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DOE ORDER# 4700.1

95 RF01142, EG&G ROCKY FLATS

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95-RF-01142

F. R. Lockhart
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DOE, RFFO

ANSWERS TO COLORADO DEPARTMENT OF PUBLIC HEALTH AND ENVIRONMENT
QUESTIONS - SRK-015-95

Colorado Department of Public Health and Environment has asked the Solar Ponds organization at EG&G, Rocky Flats to answer two questions. The response is presented below.

QUESTION 1

During recent meetings with the regulators, a question arose concerning the correlation of total alpha and isotope concentrations in the pond sludge: Why doesn't a better correlation of gross alpha and the sum of specific isotopes exist?

ANSWER 1

Several factors contribute to the low correlation of gross alpha to isotopic measurements, as discussed below. The lack of correlation is acceptable because the measurements have difference uses: gross alpha results are used for screening and the isotopic results are used for more demanding characterization needs.

Pond Operations Factors

To understand the characterization data base, certain information about pond heterogeneity and operations must be considered. Results of individual samples at different times and from different locations will vary sometimes drastically. The data must be averaged to gain an understanding of the overall content of the ponds, and individual samples are not representative of the entire sludge inventory.

Corrective actions began with the removal of sludge from the 207-A pond in 1986. The sludge from this pond was made into approximately 19,000 pondcrete blocks. This pondcrete operation ended in May 1989 when all of the sludge was removed from the 207-A pond and the pond was rinsed "clean". The sludge that remains in the clarifier, today, is from the 207-A pond. Additionally, approximately 7,000 pondcrete blocks produced during this operation remain on site today.

The sludge in the 207-A pond was not homogenized prior to the pondcrete operation. Characterization data gathered by R. F. Weston in 1986 for the 207-A pond demonstrated the variability of the contaminant concentrations based upon the location of the sample collection point in the pond. Therefore, it is expected that the pondcrete population would have exhibited this same variability in characterization.

In preparation for the clean-out of the remaining ponds, R. F. Weston was contracted in 1990 to characterize the ponds. This effort also produced isotopic determinations for the remaining ponds. Halliburton was contracted in 1991 to provide waste solidification services for the ponds. To limit their corporate liability, Halliburton re-characterized the ponds. By this time, an emergency operation to prevent the 207-B ponds from overflowing had transferred 207-B north pond waste into the empty 207-A pond.

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Until 1993, the Interceptor Trench System discharged into the B-ponds. In normal operations, water and probably some sludge was transferred among the three B-ponds to maintain the freeboard requirements in these ponds. This physical mixing has eliminated to some extent a discrete identity for the three B-ponds as well as for 207-A pond which received the B-pond waste. Halliburton at this time made no attempt to consolidate the B and A pond sludges and characterize the product. Therefore, to characterize the consolidated sludge, the discrete data from each pond should be averaged.

While pond 207-C did not experience the consolidation and water movement that occurred in Ponds 207 A/B, the pond contents were not (and are not) homogeneous. Again, results from individual samples will vary and an overall understanding of C Pond depends on averaged data.

Analytical and Sampling Factors

The correlation between the gross alpha results and the sum of isotopic results is expected to be marginal. In some cases the gross alpha result can be higher than the isotopic sum and in some cases the opposite can occur. The situation is sample-specific. The major analytical and sampling reasons why the correlation is expected to be poor are summarized below and detailed in Appendix A (see Attachment 1):

- The gross alpha methodology is not inherently an accurate technique, it is a screening technique,
- The gross alpha method measures emissions from all alpha-emitting nuclides while the isotopic method measures alpha from specific nuclides,
- The selection of the isotope used to calibrate the gross alpha instrument can cause variability,
- High levels of solids in the sample reduce the accuracy and precision of the gross alpha method, and
- The Solar Ponds sludge is heterogeneous, especially the sludge from 207C, and therefore it is difficult to take individually reproducible samples.

The isotopic technique is a more accurate methodology which eliminates much of the error inherent in the gross alpha method. Because of the precision and accuracy of the isotopic methodology, it is the method of choice for more demanding characterization needs. The results from the gross alpha method are used for less demanding situations such as DOT shipping determinations and general screening needs.

QUESTION 2

At a recent meeting with the regulators, they felt that the Pondcrete analytical results were higher than either the Pond A or the clarifier results. This isn't a reasonable expectation because the Pondcrete material has been "diluted" with cement and thus should be lower than its feed material, the Pond A and clarifier sludge. Thus they asked that the Solar Ponds organization address this issue.

ANSWER 2

In order to answer this question the analytical results for a number of analytes for Pondcrete, Pond A, and the clarifier were compared. Rather than compare **all** the analytes, a representative suite of analytes was chosen to answer the question. The grouping of analytes chosen is the suite of metals on the Land Disposal Restrictions (LDR) list. They are: Antimony (Sb), Arsenic (As), Barium (Ba), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg), Nickel (Ni), Selenium (Se), and Silver (Ag). In addition, cyanide and gross

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alpha plus beta were included on the list in order to have some nonmetals involved in the comparison.

