Radiation Surveillance Associates, Inc.
1771 South 900 West, Suite #10
Salt Lake City, Ut 84105

Report to

U.S. Nuclear Regulatory Commission
Regulatory Issues Section
Low Level Waste Management and Decommissioning

December 30, 1992

Re: Molycorp, Washington, Pa. Facility and RSA Report,
"A Subsurface Survey for Thorium Content,"
Dated December 27, 1990.

Justification of the Calibration Factor used for Borehole Measurements of Underground Radiation Exposure Rates and Average ^{232}Th Concentration and Response to NRC Comments Dated October 29, 1992.

McDonald E. Wrenn, Ph.D., CHP
William Delaney, M.S.
Luiz Bertelli, Ph.D.
Narayani P. Singh, Ph.D.

TABLE OF CONTENTS

FIGURES

TABLES

TABLE OF CONTENTS

FIGURES

TABLES

INTRODUCTION:

In 1990 RSA conducted a surface and subsurface radiation survey for gamma exposure rate around the pond area of the Molycorp Washington Pennsylvania site. The results were submitted to Molycorp in a report dated December 27, 1990 which has been recently reviewed by the NRC in a report entitled 'NRC Comments on Report Entitled, "A Sub-Surface Survey for Thorium Content at the Molycorp Plant Site in Washington, Pennsylvania,"' and transmitted to Ms. Barbara Dankmeyer, Molycorp Resident Manager, in a letter from Chad Glenn, NRC Project manager dated October 29, 1992.

In this survey the surface gamma radiation measurements were made at a variety of places on site with particular attention to the pond area; 32 boreholes were drilled and logged with a sodium iodide probe to measure exposure rate, which is related to average concentration of gamma emitters in soils.

The original intent of the summary was to measure the extent of the subsurface concentration of radioactive materials and quantitatively assess the concentrations and amounts of ^{232}Th present, laterally and as a function of depth in the area of the ponds. In order to be quantitative, an extensive calibration program was undertaken to relate the ambient gamma background both on the surface and in the boreholes to the ^{232}Th content of the underlying soils. Whenever the gamma radiation measurements exceeded the background gamma levels substantially it could be assumed that the material responsible for that increase was ^{232}Th and its daughters in equilibrium. This assumption was quite reasonable based on the history of operation of the plant and previous measurements of thorium in slag from the Molycorp operations. Information presented later in this report shows that the assumption of equilibrium was justified.

The calibration procedure is described in great detail in the 1990 report but a brief summary will be given here. In a ground survey of external radiation in 1990, a set of external exposure measurements was made with a calibrated pressurized ionization chamber (PIC) traceable to NIST. At each location where absolute exposure rate measurements were made with the PIC measurements were also made with a sodium iodide scintillometer (model 19 Ludlum) and with a

sodium iodide (NaI) probe and photomultiplier tube which was capable of being lowered into the ground inside the boreholes. The sodium iodide probe and scintillometer were cross calibrated against the pressurized ionization chamber on the surface and the calibration curves presented in that report. Thus the readout of both NaI instruments were calibrated against the exposure rate in μR/hr due to gamma rays from a distributed environmental source, predominantly due to ^{232}Th and its daughters.

The basis for the conversion from the gamma exposure rate to the average concentration in surrounding soil was given by Beck (1972), and his conversion factor, which was subsequently adopted by the NCRP, (NCRP-50, 1976) gives the exposure rate due to a semi infinite slab of soil with uniformly distributed ^{232}Th in equilibrium with its daughters as $2.82\ \mu R \bullet hr^{-1}/pCi \bullet g^{-1}$. This conversion factor is only applicable to distributed sources.

In a review of the 1990 RSA report the NRC indicated that they were not convinced that the calibration and subsequent interpretation relating exposure rate to average ^{232}Th concentration in soil was a valid one. RSA points out that the use of external gamma exposure rate and gamma spectrometry to assess average concentration of thorium in soil is a technique recognized in both the scientific literature and the NCRP publications. Moreover gamma ray exposure rate measurements of this type result from the average radioactivity concentration over reasonably large volumes of soil, and are directly related to the potential for human exposure, since they result from direct radiation measurements.

In the report that follows we have laid out the rationale and additional information for accepting the calibration factors derived in the RSA 1990 Report and present additional information on the isotopic composition of the thorium in the slag pile. Additional information is also provided on thorium isotopes found underground in borehole #29 and #32, from which core samples were obtained and radiochemical analysis for the alpha emitting isotopes of thorium made.

BACKGROUND RADIATION:

Gamma Exposure Rates for Unit ^{232}Th, ^{238}U and ^{40}K Sources in Soil

NCRP-50, based on the work of Beck, showed that the exposure rate at 1 meter above the soil for uniformly distributed natural emitters is 2.82 $\mu R \bullet hr^{-1}/pCi \bullet g^{-1}$ ^{232}Th. Figure 1 shows graphically the exposure rate in air one meter above the ground for the major nuclides found in nature, the uranium series, thorium series, and ^{40}K under equilibrium conditions of uniform distribution in depth and lateral extent at a concentration of 1 pCi/g in soil.

Fractional Gamma Exposure Rate in Surface Air Due to Natural Sources as a Function of Depth

NCRP-94 and Beck (1972) show the contribution to the exposure rate at 1 meter above the soil due to gamma emitting sources at various depths in soil for a typical natural emitter source composition. Although the gamma spectrum of energies from a typical natural emitter composition has a slightly lower average energy than that from ^{232}Th and its daughter products, the graph shown in Figure 2 can be used to illustrate a basic point about averaging. This graph has been reproduced from Beck (1972) with permission of the author. About 90% of the total exposure rate comes from radioactivity distributed in the top 20 centimeters (about 8 inches) of soil.

Specific Activity of Thorium in Slag

Beck's work implies that underground most of the gamma ray exposure from ^{232}Th and its daughters which reaches a detector in a borehole will originate from within a sphere with a radius of approximately a foot, or alternatively with a diameter of 2 or more feet. This means that, although gamma ray measurement provide a reasonably local measure of the background, they average over a relatively large volume compared to the volume of a soil sample such as those taken from the cores from boreholes 29 and 32 (see page 12). Since the concentration of ^{232}Th in the slag pile is known to average 1250 pCi/g (see Table 1) (AHP, 1975,) and since pieces of slag are probably not uniformly distributed underground, increased backgrounds underground must result from combinations of thorium bearing slag mixed with other materials.

Molycorp, Washington Pa

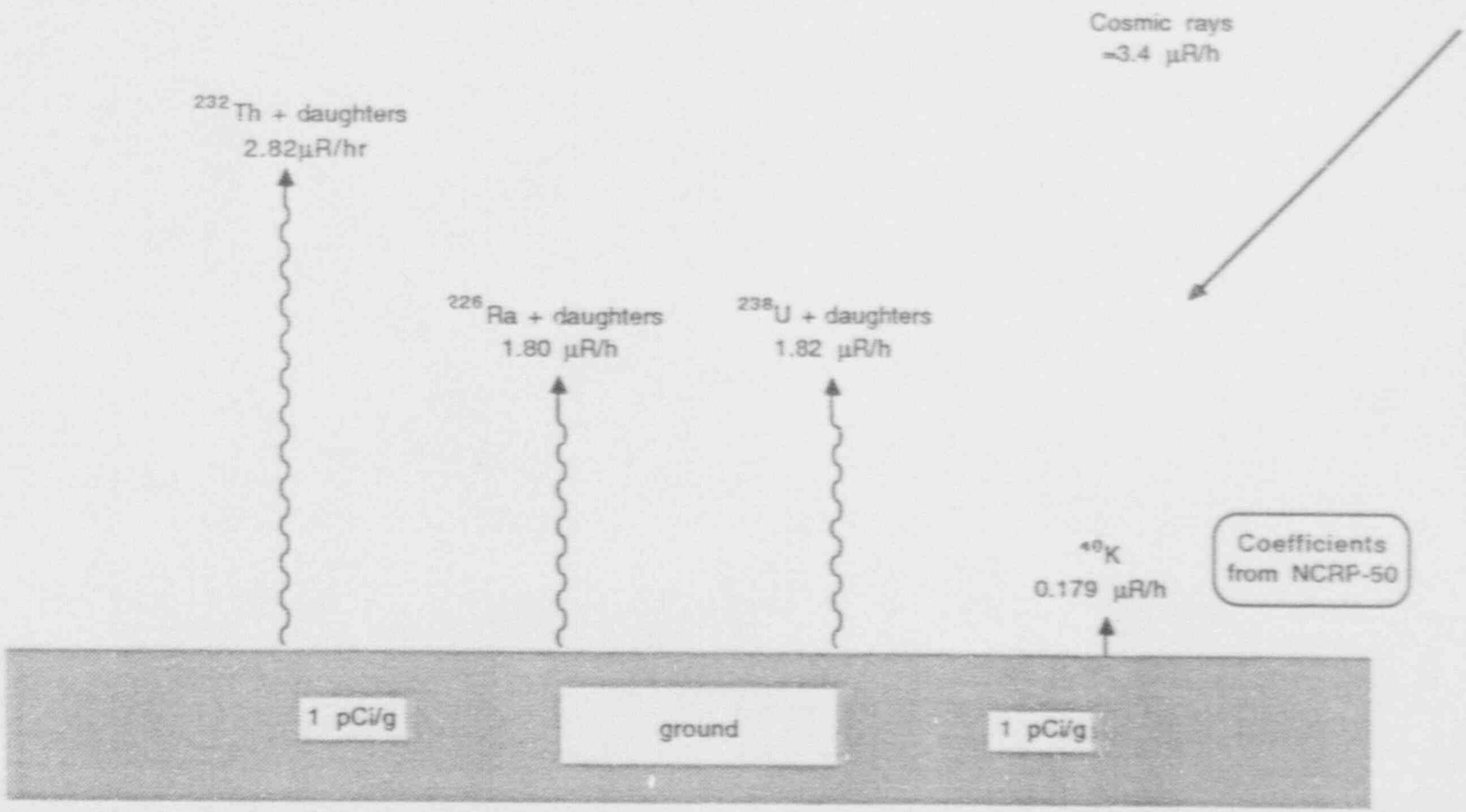


Figure 1: Exposure rate at one meter above the ground for uniformly distributed natural emitters (at a concentration of 1 pCi/g)

RSA, 12/29/92

4

Figure 2. Contribution of Total Exposure Rate at One Meter Above the Ground from Natural Sources as a Function of Soil Thickness.

