APPENDIX A

ADDITIONAL GEOLOGICAL INFORMATION – GEOLOGY OF MARCELLUS SHALE AND OTHER PENNSYLVANIA SHALE FORMATIONS

Appendix A

Additional Geological Information – Geology of Marcellus Shale and Other Pennsylvania Shale Formations

The following information is provided by Dr. Robert C. Smith II, retired geologist with the Pennsylvania Geological Survey. Dr. Smith has extensive knowledge of Pennsylvania geology and has been a consultant for the DEP Bureau of Radiation Protection, Radon Division, helping with the understanding of Rn and geology. The information below is not part of the original scope of work for the TENORM study, but rather explanatory and supportive geology information as it relates to TENORM issues.

The Lockatong Formation is primarily recognized only in the high population density Bucks and Montgomery counties in the Newark Basin of southeastern Pennsylvania. Demographic concerns can be expected to inhibit natural gas development from the Lockatong in Pennsylvania and across the Delaware River in New Jersey. However, the Lockatong and its companion Stockton Formation remain serious concerns for indoor Rn and locally for radiums in groundwater.

In addition to the above, in northwestern Pennsylvania the Rhinestreet Member of the West Falls Formation associated with the Belpre volcanic ash, and the Pipe Creek Member of the Java Formation associated with the Center Hill volcanic ash bed, are black shales having natural gas potential. (The association of black shales with volcanic ash beds is considered favorable for natural gas recovery but beyond the scope of this report. It is mentioned here only because development might migrate away from areas where the black shales are thickest or even most organic-rich.) Therefore, they may yield TENORM issues; however, because they are recognized only at depth, they will not yield indoor Rn problems when undisturbed.

Two samples of black shale and one of a high-graded black shale sample containing major rounded phosphate nodules and barite veinlets were collected from the Shellsville Member of the Dauphin Formation of the Hamburg Sequence, Lebanon County. The shale is reported to be of Ordovician age. Because the area has undergone multiple tectonic events, whatever natural gas potential there once was is now minimal. Those data are useful for understanding and projecting indoor Rn hotspots, but are not discussed further herein because they are not expected to yield TENORM as drill cuttings or flowback fluids.

Antes Formation

The Antes Formation or, variously, Antes Member of the Reedsville Formation, or “Utica of drillers,” was deposited at the end of an approximately 100 million-year period of carbonate deposition on a continental shelf. Indeed, many marine black shales in Pennsylvania occur at the end of carbonate shelf deposition. The carbonate shelves were disrupted when a series of volcanic island arcs collided with the coast of the continent of Laurentia, of which Pennsylvania was an integral part. The island arcs themselves ranged in age from approximately 458 to 448 million years ago (Ma) and are believed to have struck Laurentia from the southeast to the northwest. They left volcanic ash bed debris across much of the eastern portion of the U.S. In Pennsylvania, the Upper Ordovician volcanic ash beds are best seen at the Union Furnace section, Huntingdon County (Smith, Way, and Berkheiser 1986), as whitish gray layers of volcanically derived smectite clays ranging in thickness from approximately 2 to 20 centimeters (cm). The fresh ash layers were probably about twice that thick when they first fell on the carbonate shelf, killing many carbonate-based organisms in the process.

The arc-continent impact itself occurred during the Taconic Orogeny, which Wise et al. 2007 have dated at 450 Ma. The Antes Formation black shales were then deposited over the drown carbonate shelf in restricted, reducing marine environments that permitted preservation of organic material. The volcanics in the newly elevated highlands may have provided some of the U as metastable volcanic glass devitrified over time. In the Ridge and Valley physiographic province (located to the east, southeast, and south of U.S. 220 in Cumberland Valley and its continuation to the northeast, Bald Eagle Valley and beyond), the Antes was thoroughly folded and thrust-faulted during the Alleghanian Orogeny at approximately 275 Ma, destroying reasonable hope of natural gas preservation in that province, but not removing the U. Such destruction is not surprising considering that it was Africa hitting Laurentia. However, beneath the plateau's physiographic province much farther from the impact zone, Alleghanian folding and faulting were minimal and the natural gas reserves as well as the associated U remain largely intact. Erosion is generally agreed to have removed 4 kilometers (km) of sediment in the Ridge and Valley and perhaps a little less in the plateaus since the Alleghanian Orogeny (Smith 2003). The Antes itself is Upper Ordovician in age.

