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GEOLOGIC, GEOCHEMICAL, AND GEOGRAPHIC CONTROLS ON NORM IN PRODUCED WATER FROM TEXAS OIL, GAS, AND GEOTHERMAL RESERVOIRS

Final Report

By
R. Fisher

August 1995

Performed Under Contract No. DE-AC22-92MT92011

The University of Texas at Austin
Austin, Texas

Bartlesville Project Office
U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma

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ABSTRACT

Water from Texas oil, gas, and geothermal wells contains natural radioactivity that ranges from several hundred to several thousand picocuries per liter (pCi/L). This natural radioactivity in produced fluids and the scale that forms in producing and processing equipment can lead to increased concerns for worker safety and additional costs for handling and disposing of water and scale.

Naturally occurring radioactive materials (NORM) in oil and gas operations are mainly caused by concentrations of radium-226 (^{226}Ra) and radium-228 (^{228}Ra), daughter products of uranium-238 (^{238}U) and thorium-232 (^{232}Th), respectively, in barite scale. We examined (1) the geographic distribution of high NORM levels in oil-producing and gas-processing equipment, (2) geologic controls on uranium (U), thorium (Th), and radium (Ra) in sedimentary basins and reservoirs, (3) mineralogy of NORM scale, (4) chemical variability and potential to form barite scale in Texas formation waters, (5) Ra activity in Texas formation waters, and (6) geochemical controls on Ra isotopes in formation water and barite scale to explore natural controls on radioactivity. Our approach combined extensive compilations of published data, collection and analyses of new water samples and scale material, and geochemical modeling of scale precipitation and Ra incorporation in barite.

Ra is ubiquitous at low levels in sedimentary reservoir rocks; significantly higher activities occur in black shales, accessory mineral accumulations, and carbonaceous materials derived from hydrocarbons. Geologically short half-lives of ^{226}Ra and ^{228}Ra, coupled with slow natural flow velocities and relatively short transport distances during reservoir production, result in local lithologic variations being a major control on NORM occurrences.

To evaluate geologic and geochemical controls on NORM, we investigated the chemical and radioisotope composition of 153 formation waters from oil, gas, and geothermal wells in the Central Basin Platform (West Texas), Delaware Basin (southeastern New Mexico), Edwards Group (south-central Texas), Texas Panhandle, and the Texas and Louisiana Gulf Coast. Producing strata range from pre-Pennsylvanian to Tertiary, water salinity ranges from 1,170 to 334,000 mg/L, and Ra isotope activity ranges from 0.1 to 5,150 pCi/L. Ra activity correlates poorly with salinity and chlorinity in Gulf Coast

reservoirs but not elsewhere in the state. Formation water composition does, however, control the type of scale that can form. Scale mineralogy in turn determines how much Ra can coprecipitate in scale minerals. Geologic factors, such as reservoir lithology and grain size, and geochemical factors, such as reservoir temperature and radium/barium and barium/sulfate ratios, control the amount of Ra included in barite scale. Although we find no statewide predictors of NORM levels in oil and gas operations, there are useful associations of NORM with geologic, geochemical, and production parameters on the play, field, and reservoir scale.

INTRODUCTION

Natural Radioactivity in Oil and Gas Production

Small quantities of naturally occurring radioactive materials (NORM) occur in nearly all geologic media and contained fluids. The sources of radiation range from long-lived isotopes such as potassium-40 (^{40}K), uranium-238 (^{238}U), and thorium-232 (^{232}Th), each having half-lives of millions to billions of years, to short-lived isotopes that may exist for seconds or less. Natural radioactivity can be concentrated to high levels by both natural (for example, ore-forming) or human (for example, mining, beneficiation, and manufacturing) processes. Potential health and safety problems arise when society is exposed to high radioactivity levels; increased expenses may be incurred when radioactive material must be safely handled, processed, stored, and disposed.

Since the early reports of NORM in Canadian oil fields in 1904 (Wilson, 1994) and in Russian oil fields in the 1930's (Kolb and Wojcik, 1985), it has increasingly been recognized that small amounts of radioactive materials commonly are produced from oil and gas reservoirs along with hydrocarbons, water, and sludge. Health, safety, and environmental concerns began to develop during the early 1980's and 1990's as measurable levels of radioactivity were found in oil-producing and gas-processing facilities in the North Sea and along the U.S. Gulf Coast, in hardware and playground equipment made from recycled oil- and gas-field tubing, and in produced waters discharged into coastal environments. A recent national survey of NORM in oil-producing and gas-processing equipment sponsored by the American Petroleum Institute (API) found radioactivity in all major oil- and gas-producing states ranging from background levels to values approaching those found in uranium mill tailings (Otto, 1989). Thus, NORM production and accumulation are a natural consequence of extracting hydrocarbons from Earth's crust.

NORM in oil- and gas-field operations occurs as produced water; sludges, sands, and mineral scale precipitated in downhole or aboveground piping, valves, or gauges; thin platings on the inner surfaces of gas processing and transporting equipment; or a gas. (Smith, 1987; Baird and others, 1990; White, 1992). Most radioactivity in oil and gas field operations is produced by members of the ^{238}U and ^{232}Th decay series (fig. 1). Because the different elements in the decay series have different chemical

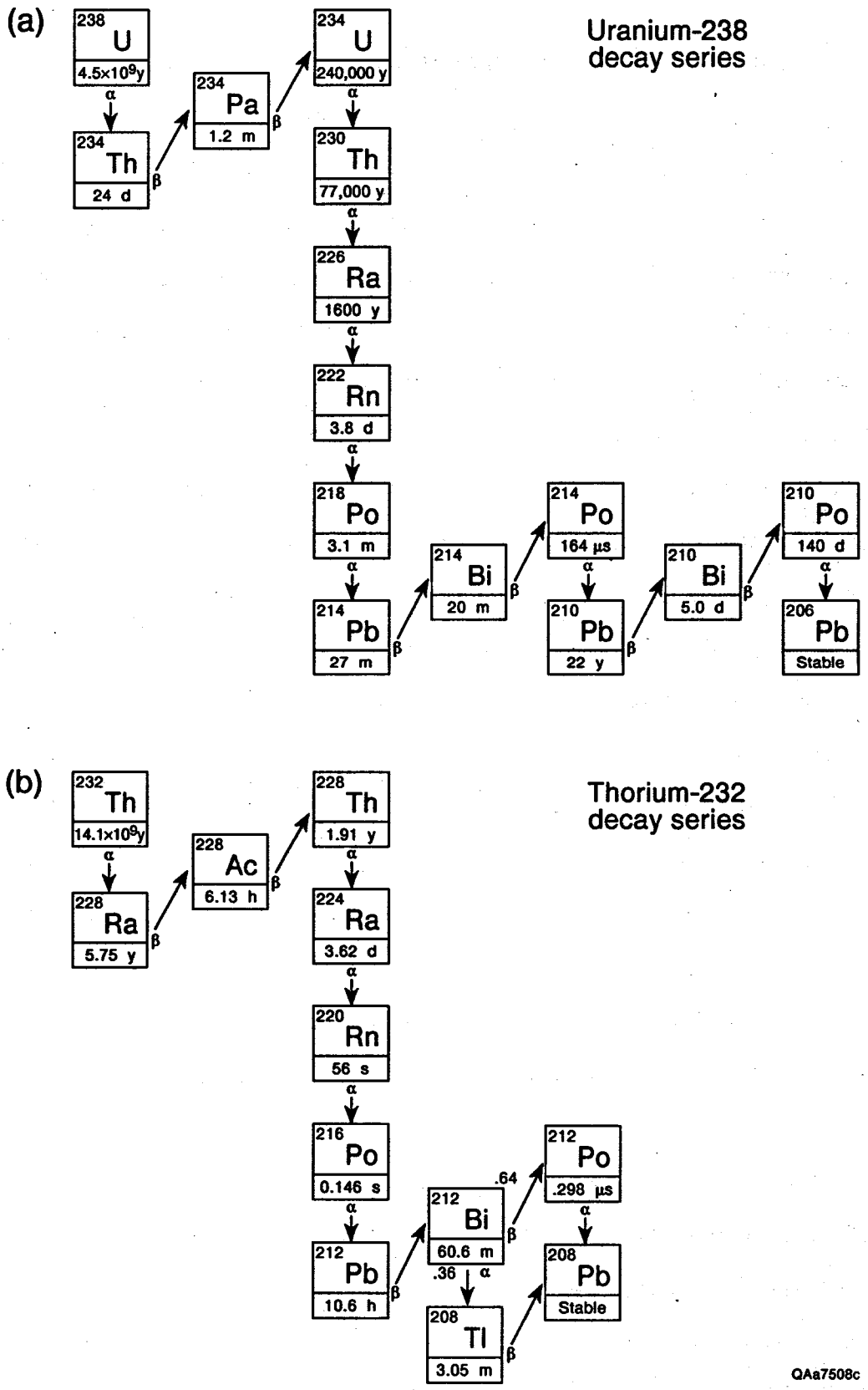

Figure 1. Uranium-238 (^{238}U) and thorium-232 (^{232}Th) decay series and half-lives of isotopes. Uranium (U), thorium (Th), protactinium (Pa), and actinium (Ac) are generally immobile under reservoir conditions; radium (Ra) can be transported in saline waters.

properties and solubilities under reservoir and production conditions, only certain radioactive species are mobile and can be transported with hydrocarbons to surface facilities.

In produced water, scale, and sludge accumulations, most of the radioactivity is caused by radium-226 (^{226}Ra) and radium-228 (^{228}Ra). In gas-processing facilities lead-210 (^{210}Pb), a decay product in the ^{238}U series, can accumulate as thin platings on the inner surfaces of pipes. Radon (Rn) gas (radon-222 [^{222}Rn] or radon-220 [^{220}Rn]), a daughter product of radium (Ra) decay in both the ^{238}U and ^{232}Th series, is also produced but is typically released to the atmosphere before it reaches hazardous levels. Effective concentrations of radionuclides are generally reported in terms of radioactivity in units of curie (Ci), picocurie (pCi = 10^{-12} Ci), Becquerel (Bq), disintegrations per second (dps), or disintegrations per minute (dpm), whereas radiation effects are reported in terms of dosages (units of rad, rem, or roentgen) (table 1). Produced water contains NORM at approximately the same concentrations or activities as formation water in the reservoir. NORM levels in produced water range from essentially background values to activities as high as several thousand picocuries per liter (pCi/L) (White, 1992). Sludge coatings on reservoir grains or other particulates derived from the well system, sands, mineral scale, and pipe platings contain elevated levels of NORM relative to produced water because radionuclides have been precipitated as minerals or coatings on reservoir material or other particulates derived from the well system. Sludges in production equipment typically contain ^{226}Ra and ^{228}Ra in amounts ranging as high as several hundred picocuries per gram (pCi/g) (Baird and others, 1990). NORM in oil- and gas-field equipment can reach very high activities because Ra isotopes are incorporated in mineral scale over long periods of time and are extracted from large volumes of produced water. NORM levels in scale can reach activities as high as several thousand pCi/g (Baird and others, 1990).

Health, Safety, and Environmental Issues

It is beyond the scope of this report to review the principles of radioactivity and health physics; only brief reviews are provided as background for the study. Radioactivity is the process by which the nuclei of unstable atoms undergo spontaneous transformations to ultimately achieve a stable state. These transformations are accomplished through emission of particles and radiant energy. Products (daughters)

Table 1. Units of radioactivity.

Curie (Ci)	The quantity of any radioactive material that produces 3.7×10^{10} disintegrations per second (dps).
Picocurie (pCi)	The quantity of any radioactive material that produces 1×10^{-12} Ci or 3.7×10^{-2} dps.
Becquerel (Bq)	A unit of radioactivity defined as 1 dps. The Bq is the Standard International Unit (SI) of radioactivity; equal to 27.03 pCi.
Rad	A unit of absorbed dose defined as the quantity of radiation or energy absorbed per unit mass. One rad equals 100 ergs per gram of material.
Rem	The dosage of any ionizing radiation that will produce a biological effect equivalent to that produced by one roentgen of X-ray or gamma-ray radiation.
Roentgen (R)	The quantity of X-ray or gamma-ray radiation that will produce 1 electrostatic unit (esu) of charge of either sign in 1 cubic centimeter of dry air at 0°C and 760 mm of mercury pressure; equal to 2.58×10^{-4} coulombs per kilogram of dry air.

of radioactive decay may themselves be radioactive or may be stable. Radioactive decay involves the emission of three different types of energy referred to as alpha particles, beta particles, and gamma rays. Alpha particles consist of two protons and two neutrons and so have a charge of +2. Alpha particles have relatively low energy; even a single sheet of paper is sufficient to stop an alpha particle. Beta particles are identical to electrons in mass but may have either positive (+1) or negative (-1) charge. Beta particles have intermediate energy; they can penetrate a piece of paper but will be stopped by a 1-cm-thick sheet of aluminum. Gamma rays are quanta of electromagnetic wave energy similar to X-rays but much more energetic. The actual energy of gamma radiation varies as a function of radiation frequency. Gamma rays are highly energetic; many radioactive materials produce gamma rays that can penetrate several centimeters of lead. Gamma-ray emission may accompany alpha or beta decay if the decay product nuclei remain in an excited state.

Because most of the radioactivity associated with NORM is caused by ^{226}Ra and ^{228}Ra, studies of the potential hazardous effects of NORM focus on the chemistry of Ra and its progeny in ecosystems and organisms. Ra has an ionic charge (+2) and radius similar to that of other Group 2A elements (1.48 angstroms in 8-fold coordination, versus 1.12, 1.26, and 1.42 angstroms for calcium (Ca), strontium (Sr), and barium (Ba), respectively (Shannon, 1976). Of the Group 2A elements, Ca is the most abundant in the tissues of living organisms (biomass), and therefore the effects of Ra substitution for Ca are of greatest concern. Ingested Ra has been associated with bone cancer, bone sarcoma, and head carcinoma, the last of which is presumably caused by production of Rn gas that accumulates in head cavities (Mays and others, 1985). Rn, a decay product of Ra, exists as a gas and is associated with occurrences of lung cancer (Wanty and Schoen, 1993). Polonium (Po), a decay product of Rn, adheres to particulates in the air, is readily inhaled, and also is associated with lung cancer (Wanty and Schoen, 1993).

The severity of NORM exposure depends on the type (energy) of radioactive decay, the amount of radiation exposure, and the organ or tissue that receives radiation exposure. NORM associated with oil and gas production causes health, safety, and environmental concern at two levels: (1) potential effects on the general public and (2) potential effects on oil- and gas-field workers. Recent reviews of health and

safety issues have been provided by Snavely (1989), Baird and others (1990), White (1992), Gundersen and Wanty (1993), and Wilson (1994) and are only briefly summarized here.

The threat of NORM from oil and gas operations to the general public arises from the way in which produced water or NORM scale and sludge are disposed. If produced water contaminates drinking-water supplies, NORM can be ingested and assimilated into the body. NORM may be incorporated into the food chain as contaminated plant or animal material resulting from produced water discharge or uptake of scale, sludge, or dust. If contaminated food is then consumed by humans, Ra is concentrated in the bones. Exposure to radioactive equipment also poses potential low-level but long-term health problems.

Threats to oil- and gas-field workers are more direct. Exposure to radiation and/or inhalation of Rn or Po during normal operations are generally limited because radioactivity is shielded by the containing hardware and Rn gas seldom accumulates to harmful levels in the work environment. However, maintenance and cleaning of tubing and equipment to remove NORM scale from pipes and tubing generate small particles that can be inhaled and also increase surface area to promote Rn emission. Ingestion of NORM can lead to Ra accumulation in the skeleton, whereas inhalation of radioactive particles or gases can cause radiation to accumulate in the lungs.

Because NORM can present serious health, safety, and environmental impacts, various state and federal agencies have established or are in the process of writing regulations to control NORM production, handling, and disposal. These regulations are currently still in a state of flux and will not be summarized in this report. Recent reviews are provided by Smith (1987), Snavely (1989), Baird and others (1990), and Wilson (1994).

Natural Radioactivity in U.S. Oil-Producing and Gas-Processing Facilities

Prior to 1989, few published data existed to quantify the extent of NORM in U.S. oil and gas operations. Many of the major producing companies had surveyed their equipment to evaluate the extent of precautions needed, but the data were not publicly available and did not exist in readily comparable forms. Recognizing this need for basic information, API sponsored a nationwide survey in which participating petroleum companies collected radiation measurements at their facilities using standardized

equipment and measurement protocols and submitted the results for statistical analysis and aggregation. The results (Otto, 1989) provided the first synopsis of NORM in U.S. oil-producing and gas-processing facilities. Significant limitations to the API study are that (1) data were not collected in a statistically designed sampling plan and therefore extrapolating data to unsampled areas is invalid, (2) scintillation detector readings were taken external to equipment, thus variable amounts of radiation were shielded from the detector, (3) NORM in produced water was not measured, (4) there was no way to evaluate the history or length of time on-line of the equipment tested, (5) whether the equipment handled produced fluids from a single formation or commingled fluids was not recorded, (6) readings were taken where there was reason to suspect high NORM levels, thus the results may be biased toward high radiation readings, (7) geologic basins or formations that yielded the NORM were not identified in the report, and (8) the forms of NORM (scale mineralogy, sludge composition, pipe lining, etc.) were not investigated (Otto, 1989). Despite these limitations, the study provides an important framework for evaluating the extent of NORM in petroleum-producing and gas-processing facilities.

