DOE/BC/15035-1
(OSTI ID: 14126)

Evaluations of Radionuclides of Uranium, Thorium, and Radium Associated
With Produced Fluids, Precipitates, and Sludges from Oil, Gas, and Oilfield
Brine Injection Wells in Mississippi

Semi-Annual Technical Progress Report
March 1, 1998-August 31, 1998

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Report Issue Date: September 24, 1998

Performed Under Contract No. DE-FG26-97BC15035

MS Department of Environmental Quality
Office of Geology
Jackson Mississippi

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Evaluations of Radionuclides of Uranium, Thorium, and Radium Associated with
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October 1999

Work Performed Under Contract DE-FG26-97BC15035

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ABSTRACT

There is an unsurpassed lack of scientific data with respect to the concentrations and isotopic compositions of uranium, thorium, and radium in the produced formation fluids (brine), precipitates, and sludges generated with the operation of oil and gas wells in Mississippi. These radioactive elements when contained in the formation fluids have been given the term NORM, which is an acronym for naturally occurring radioactive materials. When they are technologically enhanced during oil and gas production activities resulting in the formation of scale (precipitates) and sludges they are termed TENORM (technologically enhanced naturally occurring radioactive materials). As a result of this lack of data no scientifically sound theses may be developed concerning the presence of these radionuclides in the fluid (brine), precipitate (scale), or sludge phases. Also there is little or no published information on the relative amounts or isotopic compositions of NORM in Mississippi. In relation to this lack of information, Mississippi oil and gas production produces vast amounts of formation water. Over the period of just one year, 1997 for example, Mississippi produced over 39,372,963,584 liters (10,402,368,186 gallons or 247,675,433 barrels) of formation water associated with hydrocarbon production from 41 oil and gas producing counties across the state.

Initial published studies have indicated that the main contributor to NORM in oil and gas production is radium. Further, assumptions have been made concerning this issue especially with respect to the isotopic composition of the radium, i.e. ^{228}Ra versus ^{226}Ra , found in NORM. ^{228}Ra is a product in the decay chain of $^{232}\text{thorium}$ and ^{226}Ra is the daughter product of the naturally occurring $^{238}\text{uranium}$ decay series. Few studies have been made concerning the isotopic composition of naturally occurring radium. It has been assumed that ^{228}Ra and ^{226}Ra are present in equal amounts. This assumption has not been supported or refuted in the literature. The underlying significance is that ^{226}Ra , which has a half-life of approximately 1,620 years, undergoes radioactive decay by emitting an alpha particle and a gamma ray; and ^{228}Ra , which has a half-life of approximately 5.76 years, undergoes radioactive decay by beta particle emission. Of these three radiation emissions, gamma emissions have been documented to be the most worrisome because of their capability to travel through steel, iron, etc.; they have a "whole body" penetrating ability because they can travel a considerable distance in body tissue. However, based on the "quality" of these emissions, the radiation which has the greatest potential of causing biologic damage is alpha radiation. An alpha particle is comprised of two protons and two neutrons and is basically a helium atom without its orbital electrons. Because of its high mass and net electrical charge of $+2e$, an alpha particle may be stopped effectively by a single sheet of paper or a few centimeters in air.

The intent of this study however is not to assess radiation risk associated with NORM or TENORM but to contribute primary, unbiased data which will provide the knowledge base from which rational, informed, social, economic, and environmentally sound

decisions may be made. The NORM/TENORM database that will be developed during the course of this study will be extremely useful in any epidemiological studies and inferences concerning the issue.

It is anticipated that this database development will include identification of relevant references in the geological literature, acquisition of necessary petrophysical well logs, identification of oil and gas pools from these logs, and provision of guidance as to implications of rock type and petrogenesis as to the occurrence of NORM in Mississippi. This information and the database that will be developed may also be usefully applied to other areas of the United States where NORM is an issue of consideration and importance.

Where indicated and available, well sample cuttings and/or core chips of producing reservoirs with high NORM concentrations will be examined. Additional studies where warranted on these sample cuttings and/or core chips may include thin sections, electron microscopy, and/or X-ray diffractograms.