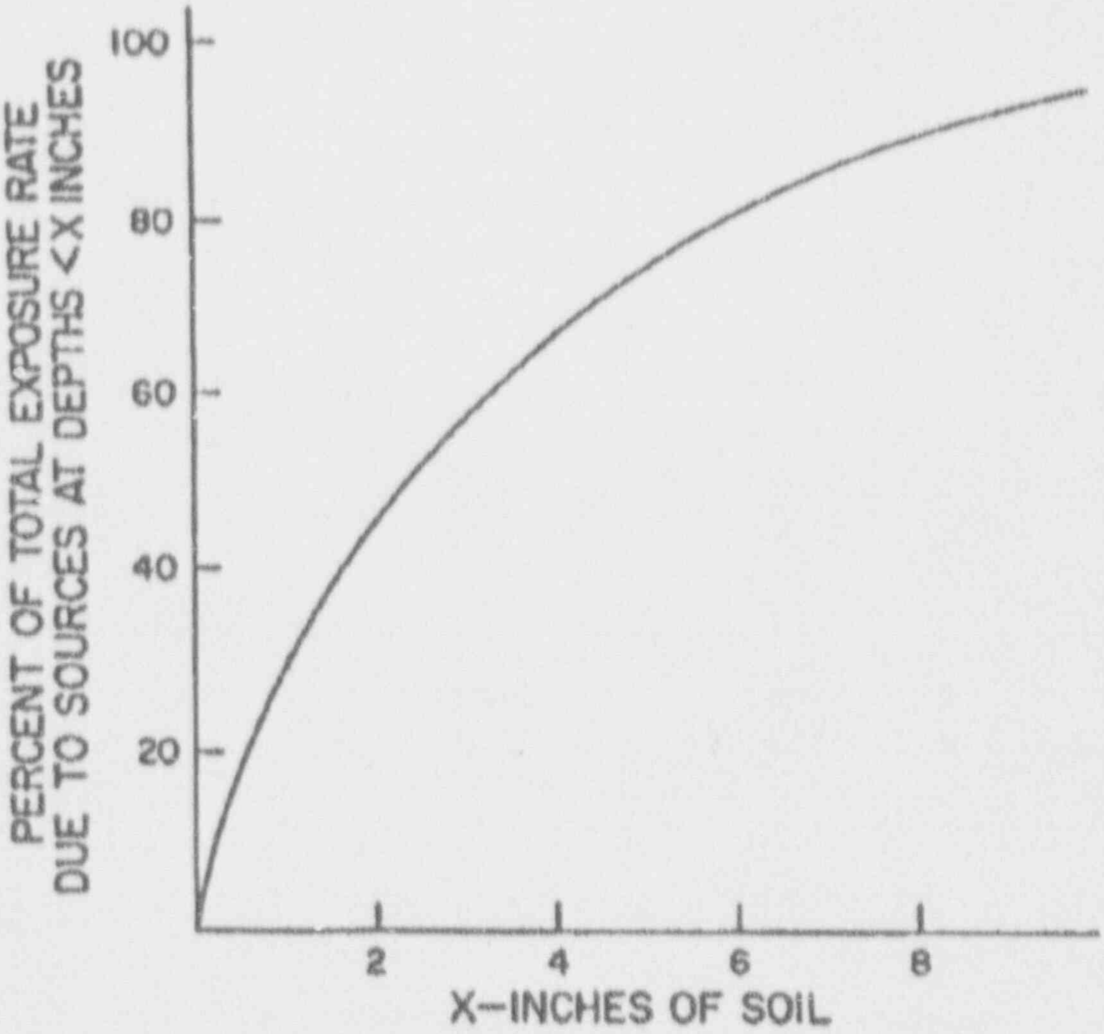


Table 1. **Information About the Slag Pile**

Volume:		2.494×10^5 ft^3
Mass:		2.245×10^7 lbs
Density:		90 lbs/ft^3
Concentration of Th:		11.4 ± 0.2 mg Th/g
	or	1.14%
	or	1250 pCi/g ^{232}Th
Degree of Equilibrium		^{232}Th = ^{228}Th (~100%)
Total Activity:		12.7 Ci ^{232}Th

• Applied Health Physics Report dated May 22, 1975

SURFACE & SUBSURFACE CALIBRATION PROCEDURES:

Summary of Procedures

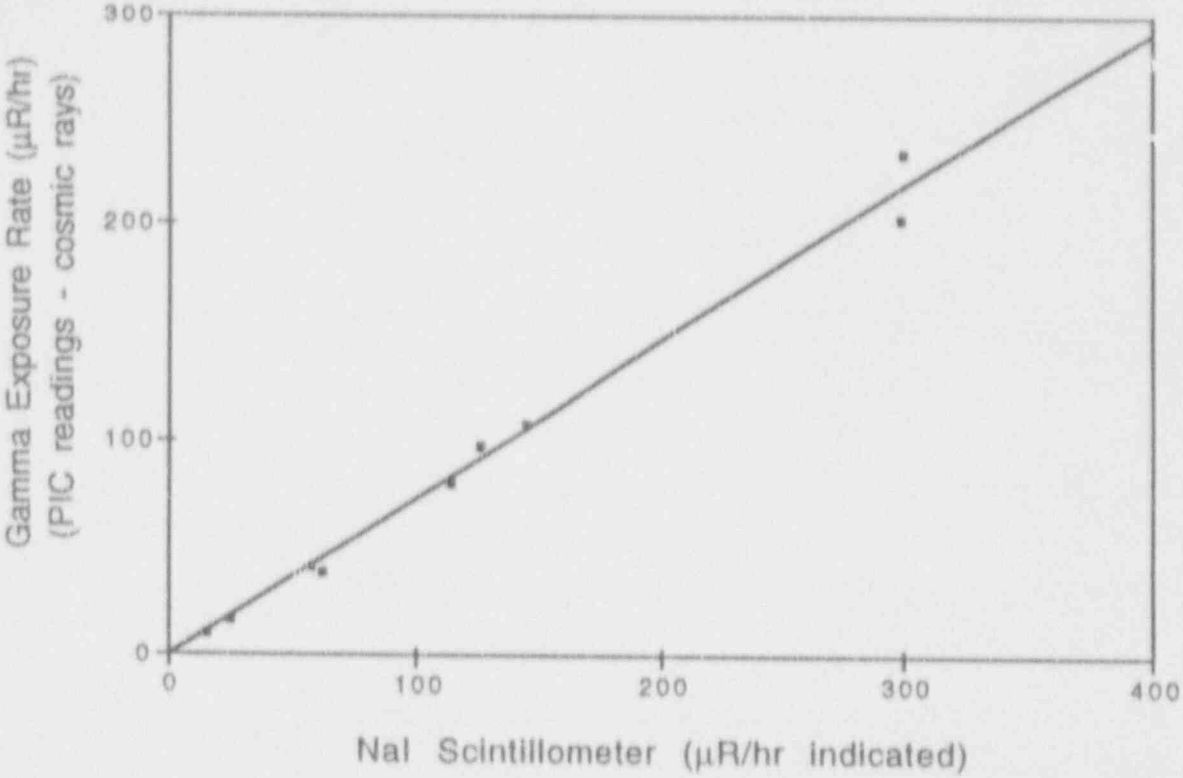
The RSA 1990 Report describes in detail the PIC calibration and the results of the pressurized ionization chamber (μR/hr) vs. in the response of the NaI scintillometer and cpm in the NaI well logging crystal (probe). For convenience the plot of the total ionization less that due to cosmic rays (i.e., due only to gamma rays) measured in the pressurized ionization chamber vs. the scintillometer readings are shown in Figure 3 (Figure 1 in the RSA Report, 1990). The correlation is very good over the range of exposure rates measured indicating that the scintillometer can be used for absolute gamma rays exposure measurements. In Figure 4 the results of the same calibration procedure are shown for the well logging probe inside PVC pipe in the configuration we used in the underground logging of boreholes 1-32.

Because the calibration coefficient was obtained in an area where the environmental radiation field is primarily due to thorium and its daughters distributed as volumetric sources in the surrounding material, the calibration factor derived is valid f ^{232}Th in a volumetric distribution We will show later in this report that most of the radioactivity responsible for the increased gamma background is from ^{232}Th and its daughters in equilibrium.

Since the boreholes were cased with 2 inch diameter PVC pipe and the probe lowered inside a 1 inch diameter PVC pipe the appropriate calibration factor is given in Graph 5 of Figure 2 (RSA 1990), which is reproduced here as Figure 4. The appropriate calibration and conversion factors are as follows:

Summary of Calibration and Conversion Factors

12.6±0.3 μR/hr /1000 cpm	directly measured, Fig. 4, NaI Probe
5.64 μR/hr /pCi/g	from NCRP-50,94, Beck, 72, adjusted for 4π, k_2 in Appendix B
448 cpm / pCi/g	inferred from the two above
0.728 true/indicated	NaI Scintillometer, Fig. 3 (μR/hr)



Least Squares Fit to a Line Constrained to Pass Through Zero:

Slope (compensation factor): 0.728 ± 0.018

y intercept = 0

(Computed using the statistical software package StatWorks on a Macintosh computer.)

Figure 3: Least squares fit of the calibration factor for the NaI scintillometer gamma measurements.

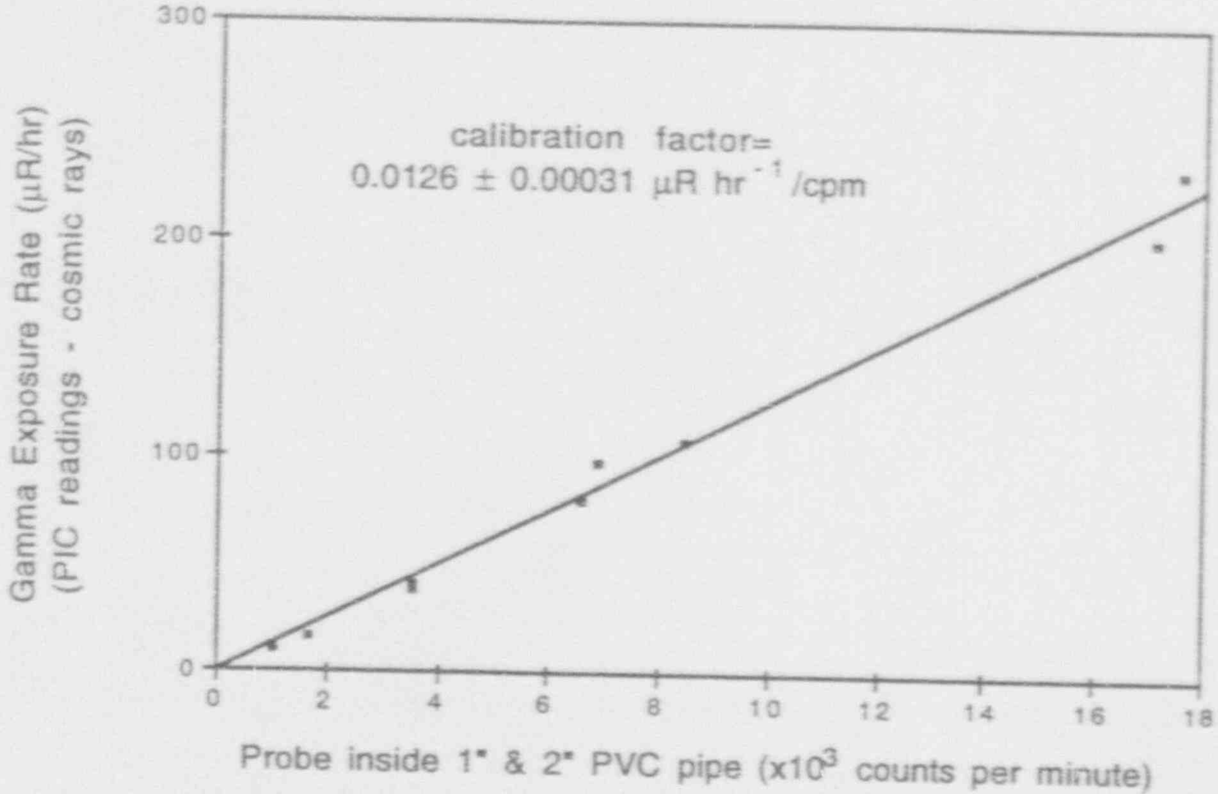


Figure 4: Least squares fit of the calibration factor for the NaI probe over a 2π geometry for a volumetrically distributed source of Th-232 and daughters

The calibration factor for 4 π geometry was obtained by multiplying the 2 π calibration factor by two. We have also made a correction for solid angle which did not appear in the RSA 1990 Report. (See Appendix C.) The RSA 1990 Report did not give estimates of average ^{232}Th content in the first foot and one half of surface soil because a correction for the reduction in the expected response associated with the solid angle subtended by the top of the hole had not been made. This correction, although approximate, should be reasonably good for the shallow depth readings and we have included its derivation in this document so that concentrations of ^{232}Th in the first several feet below the surface can be inferred from the results of gamma exposure rates established in the well logging conducted for the RSA 1990 Report. This correction is shown in the Appendix C.