Mandata Formation

Like the Antes Formation, the Mandata Formation also formed following a period of carbonate deposition. In this case, however, the duration of carbonate deposition was roughly an order of magnitude shorter and only included, from bottom up, the Silurian Wills Creek Formation calcareous hypersaline shale; the Tonoloway Formation sabka environment hypersaline; algal laminate limestones; the Keyser Formation limestones; the thin, petroliferous-smelling Coeymans; and thin, fossiliferous New Scotland Formation cherty limestones. Following New Scotland deposition, carbonate formation ceased for a time and glauconite-bearing marine phosphate nodules accumulated U from the new, black shale depositional environment which, like the Antes long before, received and preserved organic matter in a restricted marine environment. Interestingly, the three Bald Hill Bentonites (volcanic ash beds) are found on the New Scotland-Mandata contact. They were found in Pennsylvania by first being hypothesized to be present because of the carbonate to black shale environment change (Smith, Way, and Berkheiser 1988). Bald Hill Bentonite C has been dated at 417 Ma (Smith 2010, reporting work of J. Ramezani) and is the effective boundary between the Silurian and the Devonian in Pennsylvania. Where exposed in the Ridge and Valley, the high organic zone is several meters thick, but an easy natural gas bonus if one already has a deep bore hole for a primary target. The Mandata, like the Antes, Marcellus, and Burket, suffered the same thrust faulting and folding in the Ridge and Valley during the Alleghanian Orogeny. Likewise, conditions beneath the plateaus were far more tranquil. The organic-rich zone may only be several meters thick. In those cases where horizontal drilling encounters the glauconitic phosphate nodule horizon, the distribution of U and its daughters can be expected to be inhomogeneous and associated with the slightly higher-density phosphate nodule fragments that might concentrate during deposition.

Marcellus Formation

Because it is the most important economically and presently the greatest source of TENORM via cuttings and flowback fluids, the Marcellus Formation marine black shale has already been covered in some detail. For our purposes here, it need only be repeated that the Marcellus was deposited following the Onondaga Formation Limestone and that Way and Smith provided monazites from Tioga Ash Bed B (Way and Smith 1986) for dating to Mary Roden-Tice who, with Parrish and Miller (1989), obtained an age of 390 Ma ±0.5 Ma, for the lower portion of the Marcellus Formation. In many places, the organic-rich portion is tens of meters thick. To reduce the TENORM burden of cuttings brought to the surface, some operators may choose to do the horizontal drilling in the upper portion of the Onondaga Formation just below the Marcellus. However, it is expected that flowback fluids from the Onondaga will be in communication with the Marcellus such that minimal correlation would be expected between TENORM levels in the cuttings and those in the flowback fluids.

It should also be noted here that properly collected and preserved flowback fluids will retain much of their TENORM burden as received and analyzed by a laboratory. Bulk flowback fluids exposed to atmospheric oxygen will, however, transfer much of their burden to sludges and cuttings as bisulfide (HS^-) oxidizes to sulfate and ferrous iron oxidizes to ferrioxyhydroxides. Both of these latter processes are expected to nearly quantitatively remove radiums from solution. Conversely, the onset of oxidation may initiate mechanisms that will mobilize U.

Burket Member of the Harrell Formation

The Burket Member black marine shale was deposited following the relatively inconspicuous Tully Limestone. The Harrell Formation was named after Horrell Station, Blair County, documenting the fact that geology is, at times, an inexact science. The top of the Tully Limestone marks the boundary between the Middle and Upper Devonian periods. To date, no volcanic ash beds have been verified in the transition. The organic-rich portion of the Burket might only be several meters thick in the Ridge and Valley. Nevertheless, it presents an interesting secondary natural gas target already being utilized.

Lockatong Formation

Unlike all of the Paleozoic-age, marine black shales discussed above, the Lockatong is of much younger, post-Paleozoic Mesozoic Age, specifically formed in the much younger Triassic System. Further asserting its distinctive nature, it is not a marine deposit, but rather terrestrial, subaerial black, reduced shale deposited in a hypersaline lake. It is nearly always associated with the oxidized Stockton formation and both are enriched in U at many locations in Bucks County in particular. Several mechanisms are recognized to have enriched the Lockatong and portions of the Stockton Formation in U: reduction of the soluble hexavalent uranyl ion into the insoluble uranic ion in black shale, redox boundaries at Lockatong-Stockton contacts (Christine E. Turner-Peterson 1980); reduction by fossil wood charcoal in the base of otherwise oxidized stream channels; and, possibly even roll fronts utilizing natural gas as a reductant. As a result, widespread indoor Rn is a problem in the Newark Basin, but much less so in the Gettysburg Basin. Both the locally uraniferous Reading Prong to the north (Smith and Barnes 2013) and various granitic gneisses to the southeast provide more U into the Newark Basin than other sources provided into the more westerly Gettysburg Basin. Note also that the immense Cole's Hill U deposit near Gretna, Virginia, is located along the base of a Mesozoic basin and underlying gneisses.

As it was not deposited until millions of years after the Taconic and Alleghanian orogenies, the Lockatong has obviously not had its natural gas and possible liquid hydrocarbon potential reduced by deformation. However, in place of those two orogenies, sediments in the Newark Basin have been locally baked into porcelain-like hornfels by 201.509 Ma (±0.035 Ma) (Blackburn and others, 2013) contact metamorphism caused by the York Haven Diabase, which is estimated to have intruded at 1,050°C (Smith 1973, Smith, Rose, and Lanning 1975). However, because the diabase intruded with a substantial hydraulic head which typically pushed it to within a kilometer or two of the surface during the latest Triassic, baking may not be overly severe at depth except near magma conduits, which supplied the presently observed diabase sheets. Extremely widespread, more gentle heating has been observed (Smith and Faill 2000, Kohn and others 1993).