The results of the API survey showed that highest median readings above background (greater than 33 μrems/h) were found along the coast of the Gulf of Mexico from east Florida to South Texas and in southeast Illinois (fig. 2a and 2b). The survey also showed that gas-processing equipment tends to have higher NORM levels than oil-producing equipment (Otto, 1989). In gas-processing facilities, reflux pumps, propane pumps and tanks, and other pumps and product lines had the highest NORM activity levels. In oil-producing facilities, water handling equipment tended to have the highest NORM activity levels (Otto, 1989).

PURPOSE AND APPROACH

The nearly universal occurrence of NORM in oil and gas production; the potentially serious health and safety concerns associated with handling, storing, and disposing of radioactive materials; the trend toward increasing regulation of radioactive materials; and the increased costs incurred by oil and gas companies as they comply with health and safety regulations raise fundamental questions about the natural distribution of radioactivity and the various controls on NORM accumulation in oil and gas

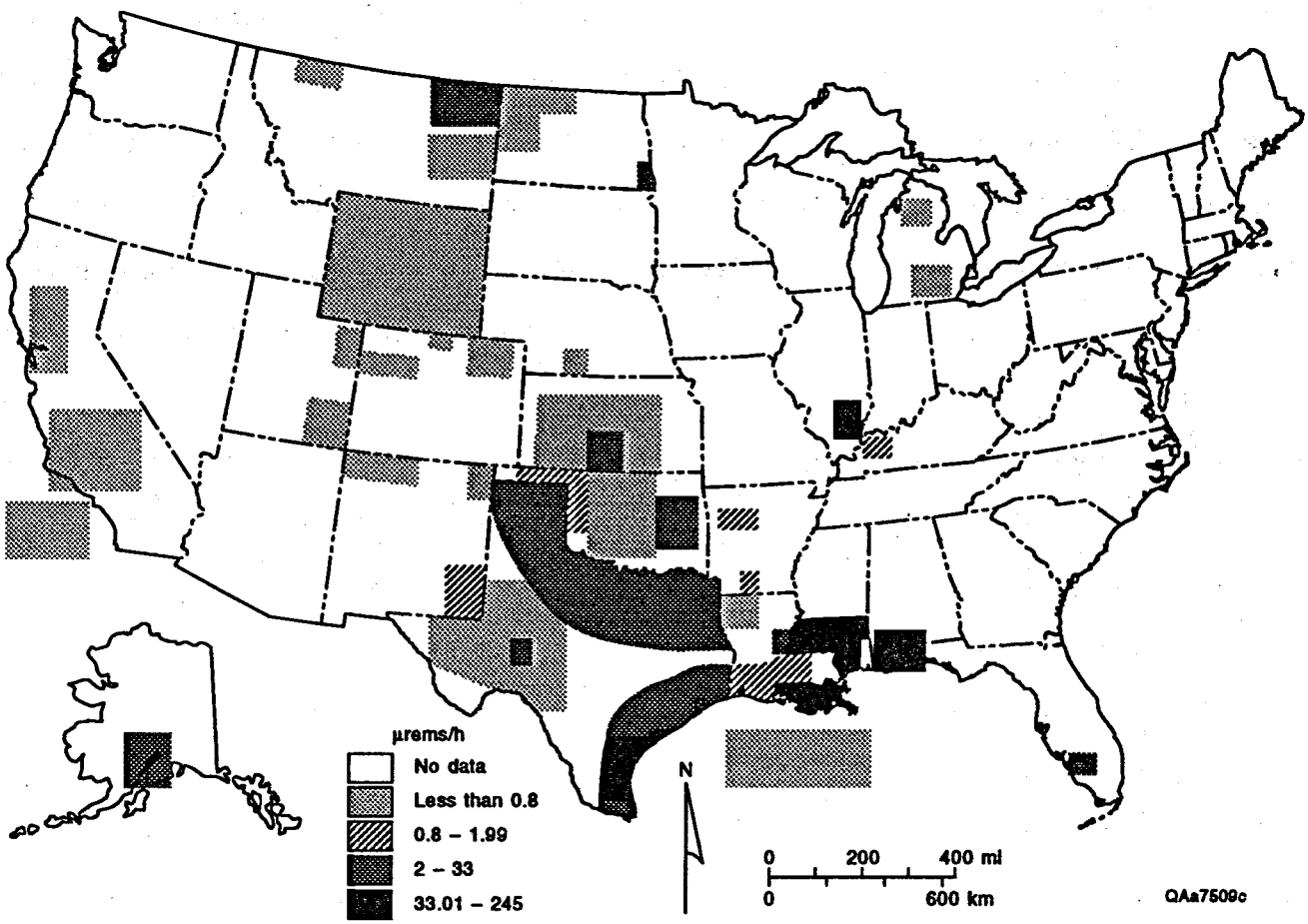

Figure 2a. Map showing regions of high NORM activity in U.S. oil-producing facilities. Values are aggregated median of difference over background in units of µrems/h (after Otto, 1989).

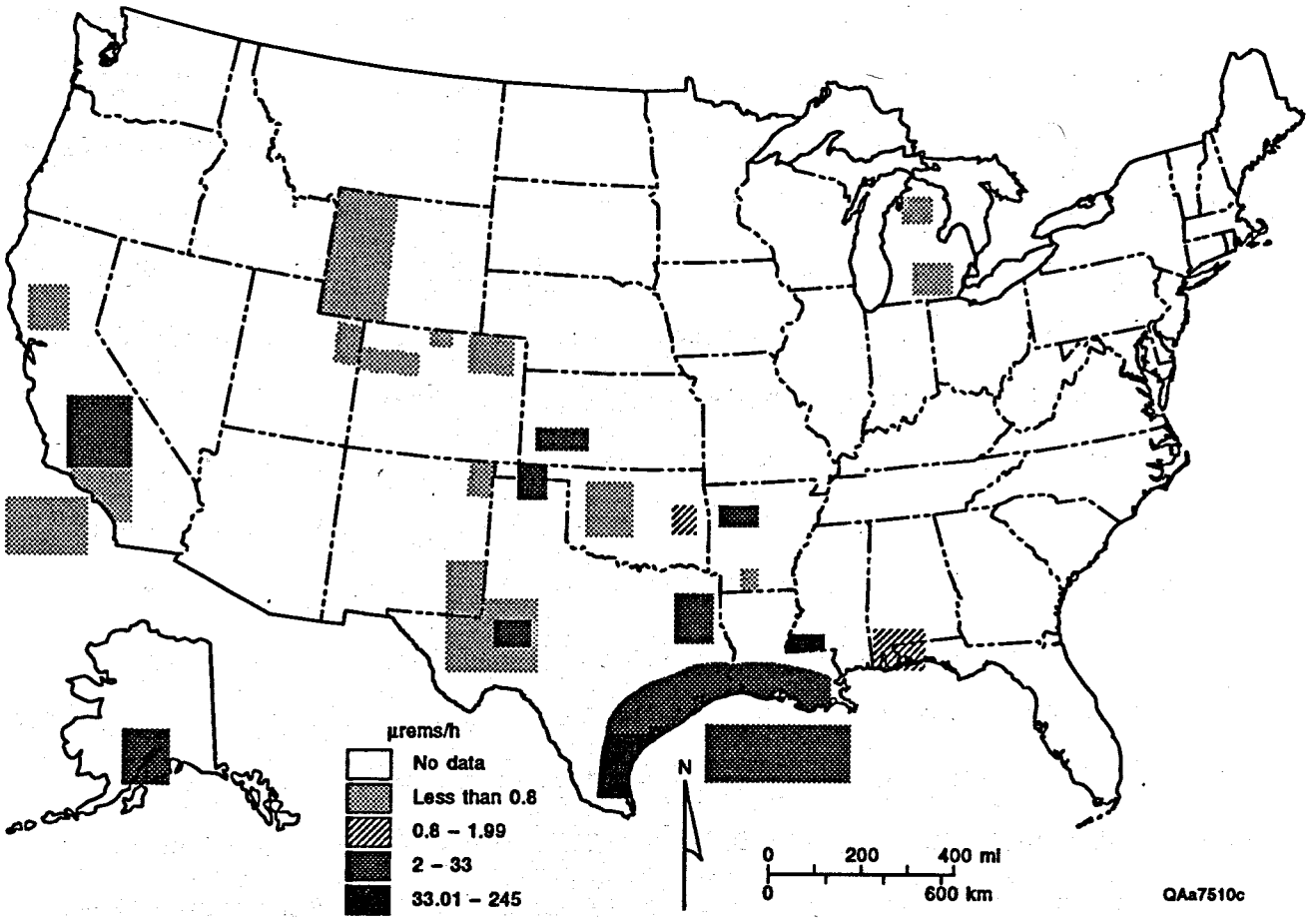

Figure 2b. Map showing regions of high NORM activity in U.S. gas-processing facilities. Values are aggregated median of difference over background in units of µrems/h (after Otto, 1989).

reservoirs. If the important factors that control or influence NORM occurrence and accumulation can be identified, exploration and production geologists and engineers will be better able to anticipate handling and disposal costs and plan drilling and development. Additionally, regulating agencies will be better able to establish rules and guidelines for handling, transporting, and disposing of oil- and gas-field NORM. These issues motivated our investigation into the geologic and geochemical controls on NORM in Texas oil-producing and gas-processing facilities.

Because of the potential health and economic impacts of NORM in oil and gas operations and the relatively few published studies of the natural controls on NORM, we investigated the geochemical, geological, and production parameters that determine the distribution of NORM in Texas oil and gas fields. Work summarized by Otto (1989), Snavely (1989), Baird and others (1990), and White (1992) clearly showed that NORM are common in the oil and gas industry. However, few studies have examined the fundamental controls on NORM in reservoirs and in production and processing facilities. Previous investigations of geochemical controls on Ra in produced water or ground water have typically been confined to specific regions or formations (for example, Adams and others, 1959; Cowart, 1981; Kraemer, 1981, 1985, 1993; Kraemer and Reid, 1984; Kraemer and Kharaka, 1986; Gilkeson and Cowart, 1987; Gascoyne, 1989; Szabo and Zapecza, 1993; Taylor, 1993) and have not attempted to distinguish between local and general controls on the mobility of radioactivity in oil, gas, and geothermal production.

This study addresses two basic questions: what controls the amount of Ra in sedimentary basins and formation waters, and what controls the precipitation of NORM-containing scale in oil-producing and gas-processing facilities? We focused on the geologic and geochemical properties of uranium (U), thorium (Th), and Ra because U and Th progeny are reportedly responsible for most NORM, and Ra is the first mobile daughter product and has the longest half-life in the decay series that ultimately leads to stable lead (Pb) isotopes. Rn, Po, and ^{210}Pb are in turn daughters of Ra decay (fig. 1). Our scope was focused on Texas oil and gas operations because hydrocarbons are produced from a wide variety of geologic and geographic environments within the state and because we have access to a large data base of produced water chemistry from oil and gas wells throughout Texas. We addressed these questions through six related investigations.

Distribution of NORM in Texas oil-producing and gas-processing facilities

Our first objective was to locate areas in Texas that are known to have high NORM levels in oil- and gas-field operations. We used the data submitted by participating oil and gas companies and complied by Otto (1989) for API to identify counties where oil-producing and gas-processing equipment had high radioactivity. We then used this information and the atlases of major Texas oil and gas fields compiled by Galloway and others (1983) and Kosters and others (1989), respectively, to identify geologic basins and structural elements associated with the high NORM activities. This information helped guide our study to particular geographic regions and suggested potential areas for sample collection.

Geologic controls on U, Th, and Ra in sedimentary basins

NORM in oil and gas fields result from accumulation of Ra isotopes, which are decay products of parent uranium and thorium. Ra isotopes in reservoir fluids are not supported by U and Th parent isotopes in the fluids; that is, Ra in solution is not produced by U and Th in solution. To predict areas likely to have high potential for NORM, therefore, it is necessary to understand the geologic and lithologic distribution of the parent isotopes and the mechanisms by which daughter products escape to the fluid phase. Two hypotheses regarding NORM in produced water and oil-producing and gas-processing equipment scale can be evaluated. The first hypothesis is that NORM is produced by locally high U and Th concentrations in the reservoir rocks. If this is generally true, NORM scale will be largely controlled by geologic formation and lithology. The second hypothesis is that NORM is released from ordinary geologic media during normal geologic processes. If this is generally true, the potential for NORM scale precipitation can be predicted largely from basin setting and history. Determining which of these hypotheses prevails will enable us to improve our ability to predict where NORM scale is most likely to accumulate in amounts that produce a health hazard.

Mineralogy of NORM scale

NORM in produced water are concentrated in equipment scale. Few specific data exist concerning the chemical or mineralogical form of the NORM-containing phases. Such information is essential to geochemically predict NORM accumulations on the basis of reservoir conditions and produced water chemistry. The NORM-containing phase must be known before we can predict how efficiently scale formation removes radioactive species from produced water. These data can then be used to geochemically model NORM accumulation. We used literature reports, geochemical evidence, and direct analyses to identify NORM-containing minerals in production scale.

Distribution of formation water types and potential to form NORM scale in Texas reservoirs

The composition of water produced from oil, gas, and geothermal wells varies significantly within the state. Water chemistry reflects basin lithology and history and also affects Ra mobility and the type and amount of scale that will precipitate when formation water is produced. Therefore, regional differences in NORM accumulation could be related to regional variations in water chemistry. To address this issue we compiled available information to investigate the distribution of formation water types in the major oil-producing and gas-processing regions of the state. We used the geochemical modeling program SOLMINEQ.88 (Kharaka and others, 1988) to compute the amount of barite that would form as pressure and temperature conditions change from those within the reservoir to those at surface production facilities. Note that "formation water" refers to water in reservoir strata under in situ conditions, whereas "produced water" refers to water from a well. Produced water may include water from single or multiple intervals, may have been treated in the reservoir or in the well bore, and may have changed in composition because of pressure and temperature changes during passage from reservoir to surface. The focus of this study is on natural controls on NORM and scale formation; therefore, we use the term "formation water" unless referring specifically to produced water.

Ra in Texas formation water

Some data already exist regarding Ra in water produced from wells drilled for geothermal research,

hydrocarbon production, and nuclear waste isolation. The results of individual studies have been interpreted separately, but the data have not been integrated to infer common parameters that control radionuclide distributions regardless of formation, lithology, or water chemistry. Existing data on Ra in formation water come mostly from wells in the Texas Gulf Coast and Panhandle regions. New data are needed to explore NORM in formation water from other geologic environments and geographic areas throughout the state. One objective of this study was to gather published information and to collect and analyze new samples to identify general geologic and chemical controls on Ra in formation water.

Geochemical controls on Ra in formation water and scale

Thermodynamic modeling of scale precipitation from various water types during production and the amount of Ra coprecipitated with various scale mineralogies provide insights into the factors that promote or retard NORM scale accumulation. We estimated the amount of Ra that would be coprecipitated in barite scale by using formation water chemical type, the temperature of scale formation, and thermodynamic data published by Langmuir and Melchior (1985) and Langmuir and Riese (1985). These results can be used to better anticipate NORM levels in equipment scale. With this information operators can be better able to plan NORM handling and disposal strategies.

Results of these six investigations are used to evaluate whether there are regional differences in the (1) Ra content of formation water, (2) potential of produced water to form scale in production equipment, (3) mineralogy of scale formed, and (4) Ra content of scale. This evaluation is accomplished using data on the chemical and radiological composition of produced waters; the chemical and mineralogical composition of production-equipment scale; a knowledge of the mineralogical composition, burial depth, and temperature of the reservoir; and thermodynamic modeling to quantify how Ra is coprecipitated in equipment scale. This information also provides a basis for identifying geographic, geologic, geochemical, and production characteristics that are likely to yield high NORM levels in produced water and equipment scale.

RESULTS

NORM in Texas Oil-Producing and Gas-Processing Facilities

The most comprehensive and consistent set of NORM data ever complied for the U.S. or any individual hydrocarbon producing state was sponsored by API (Otto, 1989). However, the way in which radioactivity was measured and reported severely restricts the usefulness of those data for our study for two reasons. First, the data are readings taken external to pipes, pumps, and other equipment. The radioactivity levels therefore reflect both the effects of some radiation shielding as well as the total amount of NORM accumulated from unknown volumes of gas, oil, and water that have passed through the equipment for an unknown length of operation. Second, data from that study are reported as aggregate radioactivity values for the county in which the oil-producing or gas-processing facilities were located. It is impossible to trace NORM levels to a particular well, field, or formation. Therefore, the data cannot be used directly to discern how different geologic and geochemical environments or production practices affect NORM accumulation. However, the API survey data are useful for identifying geographic regions where above-background radioactivity in oil-producing and gas-processing operations have been recorded.

The API survey obtained readings from 123 of the 254 counties in Texas. Highest median radiation values above background were found along the Gulf Coast crescent from South Texas to the Houston area, in North-Central and west-central Texas, and in the Texas Panhandle. Oil-producing and gas-processing facilities have the same general distribution of NORM values (fig. 3a and 3b), although there are more data for oil-production facilities than for gas-processing plants. Highest values above background for gas-processing facilities exist in the Texas Panhandle and the lower Gulf Coast; highest values above background for oil-producing facilities occur in west-central Texas (Otto, 1989) (fig. 3).

