Results of Bench-scale Testing of a Mobile On-site NORM Treatment System in Texas and New Mexico

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ABSTRACT

Naturally Occurring Radioactive Material (NORM) contained in oil field waste is becoming an increasing operational burden for oil production companies within the United States. Large volumes of NORM waste are generated by the oil and gas industry. Over the years, these wastes have been kept in barrels and drums that have been stored on oil field lease sites or left in operational equipment or have been inadvertently disposed of as non-hazardous oil field waste (NOW). NORM wastes can also be found in discarded refinery and gas treatment equipment. Recent estimates place the amount of stored NORM at 10,000,000 drums, the annual production of NORM at 142,000 drums, and the annual cost of disposal in excess of $200 million for each of the next 25 years [1]. In addition, there are increased environmental and liability concerns over typical oil field wastes as a result of the low level radioactivity present in the waste. At present there are limited methods for disposal of this waste and most of these options involve transportation of the waste to centralized facilities which results in an increased public exposure risk.

The Department of Energy Office of Fossil Energy and BPF, Inc. are co-funding a project that could reduce the cost of cleaning up NORM wastes while providing a simple and effective disposal option which eliminates the need for transportation of NORM from the production site. The primary goal of the project is the demonstration of a commercially viable, highly mobile, modular system which dissolves NORM accumulated during oil and gas production. Once dissolved, the radionuclides now in solution can be re-injected into the original formation using available salt-water injection facilities on the lease site.

This paper describes the BPF approach for treating the NORM-containing oilfield waste on the generating lease and the results achieved during bench-scale testing. The treatment system is based on a series of mobile trailer and truck mounted processing modules which can be set up at the location of stored NORM for on-site processing, thereby eliminating the need for transportation of the waste to centralized disposal facilities. The bench-scale tests are currently being completed in Texas and New Mexico.

Initial results from the bench-scale tests demonstrate the ability of the process to successfully treat a variety of NORM-containing oilfield wastes. The primary radioactive component (^{226}Ra) contained in the waste is dissolved into an aqueous solution which can be re-injected into the proper formation through an on-lease water injection or disposal well. A 100% assay is performed on the treated residual solids which are verified to have a radioactivity level below regulatory concern.

These residual solids can then be disposed of as NOW. Results from the field tests show that the treatment process reduces the concentration of ^{226}Ra in the residual solids to near background levels.

INTRODUCTION

Naturally occurring radioactive materials sometimes concentrate in the waste streams of oil and gas production operations [1]. The primary radionuclides in the NORM waste are Radium-226 (^{226}Ra) and Radium-228 (^{228}Ra). These radionuclides are formed from the radioactive decay of two principal elements, Uranium-238 (^{238}U) and Thorium-232 (^{232}Th). These elements are found in many underground formations but are not very soluble in the reservoir fluid. However, the daughter products, ^{226}Ra and ^{228}Ra, are somewhat soluble and can migrate to the surface as dissolved ions. The amount of radium actually dissolved in the reservoir fluid depends on several factors including the geology of the formation, temperature, pressure and pH of the reservoir fluid[2]. During the course of oil/water separation in production facilities, these radioactive elements can precipitate onto process equipment and storage tanks due to the change in chemical conditions from the originating formation to the surface. Over time, these radium isotopes can accumulate and become the parent radionuclides for a series of daughter products which also accumulate, including radon. Generally, these radium deposits are associated with the presence of barium sulfate scales[4].

The presence of NORM in oil field waste may present a long-term risk to human health and the environment. Presently there are no federal regulations aimed specifically at controlling this NORM waste. Several states have their own individual regulations, but have similar NORM definitions and disposal requirements. The BPF process has been designed with sufficient flexibility to meet these varying requirements.

According to a recent American Petroleum Institute [1] study, approximately 10 million drums (55 gallon each) of NORM have accumulated over the years. Currently there are five principal methods for NORM disposal [1,2]. They are:

- burial at a licensed facility
- treatment dilution
- landspreading
- downhole encapsulation
- slurry injection

Most of the above processes involve transportation of the waste to some central treatment facility, waste profiling, transport vehicle decontamination and radiochemical analysis. There are a limited number of wells available for downhole encapsulation and/or slurry injection. Also the potential impact of future regulatory changes may be a significant consideration for all the above disposal processes.