Discussion of Relative NORM Risks by Geologic Unit

Of the three principal naturally radioactive elements – K, U, and Th – only U appears to constitute significant radiological concerns. Potassium is, for practical purposes, low risk—a relative non-issue. It is largely present in relatively insoluble minerals such as muscovite, illite and potash feldspars, and therefore, does not constitute an excess nutrient issue.

Thorium is somewhat enriched in two of four Lockatong formation samples from the Newark Basin, but is unlikely to be extensively drilled soon for both demographic reasons and rather low natural gas current prices. Even in those Lockatong samples in which the Th is moderately high, it is likely to be present largely in insoluble and immobile minerals such as zircon, monazite, and thorite (Smith, et al. 1989). For practical purposes, Th is also a non-issue. The Th-232 series includes problematic Ra-228 as one of its progeny, but the amount of Ra-228 or Ra-226, in solution, is more nearly controlled by reducing conditions and absence of "normal" geochemical processes in the natural host rock at the depths penetrated by horizontal drilling, and not by an anomalously high amount of Th in the host rock (Cecil, Smith, Reilly, and Rose 1987, and Dresel and Rose 2010). Due to the high energy of some abundant gamma rays from the Th-232 series, Th may actually be a distraction to TENORM monitoring at landfills.

The U contents are elevated for all of the high organic sampled and analyzed geologic units. However, one Marcellus sample, MRCPA147 (see **Table A-1**), collected by R.C. Smith II and R. Lewis, not part of this TENORM study, was collected well above the high organic zone near the base and suggests that vertical cuttings above the Marcellus high organic zone might not require the same special treatment and/or disposal as the cuttings from horizontal drilling in the high organic zone itself. Reconnaissance monitoring may be adequate for vertical cuttings. In a few cases, astute producers might choose to do horizontal drilling to recover natural gas from the Marcellus by drilling in the Onondaga Formation just below the base of the Marcellus. Those cuttings, but not the flowback fluids that communicate between adjacent geologic formations such as the Onondaga, might also prove to be relatively innocuous.

The Burket Member of the Harrell Formation appears to lose its high organic character and even its distinct identity far to the southeast of the plateau. Therefore, it is unlikely to support worse than what, unfortunately, goes for normal Rn problems in Pennsylvania as one gets a county or two away from the edge of the plateaus. However, sample BURKLP (collected by R. C. Smith, II) suggests that the Burket may produce elevated indoor Rn levels in Lockport, Clinton County, and nearby areas. As found in the Marcellus shale samples from the TENORM study, similar increased levels of radioactivity may also arise with horizontal drilling of the Burket in the Appalachian plateau.

Somewhat prior to the TENORM study, representative rock sampling and analyses of the high organic zones of surface exposures of the corresponding black shales in the Ridge and Valley physiographic province were conducted by R. C. Smith, II, in order to interpret and project high indoor Rn contents (see **Table A-1**). These samples were analyzed by Activation Laboratories, Ltd., Ancaster, Ontario. **Table A-1** is only a partial listing of the elements analyzed. These samples were collected by cutting channels normal to bedding and compositing the corresponding chips. The sampling sites included road cuts, railroad cuts, and active and abandoned quarries which had been exposed to the atmosphere for only a few decades. Even so, the outer few inches of slightly weathered shale was wasted. Because these are surface samples, some oxidation of sulfides to sulfates has inevitably occurred, but significant remobilization of reduced U and many heavy metals is unlikely. Relatively few samples have been collected from the individual geologic units. However, based on the general lateral continuity of marine black shales and even their volcanic components, medians of the U content for each unit are believed to be predictive. Thus with these caveats in mind, from youngest to oldest, we obtained median U contents of the high organic zones of: Lockatong 26 ppm and associated Stockton 9 ppm, Burket nearest plateau 10 ppm, Marcellus 26 ppm, Mandata 9 ppm, and Utica 9 ppm. These values are in comparison to median U contents of shales of 3.7 ppm (Rose, Hawkes, and Webb 1979).

Study of additional, previously unsampled Marcellus Formation cores from the high organic zone in five deep holes spread across western, northwestern, and northern Pennsylvania is believed to be warranted.

One may speculate:

1) The high organic zone on the Marcellus Formation is likely to contain the highest radiometric burden of the natural gas targets in the plateaus of Pennsylvania and to yield the largest volume of cuttings. If producers chose to drill horizontally within the underlying Onondaga Formation limestone, the cuttings burden may be reduced, but at the possible expense of a larger volume of noxious flowback fluids from the Onondaga.