The Gulf Coast crescent includes production from Eocene, Oligocene, Miocene, and Plio-Pleistocene strata from the Houston basin (northeast coast), the Central Texas coastal basin, and the Rio Grande basin (southwest coast), as well as production from some Cretaceous strata in south-

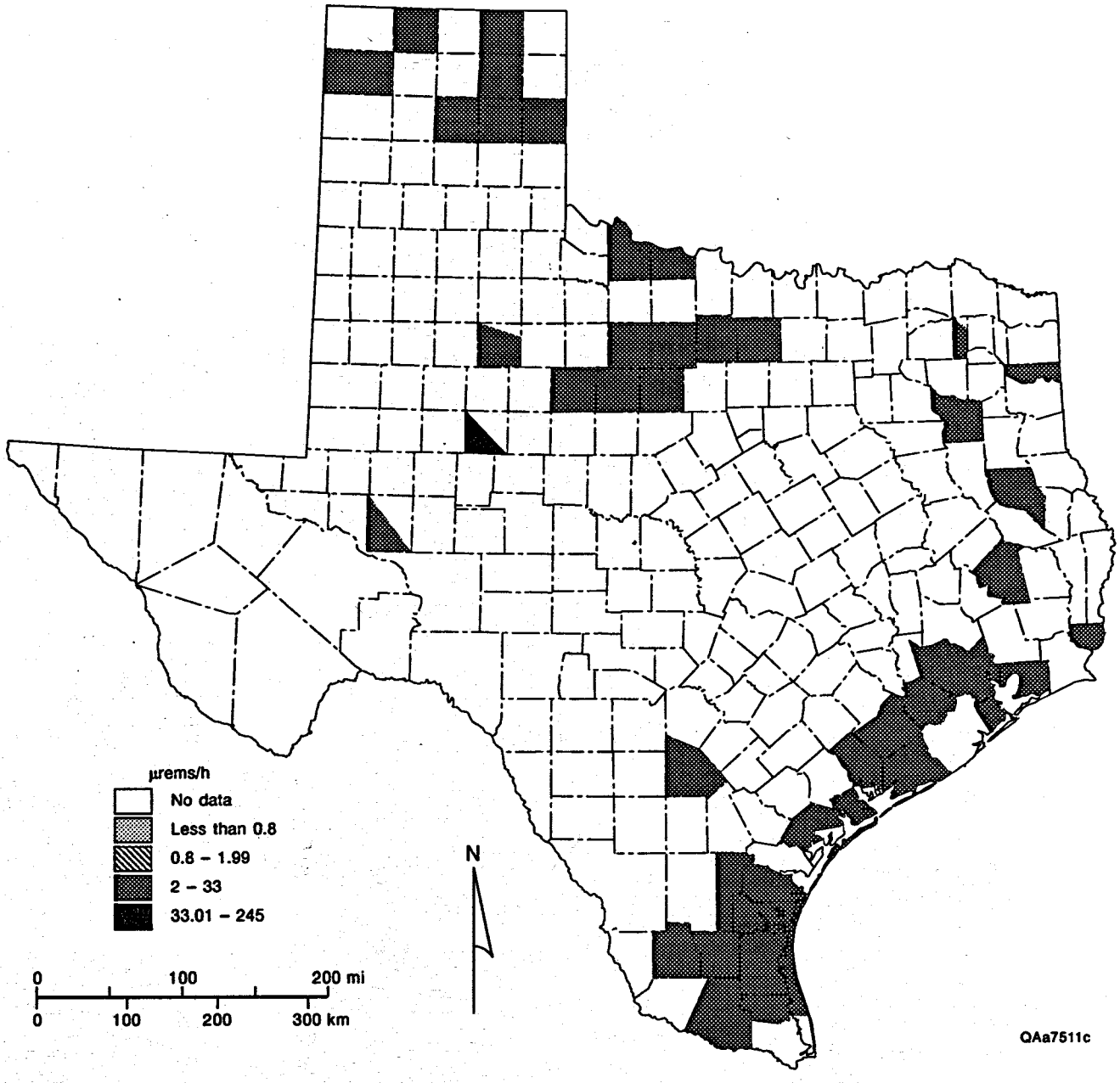

Figure 3a. Map showing regions of high NORM activity in Texas oil-producing facilities. Values are aggregated median of difference over background in units of µrems/h (after Otto, 1989).

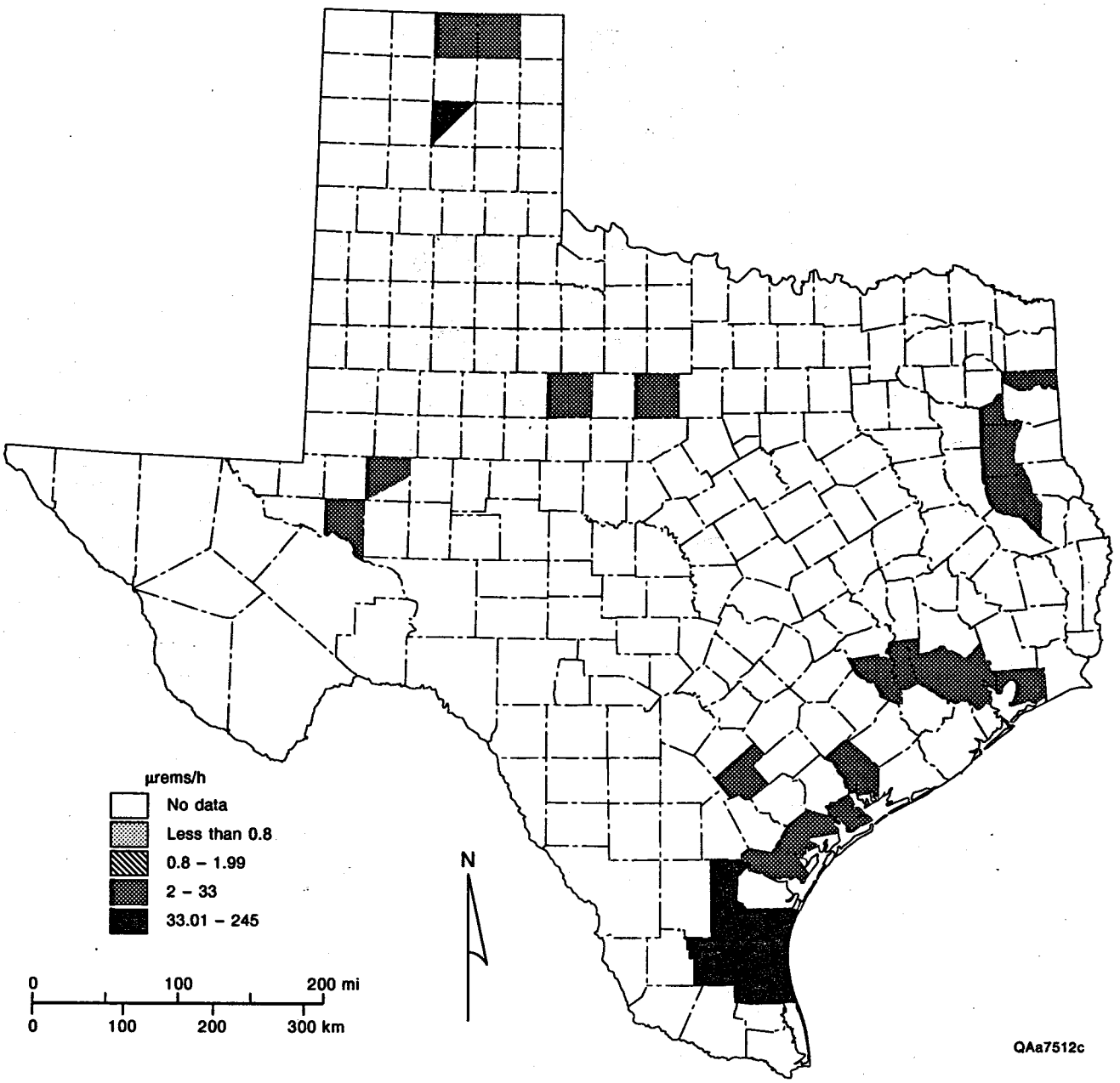

Figure 3b. Map showing regions of high NORM activity in Texas gas-processing facilities. Values are aggregated median of difference over background in units of µrems/h (after Otto, 1989).

central Texas (fig. 4). The north-central and west-central regions include the Hardeman, Fort Worth, and East Texas basins, as well as parts of the Eastern Shelf, Central Basin Platform, Midland Basin, Delaware Basin, and the Southern Shelf. The Texas Panhandle area includes the Palo Duro, Dalhart, and Anadarko Basins (fig. 4).

Elevated NORM levels above background are not associated with all the major oil-producing and gas-processing counties in Texas. Focusing on only those counties that have NORM levels in the upper 75th and 90th percentiles for oil-producing and gas-processing facilities, respectively, provides a clearer view of the location of facilities having high NORM values. By focusing on facilities that have NORM readings within the 75th and 90th percentiles of all readings throughout the state, we are better able to identify geographic regions and geologic strata where NORM levels are likely to be sufficiently high to cause concern for operators and regulators.

Twenty-three counties have median above-background radioactivity values ranging from 2 to 22 µrems/h (75th percentile), and 12 counties have median above-background values greater than 22 µrems/h (90th percentile) in oil-producing facilites (fig. 5a). Eight of these (Hidalgo, Willacy, Jim Hogg, Kenedy, Brooks, Kleberg, Jim Wells, and Nueces Counties) are located in the South Texas Gulf Coast within and adjacent to the Rio Grande basin. The major oil fields in this salt basin produce mostly from Frio strata, with minor production from fields in Vicksburg and Miocene strata (Galloway and others, 1983). Major oil fields in Refugio, Calhoun, and Jackson Counties along the central Texas Gulf Coast also produce mainly from Frio strata. In and adjacent to the Houston basin along the northern Texas Gulf Coast, Wharton, Matagorda, Fort Bend, Galveston, Chambers, Orange, and Polk Counties have major oil fields that produce largely from Miocene strata with subordinate production from Frio strata. Nacogdoches, Smith, and Kaufman Counties in East Texas are located in and adjacent to the East Texas basin where major oil fields produce from the Woodbine and Paluxy Formations. Atascosa County is located in south-central Texas along the Charlotte Fault Zone; major oil fields there produce from Cretaceous Edwards and Olmos strata. Four counties having NORM levels in the 75th percentile are located along the Amarillo Uplift and in the Anadarko Basin of the Texas Panhandle (Roberts, Carson, Gray, and Wheeler). Major oil production here is from Paleozoic strata, as is major oil production

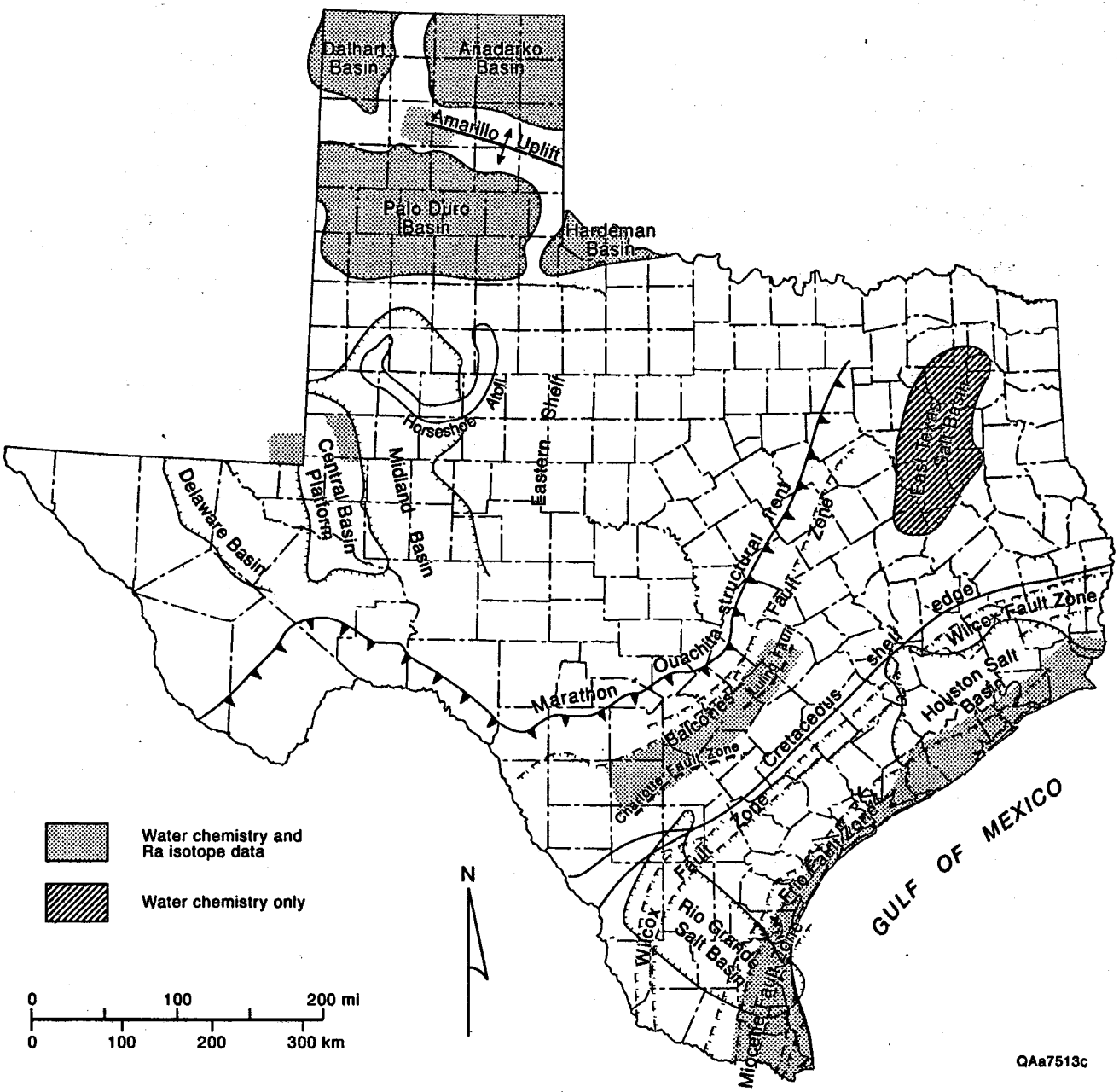

Figure 4. Map showing major structural elements in Texas and basins where water chemistry and Ra activity data are available.

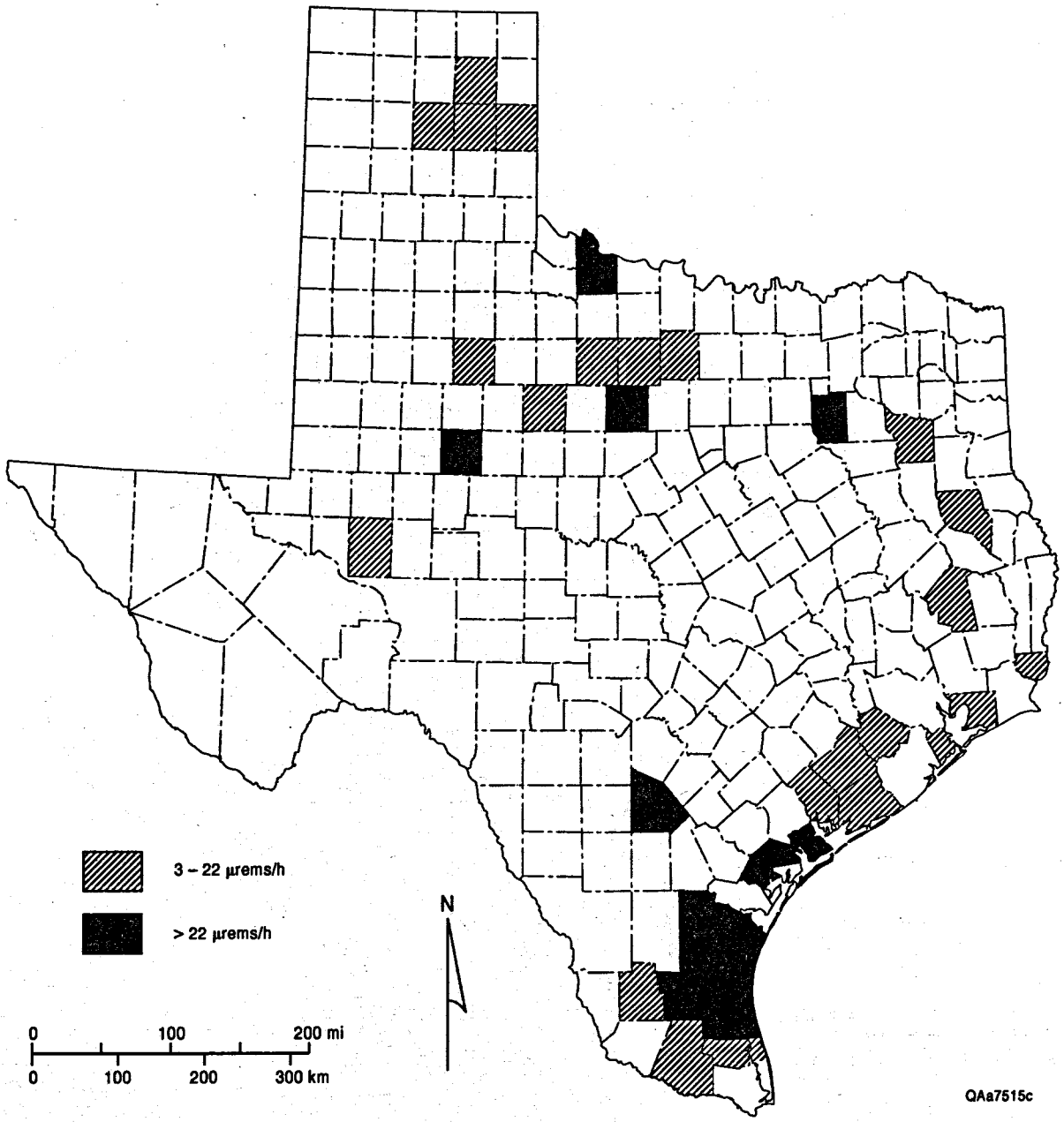

Figure 5a. Map showing counties in which NORM activity in Texas oil-producing facilities is in the 75th (3-22 µrems/h) and 90th (>22 µrems/h) percentile (data from Otto, 1989).