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EXECUTIVE SUMMARY

As previously reported during the initial "start-up" period, the background infrastructure for the project was developed for the major work required in the later phases of the investigation. A significant portion of the work involved consultations with both the Mississippi Mineral Resources Institute (MMRI) and the Research Institute of Pharmacological Science (RIPS). As a result of these discussions there is currently in place a standard procedure for sample collection, labeling, and handling of samples that is both unambiguous and straightforward. An equally important aspect of the sample collection procedure is the maintenance of custody records which can accurately document the handling of the sample(s) from the field collection site(s) to the final laboratory analysis(es). The important aspect of this task was not only to create a workable system, but to assure that all three organizations intimately understand how it will work so as to minimize the potential of errors during sample handling.

To date a total of approximately 960 liters of oil field brines has been collected from 120 wells from several different producing horizons and fields in Mississippi. As noted in the first semi-annual report, approximately 150 liters of oil field brines were initially collected from 16 wells completed in several different producing horizons in Baxterville Field, located in Lamar County, Mississippi. Baxterville Field ranks as the most prolific oil producing field in the state and has been continuously producing hydrocarbons since its discovery in November, 1944. Along with the brines which were collected from the operational oil wells completed in the Lower Tuscaloosa "stringer" sands and the Lower Tuscaloosa Massive Sand (Mesozoic Erathem, Cretaceous System, Upper Cretaceous Series, Tuscaloosa Group), 8 liters of produced formation brine were also obtained from an Eagleford gas pool at Baxterville (Upper Cretaceous Series, Lower Eutaw Group). Baxterville Field ranks third in the state in cumulative gas production. Formation brine samples were also collected at South Smithdale Field, located in Amite County, Mississippi, a Sparta gas field (Cenozoic Erathem, Tertiary System, Middle Eocene Series, Claiborne Group). Previous sampling of a Rodessa oil pool has taken place at Traxler Field, located in Smith County (Cretaceous System, Lower Cretaceous Series, Trinity Group, Glen Rose Sub-group) and at several Wilcox fields (Cenozoic Erathem, Tertiary System, Eocene Series, Wilcox Group), located in the southwestern portion of the state.

As of the date of this second semi-annual report, sampling has recovered produced brines from several different producing horizons ranging in age from the Upper Jurassic through the Upper Cretaceous at the following fields: West Paulding, Verba, and Heidelberg (all located in Jasper County); Boykin Church and Mize (Smith County); Pool Creek, Reedy Creek, Summerland, and Laurel (Jones County); East Flora and Flora (Madison County); Satartia and Tinsley (Yazoo County); Brownsville Dome (Hinds County); Tinsley (Yazoo County); and SoSo (Jasper, Smith, and Jones counties).

In addition to these samples, brine samples have also been collected at Buttahatchie, Maple Branch, and McKinley Creek fields (Monroe County), and Corinne Field (Monroe, Clay, and Lowndes Counties), all of which are located and productive from the Paleozoic-age Black Warrior Basin (Mississippian System, Chesterian Series).

INTRODUCTION

There is an unsurpassed lack of scientific data with respect to the concentrations and isotopic compositions of uranium, thorium, and radium in the produced formation fluids (brine), precipitates, and sludges generated with the operation of oil and gas wells in Mississippi. These radioactive elements when contained in the formation fluids have been given the term NORM, which is an acronym for naturally occurring radioactive materials. When they are technologically enhanced during oil and gas production activities resulting in the formation of scale (precipitates) and sludges they are termed TENORM (technologically enhanced naturally occurring radioactive materials). As used in this document, NORM and TENORM will be considered equivalent terms and the occurrence of NORM in the oilfield will be considered the result of production operations. As a result of the lack of data no scientifically sound theses may be developed concerning the presence of these radionuclides in the fluid (brine), precipitate (scale), or sludge phases. Over the period of just one year, 1997 for example, Mississippi produced over 39,372,963,584 liters (10,402,368,186 gallons or 247,675,433 barrels) of formation water associated with hydrocarbon production from 41 counties across the state.