2) Each of the other sampled target high-organic zones is likely to have around 40 percent of the burden of the Marcellus. Considering that typical shale contains 4 ppm U, perhaps this could be better conceptualized as about 28 percent of the excess burden.

3) If regulations are proposed for Marcellus shale disposal, they should be more than adequate to cover cuttings from the Burket, Mandata, and “Utica” geologic units. As there tends to be exceptions to uniformity of geologic units over time and space, a reasonable geological engineering factor might be to design for two times the maximum observed U content in the Marcellus of 42 ppm U. That is, it might be prudent to design for a maximum of 84 ppm U. Conversely, one might reduce monitoring of non-Marcellus sources by perhaps half with the proviso that adjustments will be made both ways as additional data become available.

4) As noted above, both the Rhinestreet Member of the West Falls Formation associated with the Belpre volcanic ash and the Pipe Creek Member of the Java Formation associated with the Center Hill volcanic ash bed (Berg et al. 1993) are both black shales that have natural gas potential. Neither are known to outcrop at the surface in Pennsylvania nor were deep drill cores found to be available. Because of the association with volcanic ash beds, they are likely to contain moderately high U and to be exploited commercially.

5) The Lockatong is not a marine, but rather a non-marine black shale. It is associated with the oxidized Stockton Formation. Because marine black shales lacked access to oxygen, there are very few mechanisms that can remobilize U within the geologic units to create localized extreme U enrichments. However, the Lockatong and associated Stockton had access to oxygen and have yielded a number of localized U occurrences of several types in Bucks and Montgomery counties in the Newark Basin of Pennsylvania as well as across the Delaware River in New Jersey. (Because of the immense Coles Hill U ore deposit at the base of a Mesozoic basin near Gretna in Virginia, ore grade deposits cannot be ruled out.) Thus, it can reasonably be assumed that cuttings from the Lockatong will encounter not just laterally continuous zones of perhaps 5 to 10 ppm U, but also localized zones of 50 to 100 ppm U. Further, zones of 500 to 1,000 ppm U would not be too surprising. Adding to the downside potential from a TENORM viewpoint, the adjacent Stockton sandstones and siltstones can be expected to be more porous and permeable with respect to connate brines than black shale. Thus, their yield of flowback fluids may be large.

6) All horizontal rock cutting samples that have not already been analyzed by XRF should be analyzed. This analysis would be helpful to determine the elements of their potential heavy metal toxicity.

7) Study of additional, previously unsampled Marcellus Formation cores from the high organic zone in five deep holes spread across western, northwestern, and northern Pennsylvania is believed to be warranted.

Relative Heavy Metal Contents of Selected Black Shales in Pennsylvania

Based on examination of the abridged table of geochemical analyses, the following comments are offered by oxide or element. Note the Lockatong and associated Stockton Formations in the Newark Basin and the Hamburg sequence in the Great Valley, while of great relevance for indoor Rn, are not discussed herein because they are not likely to yield TENORM in the near future.

Calcium oxide (CaO) – The Mandata Formation in surface outcrop at Everett presently contains only 0.06 percent CaO and the Marcellus Formation at Frankstown likewise only 0.06 percent. These low CaO contents suggest very limited acid neutralization capacity. Water soluble supergene sulfates built up as crusts on surface outcrops during droughts may permit bursts of acidic heavy metal-laden water following dry periods and possibly even in early spring. Such effects might also occur at disposal sites if there are any comparable cuttings and water contents that fluctuate seasonally.

Phosphorous pentoxide (P_2O_5) – It cannot be ruled out that under some circumstances polonium (Po-210) might concentrate in the phosphate mineral apatite or commonly associated glauconite. Thus, in cuttings containing > 0.2 percent P_2O_5, Po-210 enrichment cannot be entirely ruled out due to unusual geochemical environments.

Sulfur (S) is enriched in at least some samples of each marine black shale. The highest S content seems to be associated with the Antes Formation (“Utica”). Acid and potential spontaneous combustion problems need to be considered for the Antes in particular.

Arsenic (As) – The Antes, Mandata, Burket near the plateau, and especially the Marcellus are enriched in As. Some may be substituting for phosphorus in carbonate-fluorapatite. In any case, cuttings from these black shales might yield soluble As compounds depending on the activity of electrons/activity of hydrogen ions (Eh/pH) environment of the disposal site.

Barium (Ba) – Several of the marine black shales, and especially the Marcellus, contain high Ba. **Table A-1** shows two samples with very high concentrations of Ba. Sample CSMPB (101,000 ppm Ba) is from the Hamburg sequence near Harpers Tavern, Lebanon County. This sample was collected from a single block of phosphate-barite bed. Very near this area some rocks have been collected containing 95 percent barite. Barite is barium sulfate ($BaSO_4$), and this is the source of the very high Ba concentration. The other sample, M-1L (11,201 ppm Ba) from the Stockton formation in the Newark Basin (Bucks County), was near an area where barite was mined.