Derivation of Exposure Rate Underground from ^{232}Th From First Principles

The exposure rate produced in air in a borehole can also be derived from first principles as follows: The dose rate to any medium can be calculated for a radionuclide distributed uniformly in the medium at a concentration of C pCi/g with f_i fractional gamma's emitted per disintegration where E_i is the energy of gamma ray i as follows (Spiers 1968) :

$$\mu\text{rad/hr} = 2.13\ C \sum f_i E_i$$

The mean energy of the gamma rays emitted by the ^{232}Th series in equilibrium is about 0.9 MeV, and the total gamma energy emitted per disintegration of the ^{232}Th parent by members of the series in equilibrium is 2.49 MeV,($\sum f_i E_i$) a value which has been extracted from ICRP-38. (ICRP 38, 1983.)

Since the rate of gamma energy emission equals the rate of absorption in an infinite medium, the formula above gives the gamma dose rate in an infinite medium obtained from the expression above which is 5.304 $\mu\text{rad}\cdot\text{h}^{-1}/\text{pCi}\cdot\text{g}^{-1}$ ^{232}Th. By well established theory, the dose rate in air in a cavity within any medium is given by the ratio of the linear absorption coefficients in that medium to that in air. Using mineral bone as a surrogate for soil, the conversion factor for 0.9 MeV gamma rays is 0.928 rad/R. (Spiers 1968.) The expression derived above then gives 5.304/.928 = 5.72 $\mu\text{R}\cdot\text{h}^{-1}/\ \text{pCi}\cdot\text{g}^{-1}$. This compares very favorably with the 4 π calibration factor (5.64 $\mu\text{R}\cdot\text{h}^{-1}/\ \text{pCi}\cdot\text{g}^{-1}$) derived from Beck.

In short this calibration factor is valid with a high degree of accuracy to derive average ^{232}Th concentration in soil, since the NaI probe was calibrated to measure µR/hr in air, the quantity determined during the downhole logging.

Underground Background Gamma Exposure Rates

An important question is, 'What is the appropriate background to subtract both underground and above ground from the increased gamma measured in each environment?' Borehole 27 was in background soil and the 13 measurements taken from the bottom of the hole to a foot and one half below the surface averaged 1726 counts per minute, equivalent to 21.7 µR/hr using the calibration establishing the relationship between count rate in the sodium iodide probe and exposure rate. This is an underground background and in a 2 π geometry the equivalent background would be one half this or 10.9 µR/hr. The background gamma exposure rate underground in 4 inch diameter holes as well as the increased exposure rate which would be due to 5 pCi/g of ^{232}Th in soil are shown in Figure 5. In virgin soil the background gamma exposure rate is 22 µR/hr, in FeMo slag, 28 µR/hr, and the exposure rate in each media if it contained an average of 5 pCi/g ^{232}Th above normal gamma background would be 50 and 56 µR/hr respectively. The gamma exposure rate would be 163 µR/hr for 25 pCi/g of ^{232}Th above background in virgin soil..

Estimation of ^{232}Th Concentration from Underground Exposure Rate Measurements

Therefore the calculation of average ^{232}Th pCi/g in underground soil is obtained with the formulas shown in Appendix B relating concentration to the measured gamma exposure rate. The formula is summarized in simplified form below.

$$C = (Pk_1-21.7)/(5.64)*0.95*R = 0.187(Pk_1-21.7)/R$$

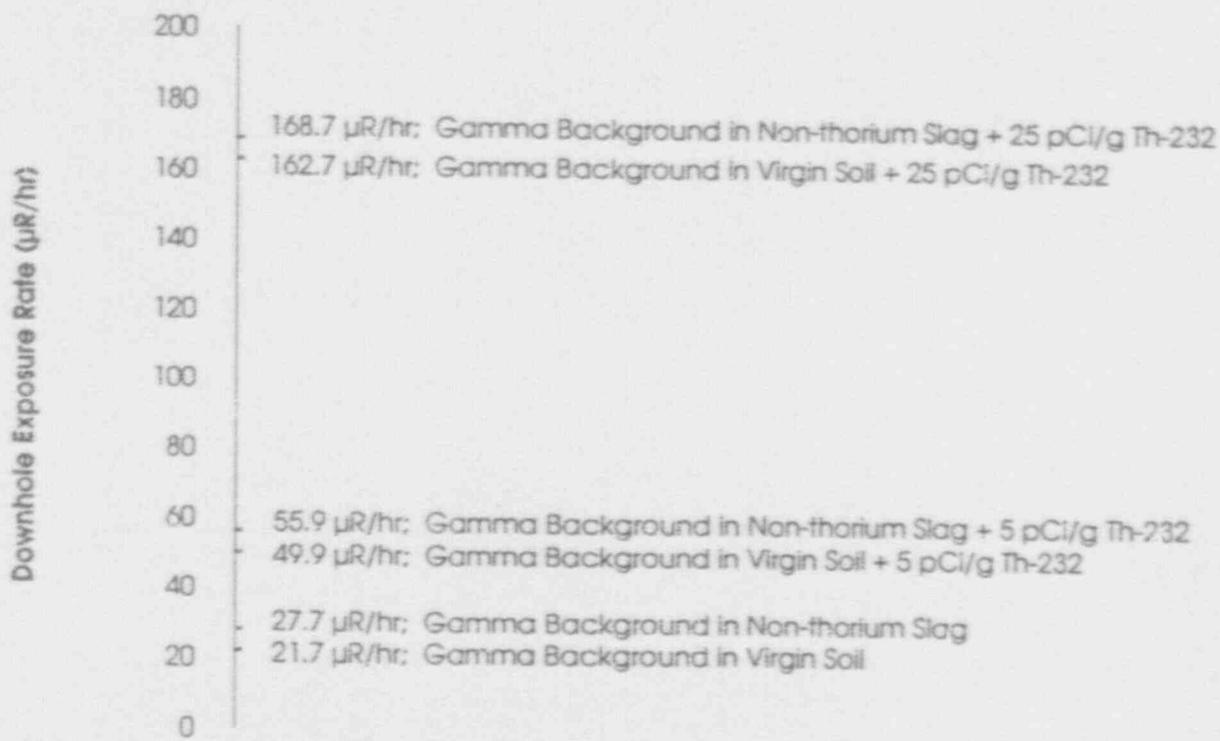
C = the concentration in pCi/g

R = the geometric correction factor, = 1 well below the surface

Pk_1 = exposure rate (µR/hr) measured underground

Because the intent of the 1990 report was to identify the horizontal and vertical distribution of underground radioactivity and not to provide information to comply with a subsequent agreement on decontamination of the site, the underground

Figure 5: Underground Background Gamma Radiation



RSA, 12/30/92

background was rounded to the first significant figure in that report (i.e., 2000 vs. 1726 cpm in virgin soil). However in this and subsequent reports we will not round off background measurements to less than three significant figures. In this report all logging results will be presented in exposure rate in μR/hr which is the primary calibrated measurement.

REVISED INFORMATION ON EXPOSURE RATE AND AVERAGE ^{232}TH CONTENT IN BOREHOLES:

The exposure rates measured underground in borehole 28 (background in non-Th bearing FeMo slag) and borehole 27 (virgin soil) are shown in Figure 6. The mean exposure rate in borehole 27 from 1.5 feet and below to bedrock was 21.7 μR/hr. The mean exposure rate in FeMo slag was 27.7 μR/hr, from 1.5 to 6 feet. The exposure rate depth profiles are shown in Figures 7 and 8 for BH's 29 and 32 from which samples were taken every 1.5 feet (See RSA 1990 Report for the sampling protocol) for subsequent radiochemical analysis. BH 32 was chosen because it was at a location just inside the north boundary of the site where the external exposure rate was among the highest found (although still localized). BH 29 was chosen from a location in the pond area which exhibited the highest local surface exposure rate .

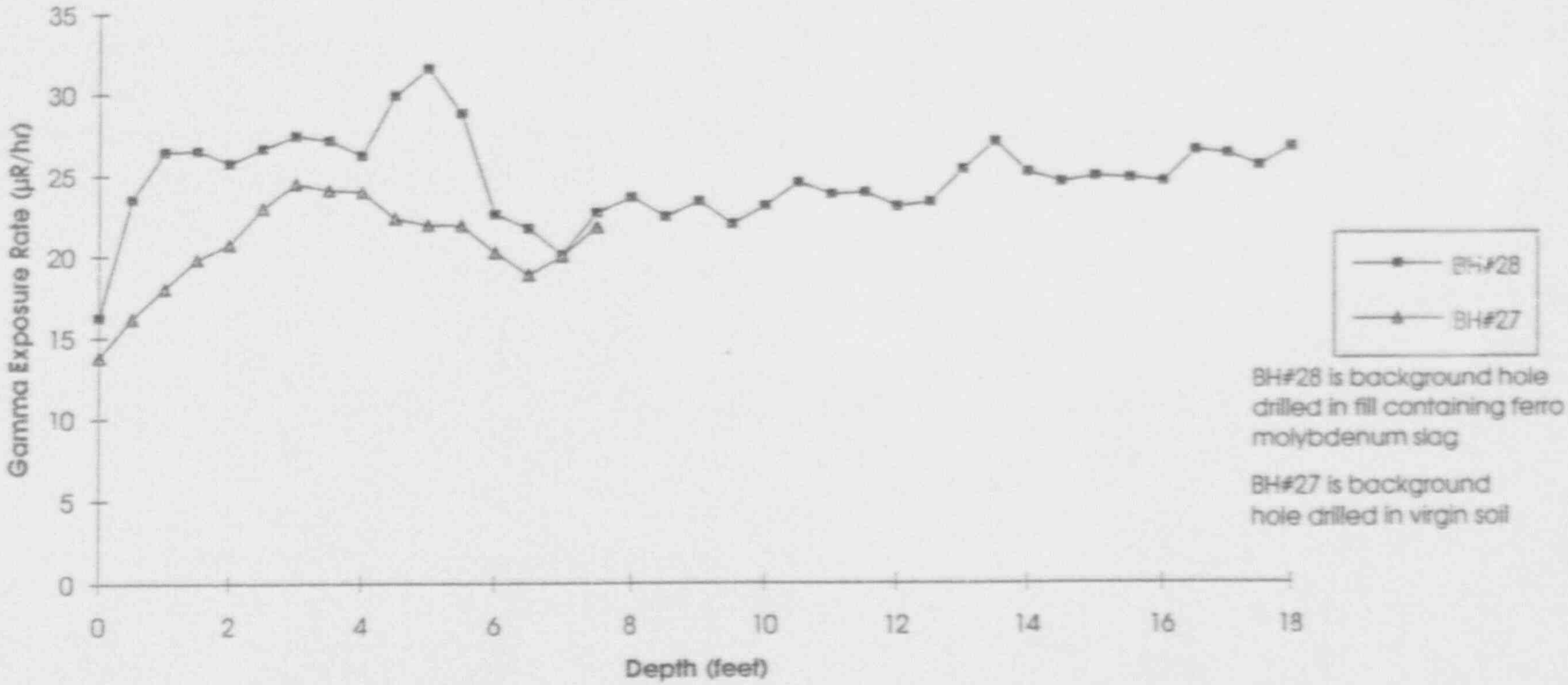
Revised tables and graphs of exposure rate (μR/hr) and. the average ^{232}Th concentration underground in all the boreholes as a function of depth will be supplied later.