The primary advantages of the BPF NORM disposal process are:

- The NORM solids are dissolved and the solution is then re-injected into the original geologic formations from which they originated. The BPF process does not require unique or special injection well parameters for NORM disposal.
- The BPF NORM disposal process is completed without the need for transportation of the radioactive waste off the lease property.
- Once the radioactive material is removed, the residual materials are no longer a NORM waste; therefore, custody of NORM waste is no longer an issue for the generator.

NORM TREATMENT APPROACH

The BPF process treats and disposes of NORM waste by dissolving the radionuclides into aqueous solutions using proprietary dissolving agents and then re-injecting these solutions into a suitable formation via a water injection system. The residual non-radioactive solid waste which can be disposed of as NOW. Thus the BPF process returns the radioactive material back to its origin. Since the entire process involves on-site treatment, there is essentially no possibility of any accidental spill or leakage outside the oilfield boundary. The process also eliminates intermediate drumming, transportation and/or long-term storage requirements for NORM waste.

The BPF bench-scale mobile system is designed around three mobile processing modules. These are designed to accommodate the treatment and disposal of NORM wastes at the lease site where the NORM is generated and/or stored. A detailed description of the processing equipment used in the bench-scale tests is described in a previous paper [3]. A general flow diagram of the process is shown in Figure 1.

A total of 500 lbs of NORM waste from two different sites have been processed in thirteen process trials using the bench-scale equipment. The trials are grouped as follows:

- Experiments #1-#4 were used to shake out the operation of the various equipment modules.
- Experiments #5-#7 were the initial process runs on the NORM from the Texas site using solvent de-oiling.
- Experiments #8-#10 were process runs on the NORM from the Texas site using thermal de-oiling.
- Experiment #11 was a final process run on the NORM from the Texas site.
- Experiments #12-#13 were process runs on the NORM from a New Mexico site.

A summary of the results achieved in these experiments is presented below.

PROCESS DESCRIPTION

The BPF bench-scale treatment process involves the following process steps:

- De-oiling (liquid extraction).
- Volume reduction by separating NORM waste from non-radioactive waste using a gamma spectrometry based sorting system.
- Dissolving the radionuclides in the NORM waste using a combination of acid and chelation steps in a batch processing module or using thermal conversion of insoluble scales to an acid soluble form.
- 100% radioassay of the residual solids using the gamma spectrometry based sorting system.
- Re-injection of the processing solutions which contain the dissolved radionuclides into the formation of origin or other suitable formation via a water injection or water disposal well at the lease site.

De-oiling

The de-oiling process is incorporated into the treatment scheme if the NORM waste contains a significant hydrocarbon content. De-oiling can be done either thermally or by using an organic solvent. In the bench-scale tests, both de-oiling methods were used and demonstrated to be effective in preparing the NORM for chemical treatment. Thermal de-oiling was performed on approximately 1 drum of NORM solids using a rotary calciner. At the selected temperature, the hydrocarbons in the waste were volatilized yielding a dry solid end product. Off gases were captured in a water-cooled condenser down stream from the calciner. Solvent de-oiling was performed on approximately 1/2 drum of NORM solids using a hydrocarbon solvent during the series of tests which comprised the bench-scale tests. The hydrocarbon contained in the NORM waste was dissolved into the organic solvent. The subsequent solid-liquid separation was accomplished with 10µm bag filters. No evidence of radioactivity in the organic fractions was observed during these tests.

Volume Reduction

The NORM waste encountered in the bench-scale tests had a homogeneous distribution of radioactivity. Because of the homogeneity, the volume reduction step was omitted.

NORM Dissolution

NORM dissolution involves a series of chemical steps. Reduction in the particle size increases the surface area and enhances the dissolution kinetics in the succeeding NORM dissolution steps. The solid byproducts from the de-oiling step were thus ground to a size of minus 60 mesh prior to further processing.

During the first stage of chemical treatment, the NORM solids were treated with a strong mineral acid. The acid dissolved most of the acid soluble fraction such as heavy metal carbonates and iron sulfide. After the reaction, solid-liquid separation was performed using a 10 micron bag filter. The solids remaining in the reactor vessel were washed with water and subsequently with a basic solution to neutralize the pH of the solids and to remove any remaining acid from the solid.