Most of this is likely present as the geologically old, insoluble mineral barite, BaSO4, and probably not of direct environmental concern. Conversely, reducing connate brine fluids present at depth in black shale formations are expected to be enriched in soluble Ba^{2+}. When the bisulfide (HS^-) and possibly hydrogen sulfide (H_2S) present at depth within these same connate fluids reach the surface and are rapidly oxidized to sulfate $SO4^{2-}$, radiobarites enriched in Ra-226 and, to a lesser extent in Ra-228, will form as insoluble precipitates. In some ways this is beneficial as the process removes soluble radiums from the connate brines, but it likely will yield intense localized hot spots where they precipitate. At least these radiobarites will likely remain relatively insoluble. The same cannot be said for all of the sulfates resulting from surface oxidation of HS^- and H_2S. Moderately soluble sulfates of alkali and especially alkaline earths may result. These resulting radiosulfates are likely to be resolubilized under a variety of changing Eh and pH conditions, not to mention simple dissolution by rainwater. The Ra burden they carry might be further concentrated downstream. If appropriate disposal methods can be found, we cannot rule out the potential benefit of concentrating the radiums for specialized disposal rather than the older "solution by dilution" methods.

An additional complication with naturally reducing connate brines from black shale formations is that the Fe^{2+} (ferrous iron) present in the brines at depth oxidizes almost immediately upon contacting oxygen in the air. This results in the production of Fe^{3+} (ferric iron) and the ultimate precipitation of ferric oxyhydroxides. These, too, may be beneficial in that the precipitates will adsorb radiums and perhaps some other progeny from solution. However, these non-crystalline ferric oxyhydroxides tend to crystallize into stable minerals over time. These more stable minerals lack the extreme surface area of the former and fail to adsorb most radionuclides. Translated loosely, radiums bound with "yellow boy" may be remobilized in landfills over time unless other geochemical traps are planned in advance.

Bromine (Br) seems to be concentrated in nearly all Marcellus and Antes high organic samples. It cannot be ruled out that some of the Br is in soluble forms such as sodium bromide (NaBr) or potassium bromide (KBr) from connate brines. Connate brines from nearly all formations can be expected to be high in chlorine (Cl) which might form complexes to solubilize metals such as copper (Cu) and mercury (Hg) in particular. The flowback fluids should be assumed to be slightly enriched in Br until proven otherwise.

Cadmium (Cd) is strongly enriched in high organic Marcellus samples. It is a toxic metal in and of itself. It may piggyback with relatively innocuous zinc and be insoluble as sulfide at depth but become solubilized as a sulfate at the surface. High Cd in the presence of high S may be troublesome.

Mercury (Hg) is less than the detection limit of 1 ppm in all of the black shale samples collected to date. However, from the standpoint of heavy metal toxicity, not radionuclide, obtaining separate analyses having a lower detection limit might be appropriate. If organic and sulfide-rich cuttings were to combust spontaneously or otherwise, vapors of Hg, As, and selenium (Se) would be particularly hazardous. Occasional thermal imaging may be in order, or at least noting anomalously snow-free or steaming piles of cuttings.

Molybdenum (Mo) geochemistry is complex. Particularly in Marcellus high organic samples, the forms and amounts of Mo should be monitored. Possibly additional analyses should be obtained by DEP's Bureau of Laboratories (BOL) for the two Marcellus samples containing more than the upper limit of the normal working range, 100 ppm. Molybdenum might become solubilized and then later precipitate in concentrated form with ferric oxyhydroxides. Because caution is needed to keep Mo out of the human and animal food chain, precipitates and the connate brines themselves should be occasionally checked for a possible Mo burden.

Nickel (Ni) is enriched in high organic Marcellus samples. Although possibly present in the black shale as iron sulfides such as pyrite or pyrrhotite where the Ni probably substitutes for iron, organometallic compounds cannot be ruled out. Whatever Ni is solubilized, it is likely to be adsorbed on ferric oxyhydroxides once they precipitate.

Lead (Pb) – Although Pb is a well-known heavy metal toxin, the levels in the sampled black shales do not appear to be of particular concern. In fact, the levels observed are typical of many shales and Pb is only included here because it is a traditional concern.

Selenium (Se) is strongly enriched in two of the high organic Marcellus samples and is toxic if enriched in the food chain for animals or humans. It is likely present within pyrite in the Marcellus. If Marcellus cuttings were to spontaneously combust, Se would likely be out-gassed as vapors, which might yield vapor-deposited solids in cooler crusts near the surface of the piles.

Thallium (Tl), a.k.a. "rat poison," is enriched to more than 1 ppm in three of four high organic Marcellus samples, all three Antes samples, both Mandata samples and the three higher organic Burket samples. It may be substituting for zinc iron sulfides and subject to mobility if pyrite oxidizes.

Uranium (U) – Because of its importance and centrality to TENORM issues, it has been discussed in more detail in the body of the report.
Thorium (Th) in the sampled black shales is typically at background levels as expected. It will contribute to the high energy gamma flux, but is not recognized as being of serious concern. This is partly because much of it is likely present in insoluble, stable minerals.

