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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, precipitates, and sludges have been given the term NORM, which is an acronym for naturally occurring radioactive materials. As a result of this lack of data no scientifically sound theses may be developed concerning the presence of these radionucleides in the fluid (brine), precipitate, 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, 1996 for example, Mississippi produced over 37,509,657,774 liters (9,909,002,712 gallons or 235,928,636 barrels) of formation water associated with hydrocarbon production from 45 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}thorium and ^{226}Ra is the daughter product of the naturally occurring ^{238}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 decays emitting both beta and gamma radiation and ^{228}Ra decays emitting beta radiation only. Of the these two radiation emissions, gamma emissions are documented to be the most worrisome because of their capability to travel through steel, iron, etc. and thus possibly have adverse effects on oilfield workers and the populace in general.

The intent of this study is to provide primary, unbiased data on NORM which will provide the knowledge base from which rational, informed, social, economic, and environmentally sound decisions may be made. The development of the NORM database which will be assimilated during the course of this study will be extremely useful in any epidemiological studies and inferences concerning the NORM issue.

It is anticipated that this 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 which will be developed may also be useful in its application 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

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 280 liters of oil field brines has been collected from 29 wells from several different producing horizons and fields in Mississippi. To date approximately 150 liters of oil field brines have been 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 (Upper Cretaceous Series, Lower Eutaw Group), also collected at Baxterville. 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.

Recent sampling has recovered produced brines from several different producing horizons at the following fields: West Paulding, Verba, and Heidelberg (all located in Jasper County); Boykin Church and Mize (Smith County); and Pool Creek (Jones County). These samples represent approximately 88 liters of the 280 liters collected thus far for analysis and cover stratigraphic horizons from the Haynesville (Upper Jurassic Series, Louark Group, Haynesville pool) through the Eutaw(Upper Cretaceous Series, Eutaw Group, Eutaw pool).

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, precipitates, and sludges have been given the term NORM, which is an acronym for 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, or sludge phases. Over the period of just one year, 1996 for example, Mississippi produced over 37,509,657,774 liters (9,909,002,712 gallons or 235,928,636 barrels) of formation water associated with hydrocarbon production from 45 counties across the state.

Initial published studies have indicated that the main contributor to NORM in oil and gas production is radium. Several assumptions have been made concerning this issue including 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}thorium and ^{226}Ra is the daughter product of the naturally occurring ^{238}uranium decay series. 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 decays emitting both beta and gamma radiation and ^{228}Ra decays emitting beta radiation only. Of the these two radiation emissions, gamma emissions are documented to be the most worrisome because of their capability to travel through steel, iron, etc. and thus possibly have adverse effects on oilfield workers and the populace in general.

It is anticipated that at the conclusion of this study that primary, unbiased data on NORM will be generated which will provide the knowledge base from which rational, informed, social, economic, and environmentally sound decisions may be made. The development of the NORM database which is being assimilated during the course of this study will be of utility in any epidemiological studies and inferences concerning the NORM issue.

RESULTS AND DISCUSSION

Preliminary Chemical And Isotopic (Radium) Characteristics And Sample Analysis Methodology - (prior to receipt of ^{226}RaCl)

A. Field collection procedures

As a result of the emulsified nature of the produced fluid at the wellhead with respect to the oil reservoir(s) samples which were collected at Baxterville Field, 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 four 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.

B. Sample processing and analysis of radium (preliminary procedures)

The laboratory methodology for determining radium in brines produced as by-products of hydrocarbon production is at this time in the final stages of development. The processing method in its current stage consists of the following procedure(s). Suspended oil and suspended solids are removed by passing the brine through 2 layers of Whatman No. 1 filter paper. In order to remove the large amount of interfering monovalent cations it was found to be necessary to add a processing step at the beginning of the radium isolation procedure. Sodium carbonate solution (10% w/v), 25 ml, is added gradually with vigorous stirring to 1 liter of filtered brine. After stirring for 10 minutes the precipitate is collected by filtration through Whatman No. 1 filter paper. The filtrate receives a second and third 25 ml aliquot of sodium carbonate solution as before. In the Baxterville Field samples that were analyzed, 90% of the detectable radioactivity that could be collected by this procedure appeared in the first precipitate. The third precipitate was very nearly at background. The Sparta sample also showed measurable radioactivity in the first two precipitates. The first two precipitates from each of the brines represented less than 10 grams of dried solids. These were redissolved with approximately 20 ml of 5 N HCl, diluted to 500 ml with deionized water, and 100 ml of concentrated sulfuric acid was added with vigorous stirring. After about 10 minutes small crystals began to appear, and continued to grow in over the next 2 hours. The crystals were collected by filtration through 2 micron glass fiber filters, the filtrate was made 2 N in nitric acid by adding concentrated nitric acid and this was then passed through a Radium Rad disk. The crystals had no detectable radioactivity while the Rad disk, counted within one hour of filtering, showed gamma and beta emission spectra characteristic of the 186 KEV gamma emission of ^{226}Ra and the 38.9 KEV beta emission from ^{228}Ra. One potential problem that remains to be addressed in the method development is the fact that precipitates form in the filtered brines if they sit for many hours. This may be due to the gradual formation of bicarbonate in the brines from carbon dioxide dissolving from the atmosphere. In the Baxterville Field samples this precipitate contained some radioactivity. We will need to either standardize the

time interval between collection and analysis or determine a means of redissolving these precipitates prior to processing in order to obtain reliable measurements of dissolved NORM at the wellhead.

