ALKALINE ADDITION PROBLEMS AT THE SKYTOP/INTERSTATE-99 SITE, CENTRAL PENNSYLVANIA[1]

Arthur W. Rose and Hubert L. Barnes[2]

Abstract. In 2002-3, approximately $8x10^5$ m^3 of pyrite-bearing Bald Eagle sandstone and Reedsville shale were removed from a large road cut through Bald Eagle Ridge near State College, PA. The rock contained an average of about 4.5% pyrite as veins and fine veinlet networks across 200 m of road cut. Smaller amounts of ZnS and other heavy metal sulfides accompany the pyrite. The rock was placed in 9 nearby locations, including large waste piles and several valley fills, two 'buttresses" and a lane elevation along about 0.8 km of hillside that was threatening to slide into the road. During excavation of the cut, pyrite was recognized as a potential problem and considerable lime was added as layers to the various piles. Despite the lime addition, highly acidic seeps emerged from the piles and fills, with pH 2.0 to 2.7, Fe 90-1500 mg/L, and acidities as high as 18,000 mg/L (as $CaCO_3$). These results clearly show that addition of lime and other alkaline materials as layers is not effective.

In experiments to test remediation methods, Bauxsol slurry was sprayed onto part of the buttress area but failed to prevent continuing acid seepages. Inspection trenches showed little penetration of the Bauxsol, and demonstrated the presence of the added lime as impermeable lime layers within the buttress. Bucket tests of mixtures of alkaline circulating fluidized-bed ash with pyritic rocks, when well mixed, gave alkaline effluents. These and similar field and lab experiments indicate that thorough mixing of alkaline materials with pyritic rock is crucial for maintaining non-acid effluent. Experiments with a slurry of $Mg(OH)_2$ show promise. However, ultimately the movable acid rock is being moved to a lined landfill and mixed with a large excess of waste lime material.

Additional key words: acid rock drainage, acid mine drainage, Bauxsol, lime addition

---

[1] Paper was presented at the 2008 National Meeting of the American Society of Mining and Reclamation, Richmond, VA, ***New Opportunities to Apply Our Science*** June 14-19, 2008. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502

[2] Arthur W. Rose (rose@ems.psu.edu) and Hubert L. Barnes are Professors Emeriti of Geochemistry, Pennsylvania State University, University Park, PA 16802.

Proceedings America Society of Mining and Reclamation, 2008 pp 927-949
DOI: 10.21000/JASMR08010927
`http://dx.doi.org/10.21000/JASMR08010927`

Introduction

The construction of the Interstate 99 highway (I-99) through Bald Eagle Mountain near State College, PA has led to a major problem of acid rock drainage (ARD) from pyrite in rock excavated from large road cuts. Attempts to remedy the problem have involved several types of alkaline addition to the broken rock. The problems encountered with the several attempts furnish lessons for alkaline addition in mining and other environments. The intent of this paper is to describe the various procedures, and record the results. The paper is a “case study” intended to make public the technologically interesting results of the various activities. The writers participated in a few of the activities, but attempt here to give an independent overview on the problems at this difficult site.

Interstate-99 is intended as a 4-lane divided highway connecting the PA Turnpike (I-76) at Bedford with I-80 near Milesburg. The route lies mainly in a valley marking the western edge of the Valley and Ridge Province in central PA. However, it was decided that the highway should cross Bald Eagle Ridge so as to pass near State College and University Park because of their high traffic density (Fig. 1). Extensive challenges to the routing arose, based on wetlands, endangered bats, weather conditions on the slopes of Bald Eagle Mountain, and other problems. The possibility of acid rock drainage was mentioned, based on recognition of pyrite in sandstone near Port Matilda, but was not seriously considered initially. Environmental challenges were finally stopped in 1998 by language inserted in the federal highway funding bill by Congressman Bud Shuster, then Chair of the House Transportation Committee, though extensive environmental studies had already been conducted.

In order to minimize the grade where the road crossed Bald Eagle Mountain, a major cut was excavated during 2002-2003 through Bald Eagle Sandstone in Bald Eagle Mountain. Although more than 20 core holes were drilled in the cut area before excavation, the significance of the pyrite problem was not recognized, perhaps in part because much of the pyrite occurred as thin veinlets,. Broken rock from the cut was placed in large piles (Seibert, Skytop, Arbogast) and in about 6 other nearby fills and piles (Fig. 1). On the advice of geologists from the PA DEP mine permitting staff, waste “lime” from a nearby lime plant was added to the broken rock in some fills and waste piles. The lime was layered in 3 m lifts at a rate of 75 kg/m^3 (128 lb/yd3) of rock.