Effective Soil Sampling Volume of ^{232}Th by Gamma Logging

The volume of soil sampled by the gamma probe downhole can also be approximated as follows: The average energy of gamma rays emitted by ^{232}Th in equilibrium with its daughters is 0.9 MeV, and the attenuation of gamma rays in soil can be adequately represented by the attenuation in aluminum. Using the mass attenuation coefficient in aluminum of 0.0301 cm^2/g, and a soil density of 1.6 g/cm^3 gives a mean free path of 21 cm.

$$1/(0.0301 \text{ cm}^2/\text{g} \times 1.6 \text{ g/cm}^3) = 20.8 \text{ cm}$$

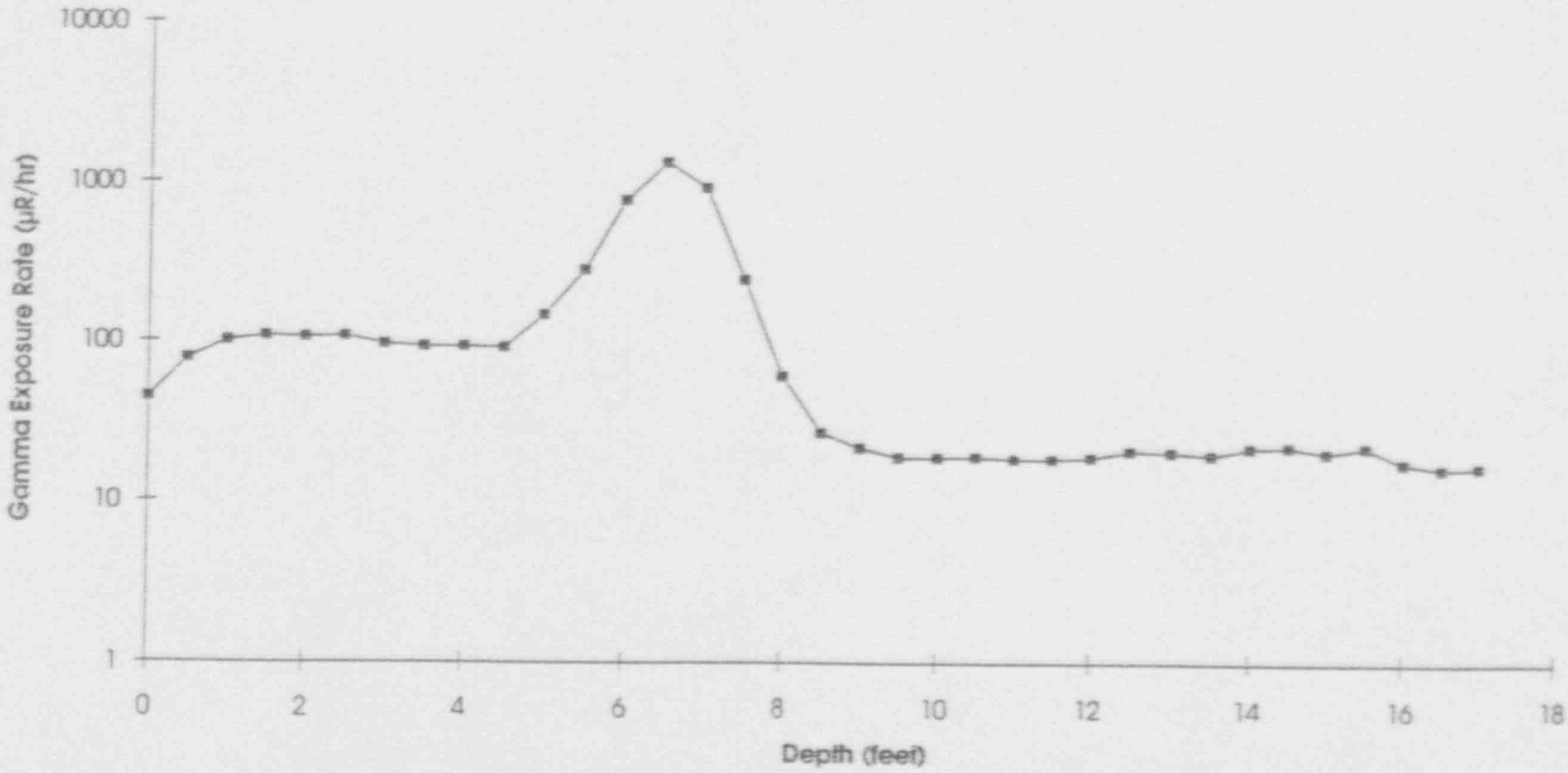
Figure 6:
Depth Profile of Gamma Exposure Rate in BH#27 and BH#28
(Molycorp, Washington Pa plant site)



14

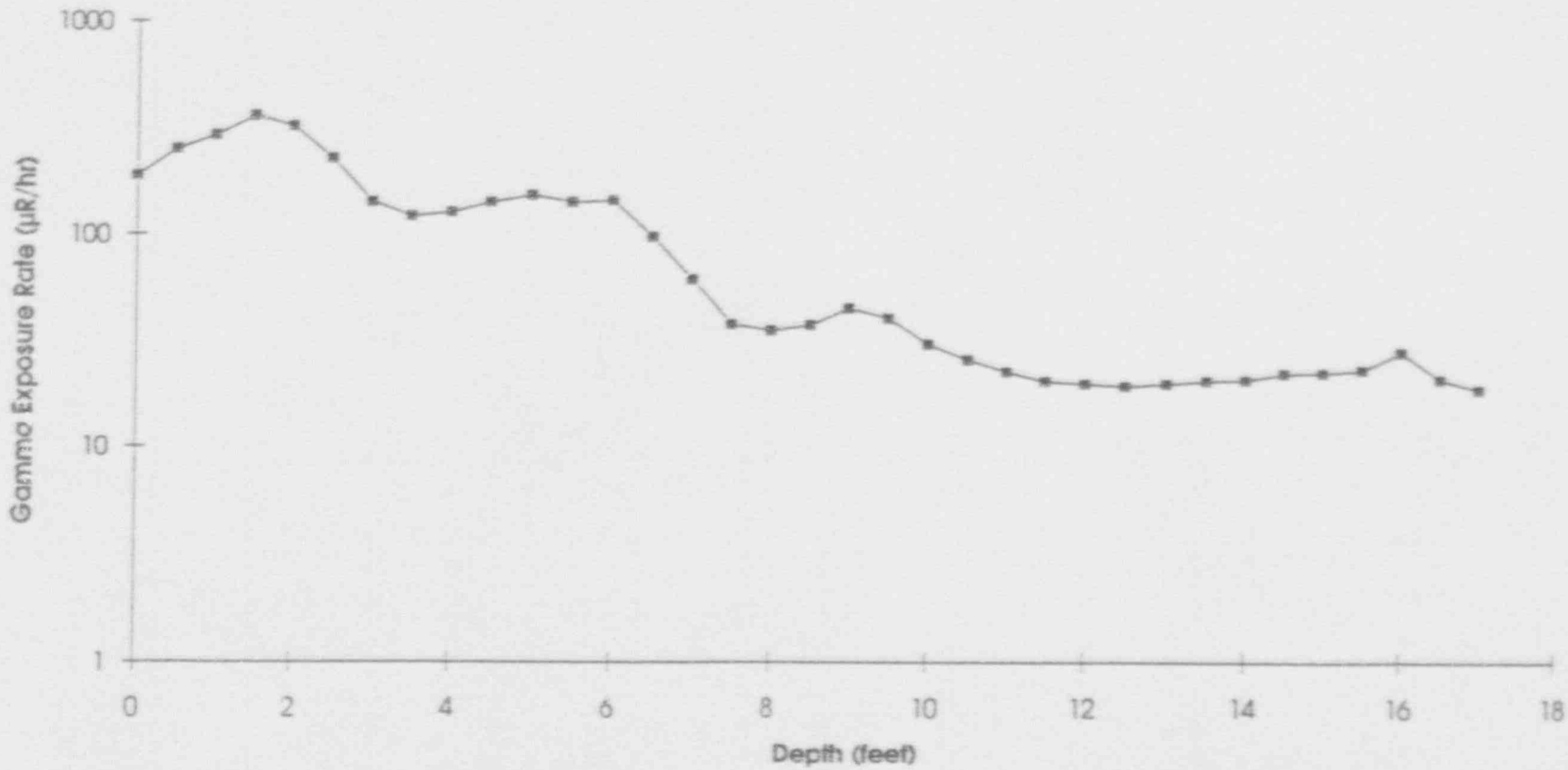
RSA, 12/29/92

Figure 7
Depth Profile of Gamma Exposure Rate in BH#29
(Molycorp, Washington Pa plant site)



RSA, 12/23/92

Figure 8
Depth Profile of Gamma Exposure Rate in BH#32
(Molycorp, Washington Pa plant site)



RSA, 12/23/92

After 2 mean free paths in soil 13.5% of the primary flux is uncollided and after 3 mean free paths 5%. Therefore a significant part of the exposure comes from a sphere with a radius between 2 and 3 mean free paths. To illustrate we take 2.5 mean free paths or 52 cm as the radius within which most of the exposure at any point at the center of a sphere of material originates. The spherical mass of soil effectively sampled by the gamma probe is accordingly about (0.94) 1 metric ton.

