Determination of Heavy Metals in NORM in Oil Exploration Waste Products

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ABSTRACT

Naturally occurring radioactive materials (NORM) contain radionuclides, such as radium, thorium, and uranium. The existence of naturally occurring radioactive materials remains an issue for oil and gas exploration because once the material becomes concentrated through human activity, it becomes a radioactive contamination hazard or a radioactive waste. The naturally occurring radioactive elements dissolve in low concentrations, but are spread over a large volume of material, usually contaminated soil. Pipes and tanks used to handle large volumes of produced water at some oil-field sites are coated with scale deposits that contain radium. This work determined the concentrations of heavy metals linked with NORM. Experiments were conducted using epithermal and thermal neutron activation analysis (NAA) and Compton suppression for radioactivity counting. Results have confirmed the determination of heavy metals and their decay products found in the radioactive scale, soil, and solid.

INTRODUCTION

- Radioactive isotopes such as $^{235/238}U$, ^{232}Th, $^{226/228}Ra$ occur naturally in rocks, soils, and underground water .
- $^{226/228}Ra$ due to their chemistry tend to accumulate in oil and gas industry byproducts.
- Of particular concern is radium levels in water, scale found in pipes, equipment, and sludge and the exposure of oil industry workers and even the general public to this NORM. .
- Several factors influence radium levels such as the rate of radium dissolution, its mobility in formation water, and the rate of radium precipitation, along with temperature and pressure changes .
- the average total radium concentration for oil and gas NORM is 7.70 x 10^3 Bq/Kg (5.735 x 10^3 Bq/Kg ^{226}Ra and 2.035 x 10^3 Bq/Kg ^{228}Ra).

EXPERIMENTAL

● **Sample collection and preparation:** Soil, solid, and piping scale samples were collected from an oil producing facility in western Texas and homogenized using a 250 µm sieve and vacuum dried for two hours in a 100 ^{0}C oven. Each sample was weighed to approximately 0.5g and placed in polyethylene vials for irradiation.

● Neutron activation analysis (NAA): Thermal and epithermal neutron activation analysis in conjunction Compton suppression were used to determine a series of trace elements. Ten samples were prepared for thermal and ten for epithermal NAA for a total of 20 samples. Each set of ten contained two solid samples, two soil samples, two scale samples, and four NIST reference materials, including coal (NIST 1632c), two coal fly ash (NIST 1633a, NIST 1633b), and San Joaquin soil (NIST 2709). For epithermal NAA, samples were irrdiated at 100 kW for 60 sec with a count time of 900 sec and a decay time of 5-10 min. A Compton detector was used for counting. For thermal NAA, samples were irrdiated at 100 kW for 60 sec with a count time of 600 sec and a decay time of 5-10 min. A normal detector was used for counting. For rotary specimen rack (RSR) NAA, samples were irrdiated at 950 kW for 1 hr with a count time of 2 hrs and a decay time of 2 weeks.

Elements	Count type	Type of radiation	Irradiation time	Decay time	Count time	Power
Sc, Fe, Co	Normal	thermal	1 hr	2 weeks	2 hrs	950 KW
Zn, Cr, Ni	Compton	thermal	1 hr	2 weeks	2 hrs	950 KW
Na, Cl, Al, Mn, Ca, V	Normal	Thermal	60 sec	5-10 min	10 min	100 KW
U, Br, Si, Ba, Sr, I, In	Compton	epithermal	60 sec	5-10 min	15 min	100 KW

● To control the variation in flux measurements in short-lived NAA which can vary up to 7% aluninum wires were irradiated with each sample.

● Calibration was mostly done using NIST 2709 San Joaquin Soil as the primary standard with the exception of uranium, bromine, chlorine and indium concentrations which were taken from NIST 1633a, NIST 1632c, NIST 1632c and liquid standard, repsectively. Once a calibration library was set up the same NIST samples were used as *unknowns*. In general all the NAA results agreed within 3-10% of the certified or information NIST values.

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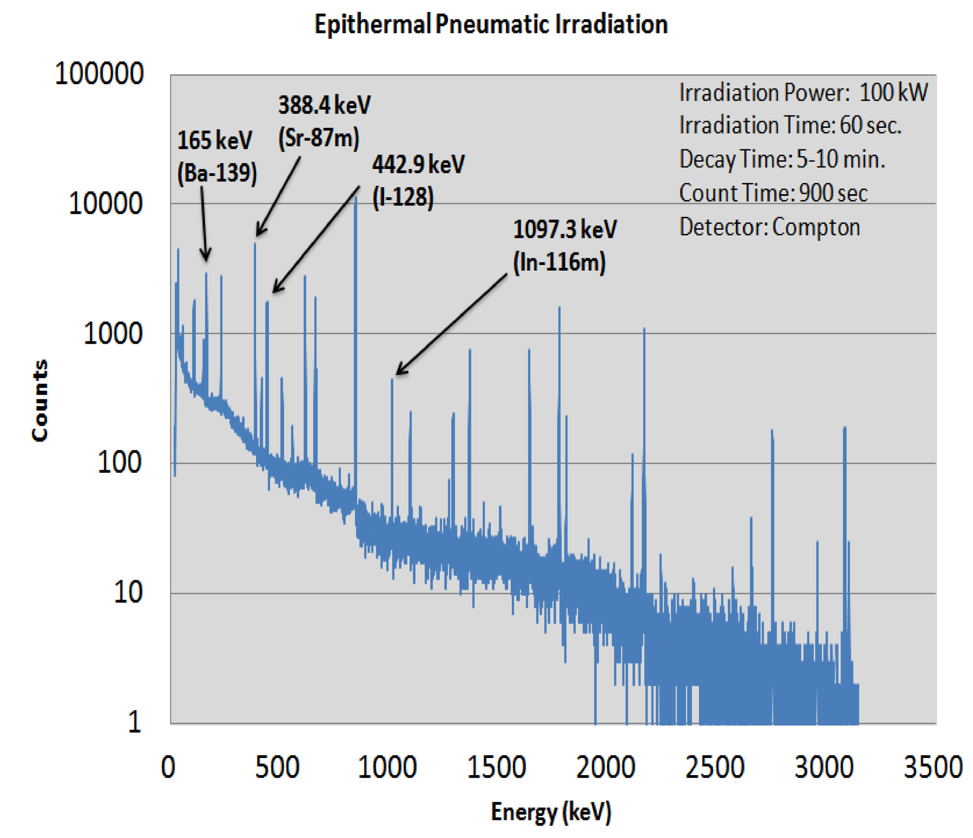