Published studies have indicated that the main contributor to NORM in oil and gas production is radium. Further, assumptions have been made concerning the isotopic composition of the radium, i.e. ^{228}Ra versus ^{226}Ra , found in NORM and TENORM. ^{228}Ra is a product in the decay chain of ^{232}Th and ^{226}Ra is the daughter product of the naturally occurring ^{238}U decay series. Few studies have been made concerning the isotopic composition of naturally occurring radium. It has been assumed that ^{228}Ra and ^{226}Ra are present in equal amounts. This assumption has yet to be supported or refuted in the literature. This study is exploring that issue, i.e. determination of the ^{226}Ra and ^{228}Ra abundances and resulting ratios. The underlying significance is that ^{226}Ra , which has a half-life of approximately 1,620 years, undergoes radioactive decay by emitting an alpha particle and a gamma ray; and ^{228}Ra , which has a half-life of approximately 5.76 years, undergoes radioactive decay by beta particle emission. Of these three radiation emissions, gamma emissions have been documented to be the most worrisome because of their capability to travel through steel, iron, etc.; they have a "whole body" penetrating ability because they can travel a considerable distance in body tissue. However, based on the "quality" of these emissions, the radiation which appears to have the greatest potential of causing biologic damage is alpha radiation. An alpha particle is comprised of two protons and two neutrons and is basically a helium atom without its orbital electrons. Because of its high mass and net electrical charge of $+2e$, an alpha particle readily interacts with matter. Because of this reactivity, an alpha particle can only travel a few centimeters in dry air (the higher the moisture content of the air, the less distance it can travel) and can be easily shielded by a single sheet of paper.

The intent of this study however is not to assess radiation risk associated with NORM or TENORM nor to assess its effects on biologic tissue. The purpose of the study is to contribute primary, unbiased data which will provide the knowledge base from which rational, informed, social, economic, and environmentally sound decisions may be made. The NORM/TENORM database that will be developed during the course of this study will be extremely useful in any epidemiological studies and inferences concerning the issue.

FIELD COLLECTION PROCEDURES

As a result of the emulsified nature of the produced fluid at the wellhead with respect to oil reservoir(s) samples which have been collected at several fields, on-site sampling procedures had to be devised to help minimize the amount of oil included in the collected, produced fluids. To help minimize the amount of oil contained in the samples, the fluid being produced at the wellhead was first collected in a 20 liter (5 gallon) sampling container equipped with an on/off valve located at its base. After the container was filled approximately two-thirds to three-quarters full, the collected fluid was allowed to sit briefly, which allowed a preliminary separation of the produced oil and water. The oil and water separated, leaving a fairly distinct two-phase fluid-oil, because of its lesser density than the brine, was the upper layer and the brine, being more dense than the oil, the lower layer. The produced brine was then transferred to a 4 liter sample container by simply opening the valve at the base of the collection container, which allowed for the water phase to be removed without introduction of large amounts of oil with the brine.

DISPOSITION OF SAMPLES

At each sample collection point approximately 8 liters of produced formation fluid is being collected. During the current chemical analysis procedure, approximately 4 liters of each sample is utilized; a portion of this (500 ml) is being acidified and stored for potential future reference. The remaining 4 liters of fluid are being stored for any additional chemical analyses which may be required or desired.

STANDARD METHOD FOR ANALYSIS OF RADIUM

The standard method that has been developed for analysis of radium in produced waters from hydrocarbon production is as follows. This method corrects for the following: 1) high and variable solute concentrations and compositions encountered in produced formation waters; and 2) radium that might become insoluble during storage of the samples. The developed method also determines the ratios of ^{226}Ra and ^{228}Ra

present in the samples.

A. Sample processing

Approximately 30 ml of each 4 liter brine sample is passed through a Whatman #1 paper filter to remove suspended oil. 10 ml of this is placed into a tared flask, weighed, dried, and reweighed to determine the density and the dissolved solute content. The pH is taken on the remainder of this aliquot.

The volume of the remainder of the 4 liter sample is measured, 100 ml of concentrated HCl is added per liter and most of this is returned to the original container and allowed to sit until all of the precipitated material has been dissolved off of the container walls. The entire sample is then recombined and filtered through 2 layers of Whatman #1 filter paper to remove suspended oil. 11 ml of the filtrate is placed in a tared vial, dried and weighed. 1.1 liter is taken for analysis of radium content, and the remainder is placed in a clean container for storage. Each sample will be analyzed for radium content 3 times by taking additional 1.1 liter aliquots with at least a 1 week interval between replicate analyses.