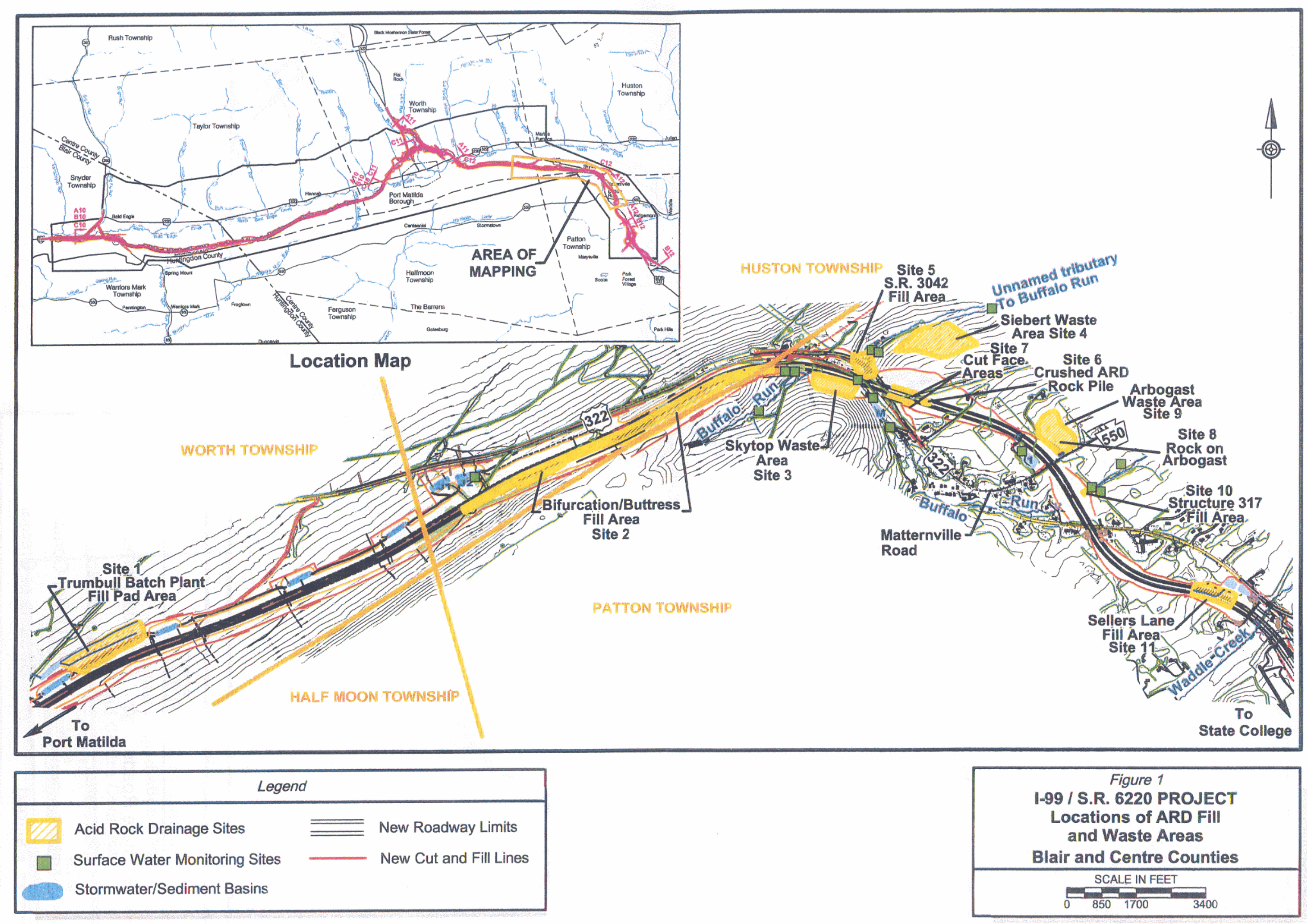

Figure 1. Map showing I-99 crossing Bald Eagle Mountain, and location of spoil piles (Skytop, Seibert, Bifurcation-Buttress, Arbogast).