Radiochemical Analysis of Slag and Core Samples

This section presents results of radiochemical and alpha spectrometric measurements of the thorium isotopes in one sample of slag and in borehole samples. In addition the uranium concentration was also measured by alpha spectrometry in one aliquot of the same sample of slag. We believe but have not yet been able to confirm that the sample of slag which RSA has analyzed and was furnished by Molycorp came from the slag pile, which according to the report of Applied Health Physics, May 22, 1975 has an average specific activity of 1250 pCi/g of ^{232}Th. (See Table 1.)

The radiochemical methods used are those reported by Singh and Wrenn (1988) using ^{229}Th as a tracer (Wrenn, et al 1978). We had a great deal of difficulty in obtaining complete dissolution of this slag. This was finally made possible by heating finely ground samples in a mixture of concentrated nitric and hydrofluoric acid. Thus the analysis of soil samples in which small particles of slag may have been admixed is particularly difficult and time consuming, more so than we had originally anticipated. This also suggests that the material is not readily leachable into the environment.

The thorium was extracted from the samples, electrodeposited on platinum disks, and counted in EG&G alpha spectrometers with solid state surface barrier detectors. All spectra were stored in a 386 computer memory and will be kept on file until the termination of this program of site evaluation and decontamination. Hard copies of the spectral data have also been made and filed.

RSA also maintains a careful program to evaluate the analytical results of any given sample. In alpha spectrometry there are many potential problems to which attention must be carefully paid. For example: If mass on the planchette exceeds 100 μg a broadening of the spectrum occurs and it is difficult to

completely resolve alpha peaks from each other. In the case of the samples here, we have used ^{229}Th as a tracer (Wrenn, 1978). ^{229}Th interferes slightly in the ^{230}Th region and therefore the non-Poisson error in the results for ^{230}Th are potentially larger than for ^{228}Th and ^{232}Th.

The radiochemical results from 11 of the samples collected underground in boreholes 29 and 32 from the sample of slag are shown in Tables 2 and 3. Figure 9 shows the alpha spectrum of the slag to which no tracer was added, and the results for this sample are shown in Table 3 as slag aliquot 4. Taking ^{232}Th as 100%, based strictly on the count rates in the regions of interest, the relative ^{228}Th content was 95.8 ± 2.5% and the relative ^{230}Th content of slag was 6.5 ± 0.5%. The absolute activity can only be established using tracer. Two measurements of aliquots of the same sample in which the results differed by approximately 20% are shown as thorium slag aliquot 1 (1018 pCi/g) and aliquot 2 (1224 pCi/g). The difference reflects variations in sample homogeneity, analytical variability, and non-Poisson error. Two analyses were made of aliquots of the same sample of slag for uranium isotopes using alpha spectrometry, once using a ^{232}U tracer and once with a ^{233}U tracer. The two results showing about 54 and 68 pCi/g of ^{238}U are reasonably consistent. This suggests that the ^{238}U is in equilibrium with the ^{230}Th. The ratio of $^{230}Th/^{232}Th$ determined by alpha spectrometry of the slag sample with tracer added is higher than that obtained when the tracer was not added. This is probably due to the inability to obtain an exact correction for the ^{229}Th tracer contribution to the ^{230}Th energy region, which varies with the mass deposited on the planchette.

The radiochemical results measured in thorium slag, around 1000-1200 pCi/g, are consistent with the Applied Health Physics Report evaluation of the average concentration of ^{232}Th in the slag pile, 1250 pCi/g ^{232}Th. (See Table 1.)

Table 2 also shows the results from alpha analyses of the core samples collected from boreholes 29 and 32. Complete results from eleven samples are presented, two are partially complete results from two samples, showing ^{232}Th only. Three samples are being processed and are not yet complete. The results for ^{230}Th are subject to revision.

Alpha Spectrum of Thorium

For The Molycorp Slag Sample From Washington, Pa.

(Without ^{229}Th Tracer)

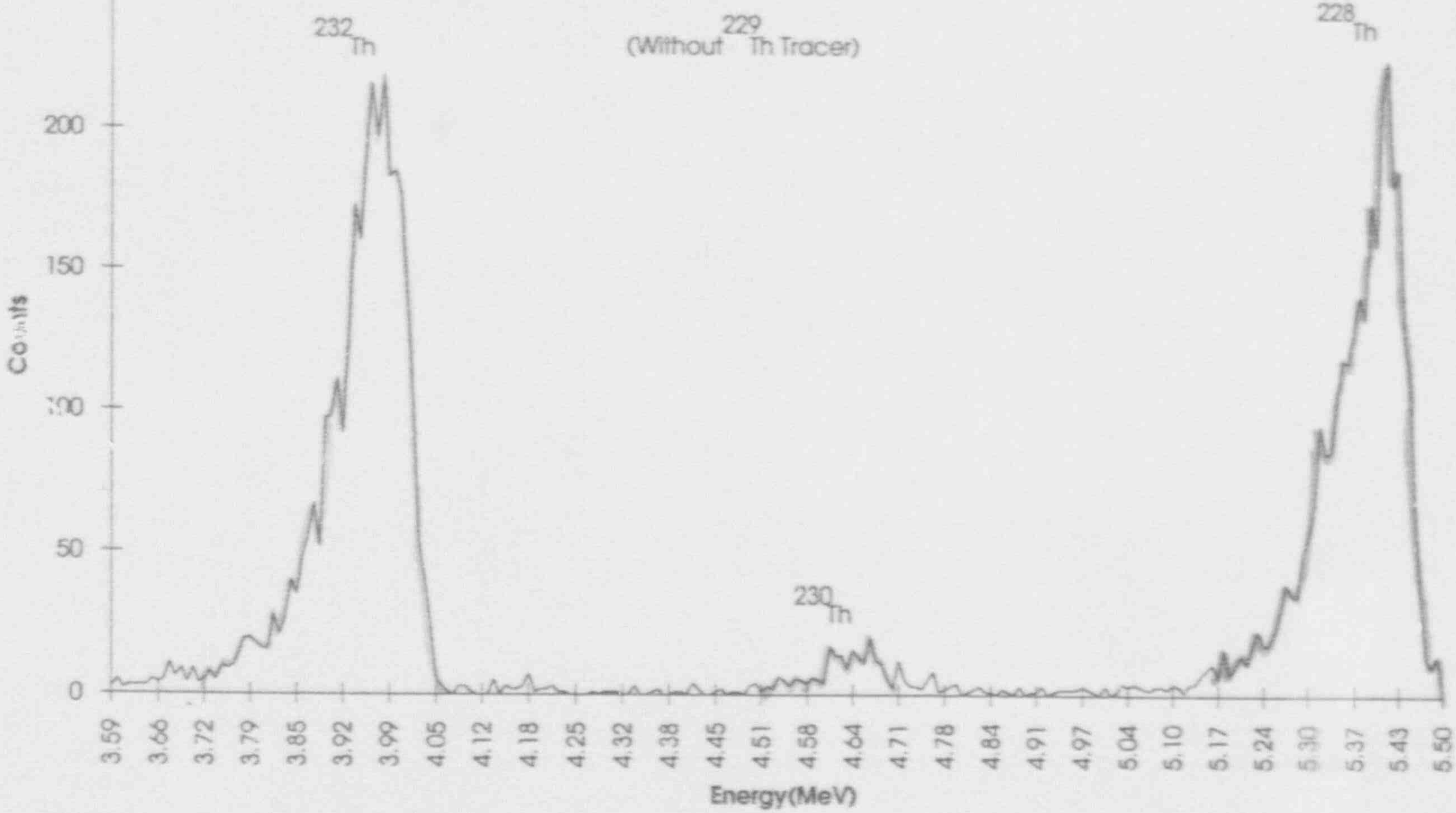


Figure 9

RSA 12/21/1992

Table 2: Alpha Spectrometric Analysis of Core Samples Taken from BH#29 and BH#32 with Corresponding Gamma Probe Measurements

Summary December 18, 1990

			NaI Probe		Activity pCi/g				
Sample #	Borehole	Depth (ft.)	cpm	µR/hr	TH-228	TH-230	TH-232	Yield	Accepted/Rejected
B29S3	B29	3	7600	95.8	5.95 ± 0.183	2.1 ± 0.078	6.16 ± 0.18	45%	Accepted 10/29/92
B29S4	B29	4.5	7202	90.7	44.02 ± 1.001	10.97 ± 0.419	45.08 ± 0.998	47%	Accepted 10/29/92
B29S9	B29	12	1501	18.9	1.32 ± 0.088	1.19 ± 0.086	1.13 ± 0.095	37%	Accepted 10/29/92
B29S10	B29	13.5	1562	19.7	3.1 ± 0.17	1.78 ± 0.214	3.05 ± 0.172	46%	Accepted 11/16/92
B29S11	B29	15	1617	20.4	0.98 ± 0.059	0.96 ± 0.068	0.86 ± 0.064	57%	Accepted 11/16/92
B29S12	B29	16.5	1293	16.3	1.89 ± 0.14	0.93 ± 0.258	1.26 ± 0.171	20%	Accepted 11/24/92
B32S3	B32	3	11233	141.5	5.89 ± 0.233	17.4 ± 0.28	5.3 ± 0.246	70%	Accepted 10/29/92
B32S4	B32	4.5	11268	142.0	30.12 ± 0.647	15.16 ± 0.363	28.27 ± 0.668	40%	Accepted 10/29/92
B32S5	B32	6	11458	144.4	N/A N/A	N/A N/A	1.36 ± 0.195	14%	Accepted 12/18/92
B32S8	B32	10.5	2047	25.8	N/A N/A	N/A N/A	1.97 ± 0.24	25%	Accepted 12/18/92
B32S9	B32	12	1574	19.8	2.56 ± 0.197	1.95 ± 0.478	2.17 ± 0.214	19%	Accepted 10/29/92
B32S10	B32	13.5	1631	20.6	6 ± 0.268	4.41 ± 0.276	5.33 ± 0.284	41%	Accepted 10/29/92
B32S11	B32	15	1773	22.3	2.18 ± 0.124	1.71 ± 0.209	2.18 ± 0.124	92%	Accepted 10/29/92

± represents one standard deviation, Poisson error, counting statistics only.

N/A: unacceptable spectral resolution to analyze for Th-228 and Th-230.

RSA, 12/29/92

Table 3: Alpha Spectrometric Analysis of Aliquots of Th Bearing Slag

Summary December 18, 1990

	Activity pCi/g				
Sample #	TH-228	TH-230	TH-232	Yield	Accepted/Rejected
Thorium Slag, aliquot 1	1018.19 ± 6.505	96.34 ± 2.117	1019.26 ± 6.501	45%	Accepted 10/29/92
Thorium Slag, aliquot 2	1223.65 ± 18.757	96.11 ± 6.377	1234.77 ± 18.672	5%	Accepted 12/18/92
Thorium Slag, aliquot 4	95.8 ± 2.50%	6.5 ± 0.50%	100%	NA	Accepted 12/8/92

	U-238 Activity	U-234 Activity	Recovery
Thorium Slag, aliquot 5	55.3 ± 0.031	53.8 ± 0.948	19%
Thorium Slag, aliquot 6	68.3	68.3	12%

1 Data acquired on 30 September 1992; analyzed with tracer.

2 Data acquired on 23 November 1992; analyzed with tracer.

4 Data acquired on 03 December 1992; analyzed without tracer.

The numbers given are ratios of the counts with respect to Th-232

5 Analyzed using U-232 as a tracer.

6 Analyzed for U-238 using U-233 as a tracer, U-234 assumed to be in equilibrium.

RSA. 1/4/93

These samples all show equilibrium between ^{228}Th and ^{232}Th. The lowest result obtained shows approximately 1 pCi/g of all three thorium isotopes, and this most likely represents a background level, being consistent with typical background concentrations in soil found elsewhere (NCRP-50, 1976).