The conclusion to heavy metal contents of black shales in Pennsylvania is that, once again, procedures designed to handle heavy metals in the Marcellus Formation should be more than adequate to handle TENORM from the other black shale units.

Reduced Rock and Fluid at Depth vs. Potentially Oxidized Disposal Sites

As mentioned in part, above, the Marcellus and other black shales of marine origin were formed, buried, and preserved in reducing environments. This perhaps appears obvious from the presence of methane, but it is mobile in some geologic environments. Confirmation of the reducing environment comes from the presence of sulfide minerals such as pyrite and the fact that significant portions of alkaline earth elements such as Ba and Ra are soluble in the connate brines at depth. The Eh on freshly produced brines are difficult to measure but also supports this. Thus, U once in a hexavalent, uranyl ion form in weathered rocks exposed to the atmosphere or in the metastable volcanic glass component of volcanic ashes, was reduced in situ in the deep, black shale basins. Once cuttings of black shales are brought to the surface, it is reasonable to assume that depending on the disposal environment, that some U might once again become oxidized and mobile, i.e., soluble. Soluble U is highly toxic.

Liming may seem like an obvious remedy to the acid-generating potential of pyrite in shales and indeed it is probably a good thing that the lower contacts of black shales tend to be interbedded with underlying limestones. However, one needs to plan carefully as the carbonate anion might increase the mobility of hexavalent U and carbonate soils accumulate radiums at depth.

Another issue to consider in the disposal of black shale cuttings is that the risk of spontaneous combustion cannot be ruled out. This is especially true for pyritic cuttings. Spontaneous combustion of natural outcrops of the Late Devonian Huron Member of the Ohio shale has occurred near Monroeville, Ohio. Finer-grained cuttings may be even more susceptible to oxidation.

Disposal of flowback fluids is perhaps even more complex because they are so unstable as they reach the surface. Bisulfide (HS^-) present at depth can be expected to oxidize immediately to the sulfate ion, effectively removing the bulk of the alkaline earths from solution. Note, however, that the solubility product for Ra sulfate still allows for high amounts of Ra^{2+} in solution, which is the divalent, soluble form of Ra-226. The second, almost instantaneous reaction is the oxidation of soluble Fe^{+2} (ferrous iron) to ferrioxyhydroxides having large adsorption capacities for radiums and other toxic heavy metals. Unfortunately, this “yellow boy” is metastable. “Yellow boy” is an orangish precipitate associated with some old coal mines. It will change to lepidocrocite and then to goethite over time, neither of which have significant adsorption capacities relative to “yellow boy;” thus, in an unengineered site, radiums might once again become soluble.

Likewise, toxic heavy metals sequestered in minerals that are stable at depth may not remain so at the surface. Careful planning is obviously needed in designing TENORM disposal sites.

Bibliography

Berg, T. M., McInerney, M. K., Way, J. H., and D. B. MacLachlan. Stratigraphic correlation chart of Pennsylvania, Pennsylvania Geological Survey, 4th series, General Geology Report G-75, third printing slightly revised, 1993.

Blackburn, T. J., Olsen, P. E., Bowring, S. A., McLean, N.M., Kent, D. V. John Puffer, Greg McHone, E. Troy Rasbury, and Mohammad Et-Touhami. Zircon U-Pb geochronology links the End-Triassic Extinction with the Central Atlantic Magmatic Province, Science, v. 340, p. 941-945, 2013.

Cecil, L. DeWayne, Smith, II, R. C., Reilly, M. A., and A. W. Rose. Radium-228 and Radium-226 in ground water of the Chickies Formation, southeastern Pennsylvania, p. 437-447 in Barbara Graves, editor, Radon, radium, and other radioactivity in groundwater, Hydrogeology impact and application to indoor airborne contamination, Proceedings of the NWWA Conference April 7-9, Somerset, New Jersey, 1987.

Dresel, P. E. and A. W. Rose. Chemistry and origin of oil and gas well brines in western Pennsylvania, Pennsylvania Geological Survey, 4th series Open File Report OFOG 10-01.0, 2010.

Haluszczak, L. O., Rose, A. W., and L. R. Kump. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA, Applied Geochemistry, v. 28, p. 55-61, 2012.

Kohn, B. P., Wagner, M. E., Lutz, T. M., and G. Organist. Anomalous Mesozoic thermal regime, central Appalachians and piedmont: evidence from zircon and sphene fission-track dating, The Journal of Geology, v. 101, p. 779-794, 1993.

Roden[-Tice], M. K., Parrish, R. R., and D. S. Miller. The absolute age of the Eifelian Tioga Ash [Bed B], Pennsylvania, Journal of Geology, v. 98, p. 282-285, 1989.

Rose, A. W., Hawkes, H. E. and J. S. Webb. Geochemistry in Mineral Exploration, second printing, Academic Press, 657 p, 1979.