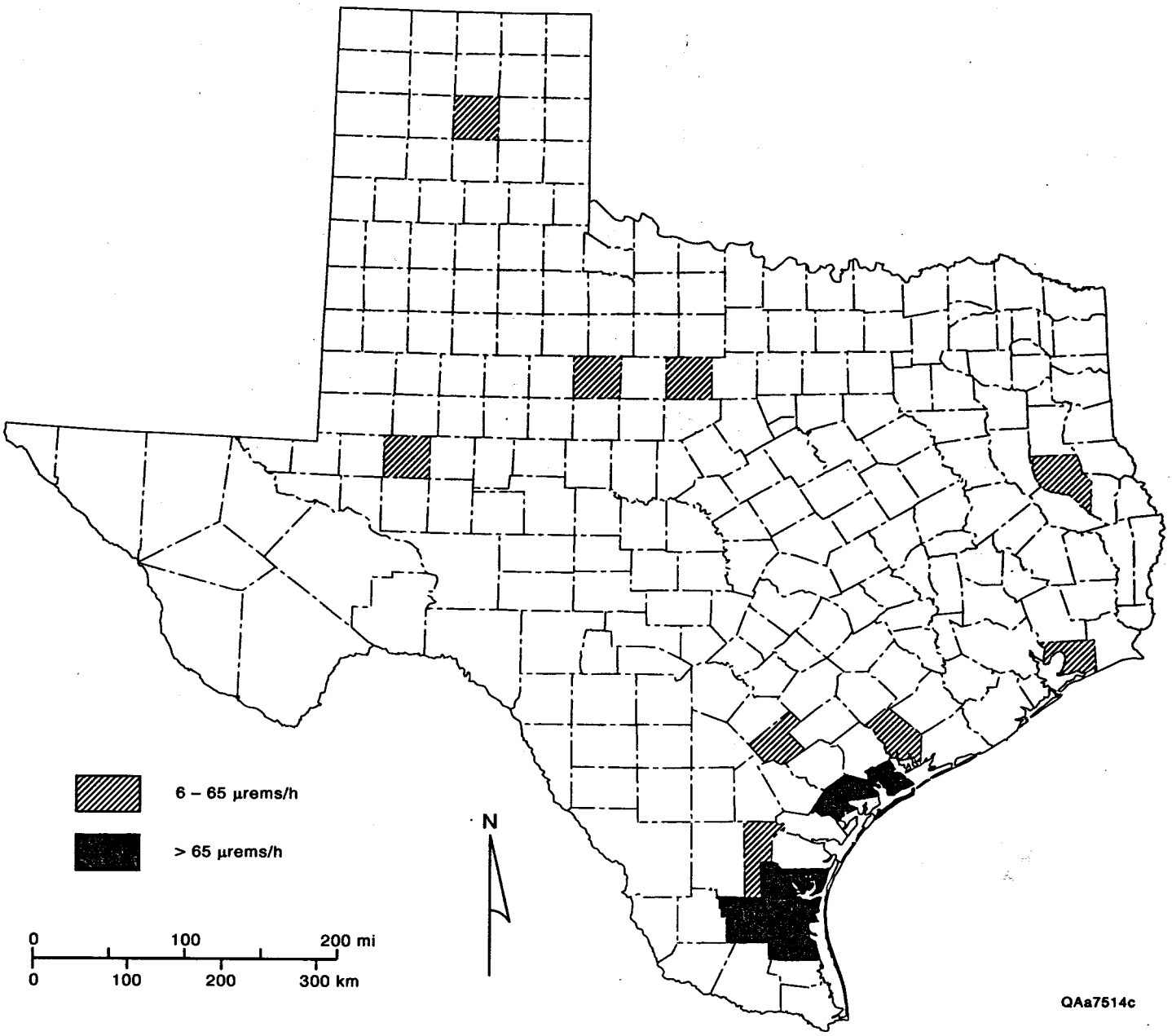

Figure 5b. Map showing counties in which NORM activity in Texas gas-processing facilities is in the 75th (6-65 µrems/h) and 90th (>65 µrems/h) percentile (data from Otto, 1989).

in Wilbarger County in the Hardeman basin, north Texas. Six counties having NORM levels in the 75th or 90th percentile are located along and adjacent to the Bend Arch in either the Fort Worth basin or the Eastern Shelf, North-Central Texas (Jack, Throckmorton, Young, Jones, Stephens, and Wilbarger). Major oil fields in these counties produce from Mississippian–Pennsylvanian strata. The remaining three counties, Mitchell, Kent, and Upton, are located in West Texas near the eastern edge of the Midland Basin, the Horseshoe Atoll, and the western portion of the Midland Basin, respectively. A variety of fields in middle to upper Pennsylvanian strata provide major oil production in these counties.

Fewer counties reported NORM activities in gas-processing facilities. Five counties have NORM levels in the 90th percentile (greater than 65 µrems/h), and nine counties have median readings in the 75th percentile (6 to 65 µrems/h). Nine of the counties reporting median values greater than 6 µrems/h and all counties reporting greater than 65 µrems/h are located along the Texas Gulf Coast (fig. 5b). Kenedy, Brooks, Kleberg, and Jim Wells Counties in the South Texas Gulf Coast are in or adjacent to the Rio Grande basin. Production from major gas fields in this basin is mostly from the Frio Formation, with additional production from Miocene strata (Kosters and others, 1989). Refugio, Calhoun, Jackson, and Karnes Counties are in the Central Texas Gulf Coast. Major gas fields in these counties produce primarily from Cenozoic strata (Wilcox, Reklaw, and Frio Formations and Miocene strata) (Kosters and others, 1989). Chambers county in the north Texas Coastal Plain is situated in the Houston basin. Major gas fields in Chambers and adjacent counties in the Houston basin produce from Frio and Miocene strata. An area of salt pillows associated with the East Texas basin encompasses Nacogdoches County in East Texas. Major gas production here is from Mesozoic strata, chiefly the Pettet and Rodessa Formations. In North-Central Texas, gas-processing facilities in Stephens and Jones Counties have NORM levels in the range of 6 to 65 µrems/h. No major gas fields exist in these counties (Kosters and others, 1989). Major gas fields in Midland county in West Texas produce from several Permian stratigraphic intervals. Major gas production in Carson county, Texas Panhandle, is predominantly from Pennsylvanian and Permian strata associated with the Amarillo Uplift and the adjacent Anadarko Basin.

Knowing which counties have high median radiation values in oil and gas equipment enables us to correlate those counties with major geologic features, producing strata, and major fields using the maps provided by Galloway and others (1983) and Kosters and others (1989). We emphasize that these correlations do not demonstrate a direct association of NORM with those strata. However, assuming that high NORM activity levels in a county reflect the radioactivity produced from the fields and formations that account for major oil and gas production in that county leads to several tentative conclusions that should be tested further. First, the geologic age of strata from which major oil and gas fields produce does not correlate strongly with county-averaged NORM levels. Second, many counties that have major oil and gas fields, and in which NORM levels were measured, do not have significantly high radioactivity associated with production and processing equipment. Third, the Rio Grande basin and the Central Texas Gulf Coast are the only regions that have NORM levels in the 90th percentile for both oil and gas facilities.

Uranium, Thorium, and Radium in Reservoirs and Formation Water

To evaluate geologic, hydrogeochemical, and production controls on NORM in oil- and gas-field operations, it is necessary to review the sources and factors that affect the mobility of radionuclides that comprise NORM. As previously discussed, ^{226}Ra and ^{228}Ra are the isotopes that produce most radioactivity in oil and gas facilities. Because the half-lives of ^{226}Ra and ^{228}Ra are geologically short (1,600 yr and 5.75 yr, respectively), Ra originally incorporated with sediments and pore water does not survive to be produced. Rather it is Ra generated from parent U and Th isotopes in the reservoir matrix that leads to NORM accumulations. The geologically short half-lives of ^{226}Ra and ^{228}Ra, combined with typical flow rates for basinal brines, indicate that Ra is not transported long distances. Typical flow rates for basinal fluids are approximately 10 cm/yr in the Texas Panhandle (Wirojanagud and others, 1986) and the Gulf Coast Basin (Harrison and Summa, 1991). In one half-life, ^{226}Ra and ^{228}Ra would move only about 160 and 0. 6 m, respectively. Flow rates can be much faster during reservoir production, but such conditions are maintained only for a few decades at most. Therefore Ra in produced water must be generated relatively near to the producing well.

The Ra isotopes are the first mobile daughter products in the ^{238}U and ^{232}Th decay series (fig. 1); hence, they present the first opportunity for transport of radioactivity from geologic media to surface facilities and human contact. Other sources of NORM in surface facilities, such as ^{222}Rn and ^{210}Pb, follow later in the decay sequence. If Ra were immobile, ^{222}Rn and ^{210}Pb would be much less likely to accumulate in surface facilities. The following section briefly summarizes the geologic occurrences of U and Th, mechanisms by which daughter Ra escapes to the fluid phase, and Ra mobility in formation water. More extensive discussions are provided in Rogers (1969a, b), Langmuir and Melchior (1985), Langmuir and Riese (1985), Gascoyne (1989), and Dickson (1990).

U and Th are typically present at the parts-per-million (ppm) level in sedimentary rocks and in the igneous and metamorphic rocks that contribute detritus to clastic sediments (Rogers, 1969a, b) (Gascoyne, 1989). Table 2 summarizes the U and Th concentrations in typical reservoir strata and in some individual minerals that occur in clastic deposits. Sandstones generally contain less than 3 ppm U and less than 8 ppm Th, whereas limestones contain less than 9 ppm of either U or Th. Evaporite strata generally contain less than 0.1 ppm U and less than 1 ppm Th. Although typical reservoir strata (sandstones, carbonates, and evaporites), as well as the common rock-forming minerals (quartz, feldspars, and micas), contain U and Th in the parts-per-million range, some sedimentary strata and accessory minerals can have parts-per-thousand concentrations (table 2). U concentrations exceeding 100 ppm are found in black shales, phosphates, coals, and asphaltites, whereas Th concentrations greater than 10 ppm are found in shales, bauxite deposits, manganese nodules, and oceanic clays (Table 2.2 of Gascoyne, 1989). Uraniferous asphaltite, a U-bearing carbonaceous material found in the Texas Panhandle and in many other geologic and geographic settings (Pierce and others, 1964), may contain several thousand parts-per-million U. Accessory minerals such as allanite, huttonite, monazite, and zircon contain U and Th concentrations that range as high as several thousand parts per million (table 2). In general, therefore, typical reservoir strata can be expected to contain parts-per-million levels of U and Th, whereas organic-rich shales, phosphate deposits, asphaltites, and accessory minerals contain concentrations of U and Th that are several orders of magnitude greater.

Table 2. Mean values and ranges of uranium and thorium concentrations (ppm) in selected rocks and minerals.

Rock or Mineral	U mean	U range	Th mean	Th range	Reference
Average shale	3.7		12		a
Average shale	3.5	3.0 - 4.0			b
Common shales	3.7	1 - 13	12	2 - 47	c
Black shale	8	3 - 250			b
Black shales		1.4 - 80		2.8 - 28	c
Black shales, metal rich	20				a
Sandstones (267 samples)	2.4		8		d
Orthoquartzites	0.45	.2 - .6	1.7	.7 - 2.0	c
Siltstones (52 samples)	2.7		8.8		d
Claystone/shale (176 samples)	4.4		11.5		d
Carbonates	2.2		1.7		e
Bentonites	5	1 - 21	24	6 - 44	c
Carbonate rocks		0.1 - 9	1.7	0.1 - 7	c
Halite	2.2	.1 - .2		.4 - .5	c
Anhydrite		0.1		0.15	c
Phosphate rock		245		3.9	c
Chert		1.9 - 3.3		0.1 - 1.6	c
Minerals from igneous rocks:					
Quartz	1.7	.1 - 10		.5 - 10	f, g
Feldspar	2.7	.1 - 10		.5 - 10	f, g
Biotite	8.1	1 - 60		.5 - 50	f, g
Muscovite		2 - 8			f
Hornblende	7.9	.2 - 60		5 - 50	f, g
Pyroxene	3.6	.1 - 50			f
Olivine	0.05		0.02		f
Allanite	200	30 - 1000	9100	1000 - 20000	f, g
Apatite	65	10 - 100	70	50 - 250	f, g
Epidote	43	20 -200	200	50 - 500	f, g
Garnet		6 - 30			f
Huttonite		3000 - 70000			f
Magnetite, opaque minerals		1 - 30		.3 - 20	f, g
Monazite	3000	500 - 3000	49700		f, g
Sphene	280	10 - 700	510	100 - 1000	f, g
Xenotime		300 - 40000			f
Zircon		100 - 6000	560	100 - 10000	f, g
Asphaltite	4000				h

References:
a: Bell, 1978
b: Swanson, 1961
c: Adams and others, 1959
d: Dypvik and Bue, 1984
e: Turekian and Wedepohl, 1961
f: Rogers and Adams, 1969a
g: Rogers and Adams, 1969b
h: Pierce and others, 1964

Under the reducing conditions present in hydrocarbon reservoirs, both U and Th are essentially immobile, as demonstrated by the exceedingly low concentrations measured in formation waters (for example, Kraemer, 1985). At reservoir pH, Eh, and temperature conditions, aqueous U exists in the +4 valence state from which it forms the highly insoluble minerals uraninite and coffinite (for example, Kraemer and Kharaka, 1986). Th occurs only in the +4 valence state and is insensitive to redox state. The minerals that have Th as a major cation are highly insoluble under reservoir conditions (Rogers, 1969a). Furthermore, at pH values greater than 3, Th in solution readily hydrolyzes to form various insoluble hydroxide species (Zukin and others, 1987). Th also has a strong tendency to adsorb onto reservoir materials (Langmuir and Chatham, 1980). For these reasons, the aqueous activities of parent ^{238}U and ^{232}Th are insufficient to support the activities of daughter ^{226}Ra and ^{228}Ra, respectively, present in formation waters and ground waters (for example, Kraemer, 1981; Kraemer and Reid, 1984; Kraemer, 1985; Kraemer and Kharaka, 1986; Kraemer, 1993).

Production of both ^{226}Ra and ^{228}Ra is the result of alpha decay (fig. 1), and recoil damage to the host mineral is generally regarded as the mechanism by which Ra is released. Fleischer and Raabe (1978), Fleischer (1982), and Rama and Moore (1984) investigated the effectiveness of alpha-decay product removal from five common minerals (mica, feldspar, pyroxene, quartz, and natural glass). They reported that recoil ejection from grains and release by natural etching of alpha-recoil tracks are the two principal mechanisms by which alpha-decay products enter the pore water system. If parent U or Th isotopes are located on grain surfaces, Ra could be ejected directly to pore water. Intracrystalline damage caused by alpha recoil and subsequent removal of Ra from the grain is likely to be a more important release mechanism because the amount of daughter product involved is not limited to that produced by parent isotopes situated on mineral or grain surfaces. Conditions that favor escape of alpha-decay products are (1) small size and large surface-to-volume ratio of U- and Th-containing materials, (2) size, distribution, and connectivity of intragranular and intergranular pore spaces, (3) location of U and Th within or on grains, and (4) whether pore spaces are filled with water or gas (Fleischer, 1982).

Diagenetic processes may retard or promote Ra mobilization. Precipitation of cement on grain surfaces may retard alpha-recoil release of radionuclides. Essentially no U, Th, or Ra coprecipitates with authigenic phases because of the relatively low temperatures of formation (80° to 120°C) and the lack of significant U and Th in formation water. Therefore authigenic quartz or feldspar deposited on detrital grains could shield alpha-recoil products from reaching the interface between grain surface and pore water (Kraemer, 1981). A similar situation would prevail if U- and Th-containing grains were encased in authigenic cements that act as a physical barrier between recoil products and the pore water system. Albitization of detrital feldspar and conversion of detrital smectite to illite in shales and sandstones, diagenetic reactions that affect nearly all sandstones and shales in Gulf Coast strata at temperatures exceeding about 80°C (for example, (Milliken, 1988, 1989), may promote the release of Ra and other alpha-decay recoil products. Dissolution of detrital feldspars or clays and precipitation of authigenic phases release trace elements into solution. Immobile species such as U and Th would be adsorbed readily onto grain surfaces or could form traces of authigenic U- and Th-rich minerals. Alpha-recoil products from parent U and Th isotopes that are either adsorbed onto grain surfaces (Ames and others, 1983a, b) or included in finely crystalline authigenic minerals would then be closer to the water phase than before diagenesis, and release to the pore water system would be more likely.

Ra released from host minerals by alpha recoil may be removed from solution by mineral precipitation or sorption onto grain surfaces, or it may remain in solution. Previous studies have shown that Ra concentrations in ground water and formation water are always too low for saturation with respect to a pure Ra phase to be achieved (for example, Langmuir and Melchior, 1985; Langmuir and Riese, 1985). Ra concentrations in formation waters are sufficiently low so that radium sulfate ($RaSO_4$), the least soluble Ra phase, is always undersaturated by several orders of magnitude. Ra concentrations must instead be limited by solid solution formation (coprecipitation), adsorption, or both.

