OBSERVED REDUCTION OF RADON-222 GAS EMANATION FROM URANIUM TAILINGS USING A NEW CHEMICAL ENCAPSULATION PROCESS

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ABSTRACT

One of the most controversial radiological contaminants in the environment is Radon-222. Presently, uranium tailings (a major source of Radon-222) are stored in confinement dams under several feet of liquid in order to contain the Radon gas and eliminate its emission to the atmosphere. This method presents a hazard to the environment because of possible ground water contamination, and it creates a water resource problem in water-scarce areas. A method has recently been developed that contains and reduces Radon-222 gas emanation from uranium tailings ponds. This method uses a chemical process in which Radon-222 is encapsulated by solidification of uranium tailings slurry.

During evaluation, equal amounts of both the unprocessed and processed slurry were allowed to reach secular equilibrium in a sealed container. The built-up gas was then de-emanated and analyzed for Radon content using two proven radiochemical methods. Based on these radiochemical methods, the process under consideration indicated greater than 92% reduction in Radon-222 gas emanation.

Other methods of reducing Radon emanation are discussed in this presentation. Research for additional application of this process is recommended.

INTRODUCTION

Sludgemaster Inc. introduced a new chemical encapsulation process to the uranium mining and milling industry in 1981. The process solidifies and encapsulates wastes, rendering them environmentally stable. A Department of Energy (DOE) contractor performed an evaluation study to determine the percent reduction of Radon-222 gas after encapsulation by this process. The tailings, collected from a Grand Junction, Colorado abandoned mill tailings site, were of a dry-powder "blow-sand" consistency. The DOE contractor performed a Closed-can Gamma Spectral Analysis on the solidified product and found that the Radon-222 gas emanation was reduced by 82%.

Based on this success, Sludgemaster, Inc. contracted with Controls for Environmental Pollution, Inc. (CEP) to further evaluate the process for uranium mill tailings and other waste materials. This paper outlines CEP's technical evaluation of the encapsulation process. At this time, only preliminary data is available; however, CEP feels that the very positive results indicate that the process is effective. More testing is needed to substantiate this data.

Because Radon-222 has a 3.8 day half-life, it is of greater concern to man than gases like Radon-220 (Thoron, 54.5 Sec $t_{\frac{1}{2}}$) and Radon-219 (Actinon, 3.9 Sec $t_{\frac{1}{2}}$) due to its longer half-life. Radon-222 is the daughter product of Radium-226 in the Uranium-238 decay chain and is a radioactive noble gas. Gaseous Radon atoms decay to Polonium, Lead and Bismuth daughter atoms (See Fig. 1). These radionuclides attach themselves to particulates creating a radioactive aerosol. Radon-222 is a radiological health hazard, because when inhaled the immobile gaseous atoms can attach to bronchial cells and constantly bombard them.

DECAY SERIES OF RADON-222

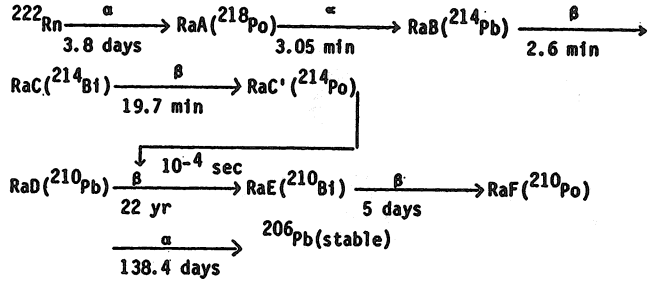

Fig. 1. Decay Series of Radon-222

Sill, C.W. (1969) reported that in the processing of Uranium ores, the radioactivity of the tailings material averages 700 pCi/g for each nuclide in the Uranium chain. He estimated that by the end of the 1970's there would be approximately 90 million tons of Uranium tailings or 58,000 Ci of each nuclide and over 125 lbs. of Radium-226.

It is estimated that bronchial exposure from Radon-222 amounts to 13.8 rad/yr from a concentration of 10.1 pCi/l. In Sill's investigation of four (4) different tailing sites, a total of thirty-six (36) samples analyzed for Radon-222 showed concentrations ranging from 5.6 pCi/l to 38.3 pCi/l. These concentrations exceed the maximum permissible concentration (MPC) of 3 pCi/l permitted by Federal Regulations for continuous exposure to the general public in uncontrolled areas.

Although many techniques for measuring Radon-222 exhalation rates have been reported, they cannot be applied to active tailings ponds because of the fluid cover (Hans 1977). The tailings at a mill are placed in an impoundment below several feet of liquid in

order to reduce radioactive emanation. Franklin, et al. (1975) conducted a test in which they used a polymeric material to seal Radon gas into the walls of Uranium mines. The results showed about a 100% reduction of the Radon gas. This approach is analogous to the approach discussed in this paper. The technique investigated in this paper encapsulates Radon gas present in the slurry by chemically solidifying it. The Sludgemaster process mixes the slurry with select chemicals that solidify it into a 90% solid end-product. (The select chemicals used in the solidification process are proprietory information.)