Smith, II, R. C. Some thoughts and speculations on radiometric dates relevant to Pennsylvania with annotated table, Proceedings of Symposium associated with the 75 Field Conference of Pennsylvania Geologists, p. 21-33, 2010.

Smith, II, R. C. Lead and zinc in central Pennsylvania, [moderately misnamed as it covers burial depths and erosion], Field Conference of Pennsylvania Geologists, 68th Guidebook, p. 63-72, 2003.

Smith, II, R. C. Geochemistry of Triassic diabase from southeastern Pennsylvania, unpublished Ph.D. thesis, The Pennsylvania State University, 262 p, 1973.

Smith, II, R. C., Barnes, J. H., and Berkheiser, S. W. Jr., and S. A. Haynes. Assessment of radon in potions of Bucks County, Pennsylvania, Pennsylvania Geological Survey, 4th series, 78 p. plus folio of hand-colored 7 1/2' topographic maps, October 1989.

Smith, II, R. C. and Barnes, J. H. Geology and Mineralogy of uranium and thorium in the Reading Prong of Berks, Lehigh, and Northampton Counties, Pennsylvania, Pennsylvania Geological Survey, 4th series, 177 p. and 1 plate, 2013, but completed 1989.

Smith, R. C. Rose, A. W., and R. M. Lanning. Geology and geochemistry of Triassic diabase in Pennsylvania, Geological Society of America, v. 86, p. 943-955, 1975.

Smith, II, R. C., Berkheiser, S. W., Jr., and Way, J. H. The Bald Hill Bentonite Beds: A Lower Devonian pyroclast-bearing unit in the Northern Appalachians [later extended to the central Appalachians] Northeastern Geology, v. 10, no. 3, p. 216-230), 1988.

Smith, II, R. C. and R. T. Faill. The Mesozoic heating event in the mid-Atlantic region, U.S.A. Geological Society of America Abstract for Poster presentation, v. 32, no. 1, p. 75, 2000.

Smith, II, R. C., Way, J. H., and S. W. Berkheiser, Jr. Bentonites in the Union Furnace Section, Huntingdon County, Pennsylvania, in Berkheiser, Jr., S.W., R. C. Smith, II, and J. H. Way, Guidebook 51st Field Conference of Pennsylvania Geologists, p. 111-119, especially p. 113. See also Appendix 1 Detailed Measured section by S. W. Berkheiser, 1986.

Turner-Peterson, C. E. Sedimentology and uranium mineralization in the Triassic-Jurassic Newark Basin, Pennsylvania and New Jersey in Uranium in sedimentary rocks: application of the facies concept, SEPM (now Society for Sedimentary Geology), p. 149-175, 1980.

Way, J. H., Jr. and R. C. Smith, II. Detailed correlations across 175 miles of the Valley and Ridge of Pennsylvania using 7 ash beds in the Tioga Zone, 51st Guidebook Field Conference of Pennsylvania Geologists, p. 55-72, 1986.

Wise, D. U., Smith, II, R. C. Jercinovic, M. J., Ganis, G. R. Onasch, C. M., Repetski, J. E., and M. L. Williams. Tectonic implications of a new 450 Ma monazite date and T/P data from the Martic Zone, Pequea Silver Mine, SE Pennsylvania, Geological Society of America Abstracts with Programs, v. 39, no., 1, p. 50, 2007.