Langmuir and Riese (1985) evaluated the coprecipitation of Ra in various minerals from both a thermodynamic and experimental perspective. Their findings can be summarized as an empirical distribution coefficient D.

$$D = (RaX/MX)_N / (Ra^{+2}/M^{+2})_m,$$

where m indicates the molal aqueous concentration of Ra and the major ion (M) that Ra substitutes for in the crystal, and N indicates the mole fraction of Ra and M in solid solution X. If the value of D is greater than 1, Ra will preferentially replace M in solid solution; if D is less than 1, Ra will be excluded from the solid solution. Langmuir and Riese (1985) investigated Ra coprecipitation in eight sulfate and carbonate minerals. The value of D decreases in the order anhydrite > celestite > anglesite > barite > aragonite > strontianite > witherite. Coprecipitation of Ra in calcite was not investigated because the large ionic size difference between Ra and Ca in the calcite structure precludes ready substitution. For the minerals investigated, D decreases with increasing temperature. Values of D are greater than 1 for anhydrite, celestite, anglesite, and barite at 25°C and greater than 1 for anhydrite, celestite, and anglesite at 100°C. None of the carbonate minerals investigated showed a preference for Ra over Ca in the crystal structure. These data indicate that the thermodynamically favored NORM scale minerals are anhydrite, celestite, anglesite, and barite, and that, for a fixed solution composition, less Ra will be incorporated in scale formed at higher temperatures than at lower temperatures. Whether these minerals actually form, however, depends on formation water composition and whether the phases become oversaturated during production.

Many workers have noted a correlation between Ra concentrations and total salinity in ground water and formation water (for example, Dickson, 1990). It has also been observed that, in dilute solutions and fresh-to-brackish ground waters, Ra is readily removed from solution by sorption onto grain surfaces. High salinity appears to be a requisite for high Ra concentrations (Dickson, 1990), although not all saline waters support high Ra activities. Experimental data confirm that Ra is extremely efficiently scavenged from dilute water by sorption processes (summarized by Dickson, 1990). In saline waters, however, high concentrations of cations such as sodium, calcium, magnesium, and potassium successfully compete for sorption sites, and high levels of Ra can be maintained in solution.

Mineralogy of NORM Scale

Predicting the conditions that favor NORM scale accumulation requires knowledge of the chemical composition and mineralogy of the phase containing radioactive species. Identifying geologic, geochemical, and production characteristics that can mitigate NORM scale accumulation; developing scale inhibitors; and designing waterflooding and commingling strategies that will not promote NORM scale accumulation all depend on an accurate knowledge of NORM scale composition. Unfortunately, most scale is a complex mixture of authigenic minerals, rust, and other contamination from the well equipment. Identifying the NORM-containing phase in such material requires detailed separation and analytical procedures. Furthermore, to quantify the rate at which NORM scale accumulates under various reservoir and production conditions, NORM scale must be collected from equipment that produces water from a single, untreated formation for a known amount of time or, more specifically, for a known amount of produced water. For these reasons, little quantitative information exists regarding the chemical or mineralogical form of the NORM-containing phase.

Most reports in the literature suggest that barite scale is the host of NORM in production equipment (for example, Gallup and Featherstone, 1983; Matty and others, 1985; Smith, 1987; Waldram, 1988; Snavely, 1989; Baird and others, 1990; Stephenson, 1992; Oddo and others, 1993; Oddo and Thomson, 1994); NORM associated with calcite is less commonly mentioned (Oddo and others, 1993). However, no available reports include mineralogical, chemical, or radiological analyses to show that the radioactivity is clearly incorporated in barite scale.

Geochemical evidence supports the contention that Ra typically coprecipitates in barite. The tendency for Ra to form a solid solution with barite has long been used to remove Ra from mine waters and U mill tailings. Langmuir and Melchior, 1985 investigated the tendency for Ra form solid solutions with sulfate and carbonate minerals that are typically present in oil and gas reservoirs. Gnanapragasam (1991) studied Ra partitioning in calcite, gypsum, and brushite, minerals that are likely to form in treated U mill tailings. Because of its ionic radius (1.48 A in 8-fold coordination [Shannon, 1976]), Ra can most readily substitute for Ba (1.42 A in 8-fold coordination) or Sr (1.26 A in 8-fold coordination). Ra substitution for Ca in NORM scale is less likely because in calcite, the most common carbonate scale

mineral, Ca is in 6-fold coordination with an ionic radius of 1.12 A (Shannon, 1976), is significantly smaller than the Ra ion. Langmuir and Riese (1985) determined or estimated distribution coefficients for Ra in the minerals anhydrite, celestite, anglesite, barite, aragonite, calcite, strontianite, witherite, and cerussite. On the basis of the measured or estimated distribution coefficients (Langmuir and Riese, 1985) and the abundances of Ca, Sr, Ba, and Pb in typical formation waters, barite and celestite are the scale minerals most likely to preferentially incorporate significant amounts of Ra.

We analyzed a suite of NORM scale samples to investigate how radioactivity is incorporated in scale minerals. Twenty scale samples were collected from a field in north Texas by Mr. Art Rood of EG&G Engineering Idaho, Inc., with the cooperation of the producing company and API. X-ray diffraction analysis showed that all samples contain barite and as many as four iron oxide or iron oxyhydroxide minerals (goethite, lepidocrocite, akaganeite, and maghemite). All scale samples also contain halite, which precipitated when residual produced water evaporated after sample collection. Total inorganic carbon analysis of acid leachates showed that the scale contained no carbonate minerals. Concentrations of major cations and activities of selected isotope are shown in table 3. Qualitative correlations between gross radioactivity and scale color showed that the lighter colored scale samples were more radioactive. This suggests that radioactivity is preferentially associated with barite (a white mineral) rather than with the iron-rich phases (red-brown to brown color). To quantitate this relation we selected 10 scale samples that ranged from nearly white to deep red in color and measured major cations in each. Results (fig. 6a and 6b) showed a strong positive correlation between Ba and ^{226}Ra activity and a strong negative correlation between Fe and ^{226}Ra activity. These results confirm that, at least in this suite of scale samples, radioactivity is associated with barite scale rather than the other phases present.

Literature reports and our suite of X-ray diffraction mineral identifications all suggest that barite is the typical NORM scale. Additionally, thermodynamic considerations indicate that Ra is more likely to form solid solutions with sulfate minerals than with carbonate minerals. Of the candidate sulfate minerals, gypsum precipitation is more likely under production conditions than anhydrite precipitation, and anglesite scale formation is limited by the naturally low quantities of Pb in formation water. Celestite

Table 3. Results of radiometric analyses provided by EG&G Engineering Idaho, Inc., and chemical analyses performed at the Bureau of Economic Geology Mineral Studies Laboratory.

SPL ID No.	MSL ID No.	^{226}Ra (pCi/g)	^{232}Th (pCi/g)	Rn (pCi/g)	Fe (µg/g)	Ba (µg/g)	Na (µg/g)	Mg (µg/g)	Sr (µg/g)	Ca (µg/g)	SiO_2 (wt. %)
PF002SC001		895.47	1508.0	0.79							
PF002SC002	94-318	2150.00	2955.0	1.60	301500	112500	51840	2440	14490	11470	2.41
PF002SC003		1977.00	2991.0	0.47							
PF002SC004		1941.00	2789.0	0.82							
PF002SC005	94-319	2156.00	2999.0	2.80	287600	159000	29520	1700	19600	8620	1.91
PF002SC006		397.70	512.5	1.00							
PF002SC007	94-320	424.75	534.0	0.90	459100	27250	9900	1270	3180	8170	4.08
PF002SC008	94-321	2747.00	4063.0	1.10	262900	198000	6310	460	28560	3810	1.50
PF002SC009		1042.10	1622.0	0.50							
PF002SC010	94-322	2321.00	3619.0	1.10	241400	208000	6610	680	29760	5540	1.58
PF002SC011		2224.00	3818.0	2.30							
PF002SC012		2629.00	393.0	2.90							
PF002SC013		716.80	1313.0	0.60							
PF002SC014	94-323	2337.00	3605.0	0.90	277300	187200	16290	1070	25600	7200	1.65
PF002SC015	94-324	2762.00	4050.0	2.00	258100	186800	15480	1170	26600	6360	1.77
PF002SC016	94-325	707.30	1295.0	0.70	369500	89340	35910	2390	11350	9630	3.47
PF002SC017	94-326	2437.00	3974.0	1.00	246000	198000	6670	1070	27830	5810	1.69
PF002SC018		658.00	1363.0	0.50							
PF002SC019		2256.00	3359.0	0.90							
PF002SC020	94-327	591.90	1502.0	0.70	398900	52080	41400	1930	7360	6940	4.37

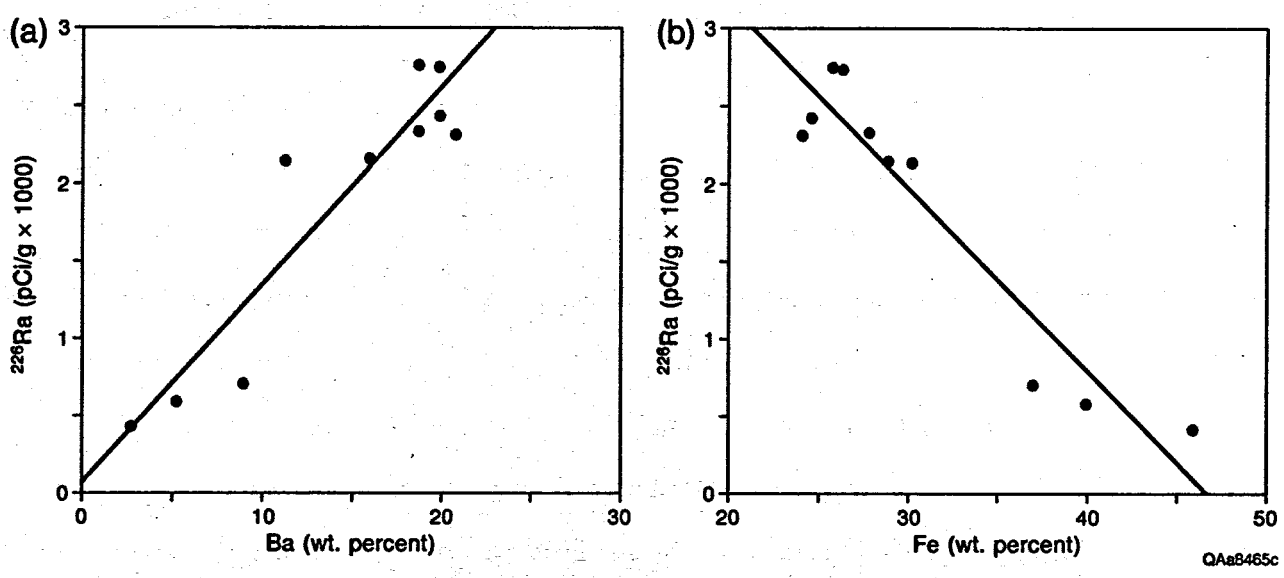

Figure 6. Plots of ^{226}Ra activity versus (a) barium and (b) total iron in NORM scale. Radium activity correlates positively (r^2=0.866) with barium content and negatively (r^2=0.901) with iron content.

is a possible scale former, but geochemical modeling of formation water compositions (following section) shows that most waters are undersaturated with respect to celestite. Formation waters are typically saturated with respect to barite under reservoir conditions (following section); thus, barite is most likely mineral to precipitate Ra in significant quantities.

Formation Water Types and Potential to Form Barite Scale in Texas Reservoirs

Previous studies have reported significantly different chemical compositions of formation water along the Texas Gulf Coast and in the Texas Panhandle. Variations in water chemistry could directly affect the occurrence of NORM in oil- and gas-field equipment in three ways. First, the salinity and chemical composition of formation water influence the mobility of Ra in sedimentary basins. Second, produced water chemistry, along with production techniques, controls the amount and type of scale that forms in oil-producing and gas-processing equipment. Scale mineralogy will in turn affect the amount of NORM removed from produced water and concentrated in equipment scale. Third, formation water chemistry records basinal processes and history. Geologic phenomena such as thermal history and large-scale diagenetic events may be important in determining Ra release from parent rocks and minerals; thus, formation water chemistry may be a useful predictor of NORM activity in production and processing equipment.

Chemical composition of water in Texas reservoirs

Studies of Texas formation water have focused primarily on the Gulf Coast and the Texas Panhandle. The Gulf Coast has been an area of intense interest both because of the enormous quantities of oil and gas produced from coastal and offshore reservoirs and because of the interest in developing geopressured-geothermal energy resources. In addition to being an important energy producing area, the Texas Panhandle was a candidate site for U.S. Department of Energy investigations to find a suitable site for high-level nuclear waste isolation during the 1980's. Formation water chemistry was investigated in both Gulf Coast and Panhandle fields to understand subsurface geochemical

conditions, hydrologic flow systems, and basinal diagenetic processes. Published data from other hydrocarbon provinces in Texas are less abundant.

Morton and Land (1987) reported that four distinct types of formation water occur in Frio Formation (Oligocene) sandstones along the Texas Gulf Coast. These types are (1) sodium-chloride water, typically highly saline, resulting from dissolution of halite, (2) sodium-acetate water resulting from shale dewatering, (3) calcium-rich water produced by extensive silicate diagenesis, and (4) a low-salinity sodium-chloride water having restricted distribution. Sodium and chloride are the predominant cation and anion, respectively, in water from Oligocene sandstones in the salt dome province of the Houston Embayment. Sodium-chloride water having generally lower salinity and high organic acid concentrations predominates along the San Marcos Arch in the Central Texas Gulf Coast. High-salinity sodium-calcium-chloride (Ca-rich) water is produced from sandstones in a small area of the South Texas Gulf Coast. Along the Rio Grande in South Texas, low-salinity sodium-chloride water prevails. Land and Macpherson (1992) and Macpherson (1992) extended this study to formation waters from all Cenozoic sandstones that could be sampled in the Texas Gulf Coast and found the same four water types with the same general distribution as reported by Morton and Land (1987). Sulfate concentrations are typically less than 100 milligrams per liter (mg/L) in all these formation water types because of bacterial sulfate reduction at ambient burial temperatures. The origin of these water types is discussed extensively in Morton and Land (1987), Land and Macpherson (1992), and Macpherson (1992) and is not repeated here. Significant to this study are the facts that (1) compositionally distinct formation waters exist in oil and gas reservoirs along the Texas coast, (2) the same compositional patterns exist in all waters sampled from Gulf Coast Cenozoic sandstones, and (3) the water compositions can be related generally to basinal geologic and hydrologic processes.

Bein and Dutton (1993) classified deep-basinal formation waters from oil and gas wells in the Texas Panhandle into sodium-chloride and calcium-chloride types. The sodium-chloride type brine is interpreted to form as meteoric water enters the basin and dissolves halite. Brines rich in calcium are interpreted to be modified connate seawater. Halite calcium-chloride and gypsum calcium-chloride waters are interpreted to be connate seawater that have been concentrated by evaporation to the point of halite

and gypsum saturation, respectively. Sulfate concentrations in these waters range from several tens to several thousand milligrams per liter.

Land and Prezbindowski (1981) and Prezbindowski (1981) investigated formation waters from the Lower Cretaceous Glen Rose and Edwards Formations, Stuart City Trend, south-central Texas. This is an area of both gas and oil production where deep saline water is diluted with meteoric water to form a brackish water zone between the basinal brines and fresh water of the Edwards aquifer. Chemical and isotopic analyses (Prezbindowski, 1981) indicate that the formation waters are characterized by molal sodium:chloride (Na:Cl) ratios less than 1 and (Cl-Na)/Mg ratios greater than 1. Sulfate concentrations in these waters range from several tens to several thousand milligrams per liter. Production depths range from 800 to 4,400 m. Land and Prezbindowski (1981), Prezbindowski (1981), and Land (1985) interpreted the deep, saline brine to be a product of halite dissolution and diagenetic reactions with silicate minerals. As the basinal brine moves upward and becomes diluted with meteoric water, additional reactions between fluid and host rock phases produce the less saline waters observed at shallower depths.

Kreitler and others (1987) investigated formation water chemistry as part of a hydrologic characterization of the East Texas Basin. These formation waters are similar to the sodium-chloride waters in the Texas Panhandle. The saline waters in this basin are interpreted to have a continental meteoric origin, sodium and chloride are the predominant ions and salinity is derived primarily from salt dissolution. Sulfate concentrations in these formation waters range from several tens to several hundred milligrams per liter.

Published chemical analyses thus indicate the presence of four volumetrically important formation water types in Texas. These are (1) a sodium-chloride water having variable salinity and sulfate concentration that is produced by evaporite dissolution, (2) a sodium-acetate water, generally less saline than seawater, that originates as water is expelled from thick shales, (3) a calcium-rich sodium-chloride water that results from evaporite dissolution coupled with extensive diagenesis of silicate minerals, and (4) a calcium-chloride water that results from evaporative concentration of seawater accompanied by diagenesis of carbonate and evaporite minerals. Mixtures of these water types with each other, with

seawater, or with meteoric water are possible. Other chemical types may exist locally, but we focused on distribution and scaling potential of the principal water types because they are most volumetrically significant in oil and gas production.