The results of this investigation could ease the environmental problems facing the Uranium industry.

MATERIALS AND METHODS

Sample Collection

CEP and Sludgemaster personnel visited three sites in February 1982 to process wastes for analysis in CEP's laboratory. At two uranium mill tailings ponds in Grants, New Mexico area, they processed slurry tailings from two (2) kinds of tailings ponds: an acid-leach pond and a basic-leach pond. For each processed sample, an equivalent amount of unprocessed slurry sample was collected. In this paper, the processed sample is also referred to as the encapsulated or solidified sample, while the unprocessed sample is referred to as the slurry or sludge.

Methods of Analysis

In the technical evaluation, CEP attempted to accomplish two objectives: 1) to determine what, if any, reduction occurred in Radon-222 emanation in the processed and unprocessed uranium mill tailings and 2) to determine what leaching occurred when the solidified tailings were subjected to variable environmental conditions.

To determine Radon-222 reduction, samples of the processed and unprocessed uranium mill tailings were analyzed by direct and indirect methods. The direct method analyzed Radon-222 gas build-up in enclosed canisters over a period of time. The indirect method measured Radon-222 daughter products.

The following environmental-simulation tests were performed in order to determine how the environment might affect the solidified product: 1) EP Toxicity on the solidified tailings, 2) acid leachability test simulating acid rain on the solidified tailings, 3) a variable-temperature test to simulate temperature extremes on the uranium mill tailings. The leachate produced from these tests was analyzed for trace metals, or radioactivity.

CEP analyzed for Radon-222, Radium-226, Lead-214, and Bismuth-214 using the Gamma Spectrometric Counting Technique. CEP also determined Total Radon emanation with an Alpha Scintillation Counting Technique.

Uranium concentration was determined by Fluorometric and Radiometric methods of analysis. To analyze for trace metals, CEP used the Inductively Coupled Plasma (ICP) and Atomic Absorption Spectrometry (AA) Techniques.

Alpha Scintillation Spectrometry Technique

Sixteen 100-gram aliquots of sample, eight (8) processed and eight (8) unprocessed, were placed in tightly sealed 500 cc stainless steel canisters. Each sample type was analyzed in duplicate. Each canister had a gas valve outlet, and through this outlet, the residual gas was evacuated by a vacuum pump at 3 liters per minute. Radon-222 was allowed to reach secular equilibrium with its short-lived Radon daughters for 12, 72, 168, and 336 hours respectively. The gas build-up was de-emanated from the canisters into a Silver, Zinc Sulfide activated scintillation cell. This was accomplished by first evacuating the scintillation cells with a vacuum pump and then connecting the scintillation cell to the canister. The scintillation cell was then placed into the scintillation chamber which was connected to a Ludlum Alpha Scintillation Counter. The Alpha Scintillation system was standardized by a certified standard supplied by the manufacturer.

Gamma Spectrometric Technique

CEP placed duplicate samples of processed and unprocessed sludge in tightly sealed containers specifically designed for Gamma counting. The containers were allowed to build up Radon-222 for twelve (12) hours. The container was then counted on the Gamma Spectrometer. An Intrinsic High Purity Germanium Diode (23% Eff) detector was used in the counting. The Gamma Spectrometric analysis determined the concentration of Radium-226, Lead-214, and Bismuth-214.

After Gamma Spectrometric counting, the gas was then transferred to a 100 cc GA-MA Radiogas container and the gas portion counted for Bismuth-214 daughter product.

EP-TOXICITY AND ACID LEACH METHODS

EP-Toxicity

Twenty-gram aliquots of the processed and unprocessed samples were placed in 500 ml plastic containers. A 0.5 N (CH_3COOH) Acetic Acid was used to lower the pH to 5.2 (EP-Toxicity procedure "ASTM Method, D19:12"). The samples were allowed to tumble and mix for twenty-four (24) hours, after which the leachate was collected by filtration through a millipore under nitrogen pressure.

Sulfuric Acid Leach (Acid Rain Simulation)

This done exactly as the EP-Toxicity method described above with on exception, 0.5 N (H_2SO_4) sulfuric acid was used to do the leaching and lowering of the pH. This was done to simulate acid-rain leaching. CEP performed a Radiochemical Analysis on the filtrate to determine Radium-226 concentration.

The filtrate was also analyzed for the concentration of Uranium. This determination used the Fluorometric method of analysis as described in ("EMSL Procedures Manual, HASL-300, Harly, J.H., (1974)").