Sample B32S3 is unusual in that it shows more ^{230}Th than ^{232}Th and possibly derives from a material other than the FeCb slag based on all analyses of FeCb slag we have seen to date (RSA 1992, AHP 1975, ORAU, 1985). Based upon results from gamma spectrometric analysis from 55 samples of surface soil taken from the site (reported by ORAU 1985) which showed elevated concentrations of ^{232}Th above background (range 10 to 1380 pCi/g) the ratio of $^{226}Ra/^{232}Th$ was 0.22, somewhat higher than our observed ratio of $^{230}Th/^{232}Th$ in one sample of slag. BH 32 was also taken from the area exhibiting the highest background in the north plant area. Further underground core samples may be required to establish the extent of this material and its origin.

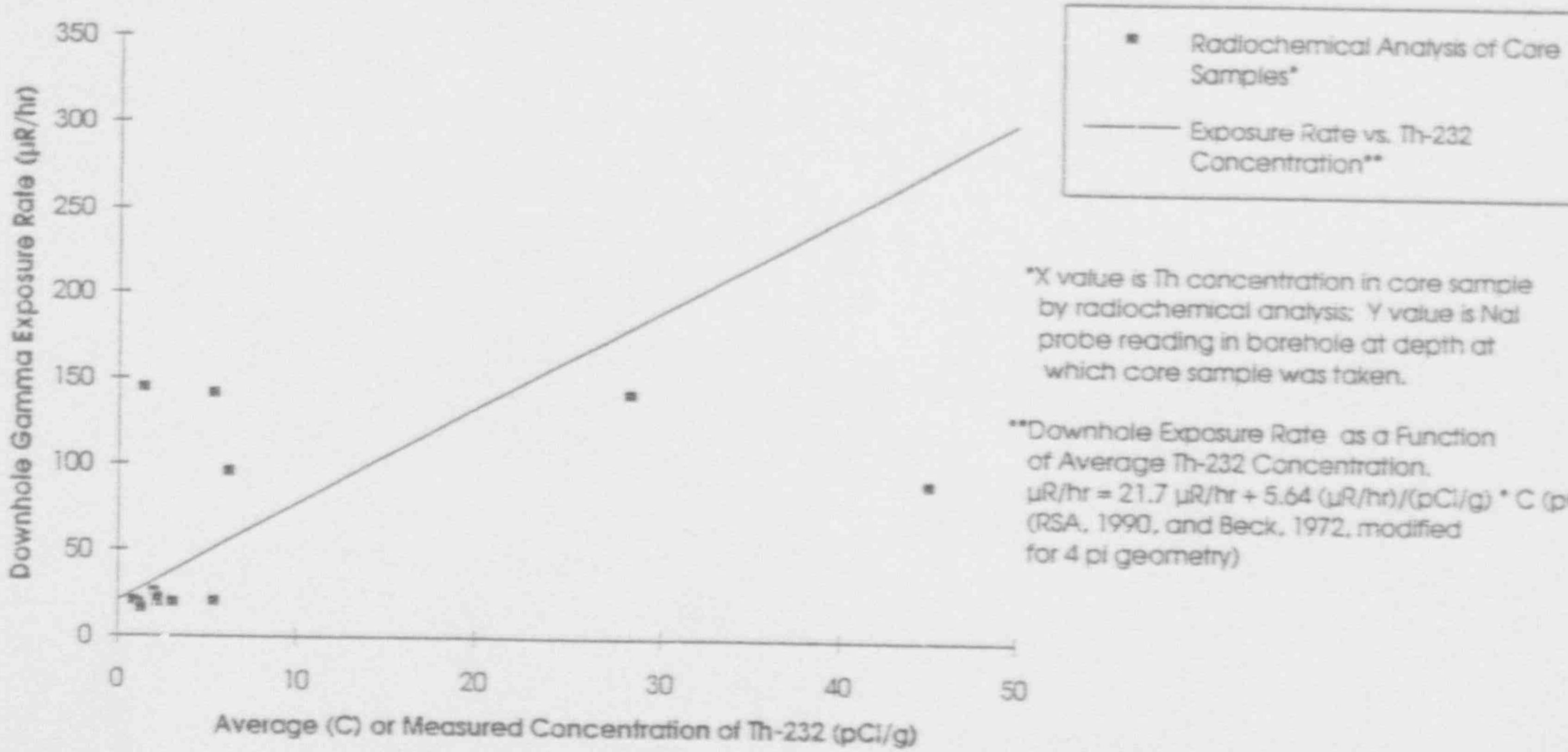
Figure 10 is a scatter plot of exposure rate (μR/hr) measured downhole (at the depth where the soil sample was taken) as a function of ^{232}Th concentration (pCi/g, measured by alpha spectrometry) of the soil sample. The line on the graph in Figure 10 is the calibration curve for the NaI probe (expressed in $\mu R \cdot hr^{-1}/pCi \cdot g^{-1}$) derived from the work by Beck and reported in the RSA 1990 report. Several of the points show less thorium than the response curve would predict and several show more. The variation is, in fact, quite large, but not surprising given the fact that the soil volume sampled was very small compared to the volume of the region sampled by the NaI gamma probe.

For example if material with a specific activity of 1250 pCi/g were mixed with background material at 1 pCi/g a very small piece or portion of the higher specific activity material could influence the average concentration measured in the alpha spectrometric analysis quite dramatically, depending on whether or not it was included in the core sample and aliquot analyzed.

The advantage of the **down hole gamma measurements** is that they **integrate the results over a larger volume of soil than a single soil sample; the results are also directly interpretable in terms of ability to produce external exposure.** Therefore RSA sees no reason to believe that the calibration factors

Figure 10

Radiochemical Analysis of Th-232 Concentration in Core Samples from BH#29 and BH#32 vs Downhole Measurements of Gamma Exposure Rate; and, Average Th-232 Concentration in Soil Calibrated against Downhole Exposure Rate.



*X value is Th concentration in core sample by radiochemical analysis; Y value is NaI probe reading in borehole at depth at which core sample was taken.

**Downhole Exposure Rate as a Function of Average Th-232 Concentration.
µR/hr = 21.7 µR/hr + 5.64 (µR/hr)/(pCi/g) * C (pCi/g)
(RSA, 1990, and Beck, 1972, modified for 4 pi geometry)

RSA, 12/23/92

developed in the RSA 1990 Report are not valid. However one needs to understand that they represent averages over much larger volumes of soil than would be taken in any reasonable size single soil or sediment sample. Even the volumes over which the downhole external gamma measurements integrate, are small compared to the volumes of material which would contribute significantly to any future exposures.

RELATIONSHIP OF ABOVE GROUND GAMMA EXPOSURE RATE TO CONCENTRATION OF ^{232}TH IN SURFACE SOILS:

The radius of material distributed in surface soil which contributes to external exposure in air is much larger than that underground, primarily because the mean free paths of gamma rays are much longer in air than in soil. Beck (personal communication citing Artuso 1981, 1992)) indicates that 95% of the exposure rate coming from a distributed natural source is due to radioactivity within a radius of 10 meters. To a dep 'ı of 20 cm a right circular cylinder of soil with a density of 1.6 g/cc would weigh about 100 metric tons. Thus gamma ray measurements in air at 1 meter above the surface effectively sample large volumes of soil and average the resulting potential for exposure. In the Site Characterization Plan and the RSA survey in 1990, a gamma grid of 20 feet spacing (about 6.5 meters) was proposed or used. The exposure rate at each measurement point, due to a disc source with a radius of 6.5 meters results from the integrated average activity of ^{232}Th in soil to a depth of 20 cm which has a mass of about 40 metric tons. To properly assay the mean activity of ^{232}Th in this volume of material by soil sampling followed by laboratory analyses would require a prohibitive number of samples and analyses. Therefore external gamma survey measurements are an accurate and effective means of assessing average soil concentration of ^{232}Th, with an exposure rate at 1 meter above a uniformly contaminated half-space of 2.82 $\mu R \cdot h^{-1}/pCi \cdot g^{-1}$.

REPLY TO THE NRC'S GENERAL COMMENTS, DATED OCT. 29, 1992 :

Based on the comments in this NRC communication we believe the NRC has not properly characterized the calibration procedure used by RSA in the 1990 report on underground radiation levels at the Molycorp Washington, Pennsylvania site. The preceding report, has the intent of making those procedures more understandable and clearer to the Staff. The preceding sections should be read before reading these replies to the NRC comments.

The measurements made down boreholes were calibrated to measure exposure rate, using a sodium iodide probe which was cross calibrated against a pressurized ionization chamber, for which the calibration is traceable to NIST. Thus the exposure rate (μR/hr) in each borehole is known as a function of depth. The results in several boreholes are plotted in the accompanying report.

Since the borehole geometry is 4 π, the exposure rate in 2 π geometry (i.e. if the overburden were removed down to the depth where the measurement was made) is very close to one half that in the 4 π geometry. In short the exposure rate measurements underground are relatable to the exposure rate which would be established if the material were exposed.

The gamma measurements produce an average over a much larger volume of soil than the volume of soil samples which were removed from the borehole; about 90% of the exposure rate in planar geometry originates above a depth of about 20 cm (derived from Beck, 1972) and the mean free path in soil of gamma rays from the ^{232}Th series is about 21 cm. Thus the exposure rate measured in a borehole at a given depth can be thought of as averages from a spherical source which has a mass about 1/2 to 1 metric ton with a diameter of 2.5 to 3 feet (see page 12).

Soil samples, on the other hand, are usually much smaller samples. In the laboratory, for alpha spectrometric analyses, between 0.1 and 1 gram are analyzed, usually about 0.1 gram. The largest core taken in the field was 2 inches in diameter. Even if all the material in a core sample six inches long were analyzed, the volume would represent less than 1% of the volume "sampled" by the gamma measurement. The in situ gamma measurement gives a much more

representative measure of the average ^{232}Th concentration than could any reasonably sized core sample. Moreover 0.1 gram of sample analyzed represents only 0.02% of the mass of the core sample taken. Since most samples analyzed were about 0.1 gram, the soil aliquot analyzed represents less than 1/1,000,000 the mass of soil effectively sampled by the gamma measurements.

It is therefore not reasonable to expect that analyses of the core samples should confirm the external gamma calibration. Also the statement by the NRC staff that "The resulting high degree of uncertainty in the derived ^{232}Th would propagate into the resulting doses to individuals calculated for times during decontamination and decommissioning and following unrestricted release" is the opposite of what is expected. Averages inferred from gamma measurements would have much less uncertainty and variability than would results from soil samples. Thus, gamma measurements are preferable over soil samples in order to minimize the uncertainties to asses the doses expected from radioactivity which is not uniformly distributed in soil.