Scales consisting of acid-insoluble barium sulfate are difficult to dissolve, since barium sulfate is insoluble in most solvents. The commercially available barium sulfate dissolvers are expensive and their use would make the treatment process uneconomical. A BPF proprietary dissolving agent was used. For large quantities of barium sulfate scales, a thermal conversion to barium carbonate is performed to avoid the use of large quantities of the BPF proprietary dissolver. The resulting barium carbonate scales are acid soluble. An economic trade-off determines the quantity of scale which warrants thermal conversion instead of chemical dissolution with the BPF proprietary dissolver.

Radioassay

A gamma-ray spectrometer with a 15% efficiency coaxial germanium crystal was used for measuring the radioactivity in both solid and liquid samples. Gammavision (a Windows-based software) was used for analyzing and calculating the radioactivity of the samples. In-process measurements of the samples for both ^{226}Ra and total activity were conducted using grab samples taken during the processing steps. In addition, a 100% assay of the entire quantity of solids was performed at the outset of each experiment and after each process step. The results obtained from these data are summarized below.

Re-injection

The aqueous solutions containing dissolved radionuclides, along with other residual liquids, is re-injected into the appropriate disposal formation. The radioactivity levels in the produced water at the Texas site are approximately 170 pCi/l of ^{226}Ra; the current injection rate of 15,000 bbls/day results in approximately 400 µCi of ^{226}Ra injected daily in normal operations. The bench-scale tests will result in a maximum injection of an additional 20 µCi of ^{226}Ra.

Residual solids which are verified to have activity below regulatory concern can be released for disposal as NOW.

RESULTS AND DISCUSSION

The initial bench-scale results are encouraging and indicate that the process reduces the radioactivity of the NORM waste, both the total radioactivity as well the concentration of total radium, to near background levels. These bench-scale tests demonstrate the ability of the process to treat a wide variety of NORM wastes.

NORM waste from two different sites were processed during these bench-scale tests. Two distinct types of NORM have been processed:

- A sludge consisting of 20% oily sludge and 80% silica having particles individually coated with scale. After treatment, approximately 67% of this material remains as residual solids.

- A dry granular solid consisting of approximately 80% acid soluble scale, approximately 10% oily fraction and approximately 10% acid-insoluble fraction. After treatment, approximately 10% of this material remains as residual solids.

Table 1 shows the chemical composition of a representative sample from each of these NORM wastes.

The effectiveness of the process was measured during each experiment by collecting grab samples of the in-process solids and solutions. The solid grab samples are washed, dried and then measured in the field using the gamma spectrometer mounted on the sorting module. The dry weight of these samples is typically about 200g. For this purpose, the system is designed to allow for the rapid loading of samples.

Figure 2 shows the result of these measurements for the solids from experiment #11 on the west Texas NORM waste. The radioactivity of the solids containing NORM has been reduced to approximately background levels after 2 hours of treatment. Data from earlier experiments indicate that the dissolution process is essentially complete within the first hour. A finer set of grab samples is planned for later runs to more precisely determine the actual process time required for completion.

Radioactivity associated with NORM is typically due to the presence of ^{226}Ra and ^{228}Ra co-precipitated in various scales, sludges and films. The radioactive elements are believed to be co-precipitated with the acid-insoluble barium sulfate fraction of the scale[4]; however, our measurements indicate that some fraction of the radioactivity is also associated with the acid soluble scales. This can be seen in Figure 2 at the NORM after acid data point.

Following processing, the total quantity of residual solids was measured in the sorting module to verify the radioactivity of the solids. A 100% assay was performed in sample increments measured sequentially in the sorting machine. Each sample increment contains approximately 1.5 kg of material. Table 2 is a summary of data showing the total quantity of material measured, the average activity level in the materials for both total radium and total activity and the standard deviations of the measured data. These results indicate that the process was successful in reducing the radioactivity in the NORM waste to near background levels. The large standard deviation reported in some of the data sets after processing are the result of sample activity levels which are below the limit of detection for the system.

In BPF experiments, the total radium activity as well as the total activity of the samples was reduced to near background radiation levels. The radioactivity of the process solutions was also measured and was in agreement with the theoretical expectation obtained from a mass balance calculation.