Scaling potential of Texas formation water

To investigate controls on NORM we must first determine whether there are systematic regional or geologic variations in the amount of NORM scale that can precipitate when oil, gas, and water are produced. Barite is the primary mineral of concern because Ra readily substitutes for Ba in the barite crystal structure and because barite is reported to be the principal NORM scale material. Ra also can coprecipitate in celestite (Langmuir and Riese, 1985); however, results of geochemical modeling using SOLMINEQ.88 (Kharaka and others, 1988) show that most formation waters throughout Texas are saturated with barite but not with celestite at reservoir temperatures. Similar results were reported by Macpherson (1989, 1992) for Gulf Coast formation waters. Because the solubility of barite decreases as temperature decreases, barite scale is the Ra-containing phase most likely to precipitate when water temperature drops during production.

Oil and natural gas in Texas are produced from a wide variety of reservoirs having correspondingly diverse pressures, temperatures, and water compositions. It is not practical to test geochemically all available formation water compositions for barite saturation, particularly when the quality of analytical data for many samples is unknown and in situ temperatures may be missing or inaccurate. Instead, we used SOLMINEQ.88 (Kharaka and others, 1988) to compute the equilibrium solubility constant of barite ($K=[Ba^{+2}][SO_4^{-2}]$) at 100°C. The temperature of formation water samples ranges from about 50° to 150°C, so 100°C represents typical temperature conditions. We neglected pressure effects because barite solubility is only slightly dependent on pressure (Templeton, 1960; Blount, 1977; Schulien, 1987) and because reservoir pressures are not available for most samples. Figure 7 shows the Ba and sulfate (SO_4) concentrations for all samples in the data base and the line relating Ba and SO_4 concentrations for barite equilibrium at 100°C. The good agreement between Ba and SO_4 in Texas formation waters compared to

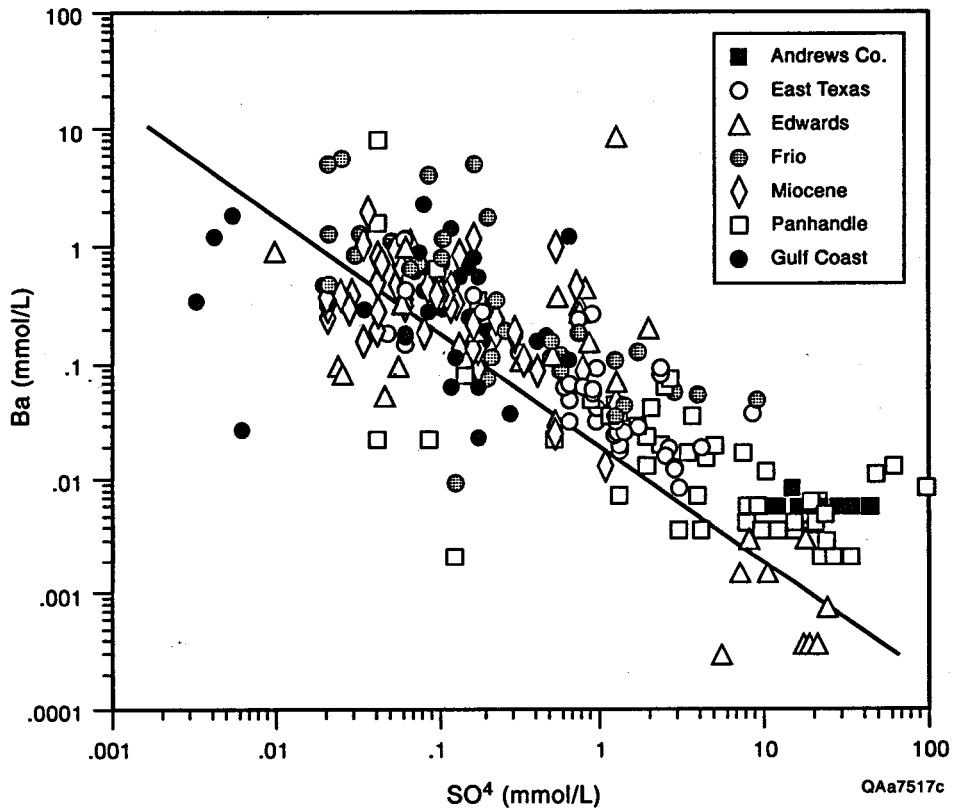

Figure 7. Plot of Ba versus SO_4 concentrations (millimoles per liter [mmol/L]) in Texas formation waters. Solid line shows the equilibrium relation between Ba and SO_4 for barite equilibrium computed by SOLMINEQ.88 and corrected for typical activity coefficients. Close agreement between predicted (line) and measured concentrations suggests most formation waters are in equilibrium with barite at reservoir temperatures.

the relation predicted for equilibrium supports the hypothesis that most waters are in equilibrium with barite under reservoir conditions.

We used SOLMINEQ.88 to compute the amount of barite that would precipitate from formation waters as temperature changes from reservoir conditions to 25°C. Calculations were performed for all samples that reported Ba and SO_4 concentrations. Results were tabulated and statistical analyses were conducted to test for significant differences between basins.

Mean values (table 4) for the amount of barite scale that can precipitate fall into three groups. Waters from the Central Basin Platform and Texas Panhandle can precipitate less than 10 cubic centimeters of barite scale per 100 barrels of water (10 cm^3/100 bbl), waters from East Texas, Frio, and Miocene reservoirs can precipitate 30 to 40 cm^3/100 bbl, and waters from the Edwards Group can precipitate more than 60 cm^3/100 bbl. Statistical analyses (95 percent confidence interval based on Student's t-Test for unpaired sample sets with unequal variances; table 4) shows that the mean value for barite precipitated from Central Basin Platform wells is significantly lower than that for any other basin represented. The mean value for barite precipitated from Panhandle wells also is significantly lower than that for any other sample set except the Edwards Group. Barite precipitated from East Texas waters is significantly lower than that precipitated from Panhandle waters. Other differences in mean values are not significant at the 95 percent confidence level. Results for the Edwards Group, however, are strongly affected by one extremely high value. Although there is no reason doubt the reported water composition, exclusion of that one sample results in a group mean of 5.6 cm^3 barite/100 bbl water (table 4). In this case the formation water samples fall into two groups: those that can precipitate less than 10 cm^3 barite/100 bbl water (Central Texas Platform, Edwards, and Panhandle waters) and those that can precipitate 30 to 65 cm^3 barite/100 bbl water (water from East Texas, Frio, and Miocene reservoirs). The change in mean value for barite precipitated from Edwards Group waters does not affect the statistical significance of differences between mean values for the various basins.

The barite scaling potential of formation waters from the studied basins generally reflects mean formation water temperature and the fact that most formation waters are saturated with barite under reservoir conditions. The Central Basin Platform and the Texas Panhandle produce the coolest

Table 4. Results of statistical analysis of amount of barite scale that can form from formation water samples showing mean values of temperature, volume of scale that can form from 100 barrels (bbl) of water, and results of Student's t-Test to evaluate significance of differences between mean values.

Basin	Temperature (°C)	Barite scale (cm^3/100 bbl)	East Texas	Edwards Group n=21	Edwards Group n=20	Gulf Coast Frio	Gulf Coast Miocene	Frio and Miocene	Panhandle
Central Basin Platform (12)	41	3.5	y	y	y	y	y	y	y
East Texas (38)	80	32.6		n	n	n	n	n	y
Edwards Group (21)	65	62.4				n	n	n	n
Edwards Group (20)	61	5.6				n	n	n	n
Gulf Coast Frio (37)	107	35.3					n	n	y
Gulf Coast Miocene (43)	93	35.5						n	y
Gulf Coast Frio and Miocene (80)	98	35.4							y
Panhandle (47)	62	9.2							

n = number of samples
y = >95 percent probability that mean values are different
n = <95 percent probability that mean values are different

formation waters, with mean temperatures of about 41°C and 62°C, respectively. Mean reservoir temperatures for water samples from the Gulf Coast are 107°C (Frio), 93°C (Miocene), and 98°C (Frio and Miocene combined). Barite solubility increases with temperature up to about 100° to 125°C, depending on salinity and pressure (Blount, 1977). Over the range of sample temperatures, hotter waters are therefore expected to precipitate greater amounts of barite than cooler waters during production.

Radium in Produced Water from Texas and Adjacent Areas

Data sources

Some data already exist regarding U, Th, and Ra in wells drilled for geothermal research, hydrocarbon production, and nuclear waste isolation. The results of these studies have been analyzed individually, but common parameters that may control radionuclide distributions regardless of basin or lithology type have yet to be explored.

In addition to the published data, new measurements were needed to study NORM in formation water throughout the state, particularly in areas where the API survey identified high NORM levels in production equipment. Our objective was to collect all available measurements of Ra and other dissolved species in produced water from oil, gas, and geothermal wells in Texas and adjacent areas so that interpretations and conclusions would not be limited to a single geologic or geographic region, nor to only the number of new samples we could obtain during the course of this study. For this reason, the data base of Ra in produced water contains values measured on samples collected as part of this study, results from various published reports, and recent Ra measurements performed on previously collected water samples.

Previous studies of Ra in Texas formation water focused on specific fields or wells. Pierce and others (1955, 1964) analyzed water, natural gas, asphaltite, and crude oil for various radioisotopes to investigate sources of U and helium in the Panhandle gas field, Texas Panhandle. Langmuir and Melchior (1985) measured radioisotope concentrations in formation waters from the Texas Panhandle

as part of an investigation into the suitability of bedded evaporite strata to host a high-level nuclear waste isolation facility. Kraemer (1981, 1985, 1993), Kraemer and Reid (1984), and Kraemer and Kharaka (1986) measured radioisotopes, including ^{226}Ra in test wells along the Texas and Louisiana Gulf Coast as part of a U.S. Department of Energy program to evaluate geothermal energy potential. Taylor (1993) plotted ^{226}Ra activities in produced-water discharges in Texas coastal waters as part of an investigation conducted by the Railroad Commission of Texas in an attempt to identify parameters that could be used to predict NORM levels.

Chemical compositions of produced water samples collected as part of this investigation were measured at the Bureau of Economic Geology Mineral Studies Laboratory (MSL) under an existing quality assurance/quality control program. Concentrations of major and most minor species are reproducible to within 5 percent, whereas trace constituents are reproducible to within 10 percent. The quality of data taken from published reports, some of which date to the mid-1960's or report only partial chemical analyses, is more difficult to evaluate. Where major cation and anion concentrations were reported, we accepted only those samples for which the charge balance (cations–anions/ cations+anions) in milliequivalents per liter was 10 percent or lower.

In addition to new samples and data extracted from the literature, we evaluated the possibility of measuring Ra activity in samples previously collected and stored under known conditions. We identified a suite of several hundred produced water samples that had been collected and analyzed for major, minor, and trace solutes as well as isotopic composition of oxygen, hydrogen, carbon, and strontium in conjunction with other research at The University of Texas at Austin's Bureau of Economic Geology and Department of Geological Sciences. These produced water samples are a significant resource for the NORM study because they were collected from a wide variety of geographic areas and geologic formations, they have already been analyzed for a large number of chemical and isotopic constituents, and they represent fields and reservoirs that have since been shut in. The field name, formation, depth of production, and storage history of these samples are well documented. It if could be shown that relevant parameters of brine composition have not changed since sample collection we could determine Ra activities in archived waters and thus greatly extend the data base. The high

salinity of most formation waters and the fact that samples were filtered and acidified upon collection should prevent the loss of Ra from stored samples caused by sorption onto the container.

Appendix 1 contains the chemical and radiometric data compiled for this study from basins throughout Texas and adjacent areas in New Mexico and the Louisiana Gulf Coast (fig. 4). The following sections describe data quality for samples from each region.

Central Basin Platform, West Texas

For this study, twelve produced water samples were collected from oil and gas wells from Martin field, Andrews County, Texas. Wells in Martin field produce from stratigraphic intervals ranging from Ordovician to Permian. Limestone, dolomite, sandstone, and chert lithologies are present. Chemical analyses were performed at the Bureau of Economic Geology MSL. ^{226}Ra and ^{228}Ra analyses were performed on seven selected samples by Core Laboratories of Casper, Wyoming, according to methods described by Demorest and Wallace (1992) and established at Core Laboratories as Standard Operating Procedures CA-GLR-06.0 and CA-GLR-07.0. These procedures were designed specifically for saline produced waters and involve chemical separation of Ra followed by counting ^{226}Ra by alpha scintillation and counting beta emission of ^{228}Ra decay products (Demorest and Wallace, 1992). Analytical errors for this set of samples are approximately 20 pCi/L for ^{226}Ra and ^{228}Ra. Detection limits are approximately 7 pCi/L for ^{226}Ra and 30 pCi/L for ^{228}Ra.

Edwards Group, south-central Texas

Water samples from the Edwards Group (Lower Cretaceous carbonate strata) were loaned to us by Dr. Lynton Land, University of Texas at Austin Department of Geological Sciences. The sample suite was collected in 1990 as part of a joint U.S. Geological Survey–University of Texas investigation of the saline portion of the Edwards aquifer. All samples had been filtered at the time of collection through 0.45 µm membrane filters and both acidified and untreated aliquots were preserved. Repeat chemical analyses performed at MSL in 1994 duplicated the major and minor ion concentrations

determined at the Department of Geological Sciences in 1990 to within the limits of analytical uncertainty. Because Ba and Ra have similar geochemical characteristics and because repeat analyses of Ba concentrations in the acidified aliquots were in good agreement with values originally measured we considered these samples to retain representative Ra concentrations. Sixteen samples covering a depth range of 165 to 3,374 m and a salinity range of 1,900 to 227,600 mg/L total dissolved solids (TDS) were analyzed for ^{226}Ra by Core Laboratories. Because only about 0.002 half-lives of ^{226}Ra had passed since the time of sample collection, we did not adjust ^{226}Ra activities for decay in storage. ^{228}Ra data were corrected to activities at the time samples were collected.

Delaware Basin, southeastern New Mexico

Herczeg and others (1988) published Ra data for saline ground waters, lakes, and springs in the Delaware Basin, southeastern New Mexico, adjacent to Andrews County, Texas. Thirteen samples were collected from wells at the Waste Isolation Pilot Project (WIPP) site, oil or gas wells, or saline springs and were judged to be similar to produced water from oil and gas wells. Producing lithologies are anhydrite, halite, carbonate, dolomitic sandstone, cherty limestone, and shaly limestone. We could not evaluate the charge balance of these samples because Herczeg and others (1988) published only partial chemical analyses. However, we have included the reported chemical concentrations and Ra activities in our data base because they augment the sample coverage of a variety of lithologies near an important oil- and gas-producing part of the state.

Texas Panhandle

Radioisotopes in formation water from the Texas Panhandle were previously investigated for two different purposes. Investigations during the 1950's and 1960's focused on the origin of helium in the Panhandle gas field, located along the Amarillo–Wichita Uplift. Studies during the 1980's measured U, Ra, and Rn radioisotope activities to interpret the suitability of bedded salt formations for high-level nuclear waste isolation. Related investigations elucidated the origin, age, and movement of

formation water in the Texas Panhandle. These various studies provide a large data base of water chemistry, Ra activity, and host rock composition.

Pierce and others (1964) published 75 formation water analyses, including ^{226}Ra concentrations. Of these, 70 had acceptable charge balances and were included in the data base. Producing formations were not identified; however, it is noted that "The highly saline brines of the Panhandle field are most likely derived from the evaporites of Leonard age, which overlie the oil and gas reservoir rocks." Leonard age strata in the Texas Panhandle include the Wichita Group (anhydrite, dolomite, and shale) and the lower Clear Fork (siltstone and shale interlaminated with dolomite and anhydrite). Pierce and others (1964) found that both Ra and Ca concentrations are highest in formation waters that have high chloride to sulfate ratios and high salinities. These relations were interpreted as reflecting the similar geochemical behavior of Ra and Ca and the effects of ion exchange. Pierce and others (1964) also conclude that Ra concentrations are not directly controlled by the U content of encasing strata. Disequilibrium ages, the time since isotopes were in equilibrium with each other, of four to five days were calculated on the basis of activity ratios for ^{226}Ra and ^{223}Ra (a decay product in the actinium series) and for ^{228}Ra and ^{224}Ra . These short ages suggest that Ra isotopes were derived from parent nuclei in the immediate vicinity of the well bore.

Langmuir and Melchior (1985), Dutton and Orr (1986), Fisher and Kreitler (1987), and Bein and Dutton (1993) investigated the composition and movement of water in strata ranging from pre-Pennsylvanian to Permian in the Texas Panhandle as part of an integrated geologic, geochemical, and hydrologic investigation to evaluate the suitability of bedded evaporite strata for a high-level nuclear waste repository. Radioisotope data for four deep-basin samples were collected as part of this work (Langmuir and Melchior, 1985). Because of the extensive data base, the variety of lithologies and formations previously sampled, and the large collection of formation water samples archived at MSL, we evaluated the chemical stability of selected samples during storage. Repeated analyses of major cations and anions as well as Ba indicated that original compositions were preserved in acidified, field-filtered samples. In one case we were able to compare the ^{226}Ra activity of a sample collected and analyzed in 1985 by Langmuir and Melchior (1985) with ^{226}Ra measured in 1994 by Core Laboratories.

Good agreement between the original and recent values indicated that ^{226}Ra activities measured as part of this study are representative of formation conditions. Therefore, 25 formation water samples collected earlier (Fisher and Kreitler, 1987; Bein and Dutton, 1993) were analyzed for ^{226}Ra and these results were combined with the data of Langmuir and Melchior (1985) to complement the Texas Panhandle data base.