A major site for disposal of pyritic rock was the "bifurcation-buttress" system. During construction of the highway on the upper NW slope of Bald Eagle Mountain, the cut face on the uphill side began sliding down into the new highway cut. To stabilize the slope its inclination was laid back to a lower angle, the uphill lane at the toe of the slope was raised about 6 m by filling along the previous grade, and a "buttress" was built along the uphill side to weight the toe of the slide. This "bifurcation and buttress" was constructed along about 2 km of the new highway (Fig. 1). Part of the material used to build this "bifurcation-buttress" system was the pyritic rock from the large cut. "Lime" was added to part of this fill also.

The ARD problem became public in November 2003 when reddish water was observed seeping from some of the spoil piles and fills, and was found to be acid rock drainage (Centre Daily Times, 2003). In March 2004, work on the 10 km section from near Port Matilda to State College was halted because of the acid seeps, and was not renewed until 2007. Between 2003 and the present, extensive effort has been, and is being, directed to remedying the acid and metal release. After several alternatives were considered, the decision was made to place about 760,000 m^3 of broken rock into a lined landfill, and mix the rock with 240 kg/m^3 (400 lb/yd^3) of "lime" to neutralize acid and inhibit its production. Cut faces and "immovable fills" will be covered with impermeable covers. The extra work needed to solve the ARD problems is reported to cost $79,000,000 (Centre Daily Times, 2007).

Several types of alkaline addition were conducted or evaluated during the project and will be discussed in this paper. Layers of "lime" were added to waste rock during initial disposal of rock from the large cut. Later, a pilot-scale trial was conducted with Bauxsol slurry. Bauxsol is a waste product from the recovery of alumina from bauxite ore (McConchie et al., 1999). Lab experiments were conducted with mixtures of alkaline fluidized-bed combustion ash and pyritic rock. Other lab experiments investigated slurries of $Mg(OH)_2$, $CaCO_3$, lime, clay and Ecotite, an alkaline waste product. The results of these treatments are discussed below.

Site Characteristics

Bald Eagle Mountain is a NE-SW-trending double ridge held up by the late Ordovician Bald Eagle Sandstone and the early Silurian Tuscarora Quartzite, separated by about 200 m of red sandstones and shales of the Upper Ordovician Juniata Formation. The mountain is the most westerly ridge of the Valley and Ridge province in Pennsylvania. Crest elevations in the vicinity are 520-570 m compared with 275 m in Bald Eagle Valley to the west and 400 m in the Nittany

Valley to the east. The I-99 route climbs the west slope of Bald Eagle Mountain in a 7 km-long grade and crosses the Tuscarora ridge at a topographic low of about 520 m near Skytop where pre-existing US 322 crosses the ridge. On the east side, the new highway passes into a large cut in the near-vertical Bald Eagle Sandstone and underlying Reedsville Shale on the north side of Buffalo Run (Fig. 2). This cut is about 600 m long and 70 m deep. The Bald Eagle Sandstone is normally a greenish-gray impure sandstone, containing quartz, illite, chlorite, minor feldspar and minor hematite and leucoxene (Thompson, 1970). About 200 m of the cut is in Bald Eagle Sandstone containing significant concentrations of pyrite as veins and veinlets.

Figure 2 shows the rock cut and the location of a series of samples collected from the rock face. The samples consisted of a random fist-sized chunk collected from the cut face beneath the obvious weathering every 0.9 m and composited into 9.15 m sections. Each 9.15 m composite was crushed and a portion ground and analyzed for S and many other elements by ACTLABS of Ancaster, Ont. using ICP-total dissolution and neutron activation and independently for total S by Geochemical Testing, Inc. of Somerset, PA. Figure 3 shows the content of sulfur in the composite samples. Sulfur contents across 193 m average 2.4 weight % and range from 0.4 to