From the beginning of the bench-scale studies, processing time has been reduced by a factor of 8. Chemical usage has been reduced by up to a factor of 4 in some process steps. The bench-scale tests have confirmed that a volume of NORM waste can be processed in one shift from start to finish. Pilot-scale equipment will be based on these results.

FUTURE ACTIVITIES

Experiments are currently being conducted to determine the effectiveness of process chemical reuse through recycling and replenishing process solutions. Modifications to the bench-scale equipment are planned which will increase the throughput to approximately 3 barrels per day. This will allow BPF to initiate NORM treatment and disposal operations during the next few months.

Injection of the bench-scale process fluids into on-site water flood injection systems will be completed in next few weeks.

The pilot-scale equipment designs are nearing completion and will be constructed over the next several months. The equipment consists of three trailer mounted modules, the sorting/assay module, the solvent extraction module, and the thermal conversion module. The design throughput of the pilot-scale equipment is 25 barrels per day on a one shift basis. The pilot-scale field tests are currently scheduled for the summer of 1997.

Included in the modifications for the pilot-scale equipment are:

- A 50% efficiency germanium detector
- The introduction of hydrocyclones for solid-liquid separation
- Semi-continuous processing of solids
- Solvent recycling and replenishment

ACKNOWLEDGMENTS

Research sponsored by the U.S. Department of Energy's Pittsburgh Energy Technology Center through the Bartlesville Project Office, under a financial assistance award DE-FC21-95MT30081 with BPF, Inc. 205 East Center St., Duncanville, TX 75116; FAX (972) 709-3899; TEL (972) 709-3890.

The authors gratefully acknowledge the contribution of the COR John Ford and the NEPA Compliance Officer, David Alleman, both of the Bartlesville Project Office, for their continued technical and administrative support of this project. We also appreciate the continued technical support received from Karen Smith at Argonne National Laboratory.

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TABLES

	T	NM
Total Water Soluble (%)	2.77	0.53
Total Acid Soluble (%)	4.49	38.38
Iron as Sulfide	13.95	32.92
Calcium as Carbonate	10.39	5.31
Magnesium as Carbonate	0.34	0.13
Sulfate as Calcium Sulfate	0.41	0
Unidentified	1.94	0.02
Total Organic (%)	9.1	57.5
Solvent soluble	5.74	34
Ignition loss	3.35	23.51
Total Acid Insoluble (%)	81.09	3.59
Barium Sulfate	0	0
Other Acid Insoluble	61.12	3.59

Table 1. Composition of representative samples of NORM waste from the Texas and New Mexico sites.

Experiment #9	Mass	Total Ra	σ	Total	σ
	(g)	(pCi/g)	(pCi/g)	(pCi/g)	(pCi/g)
Untreated NORM	14064	253.17	10.86	1419	114.9
NORM After Solvent Treatment	6149	5.15	4.04	227	100
Experiment #10					
Untreated NORM	13732	349.03	9.46	1460	160.6
NORM After Solvent Treatment	7283	8.76	1.69	94.1	23
Experiment #11					
Untreated NORM	12127	351.3	22.04	1440	119.4
NORM After Acid Treatment	8945	249.55	20.4	1119	117
NORM After Solvent Treatment	6430	4.95	1.17	53.6	4.6
Experiment #12					
Untreated NORM	17720	8.64	1.42	48.4	--
NORM After Acid Treatment	3719	17.42	8.22	101	8.2
NORM After Solvent Treatment	1352	4.21	4.3	30.6	9.1
Experiment #13					
Untreated NORM	12803	10.48	1.97	56.9	7.6
NORM After Acid Treatment	2664	24.17	4.44	53	22
NORM After Solvent Treatment	1336	2.16	0.93	9.2	6.4

Table 2. Summary of the activity measurements from the 100% assay at the conclusion of each processing experiment.