The NRC also states that, "Precise determination of the extent and quantity of residual activity is a prerequisite to assessing doses to be used as basis for NRC decommissioning decisions". Although RSA agrees that the extent and quantity of contamination should be established, we do not believe it would be reasonable to require that the scale of variation to be investigated be on the order of inches or feet, since both external and internal exposures which might be delivered would be determined by radioactivity concentrations averaged over much greater distances.

Since the slag pile is composed of material which has a mean specific activity of 1250 pCi/g ^{232}Th, and since some of this material is still distributed in small pieces on site, we believe that averages which are more closely related to expected radiation doses rather than maximum specific activities which can be found in small samples, should be used for both dose estimation and compliance determinations.

We believe that it is appropriate that Molycorp use the quantitative determination of average ^{232}Th concentration underground determined with in situ gamma

measurements as a basis to establish cleanup criteria, as a basis for the dose assessment, and to demonstrate compliance.

Also referring to the downhole measurements, the NRC stated that, "additional information would be required to demonstrate the accuracy of the calculated concentrations. This demonstration should be based on direct measurement of soil concentrations via sample analysis, portable survey meter, or some combination of the methods." We point our that the measurement of count rate underground in a NaI crystal with a scaler to record counts over preset time intervals is equivalent to a survey meter. Therefore the calibration RSA performed is consistent with this recommendation of the NRC.

Molycorp did not agree to a cleanup level of 5 pCi/g in the July 8, 1992 meeting with the NRC. In fact it was specifically emphasized in the technical briefing that Molycorp intends to consider a modified Option 2 (25 pCi/g ^{232}Th) for subsurface levels. It was stated that surface radiation levels above background would not exceed the equivalent of that produced by an average of 5 pCi/g ^{232}Th in equilibrium, or a total of 14.1 μR/hr above background measured 1 meter above the surface averaged over a 10 meter grid spacing. The Molycorp proposals were identified in the table entitled "Proposed Actions" which was given to the NRC on July 8th during the briefing by Molycorp, and this table was retransmitted by the NRC to Molycorp as an enclosure to their memorandum dated July 31, 1992.

REPLY TO THE NRC'S SPECIFIC COMMENTS, DATED OCT. 29, 1922:

1. The results of 11 of the 16 core soil samples taken underground are given in the preceding report (RSA 12/30/92). The delay in its availability was occasioned by the need to develop a new technique to completely dissolve the refractory particles of slag. This was accomplished by heating pulverized samples in combined, heated concentrated nitric and hydrofluoric acid.

2. The background count rate underground established in virgin soil was 1726 cpm and is discussed in detail in the preceding report. The 2000 cpm figure plotted in the RSA 1990 Report was a rounded number used for the purposes of the RSA 1990 Report. We agree that the results in borehole #28 do not represent

natural soil background nor were they intended to. They do, however, over the first six feet of depth, represent background in slag which was produced from other processes than the ones involving FeCb ore or concentrate which was licensed by the NRC. A plot of exposure rate vs. depth in FeMo slag is given in Figure 6. Thus it may well be an appropriate background above which to measure compliance.

3. The NRC staff asks, "Why would cosmic rays not produce a response in a NaI scintillation detector as they would in an ion chamber?" Cosmic rays are known to produce less of a response in NaI count rate instruments than do gamma rays. The reason can be illustrated as follows. A fast meson (mesons comprise most of the cosmic ray flux at sea level) passing through an inch of NaI would deposit about 20 MeV of energy, but would be recorded by the PM tube and electronic scaler as one event. A 0.2 MeV gamma ray would likewise be recorded as one event. Thus MeV for MeV deposited in the crystal, the associated count rate meter would respond 100 times more strongly to the gamma rays than the cosmic rays. A pressurized ion chamber on the other hand integrates charge, and hence ion pairs produced in the sensitive volume, and therefore responds to cosmic rays almost equally with gamma rays per unit of deposited energy and therefore also with respect to exposure and dose. A useful reference for this subject area is NCRP-50.

4. The response to the request for identification of the water wells and their relationship to the ORAU report will be provided by Molycorp staff as RSA was not involved in the location or construction of these wells. RSA has not yet made any study of radioactivity in well water samples. However some information is available from Molycorp. This information will be furnished in the report of the results of the Site Characterization Study and possibly also during pond closure.

5. The contention of the NRC that the value 0.01% thorium would be used as a criteria for excavation of radioactive contaminated material is the NRC's own conclusion. It was not our intent in the RSA 1990 Report to suggest that 0.01% be used as a level for decontamination. The NRC and Molycorp have subsequently agreed on a process which involves extensive site characterization, a dosimetric analysis and development of a site decommissioning plan. It would accordingly be premature now to select levels of activity to which the

decommissioning will be accomplished. The underground radiation exposure rate measurements will be used to evaluate the average concentration of ^{232}Th and also in the dosimetric evaluations, including those involving assumed future scenarios of exposure.

6. In this comment, the reviewer uses the number 9.33 μR/hr, taken from page 33, as the natural background for the site. The text on page 33 does not claim that 9.33 μR/hr, taken at location PIC18, is an adequate measure of natural background for the site. This single PIC reading, taken on Molycorp property immediately adjacent to the site, should not be interpreted as establishing background. RSA did not include a program to measure the natural gamma background in the vicinity of the site as part of the 1990 study. The text on page 33 simply points out that the 9.33 μR/hr reading does not result from a gamma spectrum representative of thorium because it is due to naturally occurring emitters, and is only partly due to thorium.

The statement that 31 μR/hr is roughly twice background is based on a natural background exposure rate of 11 μR/hr reported in the ORAU 1985 report on the site. RSA assumed that ORAU was reporting gamma background (since the readings were taken with NaI instruments, which don't respond appreciably to cosmic) so for the executive summary we added 4 μR/hr cosmic radiation to the natural gamma to obtain 15 μR/hr. Twice 15 is 30 μR/hr. Therefore, the conclusion as we stated it in the report, based on our understanding of the natural radiation background at the time, was correct. More recent work by RSA at the Washington Pennsylvania site indicates that the natural background for the area may be less than that reported by ORAU. Appendix A gives the results of 12 off-site PIC measurements made in the summer of 1992, which averaged 10.5 μR/hr gamma's plus cosmic. Molycorp will include a rigorous study of the natural radiation background for the plant site as part of the Site Characterization Report.

As a matter of definition, RSA and Molycorp request the NRC to make a distinction between natural external background and natural gamma background, since the two are not the same. Natural background, as measured by the PIC, includes both gamma and cosmic radiation. Twice external natural background, therefore, is twice the measured exposure rate with a pressurized ionization

chamber. For external radiation when we use the term "twice natural background," we mean double gamma plus cosmic.

The reviewer also pointed out that in examining Site Map III in the RSA 1990 Report, it appeared to him or her that readings exceeded the natural background by a factor of two or more over much of the site. The two reasons why these conclusions are incorrect follow:

(a) The numbers reported on the map are based on a calibration factor that was derived by measurements made over a distributed thorium source. The calibration is accurate when used over soil contaminated with sufficient amounts of thorium that the radiation being measured comes predominately from thorium and its daughters. When the measurements are made over soil that is not contaminated above normal background with thorium, the spectrum is only partly due to thorium, and the gamma ray spectrum emitted from the soil is softer (i.e., has a lower energy frequency distribution) than that for Th. Using the calibration factor established for thorium contaminated areas for measurements taken over uncontaminated soil has the effect of overestimating the gamma background. The calibration factor used for the NaI survey meter in the 1990 report (0.73 true/indicated) is valid for exposure rates that exceed 20 μR/hr, but at the lower exposure rates and softer gamma spectra, characteristic of natural background, the calibration factor is closer to 0.6. Offsite, in clearly natural background areas, the true indicated gamma exposure ratio is approximately 0.55. (See Appendix A.) For the purposes of the 1990 report, RSA considered this overestimation to be a second order effect, and therefore we did not include a correction for it. In the Site Characterization Report, we will make a correction for this factor.

(b) Much of the Molycorp site is covered with fill. The fill includes ferro-molybdenum slag and other material from decades of industrial activity at the site. Except for the FeCb slag buried in portions of the site, none of the fill is licensed radioactive material. However, because the Washington Pennsylvania area has an unusually low natural external gamma radiation background (generally under 8 μR/hr), this non-licensed, non-radioactive fill will tend to raise the background just by dint of the fact that it was brought into the area from somewhere else. Since the natural gamma background in

Washington Pennsylvania is naturally low, material brought in from outside will probably tend to raise the natural background, rather than lower it.

Based on the newly available data given in Appendix A, it would be correct to say that the natural gamma background is about 8 μR/hr, and that 16 μR/hr is twice gamma background. 22.8 μR/hr [= 2*(8 μR/hr gamma + 3.4 μR/hr cosmic)] is double the external natural background. The NRC staff suggestion that "residual contamination levels appear to contribute significantly to the surface exposure rates over a large portion of the study area," is incorrect. There are 422 readings reported on Site Map III in the 1990 report. Of those readings, only 92, or 22%, are above 22.8 μR/hr. Of those 92 elevated readings, 34 are located in a limited area adjacent to the north fence line. For the readings taken outside of this limited area along the north fence line, only 14% are elevated above twice natural background.

7. We agree with the comments of the NRC in the first paragraph and will attempt to construct cross sectional maps of underground contamination when a greater density of borehole information becomes available.

8. The 25 μR/hr level alluded to on the July 8, 1992 meeting is not inconsistent with the 30 μR/hr cited in the RSA 1990 report for total external exposure. In fact with 30 μR/hr total external exposure rate the gamma contribution would be approximately 26 μR/hr.

Based on measurements of background off site made since the July 8th meeting our calculations suggest that 22 or 23 μR/hr of gamma might be a more appropriate level as being equivalent to the exposure rate from gamma background plus an average 5 pCi/g ^{232}Th in surface soil. We will however await the results of a more extensive background survey during the site characterization study, before deriving this gamma exposure rate equivalent to 5 pCi/g ^{232}Th above background.

9. A reply to these comments will be made by Molycorp staff. However we believe that a number of pilot studies such as those suggested by the NRC will be both useful and essential to effectively plan for decontaminating the site. In its review of the report the NRC staff indicated that it was not convinced that the

downhole calibration was a valid one. RSA points out that use of external gamma to assess average concentration of thorium in soil is a technique recognized in both the scientific literature and the NCRP publications. Moreover gamma measurements of this type average over reasonably large variations, and are directly related to the potential for human exposure, being direct radiation measurements. Use of gamma measurement to infer average ^{232}Th concentrations should produce less variability in estimation of doses than should soil sampling. In this report we have laid out the rationale and additional information for accepting the calibration factors derived in the RSA 1990 Report and present additional information on the isotopic composition of thorium in the slag pile and additional information on thorium isotopes found underground in boreholes 29 and 32.

Bibliography

Applied Health Physics Report, dated May 22, 1975, Summary of Actions Taken During 1972-1974 to Comply With Requirements of the Nuclear Regulatory Commission.