A comparison of the Halliburton analytical data for the above analyte list for Pondcrete and Clarifier sludge is presented in Appendix B (see Attachment 2). The data show that in almost all cases the Clarifier sludge analytical data is higher than the Pondcrete data. The average ratio of clarifier to Pondcrete data is 2.1. (Only two of the analytes didn't follow the trend, they are Ba and Hg.)

Please be advised that because the material is very heterogeneous, these data should only be used to show general trends such as the Pondcrete comparison.

Please contact me or Mark Peters at extension 6992 with any further questions on this issue.



S. R. Keith
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EG&G Rocky Flats, Inc.

MAP:pjm

Attachments:
As Stated (2)

Orig. and 1 cc - F. R. Lockhart

cc:
S. Howard - DOE, RFFO (SAIC)
M. A. Witherill - " " "

Appendix A

The information presented below pulls together the technical reasons why there should be a poor correlation between the results for gross alpha and the sum of the isotopics (pU, Am, U).

General

- The gross alpha method theoretically measures all the alpha emitting isotopes but the isotopic method only measures the alpha's from U + Pu + Am. Therefore, the sum of isotopic results should be lower than the gross alpha results if daughter products from the U or Th series are present in the sample. Alpha emitting isotopes from these series such as Po, Th, Ra, Rn, Bi will cause a higher gross alpha measurement.
- The Solar Pond material is known to be heterogeneous and is difficult to representatively sample. This aspect of the material makes it difficult to sample exactly the same material even from the same location. Thus, the protocol of taking a sample for gross alpha and another for isotopics has the potential of generating different results because of sample differences.

Gross Alpha Determination

- The gross alpha method is not an accurate analytical method and can produce large errors which could be part of the reason for the poor correlation. For example, the precision of the RCRA SW-846 gross alpha method (Method #9310) averaged 22% (2 sigma) at the 95% confidence level for water samples. This RCRA water method is similar to the gross alpha methods used by the analytical labs which analyzed the Solar Ponds water samples.
- The solids content of the water samples is a major factor in the accuracy and precision the gross alpha method can achieve. As the solids content in the water increases and results in increased solids deposition on the planchet, the precision and accuracy decreases. The gross alpha method attempts to address the alpha attenuation caused by solids deposition on the planchet by calibrating this attenuation against a standard containing a similar amount of solids on the planchet. However, if the solids on the standard (eg., river silt) absorbs alpha's more or less than the actual solids (Solar Ponds crystals) the alpha result can be low or high. The Solar Ponds samples contain a significant concentration of dissolved solids (typically as high as 460,000 mg/L.) and this could result in poor gross alpha accuracy as well as poor precision. Therefore, the Solar Ponds' water and sludge samples will suffer significantly from this problem. (Solar Ponds' dried sludge will not have this problem).
- For solid samples some labs use a preparation step for the gross alpha method called "direct mount" wherein the solid sample is mounted directly onto the planchet without a previous dissolution step. (If the sample is first dissolved and the solution evaporated onto the planchet the accuracy and precision of the gross alpha method is much improved.) Consequently, if the solid is mounted directly onto the planchet, a good percentage of the alpha particles are shielded from the detector and will not be measured resulting in a low bias for the gross alpha measurement. The lab that supplied the Solar Pond gross alpha results used the direct mount method. This problem would affect only the Solar Ponds' dry solids sludge samples.
- Some of the poor correlation between the gross alpha and the sum of the isotopics may be due to the fact that the instrument which measures the gross alpha (Gas-Flow Proportional Counter) is calibrated with the alpha from the Am-241 isotope and the major isotope in some Solar Pond samples is U which can cause a low bias in the gross alpha measurement. The book, "Standard Methods for the Examination of Water and Waste water (h18th ed.)" states: "Gross Alpha and gross beta results

will not provide accurate information about radionuclides having energies significantly different from the energy of the calibration standard." The gross alpha analytical methods used to measure gross alpha's in Solar Ponds samples used Am-241 to calibrate the Gas Flow Proportional Counter and since many of the samples have high proportions of uranium, low gross alpha results could result.

Isotopics Methodology

The isotopic method is a more accurate analytical technique which:

- eliminates the high solids errors present the gross alpha method,
- chemically separates the U, Pu and Am species and measures their alpha concentrations individually,
- uses more sensitive and accurate analytical instrumentation for the final alpha measurement,
- only measures the alpha's of the isotopes U, Pu, Am.

Analyte	Mean Concentration, mg/kg		Ratio:
	Pondcrete	Clarifier Sludge	Clarifier/Pondcrete
Cyanide, Tot.	13.9	64.3	4.63
Sb	NA	NA	
As	ND	12	
Ba	227	183	0.81
Cd	1670	3660	2.19
Cr	1010	2480	2.46
Pb	75.1	161	2.14
Hg	29	9	0.31
Ni	329	700	2.13
Se	ND	ND	
Ag	60	135	2.25
Gross A/B	2700	5945	2.20
		Average=	2.12
ND=None Detected			
NA=Not Analyzed			
Reference:			
Deliverable (Combined 224A, 224E) "Pond Sludge Waste Characterization Report and Clarifier Sludge Waste Characterization Report", Halliburton, March 1992.			