Variable Temperature Method (Seasonal Conditions Simulation)

Hundred (100) gram samples of the solidified and the slurry material were placed in canisters and allowed to reach secular equilibrium in a refrigerator at a temperature below 0°C for twelve (12) hours. Equivalent amounts of sample were allowed to reach secular equilibrium at a temperature of 40°C for

twelve (12) hours. They were then de-emanated and counted by the Alpha Scintillation Technique.

RESULTS AND DISCUSSION

The average values of Radon-222 emanation reduction obtained as a result of encapsulation of the slurry tailings are given in Table I (Alpha Scintillation Technique). Table I also presents the results of the relative percent reduction of Radon-222 determined through short-lived Radon daughters (Gamma Spectral Technique). In Table I numbers A1 through A4 represent solidifed samples from the Uranium tailings pond that used an acid leach, while those numbered B1 through B4 are samples from the basic-leach Uranium tailings pond. The average Radon-222 emanation reduction for both ponds is 93.51% after encapsulation. The average reduction for acid leach tailings is 93.42%, while that of the basic-leach tailings is 93.60%. When the samples were allowed to build up Radon gas and reach secular equilibrium over a time period between twelve (12) hours and three hundred and thirty six (336) hours, the percent Radon reduction remained relatively the same. Within this time, gases like Radon-220 (Thoron, 54.5 Sec $t_{\frac{1}{2}}$) and Radon-219 (Actinon, 3.9 Sec $t_{\frac{1}{2}}$) do not contribute to the activity measurement because of their short half-lives. The longer period of build up did not show any significant difference in relative percent reduction, because Radon-222, being in the Uranium (4n+2) decay series, was being generated as the short-lived daughters were decaying.

Table I illustrates the percent Radon-222 reduction from Lead-214 and Bismuth-214, which are Radon daughters in equilibrium with Radon-222. This data was obtained using the Gamma Spectral Technique which utilizes an intrinsic high purity germanium diode detector. The results show a 76% reduction of Lead-214 and a 66% reduction of Bismuth-214 in the solidified sample. A 90% reduction in Bismuth-214 was also obtained using a slightly different analytical technique, as shown in Table I. These results are in agreement with the work of Countess, R.J. (1976), in his investigation of Radon-222 flux with charcoal canisters. He reported that Radon flux from the surface of a Uranium mill tailings pile was about 1.2×10^4 pCi m^{-2} min^{-1}. Radon flux, he noted, will increase to approximately two-thirds of its maximum accumulation in a canister in six (6) days and that little will be gained by longer exposures. The results of the investigation of Franklin, et al. (1975), in which polymeric materials were used to seal Radon-222 in the walls of a Uranium mine, are also in agreement with the results of this investigation.

Uranium concentration results given in Table II show that there is a greater Uranium concentration of 10.4% in the solidified Uranium tailings than in the slurry. This demonstrates the Sludgemaster process does not dilute Uranium concentration.

Radium-226 concentration in the leachate was determined by the Gamma Spectral Technique. Results indicate that the leachate from the EP-Toxicity method showed non-detectable concentration (less than 0.6 pCi/l) of Radium-226, while the leachate from the Acid Rain experiment (0.5 N H_2SO_4) showed 2.39±0.25 pCi/l Radium-226 (See Table III). Based on the EP-Toxicity method, leachable Radium-226 from the encapsulated material would be very low. However, acid rain conditions (rain or moisture above 0.5 N H_2SO_4 concentration) could cause a small amount of Radium-226 leaching into the surrounding soil.

Sample #	Time for Equilibrium	SOLIDIFIED counting rate (cpm)	SLURRY counting rate (cpm)	% Reduction of Radon-222
A-1	12 hours	5.50×10^2	6.87×10^3	92.00
A-2	3 days	2.50×10^2	3.98×10^3	93.72
A-3	7 days	6.00×10^2	8.50×10^3	92.94
A-4	2 weeks	3.90×10^2	7.80×10^3	95.00
B-1	12 hours	4.00×10^2	5.40×10^3	91.48
B-2	3 days	4.00×10^2	8.10×10^3	95.06
B-3	7 days	4.50×10^2	6.89×10^3	93.47
B-4	2 weeks	2.80×10^2	4.98×10^3	94.38
			Mean	93.51

GAMMA SPECTRAL TECHNIQUE

(Intrinsic (HPGE) Detector 23% Eff)

Sample #	Isotope	SOLIDIFIED	SLURRY	% Reduction
A-1	Pb-214[a]	5.44×10^2 pCi/gm	2.36×10^3 pCi/gm	76%
A-1	Bi-214[a]	7.58×10^2 pCi/gm	2.22×10^3 pCi/gm	66%
A-1	Bi-214[b]	9.68×10^3 pCi/Total	9.80×10^3 pCi/Total	90%

[a]The solid sample was sealed in a metal can for 12 hours to reach secular equilibrium.