Artuso, J.F. Conversion of Pulse Height Spectra to Exposure Rates for Circular Sources, EGG 1183-2442, Santa Barbara, December 1981.

Beck, H.L. The Physics of Environmental Gamma Radiation Fields, Proceedings of the Second International Symposium on the Natural Radiation Environment, Houston, Texas, 1972.

Hubbell, J.H. Power Series Buildup Factor Formulation. Application to Rectangular and Off Axis Disc Source Problems, Journal of Research of the National Bureau of Standards, C. Engineering and Instrumentation, Vol. 67C, No. 4, Oct.-Dec. 1963.

ICRP Publication 38, Radionuclide Transformations, Energy and Intensity of Emissions, ICRP, Pergamon Press, Vol. 11-13, 1983.

NCRP-50, Environmental Radiation Measurements, NCRP Publication, 1976.

NCRP-94, Exposure of the Population in the U.S. and Canada from Natural Background Radiation, NCRP Publications, 1987.

Oak Ridge Associated Universities Report dated August 12, 1985, Radiological Survey of Molybdenum Corporation of America, Washington, Pennsylvania, 1985

Radiological Health Handbook, U.S. Department, HEW, PHS, Rockville, MD, 1970, pp. 110, 137 and 145.

Spiers, Radioisotopes in the Human Body, Academic Press, New York and London, 1968, pp. 19 and 84.

Singh, N.P. and Wrenn, M.E., Determinations of Actinides in Biological and Environmental Samples, The Science of the Total Environment, 70 ,1988 pp. 187-203

Wrenn, M.E., Singh, N.P., Ibrahim, S.A., and Cohen, N., Thorium-229 as an isotopic tracer for the radiochemical determination of thorium isotopes in biological samples, Anal. Chem. 50: 1712 (1978).

Appendix A: Off-site PIC Readings, Molycorp, Washington Pa Plant

Pressurized Ionization Chamber								Scintillometer
PIC Location Number	date	time	µR	minutes	seconds	Total (µR/hr)	Gamma (PIC - cosmic)	Ludlum Model 19 (RSA)
#10	8/24/92	4:15 PM	2	11	54	10.08	6.68	12.60
#11	8/25/92	12:09 PM	2	11	46	10.20	6.80	12.62
#12	8/25/92	1:00 PM	2	12	10	9.86	6.46	11.75
#13	8/25/92	2:15 PM	2	11	11	10.73	7.33	13.00
#14	8/25/92	3:15 PM	2	10	17	11.67	8.27	14.55
#15	8/25/92	4:15 PM	2	10	53	11.03	7.63	12.80
#16	8/25/92	4:45 PM	3	17	29	10.30	6.90	12.18
#17	8/25/92	5:45 PM	2	11	57	10.04	6.64	12.25
#18	8/25/92	6:30 PM	2	11	32	10.40	7.00	13.20
#19	8/26/92	10:00 AM	2	11	6	10.81	7.41	13.13
#20	8/26/92	11:30 AM	2	12	13	9.82	6.42	11.83
#21	8/26/92	12:00 PM	2	10	45	11.16	7.76	14.28
					Average	10.51	7.11	12.85
					Standard Deviation	0.574	0.574	0.870

Appendix B

Calibration of NaI Probe for Exposure Rate and Calculation of Average ^{232}Th Content

$$E=(P-B)k_1$$

$$C=\frac{E}{A\cdot k_2\cdot R}$$

$E=$ exposure rate measured downhole in excess of background ($\mu R/hr$)

$C=$ average concentration of ^{232}Th in soil (pCi/g)

$P=$ NaI probe measured count rate (cpm)

$B=$ background count rate (cpm)

$A=0.95=$ compensation factor included to compensate for attenuation of gamma rays due to the presence of water in the soil

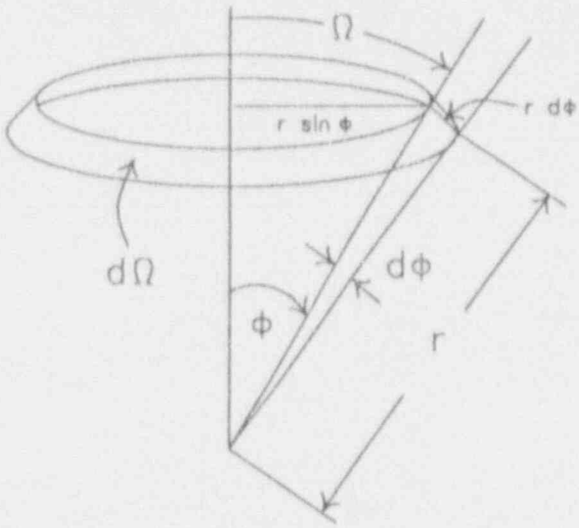
$R=$ Fractional reduction in NaI probe response due to geometry

$k_1=12.6\ \mu R\cdot hr^{-1}/1000$ cpm $=$ Calibration factor established in field with ^{232}Th distributed source (probe inside 2" and 1" Schedule 40 PVC pipe)

$k_2=\ 5.64\ \mu R\cdot hr^{-1}/pCi\cdot g^{-1}=$ Beck's conversion factor adjusted for 4π geometry

Appendix C

Correction for Deviation from 4π Geometry Due to Opening at Top of Borehole

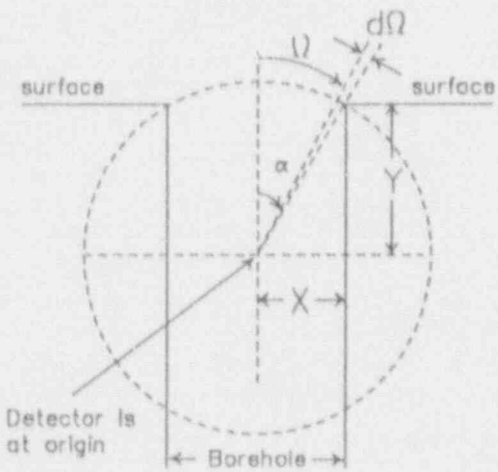


ϕ = azmuthal angle from spherical coordinates

Ω = solid angle

$d\Omega = area / r^2 = (2\pi r \sin\phi)(r d\phi) / r^2$

$= 2\pi \sin\phi \; d\phi$



α = the angle formed by the y axis and the line from the detector to the rim of the borehole

X = radius of borehole

Y = depth of detector in borehole

$$\Omega = \int_0^\alpha 2\pi \sin(\phi) d\phi = -2\pi\left[\cos(\phi)\right]_0^\alpha = 2\pi\left[1-\cos(\alpha)\right] = 2\pi\left[1 - Y/\sqrt{X^2+Y^2}\right]$$

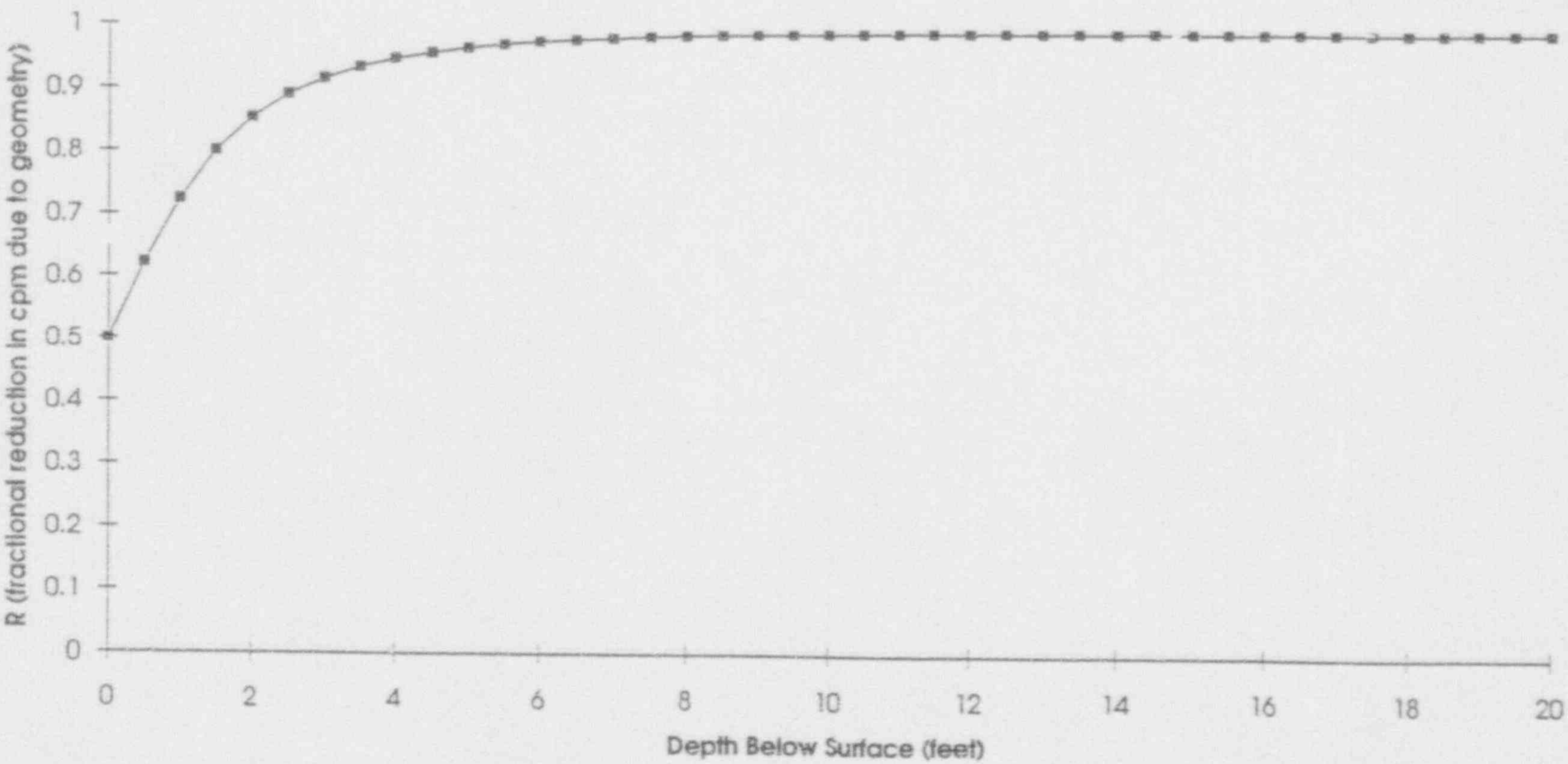
4π = solid angle encompassing entire sphere

R = fractional reduction in cpm due to absence of radiation source from solid angle Ω

$$R = \frac{4\pi - \Omega}{4\pi} = \frac{4\pi - 2\pi\left[1 - Y/\sqrt{X^2+Y^2}\right]}{4\pi} = \frac{1}{2}\left[1 + Y/\sqrt{X^2+Y^2}\right]$$

Appendix C (continued)

Plot of Fractional Reduction in NaI Count Rate Due to Geometry at Top of Hole, as a Function of Depth, for a 4 Foot Diameter Borehole



RSA, 12/30/92