>d</sup>  | 1.0 <sup>c</sup><br>1.0 <sup>d</sup> | Benzene     | 0.002                        | 1,000 ft from failure |
|                            |  |                                      | Arsenic     | 0.0006                       | 1,000 ft from failure |
|                            |  |                                      | Cadmium     | 0.0003                       | 1,000 ft from failure |
|                            |  |                                      | Chromium    | $8.5 \times 10^{-5}$         | 1,000 ft from failure |

a Cavern seal failure with casing failure at shallow depth.

b Cavern roof collapse with cavern seal failure and casing failure at shallow depth.

c Cavern seal failure with casing failure at depth of the cavern.

d Cracked, leaky interbeds, cavern roof collapse with intact cavern seal, and cavern roof collapse with cavern seal failure and casing failure at depth.

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