[b]After reaching secular equilibrium (12 hours), the gas was transferred to a counting cell.

Table I. Solidification of Uranium Tailings - Radon-222 Reduction Alpha Scintillation Technique

Sample #	SLURRY (ug/g)	SOLIDIFICATION (ug/g)
A-1	29.8	31.0
A-2	29.8	30.4
A-3	32.2	38.4
A-4	31.9	38.1
	x = 30.9	x = 34.5

NOTE: Based on the above results a 10.4% greater Uranium concentration was found in the solidified tailings.

Table II. Solidification Uranium Tailings - Uranium Concentration

Analysis	SLURRY	SOLIDIFIED	SOLIDIFIED** EP-Toxicity	SOLIDIFIED Acid Rain* Leach
Radium-226	$(1.97 \pm 0.002)10^3$ pCi/gm	$(5.57 \pm 0.005)10^2$ pCi/gm	< 0.6 pCi/l	2.39 ± 0.25 pCi/l

*Simulation of Acid Rain when the atmosphere has significant concentration of sulfur dioxide. Samples were therefore leached in 0.5 N H_2SO_4.

**Normal leaching process with 0.5 N Acetic Acid (ASTM D19:12 Method).

Table III. Leach Studies - Uranium Tailings

An 85% Radon-222 reduction was observed in a sample that was allowed to reach secular equilibrium at a temperature below freezing point (0°C) for twelve (12) hours (see Table IV). Another sample was allowed to reach secular equilibrium at an elevated temperature of 40°C for twelve (12) hours. When de-emanated, Radon-222 reduction was 93.05%. The percent Radon-222 emanation reduction of the solidified material compares favorably to the data presented in Table I.

Table V illustrates the concentration of trace metals in the leachates and the unleached solidified sample. Ten elements were analyzed by the use of an Inductive Coupled Plasma Spectroscopy (ICP) instrument. A total digestion of the solidified Uranium tailings sample was analyzed and results compared to the leach extracts. The total Iron concentration in the solidified sample was 14,900 ug/gm, while the leach extracts from both the EP-Toxicity method and the sulfuric acid leach showed a concentration less than 0.1 mg/l. Vanadium showed a total of 520 ug/g (solidified sample) and less than 0.1 mg/l in both leachates. Barium was the next highest with a total of 360 ug/g (solidified sample) and less than 0.1 mg/l in both leachates. Other elements determined were as follows: Arsenic, Cadmium, Chromium, Lead, Molybdenum, Selenium, and Silver (see Table IV). The above leach study indicates that the Sludgemaster process of solidification is successful in encapsulating toxic metals in the solidified Uranium tailings.

	SLURRY count rate (cpm)	SOLIDIFIED count rate (cpm)	Equilibrium Time	% Reduction
Freeze Dried (-2.2°C)	1.05×10^3	2.20×10^2	12 hours	85.0
Temperature Acclimated (60°C)	9.07×10^3	6.50×10^2	12 hours	93.05

Table IV. Comparison Alpha Spectrometric Counts Between Freeze Dried and Temperature Acclimated Uranium Tailings Samples.

Analysis	SOLIDIFIED Tailings ug/gm	EP-TOXICITY* mg/l	ACID RAIN** mg/l
Arsenic	75	0.6	0.3
Barium	360	< 0.1	< 0.1
Cadmium	< 10	< 0.1	< 0.1
Chromium	< 10	< 0.1	< 0.1
Iron	14,900	< 0.1	< 0.1
Lead	< 10	0.2	< 0.1
Molybdenum	< 10	< 0.1	< 0.1
Selenium	< 10	< 0.1	0.1
Silver	< 10	< 0.1	< 0.1
Vanadium	520	< 0.1	< 0.1

*Simulation of Acid Rain when the atmosphere has significant concentration of sulfur dioxide. Samples were therefore leached in 0.5 N H_2SO_4.

**Normal leaching process with 0.5 N Acetic Acid (ASTM D19:12 Method).

Table V. Leach Studies - Solidified Uranium Tailings.

CONCLUSION AND SUMMARY

The results of the various aspects of this study indicate that the Sludgemaster process of encapsulation is not only capable of reducing the percent of Radon-222 emanation but also reduces the possibility of the leaching of toxic elements. Radon-222 emanation after solidification showed a 93.51% reduction from the slurry. The Gamma Spectral Analyses of short-lived Radon daughters supported the above findings.

Further studies are needed to confirm the results of this investigation; however, the present findings indicate that the Sludgemaster process of encapsulation could substantially reduce Radon-222 exhalation to the environment from Uranium tailings ponds and reduce toxic leachates from hazardous waste.

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