Table A-1. Rock Formation Samples Analysis

Sample Name and Formation	Location, County	U	Th	K2O	P2O5	As	Ba	Br	S	Tl	V
Analyte Symbol:		U	Th	K2O	P2O5	As	Ba	Br	S	Tl	V
Unit Symbol:		ppm	ppm	%	%	ppm	ppm	ppm	%	ppm	ppm
Detection Limit:		0.01	0.05	0.01	0.01	1	1	0.5	0.001	0.05	5
Analysis Method:		FUS-MS	FUS-MS	FUS-ICP	FUS-ICP	INAA	FUS-ICP	INAA	TD-ICP	FUS-MS	FUS-ICP
ANTES = "UTICA"	Oak Hall, Centre County	14.8	11.1	2.32	0.25	32	309	3.1	4.41	0.50	111
ANTES = "UTICA"	Reedsville, Mifflin County	9.08	10.7	3.04	0.15	35	960	2.2	2.23	1.42	138
ANTES = "UTCA"	Antes Gap, Lycoming County	7.76	8.88	2.91	0.27	9	371	3.4	1.04	1.00	130
MARCELLUS	Hares Valley, Huntingdon	23.1	10.8	2.51	0.08	50	645	4.6	2.81	2.14	500
MARCELLUS	Frankstown, Blair	26.6	9.13	1.81	0.11	92	1060	9.2	0.919	9.58	596
Tioga Ash Bed F in Marcellus	Frankstown, Blair	42.3	37.0	1.70	0.11	49	1100	1.0	N.A.	N.A.	260
MARCELLUS	Selinsgrove Junction, Northumb.	25.0	7.69	2.07	0.09	32	1232	4.4	3.08	0.65	399
MARCELLUS	Wardville, Perry/Juniata	25.4	8.61	3.18	0.09	37	2328	3.3	0.197	1.29	497
MARCELLUS	S. Sunbury, Northumberland	3.23	13.1	3.41	0.10	8	860	2.2	0.761	0.96	134
MANDATA	Everett, Bedford	7.71	11.9	4.31	0.26	28	319	2.3	0.182	1.93	177
MANDATA	Hollidaysburg, Blair	10.4	9.00	4.21	0.43	19	837	3.7	1.22	1.25	159
HAMBURG	Fredericksburg, Lebanon	10.9	7.50	2.66	0.60	18	392	3.3	0.008	0.72	346
HAMBURG	Harpers Tavern, Lebanon	18.7	10.9	5.12	1.74	43	1972	2.4	0.062	1.66	756
HAMBURG	Harpers Tavern, Lebanon	46.2	3.95	0.72	19.12	4	101100	< 0.5	0.341	0.29	62
BURKET	Lockport, Clinton	12.9	10.6	4.05	0.22	32	733	4.1	0.893	2.60	348
BURKET	Amity Hall, Perry	4.82	14.7	4.57	0.09	21	618	< 0.5	0.499	2.21	209
BURKET	Newry, Blair	7.43	12.2	4.09	0.10	45	750	< 0.5	1.53	2.85	279
BURKET	Grazierville, Blair	3.72	14.0	3.76	0.11	8	700	2.1	0.387	0.92	155
BURKET	Liverpool, Perry	3.54	15.2	3.91	0.13	12	549	< 0.5	0.021	0.90	154
LOCKATONG, Newark Basin	Pipersville, Bucks	39.6	14.3	4.87	0.28	58	578	< 0.5	0.60	1.17	162
LOCKATONG, Newark Basin	Jamison, Bucks	26.9	19.6	4.17	0.41	94	683	< 0.5	0.516	1.18	122
LOCKATONG, Newark Basin	Tradesville, Bucks	25.1	35.3	4.57	0.66	7	735	< 0.5	0.162	1.71	176
LOCKATONG, Newark Basin	Danboro, Bucks	8.13	26.8	3.34	0.45	10	542	< 0.5	0.336	0.41	117

Table A-1. Rock Formation Samples Analysis (Continued)

Sample Name and Formation	Location, County	U	Th	K2O	P2O5	As	Ba	Br	S	Tl	V
Analyte Symbol:		**U**	**Th**	**K2O**	**P2O5**	**As**	**Ba**	**Br**	**S**	**Tl**	**V**
Unit Symbol:		**ppm**	**ppm**	**%**	**%**	**ppm**	**ppm**	**ppm**	**%**	**ppm**	**ppm**
Detection Limit:		**0.01**	**0.05**	**0.01**	**0.01**	**1**	**1**	**0.5**	**0.001**	**0.05**	**5**
Analysis Method:		**FUS-MS**	**FUS-MS**	**FUS-ICP**	**FUS-ICP**	**INAA**	**FUS-ICP**	**INAA**	**TD-ICP**	**FUS-MS**	**FUS-ICP**
STOCKTON, Newark Basin	**Lumberville, Bucks**	**9.04**	**11.6**	**2.00**	**0.26**	**14**	**11210**	**< 0.5**	**0.191**	**0.51**	**101**
STOCKTON, Newark Basin	**Newtown, Bucks**	**25.5**	**16.0**	**0.89**	**0.15**	**< 1**	**296**	**< 0.5**	**0.007**	**0.58**	**38**
STOCKTON, Newark Basin	**Carversville, Bucks**	**5.21**	**16.7**	**4.40**	**0.15**	**4**	**810**	**< 0.5**	**0.007**	**1.14**	**131**
Middle Ord. Bentonite 5	Union Furnace, Huntg./Blair	4.28	20.0	6.26	0.06	4	194	1.5	1.83	1.31	14
Middle Ord. Bentonite 11	Union Furnace, Huntg./Blair	4.31	22.8	6.25	0.06	8	280	1.3	0.86	0.80	16
Middle Ord. Bentonite 12	Union Furnace, Huntg./Blair	7.95	31.3	5.15	0.15	7	227	1.1	0.38	1.07	33
Middle Ord. Bentonite 13	Union Furnace, Huntg./Blair	5.10	17.4	3.81	0.14	13	229	1.8	0.17	0.67	46
Middle Ord. Bentonite 14	Union Furnace, Huntg./Blair	8.77	15.0	6.25	0.05	10	278	1.2	0.12	1.19	13
Middle Ord. Bentonite 15	Union Furnace, Huntg./Blair	7.44	25.3	5.50	0.07	10	345	<.5	0.67	0.89	18
Middle Ord. Bentonite 16	Union Furnace, Huntg./Blair	5.77	31.2	5.56	0.09	6	335	1.4	0.10	0.88	17