Texas Gulf Coast

Formation water samples from wells along the Texas and Louisiana Gulf Coast were analyzed for Ra isotope activity as part of geothermal energy tests and as part of a Railroad Commission of Texas NORM investigation. Kraemer and Reid (1984) reported ^{228}Ra and ^{228}Ra activities in wells drilled for U.S. Department of Energy geothermal energy tests. Tested intervals were in the Tertiary Frio and Cretaceous Tuscaloosa sandstones at depths ranging from 2,984 to 6,238 m. Chemical data were not presented in Kraemer and Reid (1984) but are available elsewhere (Kharaka and others, 1977; Kharaka, 1978a, b; Kraemer and Kharaka, 1986; Kraemer, 1993). Kraemer and Reid (1984) reported that Ra activity correlates better with total salinity than with any other parameter. A study by the Railroad Commission of Texas (Taylor, 1993) presented ^{226}Ra values for offshore oil and gas wells without full chemical analyses. Plotted data show that Ra levels in produced waters from offshore wells in the Gulf of Mexico are higher in Oligocene Frio reservoirs than in overlying Miocene reservoirs. In waters from both Frio and Miocene formations, Ra levels increase with increasing salinity. These data suggest that Ra may be more readily mobilized from deeper, hotter formations and that high salinity tends to prevent Ra immobilization by processes such as ion exchange or sorption.

Relations between radium activity, location, and water chemistry

For analytical reasons, ^{226}Ra is more commonly determined than ^{228}Ra. Even though the two Ra isotopes are members of different decay series, most studies find a close correlation. Our data set (Appendix 1) contains 153 measurements of water chemistry and ^{226}Ra activity; 20 of these samples

were also analyzed for ^{228}Ra. The correlation between ^{226}Ra and ^{228}Ra (fig. 8) is excellent (r^2=0.96; slope of regression line = 1.03); therefore, the following discussions based on ^{226}Ra data can be extrapolated to ^{228}Ra activities.

^{226}Ra activities in formation waters (Appendix 1) range from 0.1 to 5,150 pCi/L; 95 percent of the values fall between 2.0 and 2,290 pCi/L. Fourteen waters (9 percent of samples) have values greater than 1,000 pCi/L, and 17 samples (11 percent of samples) have values between 500 and 1,000 pCi/L. There is little apparent geographic control on ^{226}Ra activity values. Formation water samples that have more than 1,000 pCi/L ^{226}Ra are found in the Central Basin Platform (2 samples), Delaware Basin (1 sample), the Gulf Coast (1 sample), and the Texas Panhandle (10 samples), and values greater than 500 pCi/L occur in each of the sample groups (Appendix 1).

Mean values of ^{226}Ra activity range from 140 pCi/L in water from the Edwards Group to 958 pCi/L in water from the Central Basin Platform (table 5). The Student's t-Test was used to determine whether differences in mean Ra activities varied significantly among the sample groups. Results suggest that ^{226}Ra activity in formation water from wells in the Central Basin Platform is significantly (95 percent confidence level or higher) greater than in water from the other basins sampled and that ^{226}Ra activity in water of the Edwards Group is significantly lower than in water from the Texas Panhandle (table 5). However, the high mean ^{226}Ra value for water from the Central Basin Platform reflects the fact that two samples have ^{226}Ra activities greater than 2,000 pCi/L, whereas the other five samples are all less than 800 pCi/L. If the two exceptionally high values are omitted, the mean value for Central Basin Platform waters is 431 pCi/L, and this mean value is not significantly different from mean values for ^{226}Ra in the other basins (table 5).

Previous studies reported a general correlation between Ra activity and salinity in formation water; no other correlations between Ra and water chemistry, production depth, or temperature were noted. Kraemer and Reid (1984) found a correlation between Ra activity and TDS for produced water samples from Gulf Coast reservoirs in Texas and Louisiana. A plot of log ^{226}Ra activity versus log TDS for water from geopressured-geothermal wells yielded a correlation coefficient (r^2) of 0.81 whereas a similar plot that included data from commercial oil and gas wells yielded an r^2 value of 0.52 (Kraemer and

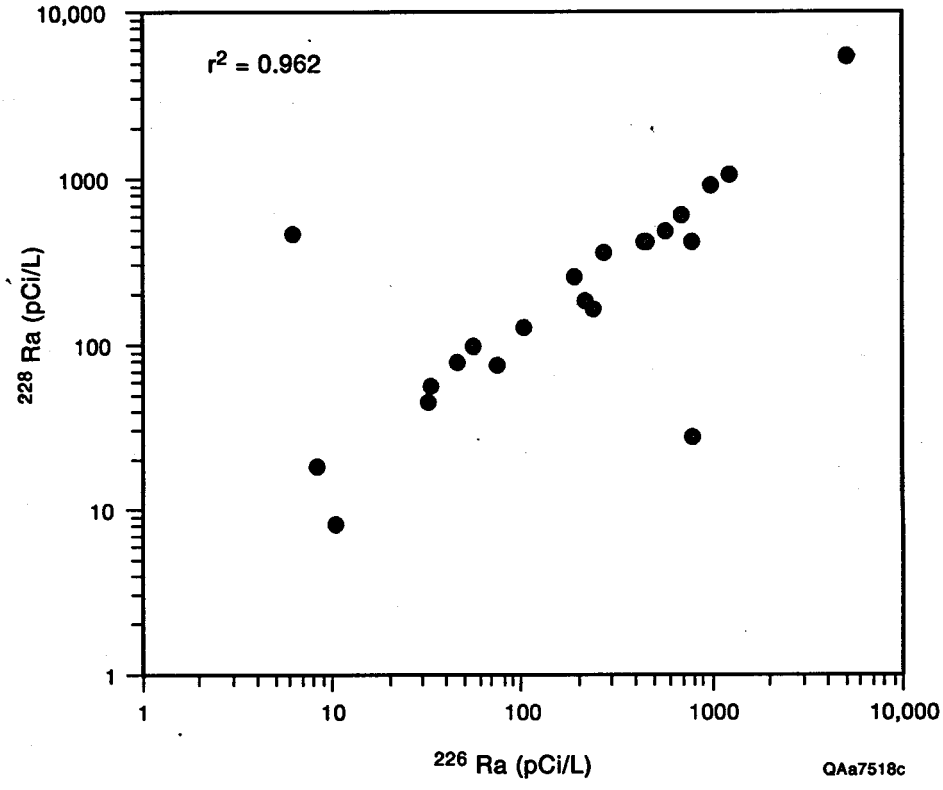

Figure 8. Plot of ^{226}Ra activity versus ^{228}Ra activity. Excellent correlation between the two radioisotopes indicates that activity of the less commonly measured ^{228}Ra isotope can be predicted from the activity of ^{226}Ra.

Table 5. Results of statistical analysis of ^{226}Ra activity in formation water samples showing mean values and results of Student's t-Test to evaluate significance of differences between mean values. T-Test values less than 0.0500 indicate that mean values are different at the 95 percent confidence level or greater.

	Mean pCi/L	Delaware Basin	Edwards Group	Gulf Coast	Panhandle
Central Basin Platform (n=7)	958	0.0050	0.0003	0.0017	0.0123
Central Basin Platform (n=5)	431	0.3014	0.0727	0.3409	0.6402
Delaware Basin (n=11)	284		0.2956	0.6036	0.5210
Edwards Group (n=16)	140			0.6209	0.0273
Gulf Coast (n=20)	296				0.1804
Panhandle (n=99)	370				

n = number of samples

Reid, 1984). Data plots of Taylor (1993) show the same general trend for produced waters from offshore Gulf Coast oil and gas wells that produce from the same formations as the wells sampled by Kraemer and Reid (1984). Pierce and others (1964) reported that Texas Panhandle waters that have high Ra activities also have high Cl concentrations, although many waters with high chlorinity have low Ra contents. The correlation coefficient r^2 for log ^{226}Ra and log Cl for data reported by Pierce and others (1964) is 0.56.

We cannot explore statewide correlations between Ra and TDS because not all samples included in our data base were analyzed for the full suite of major and minor ions. However, for samples with complete analyses, Cl correlates well with TDS (r^2=0.995) (fig. 9). Thus correlations that are significant with TDS should also be significant with Cl. Figure 10 shows the relation between ^{226}Ra activity and Cl for all samples in Appendix 1; table 6 lists correlation coefficients relating log ^{226}Ra activity and log Cl content. Clearly the relation between ^{226}Ra and Cl that holds for Gulf Coast sandstones is not universal. Sample sets with the highest correlation coefficients are those in which all waters were derived from similar lithologies, for example, water samples from Gulf Coast sandstones (r^2=0.71) and those from Edwards Group carbonates (r^2=0.63). Data sets that contain different types of water samples (Delaware Basin) or waters hosted by different lithologies (Central Basin Platform) have only poor correlations between ^{226}Ra and Cl (table 6). Figure 10 does illustrate that low-salinity waters do not support high Ra activities. ^{226}Ra activities greater than 200 pCi/L are found only in waters that have more than about 20,000 mg/L Cl (36,000 mg/L TDS).

Statistical correlations between radioactivity and other dissolved constituents were determined to explore hydrochemical controls on ^{226}Ra activity in formation water (table 6). Correlations were considered geologically significant only if they accounted for more than 50 percent of the variation in Ra activity, that is, only if r^2 was greater than 0.5. Correlations were sought between log Ra activity and the log of major ion concentrations because Ra activity and ionic concentrations fit a log-normal distribution more closely than a normal distribution. Results (table 6) show that there is no strong correlation between depth, temperature, or major ion concentrations for all formation waters examined, formation waters from the Delaware Basin, or formation waters from the Texas Panhandle.

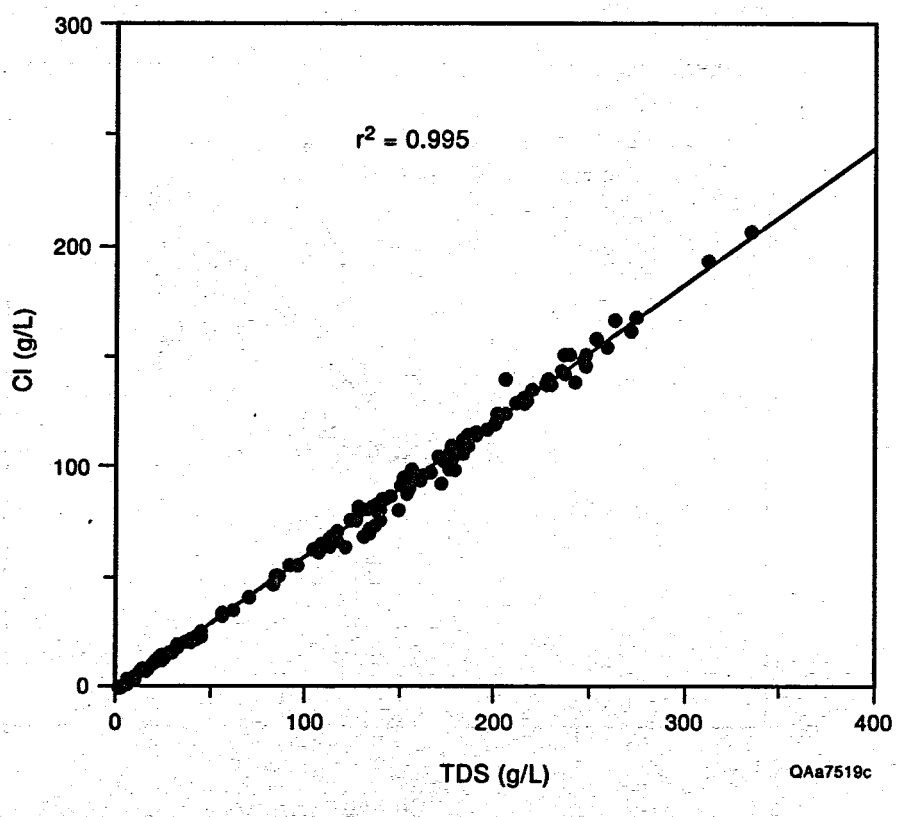

Figure 9. Plot of total dissolved solids (TDS) versus chloride (Cl) concentrations for produced waters that have been analyzed for ^{226}Ra or ^{228}Ra activity. Excellent correlation indicates that relations between ^{226}Ra or ^{228}Ra activity and TDS should also hold for relations between ^{226}Ra or ^{228}Ra activity and Cl.

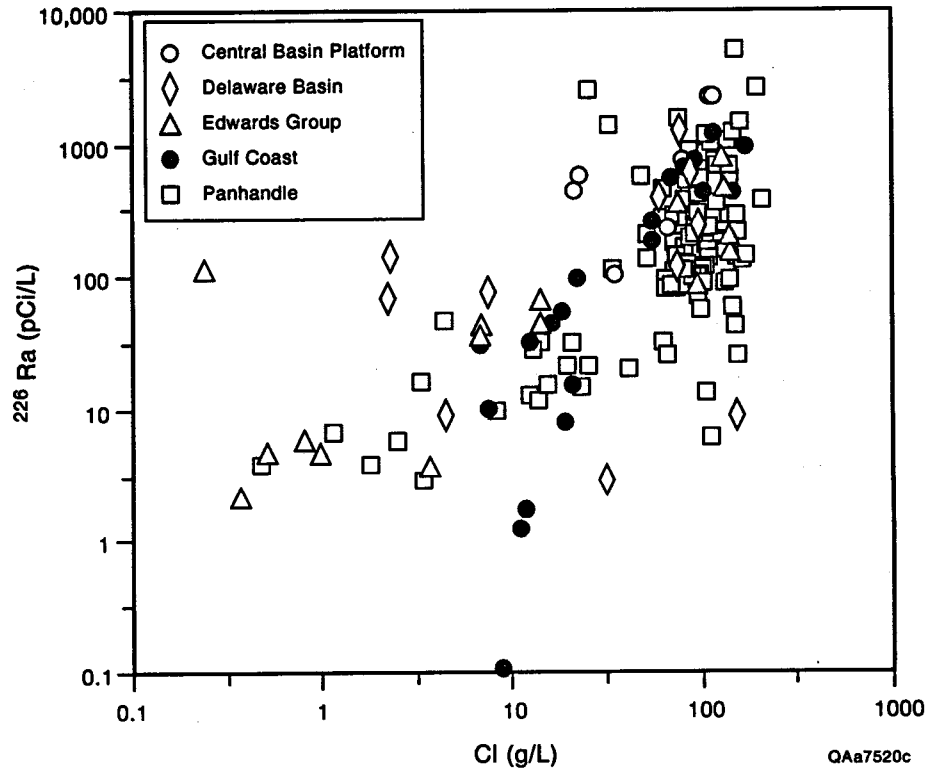

Figure 10. Plot of chloride (log Cl) concentration versus ^{226}Ra activity (log ^{226}Ra) for produced waters. Waters having high Ra activity also have high chlorinity. However, the direct correlation between chlorinity or salinity and Ra activity observed by Kraemer and Reid (1984) for Gulf Coast geothermal wells is not generally observed.

Table 6. Correlation coefficients (r^2) showing relations between radium activity and other hydrochemical parameters.

	All samples log ^{226}Ra	Central Basin Platform log ^{226}Ra	Delaware Basin log ^{226}Ra	Edwards Group log ^{226}Ra	Gulf Coast log ^{226}Ra	Panhandle log ^{226}Ra
Depth (m)	< 0.5	< 0.5	na	< 0.5	0.556	< 0.5
Temp. (C)	< 0.5	< 0.5	na	< 0.5	< 0.5	< 0.5
log Na	< 0.5	< 0.5	na	0.648	0.695	< 0.5
log K	< 0.5	< 0.5	na	0.667	0.637	< 0.5
log Ca	< 0.5	< 0.5	na	0.674	0.722	< 0.5
log Mg	< 0.5	< 0.5	na	0.550	0.695	< 0.5
log Ba	< 0.5	< 0.5	na	0.682	0.548	< 0.5
log Cl	< 0.5	< 0.5	< 0.5	0.630	0.709	< 0.5
log SO_4	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
log Alkalinity	< 0.5	-0.972	< 0.5	< 0.5	< 0.5	< 0.5
log TDS	< 0.5	< 0.5	na	0.689	0.707	< 0.5

We attribute this lack of correlation to the diverse reservoir lithologies from which water is produced. Correlations between Ra activity and water chemistry are best for waters from the Edwards Group and the Gulf Coast (table 6). We interpreted this relation to indicate that general water chemistry can be a good predictor of Ra activity if a set of water samples represents similar reservoir lithologies or a group of similar lithologies.

Relations between Ra activity and formation water type were also investigated by calculating correlations between ^{226}Ra and those parameters used by Morton and Land (1987) and Bein and Dutton (1993) to identify the different water types. The results generally show that correlations are better with salinity or chlorinity than with the parameters that define water types. The available data do not suggest that chemically distinct formation water types have systematically different Ra activities.

Geochemical Controls on NORM in Scale

Natural radioactivity of the equipment scale that ultimately accumulates in production and processing equipment is complexly dependent on several variables. One is the capacity of the formation water to precipitate Ra-containing scale when water, oil, and gas are produced. A second is the Ra activity of the formation water or, more precisely, the activity ratio of Ra to major cations for which Ra can substitute in scale minerals. The third major variable is the way in which Ra is included in scale minerals.

Several lines of evidence point to barite as the major scale component that can preferentially incorporate Ra. Because nearly all formation waters we tested are near or at saturation with barite under reservoir conditions and because barite solubility decreases with decreasing temperature below about 125°C, barite scale will form as most waters are produced. The amount of barite scale that can form depends both on the temperature difference between reservoir and surface and on the proportions of Ba and SO_4 in solution. Barite precipitation removes Ba and SO_4 in equal molal amounts; thus, a water can be highly oversaturated with barite at surface conditions but deposit little material because scale precipitation is limited by the amount of the least abundant ion. Ra activity and the Ra/Ba ratio in formation water are highly variable in reservoirs throughout the state. Furthermore, although high Ra

activity is generally associated with high salinity, there is no systematic relation between Ra/Ba ratio and total salinity. Thus, Ra activity alone cannot be used to predict NORM activity in scale.