B. Analysis of radium

The 1.1 liter acidified brine sample is divided into two 550 ml aliquots. One aliquot is spiked with 25 nCi of ^{226}Ra by adding 50 μl of 0.5 $\mu\text{Ci/ml}$ $^{226}\text{RaCl}_2$. Then 25g of powdered anhydrous Na_2CO_3 is added gradually to each 550 ml brine sample and stirred until completely dissolved. Then 32% w/v Na_2CO_3 in water is added slowly, dropwise, under the control of a peristaltic pump, with stirring until the solution color changes from bright yellow to dark amber. An additional 100 ml of 32% w/v Na_2CO_3 is added dropwise, and the mixture is stirred for 15 minutes and filtered through Whatman #1 filter paper. The filtrate receives another 100 ml addition of sodium carbonate solution as before, followed by filtering. This step is repeated until no further precipitate forms with added sodium carbonate. This procedure results in quantitative precipitation of the radium from the brine solution and it separates the radium from the monovalent cations, which are the major sources of interference with radium binding to the 3-M Company Radium Rad Disks. The precipitates are combined and redissolved to a resultant 1 liter volume with 2 N nitric acid. This solution is prefiltered through Whatman 0.45 μm cellulose nitrate membrane filters and then filtered through Radium Rad Disks. Depending upon the amount and composition of the salts from the brine, 40 to 100% of the radium from the sample is captured on the Rad Disk by this procedure. Because of the large variability in recovery from one brine to another it is necessary to run a spiked sample as an internal standard to determine recovery for each brine sample.

The Rad Disk is then immediately counted for 30 minutes in a gamma counter to

quantify the 186 KeV gamma emission of ^{226}Ra . If the Rad Disks are allowed to age daughter isotopes grow in and interfere with the quantification. The Rad Disks from the unspiked samples are then placed in a desiccator jar under vacuum with CaSO_4 desiccant and activated charcoal and aged for 2 weeks. This allows ^{228}Ac , a daughter of ^{228}Ra , to grow in and equilibrate. Storage with desiccant and activated charcoal under vacuum helps to pull off and adsorb volatile ^{222}Rn , the first daughter of ^{226}Ra . This minimizes possible interference with quantification of ^{228}Ac . The aged Rad Disks are then counted for 30 minutes in a gamma counter to quantify the 911 and 969 KeV emissions of ^{228}Ac . The content of ^{228}Ra is determined from this by calculation. Similarly, the amounts of ^{238}U and ^{232}Th that were, theoretically, in equilibrium with the brines in the substratum are calculated.

Each brine is analyzed through 2 complete replicates of spiked and unspiked aliquots with at least one week between replicate analyses. When the two spiked replicates are within 10% of one another the analysis is considered accurate. If the two spiked replicates are greater than 10% different, then a third replicate analysis of both spiked and unspiked is performed. Occasionally, when there are several brine samples from a single field, and they all have similar pH and solute concentrations, and the radium recoveries are within 10% of one another from at least half of the brines from that field, then only one spiked replicate is run for the remaining brines. The analysis is considered complete if the single analysis falls within 10% of the average for the field. Samples containing less than 25 g/l of dissolved solutes are not analyzed further because the amounts of radium-226 and radium-228 contained therein, even when spiked, are less than experimental error.

C. Summary of preliminary chemical and isotopic data

To date 54 brine samples have been completed from 14 fields and partial analyses have been performed on 49 additional samples and 4 additional fields. Brine pH values have ranged from 3.66 to 7.72 with an average of 5.7. It has been observed that the pH values can change by as much as 0.5 pH units upon storage. This is most probably due to uptake of CO_2 from the atmosphere. Dissolved solutes have ranged from 2.45 g/l to 315.8 g/l with an average of 176 g/l. ^{226}Ra levels have ranged from 0.142 to 17.92 pM/l with an average of 6.04 pM/l. ^{228}Ra levels have ranged from 0.02 to 3.41 fM/l with an average of 0.7 fM/l. The isotopic ratio of radium-226 to radium-228 has a range from 1106 to 21,229 and averages 9047. This is significant in that literature searches have indicated that the assumption is the equilibrated ratio of the two isotopes would be 1:1. Ramifications of this measured isotopic ratio is currently being researched and will be incorporated into the final report.