C. Preliminary chemical and isotopic data

Preliminary basic chemical characteristic/isotopic studies have examined the Sparta gas brine and the brines from a portion of the Baxterville Field samples which were collected. The Sparta brine was relatively free of suspended oil and also relatively low in total dissolved solute content. After the suspended oil and solids were removed the sample had a pH of 5.88, a density of 1.068 g/ml, and a total solute content of 119.5 g/l. Upon analysis this sample was found to have a small amount of NORM, within the range of 10 pCi/l over background. Because this sample's activity is so low data do not allow the calculation of the isotopic composition of radium contained therein.

Once in the laboratory, the Baxterville samples that were analyzed had relatively high suspended oil content and relatively high dissolved solute content. After removing the suspended oil and suspended solids these samples had pH values ranging from 5.25 to 5.98, densities of 1.138 to 1.145 g/ml, and total solutes of 230.6 to 242.3 g/l. The Baxterville samples that were analyzed had NORM activities in the range of 100 pCi/l over background levels. Preliminary calculations for a Baxterville Field sample have yielded the following isotopic concentrations of radium:

1) Ratio of $^{226}Ra/^{228}Ra$ = 770:1;
2) Isotopic concentration of ^{226}Ra = 17 picomoles/liter (1.7×10^{-11} moles/liter);
3) Isotopic concentration of ^{228}Ra = 22 femtomoles/liter (2.2×10^{-14} moles/liter).

Standardized Method For Analysis of Radium - Current And Final Methodology

The analytical isotopic methodology work has now been completed. A previous delay that was encountered was in the receiving of radium chloride from Ohio State University. The radium chloride, which was needed to spike the samples in order to determine the effectiveness of the procedure that has been developed, has been received. The delay in receiving shipment has been the result of the lack of an adequate shipping container due to radioactivity of the radium chloride.

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 high and variable solute concentrations and compositions likely to be encountered in produced waters, it corrects for radium that might become insoluble during storage of the samples, and it 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 filter paper to remove suspended oil. 10 ml of this is placed into a tared flask, weighed, dried, and re-weighed 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

50 g of powdered anhydrous Na_2CO_3 is added gradually to the 1.1 liter acidified brine sample and stirred until completely dissolved. Then 35% w/v Na_2CO_3 in water is added dropwise with stirring until the solution color changes from bright yellow to dark amber. An additional 100 ml of 35% w/v Na_2CO_3 is added dropwise, 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 2 liters with 2 N nitric acid. This solution is pre-filtered through Whatman #1 filter paper and then filtered through a Radium Rad Disk. 90+% of the radium from the sample is captured on the Rad Disk by this procedure.

The Rad Disk is then <u>immediately</u> counted for 30 minutes in a gamma counter to quantify the 186 KEV gamma emission of ^{226}Ra. The Rad Disk is then <u>immediately</u> transferred into liquid scintillation cocktail and counted for 30 minutes in a liquid scintillation counter to quantify the 38.9 KEV beta emission from ^{228}Ra. If the Rad Disks are allowed to age, daughter isotopes grow in and interfere with the quantification. For every 10 brine samples that are analyzed, 1 brine sample (a different one each time) which has been spiked with 50 nCi of $^{226}RaCl$ and 1 laboratory mixture consisting of 1 liter of 1 M NaCl and 1 M $CaCl_2$ plus 100 ml of concentrated

HCl spiked with 50 nCi of ^{226}RaCl will also be carried through the entire analytical procedure. These samples will allow us to assure that recoveries are consistent and reproducible from brine sample to brine sample and from day to day.

CONCLUSION

Please note that the data presented herein should be considered only as preliminary. Since the radium chloride has been received, spiked samples have been run, the methodology has been perfected, and analyses from this point on shall utilize the methodology as outlined. Sample analysis is now proceeding on accelerated schedule on samples from the aforementioned fields, as well as many other fields/producing horizons scheduled to be collected. Presently the isotope analytical work is nearing the end of its third month of operation and should complete the analyses of 25-30 brine samples at that time. During the next five (5) months the lab will process approximately an additional 50 brine samples obtained from more oil and gas wells from various fields and reservoirs across the state.

Several oil and gas operators have granted us permission to collect samples from other fields in the state. These include East Flora, Satartia, Maxie, Jackson (which underlies much of the capital city of the state, Jackson, and is used mainly for gas storage - however in this case the sample will come from a producing gas well not connected to the storage facility), etc. These fields are productive from stratigraphic horizons ranging in age from Upper Gulfian (Selma Chalk) through Coahuilan age (Sligo). In addition to these fields, a representative cross section of producing fields and reservoirs has been arranged to be sampled in the Paleozoic-age Black Warrior Basin, located in the northeastern portion of the state. Fields which are scheduled to be sampled are Maple Branch, Shannon, Troy, and Buttahatchie River. These fields will provide a sampling of the Mississippian System, Chesterian Series, of the Parkwood-Pennington and Pride Mountain formations. Also scheduled to be sampled in the Black Warrior Basin is Maben Field, which is productive from the Knox Dolomite (Paleozoic Erathem, Ordovician System, Stones River Group).

List of Acronyms and Abbreviations:

gram . . . . . g
liter l
picocuries . . . . . pCi
milliliter . . . . . ml
MMRI . . . . . Mississippi Mineral Resources Institute
Molar . . . . . M
nanocuries . . . . . nCi
NORM . . . . . Naturally Occurring Radioactive Materials
Normal . . . . . N
RIPS . . . . . Research Institute of Pharmaceutical Science
weight per volume . . . . . w/v