Incorporation of Ra in scale minerals can be estimated on the basis of available thermodynamic data. However, much more information regarding NORM scale composition is needed before we can evaluate how accurately such estimations reflect actual conditions in oil and gas fields. Our approach to estimating the amount of NORM scale in Texas oil and gas operations was as follows. First, we assumed that barite is the mineral that hosts Ra and that Ra coprecipitation in barite follows the distribution coefficient (D) equation of Langmuir and Melchior (1985) and Langmuir and Riese (1985) between 0° and 100°C:

$$\log D = (428.2/T)-1.181,$$

where T is temperature in degrees Kelvin and D is as defined previously. Note that D increases as T decreases; lower temperatures of barite precipitation favor greater substitution of Ra for Ba. Therefore barite that precipitates in surface equipment is predicted to be more radioactive than barite that precipitates in the well bore near the producing interval. We calculated values of D for reservoir temperature and surface temperature (25°C). We also considered the case where precipitation is so rapid that there is no discrimination between Ra and Ba in the crystal lattice and therefore D=1. (2) We used the three values for D, chemical analyses of formation waters, reported or measured ^{226}Ra activity, reservoir temperature, and the amount of barite scale that would form during production (previously calculated using SOLMINEQ.88) to calculate the ^{226}Ra activity of the barite scale that would form from 100 bbl of produced water. This gives an estimate of the total radioactivity per unit of produced water. (3) We calculated the ^{226}Ra per gram of barite scale. This gives an estimate of the radioactivity per unit of scale material or the "intensity" of the NORM activity. We used the mean values of Ra activity for the Central Basin Platform, Edwards Group, Gulf Coast, and Texas Panhandle and performed the calculations for water samples for which the concentrations of Ba and SO_4 were known and reservoir temperature was known or could be estimated from reservoir depth. Results show the combined effects of statewide differences in formation water composition and Ra activity, reservoir temperature, and potential to precipitate barite during production. These values are upper limits to the

amount and radioactivity of scale expected because (1) the scale may be distributed throughout the various equipment components, (2) other scale minerals can also precipitate and essentially dilute the radioactivity caused by Ra in barite, (3) actual scale will likely be less dense that the barite minerals used to obtain the thermodynamic data, and (4) the distribution coefficient (D) may be lower in saline formation waters.

Table 7 presents the results of six calculations. The first three give mean values for the total radioactivity due to ^{226}Ra in the barite scale predicted to precipitate from 100 bbl of produced water when (1) Ra/Ba ratio in barite reflects reservoir temperature, (2) Ra/Ba ratio in barite reflects surface temperature, and (3) Ra/Ba ratio in barite reflects formation water composition. Columns 4 through 6 give mean values for the radioactivity per gram of barite scale under the same assumptions. Formation water from wells in the Central Basin Platform produces the greatest total amount of radioactivity, whereas water from wells in the Edwards Group produces the most highly radioactive scale (table 7). Waters from Gulf Coast wells produce the least amount of total radioactivity and the least radioactive scale.

We used the Student's t-Test to evaluate whether the differences between basins are statistically significant. Results (table 7) suggest that all differences between basins are significant at the 95 percent confidence level, with the exceptions that total radioactivity in scale from Edwards waters is indistinguishable from total radioactivity in scale from Gulf Coast wells and scale from Central Basin Platform and Edwards waters has the same activity (pCi/g).

SUMMARY

Natural radioactivity is commonly produced from oil, gas, and geothermal reservoirs. In some cases the fluids themselves, or the scale that forms from produced water, may be sufficiently radioactive to cause safety, environmental, or regulatory concerns as well as increased costs for special handling and disposal practices. A national survey of radioactivity in oil-producing equipment and gas-processing facilities (Otto, 1989) showed that naturally occurring radioactive materials (NORM) in Texas oil and natural gas facilities are as high as activities elsewhere in the United States and the world.

Table 7. Mean values and results of t-Test analyses of the radioactivity caused by ^{226}Ra incorporated in barite scale from formation waters under different scenarios.

			pCi/100 bbl reservoir T	pCi/100 bbl 25°C	pCi/100 bbl D=1	pCi/g scale reservoir T	pCi/g scale 25°C	pCi/g scale D=1
Central Basin Platform		Average	7.21E+06	8.44E+06	4.69E+06	4.82E+05	5.60E+05	3.11E+05
Edwards Group		Average	1.94E+06	2.35E+06	1.30E+06	1.17E+06	1.29E+06	7.16E+05
Gulf Coast		Average	1.34E+06	2.41E+06	1.34E+06	9.06E+03	1.75E+04	9.70E+03
Texas Panhandle		Average	4.29E+06	6.30E+06	3.50E+06	2.69E+05	3.85E+05	2.14E+05
Central Basin Platform	vs.	Edwards	y	y	y	n	n	n
Central Basin Platform	vs.	Gulf Coast	y	y	y	y	y	y
Central Basin Platform	vs.	Panhandle	y	y	y	y	y	y
Edwards	vs.	Gulf Coast	y	y	n	y	y	y
Edwards	vs.	Panhandle	y	y	y	y	y	y
Gulf Coast	vs.	Panhandle	y	y	y	y	y	y

pCi/100 bbl: Picocuries activity in barite scale that forms from 100 barrels of formation water
pCi/g: Picocuries activity per gram of barite scale
Reservoir T: Distribution coefficient calculated for reservoir temperature
25°C: Distribution coefficient calculated at 25°C to represent surface temperature
D=1: Distribution coefficient set to 1.0
y = >95 percent probability that mean values are different
n = <95 percent probability that mean values are different
See text for discussion

This study investigated natural controls on the amount of radioactivity in sedimentary basins and produced waters and the accumulation of natural radioactivity in oil-producing and gas-processing facilities. We focused on the isotopes ^{226}Ra and ^{228}Ra and the scale mineral barite because these are the most commonly reported sources and forms of NORM in produced water and production equipment, respectively. The goal was to identify screening criteria that could be used by plant operators and health and safety regulators to anticipate special needs in areas where NORM levels are likely to be greater than normal. Although samples and data were collected from Texas and adjacent areas in New Mexico and the Louisiana Gulf Coast, results and conclusions should generally be applicable because the level, type, and sources of NORM activity in Texas reservoirs are similar to those reported at other oil and gas operations in the United States and throughout the world.

Data obtained by measuring radioactivity in various types of oil- and gas-field equipment and aggregating values by county revealed elevated NORM activity levels in oil and gas facilities in north, north-central, east, south-central, and Gulf Coast Texas (Otto, 1989). The highest activities were found along the south Texas Gulf Coast. Results cannot be extrapolated to unsurveyed areas because sample sites were neither randomly selected nor uniformly distributed. However, the results do show that (1) not every major oil or gas field has associated high NORM levels, and (2) no major hydrocarbon producing basin in Texas is exempt from high levels of natural radioactivity.

A survey of the U and Th content of sedimentary rocks and the minerals typically encountered in sedimentary basins shows no order-of-magnitude differences in concentrations of Ra-producing elements between siliciclastic and chemical sedimentary rocks. Sandstones, common shales, carbonate rocks, and the individual minerals that compose these strata have mean U and Th contents in the 1- to 10-ppm range. In contrast, black and organic shales, U- and Th-rich accessory minerals, and carbonaceous accumulations can have U and Th concentrations in the 1,000- to 70,000-ppm range. The combination of slow natural transport velocities relative to Ra isotope half-lives and the relatively short production times of most reservoirs makes long-distance Ra transport to well bore highly unlikely. Burial diagenesis can either promote or retard alpha-recoil release of Ra from parent U- and Th-containing solids. Massive dissolution and reprecipitation or recrystallization can redistribute U and Th

from grain interiors to new phases or surface coatings on other grains where alpha-recoil products have greater access to reservoir fluids. In contrast, pore-filling and grain-coating cements can form a barrier between alpha-recoil products and the fluid phase.

To investigate geologic and hydrochemical controls on NORM activity we assembled a data base of 153 formation water samples for which chemical and Ra isotopic analyses were available. The data included new samples and analyses, results from publications, and new analyses of previously collected formation waters. The samples were obtained from reservoirs in the Texas Panhandle (Dalhart, Anadarko, Palo Duro, and Hardeman Basins and the Amarillo Uplift), the Edwards Group (south-central Texas), the Central Basin Platform (West Texas), the Texas and Louisiana Gulf Coast, and the Delaware Basin (southeastern New Mexico). Samples in the data base represent widely diverse conditions of salinity; Ra activity; reservoir depth, temperature, and lithology; and geographic location. Mean ^{226}Ra activity ranged from 958 pCi/L in the Central Basin Platform to 140 pCi/L for the Edwards Group. On the basis of the available samples, formation waters can be divided into three groups. Those from the Central Basin Platform are expected to have generally high mean ^{226}Ra activity (greater than 400 pCi/L), those from the Texas Panhandle, Gulf Coast, and Delaware Basin are expected to have intermediate mean ^{226} Ra activity (200 to 400 pCi/L), and those from the Edwards Group are expected to have low mean ^{226}Ra activity (less than 200 pCi/L). Statistical analysis, however, reveals the variability of ^{226}Ra activities and the difficulty of obtaining sufficient samples for confident predictions. Choosing random data subsets from the smaller sample groups greatly affects the mean value.

Correlations between ^{226}Ra activity and other water composition parameters shows that relations previously reported for samples from Gulf Coast reservoirs do not hold for any other group of samples nor for the combined set of analyses. We conclude that parameters such as host rock lithology and diagenetic history are as important as water chemistry in supporting high aqueous ^{226}Ra activities. One generalization that can be made is that ^{226}Ra activities greater than about 200 pCi/L require chlorinities greater than 10,000 mg/L; higher ^{226}Ra activities cannot be supported by less saline waters.

To investigate statewide variations in the capacity of formation water to precipitate NORM scale, we assembled a data base that consists of several hundred formation water analyses. Published reports, observations, and thermodynamic relations suggest that barite is the most common NORM scale. We used the geochemical modeling program SOLMINEQ.88 (Kharaka and others, 1988) to predict that amount of barite that could precipitate from formation waters of the Texas Panhandle, Gulf Coast, Edwards Group, Central Basin Platform, and Delaware Basin. We then used an experimentally derived distribution coefficient which describes how Ra will substitute for Ba in barite to estimate the radioactivity of barite scale in the various basins. These results combine both the mean ^{226}Ra activity of each basin with the barite-forming capacity of formation water from each basin. Although the absolute values of ^{226}Ra activity in scale are subject to the effects of errors in water chemistry analyses, reservoir temperatures, lack of pressure values, and uncertainty in the thermodynamic data, the results are useful for ranking the relative NORM-forming potential of produced water from different geographic and geologic settings.

Results are presented two ways. We first calculated the radioactivity of scale that could precipitate from each 100 bbl of produced water. This value reflects the mean Ra/Ba ratio in the water, the amount of barite that can form from 100 bbl of water, and the reservoir temperature. These results predict high scale radioactivities in the Central Basin Platform, intermediate activities in the Texas Panhandle, and low activities in the Edwards Group and Gulf Coast reservoirs. We also calculated that amount of radioactivity per gram of scale. This value reflects the mean Ra/Ba ratio in the water and reservoir temperature but not the total amount of barite that can precipitate. These results predict significant differences between the four formation water groups with scale radioactivities decreasing in the order Edwards Group > Central Basin Platform > Texas Panhandle > Gulf Coast.

Information for this study was gathered from all available sources. The resulting data sets included complete chemical analyses of several hundred formation waters from basins throughout the state and 153 formation water analyses that included ^{226}Ra activity. In addition, we obtained chemical, mineralogical, and radiological analyses of 20 scale samples. Although this data base is large, it inadequately represents the number of geographic, geologic, geochemical, and hydrologic variables

in Texas oil and gas fields that can affect NORM distributions in production and processing equipment. Chemical, mineralogical, and radiological characterization of NORM scale in particular is sparse. A larger data base of well-characterized water and scale samples might reveal controls on NORM distributions that could not be resolved using currently available data.

CONCLUSIONS

This investigation has found that NORM levels in produced fluids and equipment scale are controlled primarily by local geologic variables that determine the abundance of U and Th within a few hundred meters of the well bore. These locally high concentrations of Ra parent isotopes can generally be anticipated on the basis of regional and local geologic information. Other factors that influence NORM levels in oil- and gas-field operations are related to the original reservoir rock, diagenetic modifications, formation water chemistry, and production and disposal practices. Although we find no reliable state-wide quantitative predictors of NORM levels, local (reservoir- or field-scale) predictors do exist and can help operators and regulators anticipate special procedures required for the safe handling and disposal of natural radioactivity associated with hydrocarbon or geothermal production.

Geographic and Geologic Associations

The national survey sponsored by API shows general areas and counties where NORM levels in oil-producing and gas-processing equipment are above median values. These statistical data identify the South Texas Gulf Coast as particularly prone to high NORM activities. Without information concerning the reservoir strata and length of time these facilities were in operation it is impossible to determine why this is an area of high radioactivity. It is highly likely that the NORM levels in the South Texas Gulf Coast reflect the higher abundance of volcanic rock fragments carried to the Gulf of Mexico by the Rio Grande.

Transport distances are limited by the geologically short half-lives of ^{228}Ra and ^{226}Ra coupled with the slow natural fluid velocities and the relatively short production times of most reservoirs. Therefore,

long-distance transport of NORM sources is much less likely than local derivation of the radioactivity. Typical reservoir (sandstones, limestones, and dolostones) and associated lithologies (siltstones, mudstones, and shales) have U and Th concentrations in the 1- to 10-ppm range. Release of Ra isotopes from these rocks to produced fluids will be favored by small grain size (large ratio of surface area to grain volume), high and well-connected porosity, and water-filled pore spaces.

Much more important are the volumetrically small accumulations of U- and Th-rich strata such as black, organic- and metal-rich shales, lag accumulations of heavy and accessory minerals, and carbonaceous material derived from hydrocarbon deposits. The occurrence of these accumulations in a play, field, or reservoir setting can be anticipated from basic geologic information. Black, organic- and metal-rich shales form from deposition in reducing conditions that develop in deep waters when circulation is restricted. These conditions commonly occur during times of rapid sea-level rise and mark the bases of transgressive sequences. Concentrations of heavy or accessory minerals typically accumulate where transport energy is sufficiently high that less dense grains remain in transport. Accumulations of these minerals are therefore anticipated at the bases of fluvial or distributary channels or in heavily wave- or current-modified beach or shoreface deposits and in sandstones derived from igneous and metamorphic source rocks. Carbonaceous matter such as the Texas Panhandle asphaltite accumulations might be expected to occur near the margins of hydrocarbon deposits.

Diagenetic Associations

Diagenesis of reservoir rocks can either promote or reduce Ra mobility. Pore-filling or grain-coating cements can shield the U- and Th- bearing grains from pore water, thus not permitting alpha-recoil products to escape the solid material of the reservoir. Conversely, large-scale remobilization of sedimentary materials through feldspar and clay dissolution-reprecipitation reactions of recrystallization of carbonate strata can release trace U and Th from the rock matrix. Because U and Th form highly insoluble phases under reservoir conditions, this remobilization effectively moves the Ra parent isotopes to authigenic phases or grain coatings where alpha-recoil products have a much greater opportunity to

escape to the fluid phase. Which of these diagenetic effects will predominate in a reservoir cannot be predicted statewide but can be readily established by local, field-specific investigations.

Water Chemistry Associations

Although no statewide predictive associations were found between Ra activity and other water chemical parameters, good correlations do exist between Ra activity and total salinity in Gulf Coast geothermal reservoirs. In restricted geographic areas where producing reservoirs have similar lithology and burial history, a semipredictive relation was found between Ra activity and total salinity (Kraemer and Reid, 1984). Similar relations probably exist within fields but could not be established from our data set. The Texas data base does indicate that Ra activities greater than about 200 pCi/L require chlorinities greater than 20,000 mg/L. Apparently Ra can successfully compete with more abundant cations for ion exchange or sorption sites in less saline waters.

Equipment Scale Associations

Ra substitution for Ba in barite is the main mechanism by which radioactive Ra isotopes are removed from water and concentrated in equipment scale. Because most Texas formation waters are at or near barite saturation under reservoir conditions, the amount of barite scale that can form during production depends on the change in solubility between reservoir and surface conditions. The radioactivity of that scale depends on how much Ra substitutes for Ba in the mineral.

Barite solubility depends on temperature, pressure, and ionic strength of the solution. Under typical reservoir conditions, however, barite solubility is at a maximum at temperatures of about 125°C. Waters near this temperature are capable of precipitating more barite scale than hotter or colder waters. The amount of barite that actually precipitates is limited by the less abundant ion. Therefore for any degree of oversaturation at surface conditions, waters that have nearly equal molar concentrations of Ba and SO_4 will deposit the greatest amount of mineral scale. Water analyses in the Texas data base generally are abundant in either Ba or SO_4 and depleted in the complementary ion. For this reason, barite precipitation

can be significantly increased if waters are mixed either during production or waste disposal. Ra substitution for Ba in barite depends on the solution Ra/Ba ratio and temperature of precipitation. High Ra/Ba ratios and low precipitation temperatures favor Ra concentration in barite scale.

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