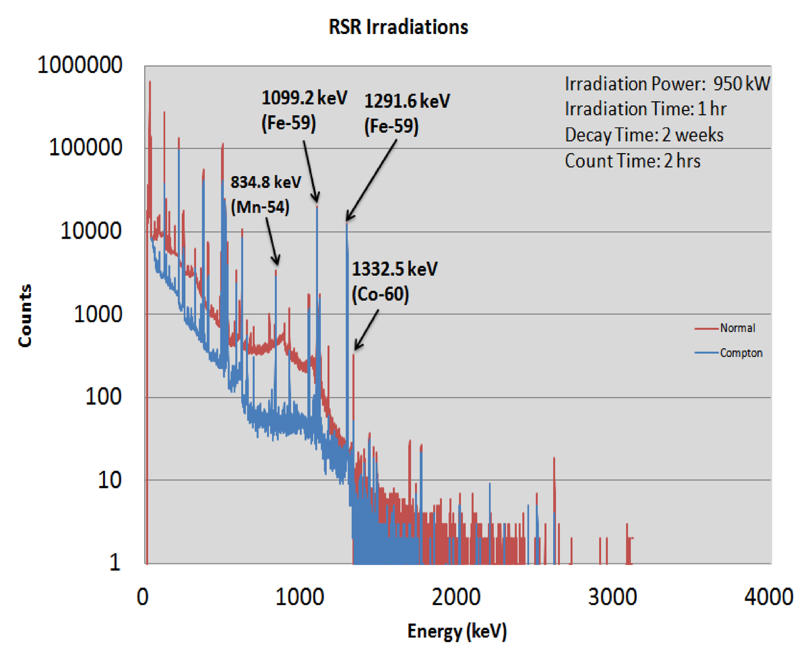

Element	Scale	Soil	Solid
Aluminum (%)	0.53 +/- 0.02	1.88 +/- 0.02	0.46 +/- 0.01
Barium (µg/g)	8936 +/- 717	34,435 +/- 2721	17,7121 +/- 13960
Bromine (µg/g)	223 +/- 11	2.9 +/- 0.6	48 +/- 3
Calcium (%)	11.2 +/- 0.7	2.4+/- 0.2	1.5 +/- 0.1
Chlorine (%)	6.41 +/- 0.48	0.04 +/- 0.01	0.71 +/- 0.05
Chromium (µg/g)	53 +/- 2	13.7 +/- 0.7	131 +/- 5
Cobalt (µg/g)	14.6 +/- 0.6	1.8 +/- 0.1	2.8+/- 0.2
Indium (µg/g)	1.64 +/- 0.08	ND*	0.84 +/-0.05
Iodine (µg/g)	31.9 +/- 2.5	3.2 +/- 0.3	10.5 +/- 0.9
Iron (%)	24.9 +/- 0.5	0.94 +/- 0.02	15.7 +/- 0.3
Manganese (µg/g)	1053 +/- 38	80 +/- 4	207 +/- 9
Nickel (µg/g)	54 +/- 9	11.7 +/- 2.5	73 +/- 9
Scandium (µg/g)	0.21 +/- 0.02	1.81 +/- 0.03	0.12 +/- 0.01
Silicon (%)	1.08 +/- 0.14	39.0 +/- 1.3	2.40 +/- 0.13
Sodium (%)	3.24 +/- 0.09	0.14 +/- 0.01	0.85 +/- 0.03
Strontium (µg/g)	12484 +/- 1389	4142 +/- 464	48,288 +/- 5362
Uranium (µg/g)	0.08 +/- 0.02	0.80 +/- 0.03	ND*
Vanadium (µg/g)	ND*	21.8 +/- 1.5	5.2 +/- 0.7
Zinc (µg/g)	288+/- 8	50 +/- 2	683 +/- 15

Ratio	Scale	Seawater
Cl/Na	1.97	1.8
Br/Cl	3.5 x 10^{-3}	6.2 x 10^{-3}
I/Cl	5 x 10^{-4}	3.3 x 10^{-6}

Conclusion Given the tighter restrictions and regulations with increasing oil and gas exploration further research is needed in understanding the effect the elements and metals may have on the evironement once they are buried as low-level waste. It is recommended that studies aslo be incorporated to understand the leaching dynamics of not only these metals but also of the radium nuclides.