Of the fields analyzed to date Brownsville and Reedy Creek have produced the highest concentrations of radium. However, even these highest concentrations are still very low.

CONCLUSION

As noted, the data presented herein are preliminary. The complete isotopic and concentration analyses for radium, thorium, and uranium will be presented with the final report of this study.

Since the radium chloride has been received, spiked samples have been run, the methodology has been perfected, and analyses have been utilizing the methodology as presented herein. Sample analysis has been proceeding on a relatively uniform schedule. Presently the analytical laboratory work has entered its ninth month of operation and as noted, 54 brine samples from 14 fields have been fully analyzed and partial analyses from 49 additional samples and 4 additional fields are in process. During the next six (6) months the lab will process approximately an additional 60 brine samples obtained from more oil and gas wells from various fields and reservoirs across the state.

In addition, we have recently placed thermoluminescent dosimeters out in the field in an area which had elevated background NORM. These dosimeters, which were designed to be sensitive to gamma rays, were placed to determine the variation in gamma radiation emitted versus distance from the apparent emitting source. One dosimeter was placed on the wall of an apparent gamma radiating source one (1) meter above ground level and another was placed at a distance of one (1) meter, at a height of one (1) meter. This procedure is currently being followed in the lab using the RaCl spike salt. From this we will be able to more accurately quantify and/or relate some of the findings of this ongoing study. The dosimeters which were placed in the field and had a residency time of one month are currently being analyzed to determine the measured gamma radiation at the field site and results should be forthcoming shortly.

Also, we have begun to collect soil samples from areas of oil and gas operations and other areas which have had none but have elevated NORM readings. These samples are being stored for future analysis as to the mobility of NORM contained therein and the concentrations of uranium, thorium, and radium and the isotopic composition of radium.

Oil and gas operators in Mississippi continue to provide us with virtually unlimited access to producing properties and it appears that the goals of the brine sampling phase of this investigation will be accomplished. It is anticipated that additional Black Warrior Basin and Mississippi Interior Salt Basin fields, as well as producing areas in the Wilcox Trend, located in the southwestern portion of the state, will be sampled during the next six (6) months.

List of Acronyms, Abbreviations, and Definitions:

1,000 electron volts	KeV
barrel(s)	42 gallons = 168 quarts = 158.97 liters = bbl(s)
bbl(s)	barrel(s)
Ci ... curie = 3.7×10^{10} disintegrations per second (dps) = 2.22×10^{12} disintegrations per minute (dpm)	
counts per minute	cpm $\approx$ disintegrations per minute
cpm	counts per minute
curie ... Ci = 3.7×10^{10} disintegrations per second (dps) = 2.22×10^{12} disintegrations per minute (dpm)	
eV	electron volt
electron volt	eV
fM	femtomole = 1×10^{-15} mole
femtomole(s)	fM = 1×10^{-15} mole(s)
g	gram
gram	g
KeV	1,000 electron volts
L or l	liter
liter	l
M	molar
μ M	micromole = 1×10^{-6} mole
micromole(s)	μ M = 1×10^{-6} mole(s)
milliliter	ml
Mississippi Mineral Resources Institute	MMRI
ml	milliliter
MMRI	Mississippi Mineral Resources Institute
molar	M
N	Normal
nanocurie(s)	nCi = 1×10^{-9} curie(s)
Naturally Occurring Radioactive Materials	NORM
nCi	1×10^{-9} curie
NORM	Naturally Occurring Radioactive Materials
Normal	N
pCi	picocurie = 1×10^{-12} curie
picocurie(s)	pCi = 1×10^{-12} curie(s)
picomole(s)	pM = 1×10^{-12} mole(s)
pM	picomole = 1×10^{-12} mole
Research Institute of Pharmaceutical Science	RIPS
RIPS	Research Institute of Pharmaceutical Science
Technologically Enhanced Naturally Occurring Radioactive Materials	TENORM
TENORM	Technologically Enhanced Naturally Occurring Radioactive Materials
w/v	weight per volume
weight per volume	w/v