FIGURES

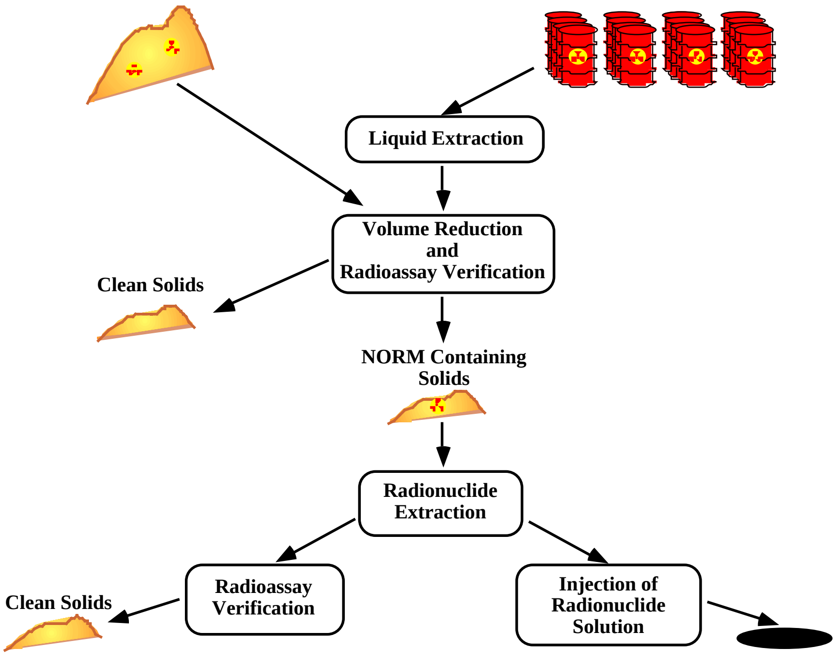

Figure 1. The general process flow diagram for the BPF NORM treatment and disposal system.

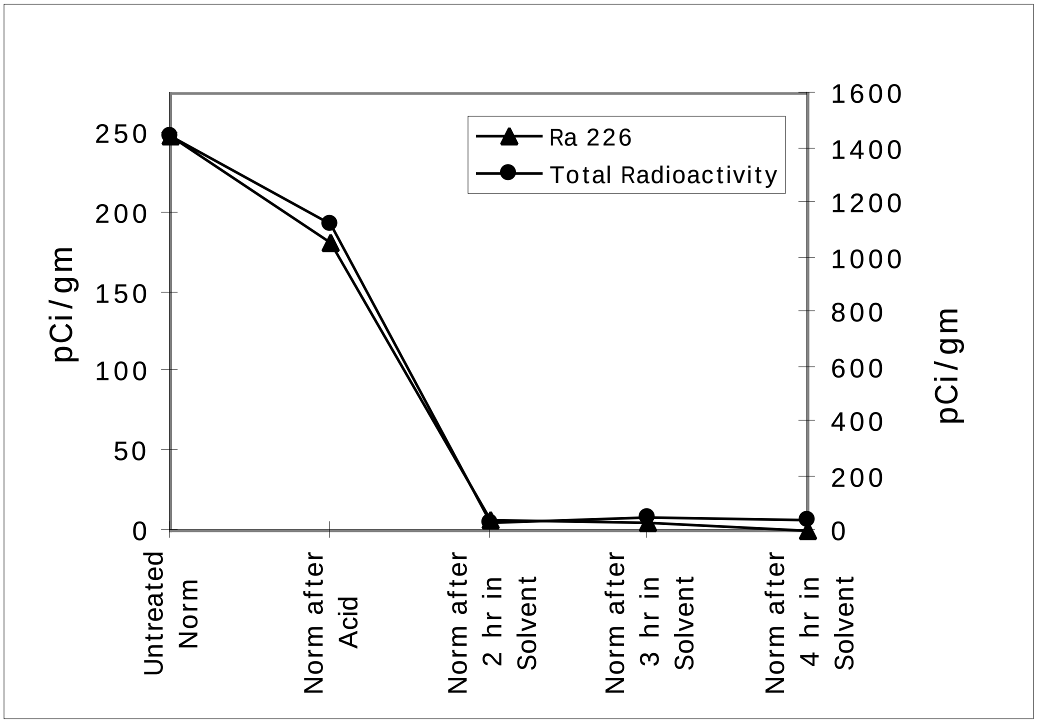

Figure 2. Radium-226 and total activity levels for grab samples from experiment #11 as a function of time in process solution.