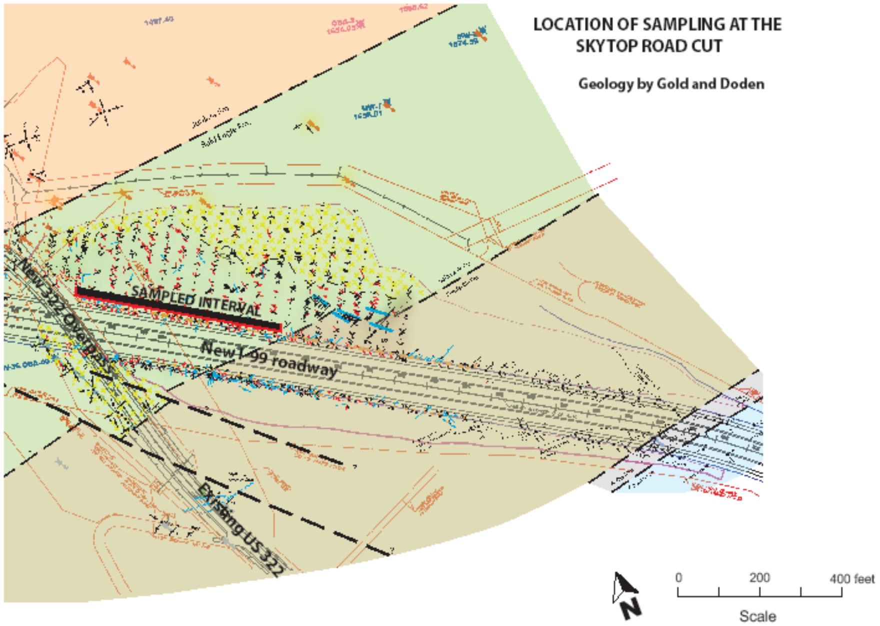

Figure 2. Geological map of the cut through Bald Eagle sandstone at Skytop, showing location of rock sample traverse. Green = Bald Eagle Sandstone, orange= Juniata red sandstone and shale, brown = Reedsville shale, blue= limestone. Yellow dots = oxidized and weathered Bald Eagle sandstone. (After Gold and Doden, personal communication, 2004).

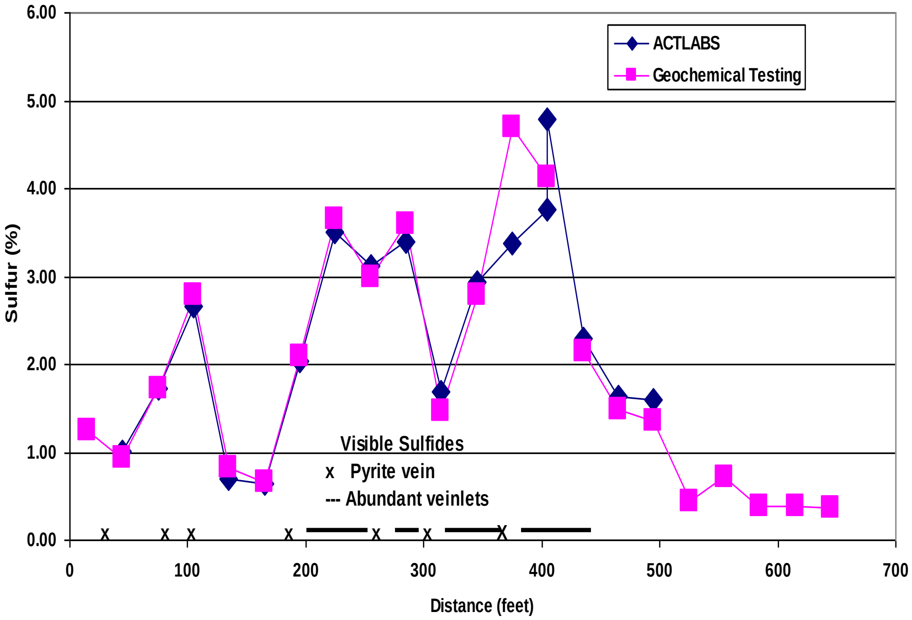

Figure 3. Sulfur content of rock composites collected across the base of the large cut face at Skytop.

4.7 weight %, equivalent to an average of 4.5% pyrite, assuming all the sulfur content to be in pyrite. The pyrite occurs mainly as a network of tiny veinlets, rarely more than 10 cm apart, plus a few larger veins up to 0.3 m in thickness. Some of the pyrite occurs as tiny needles with a large surface area, possibly accounting for rapid oxidation and acid generation. The pyrite is accompanied by quartz and minor to trace amounts of sphalerite, marcasite and pyrrhotite, lesser galena and trace amounts of minerals containing Ni, As, and other heavy metals. The pyrite and associated minerals were evidently introduced hydrothermally after the sandstone was well indurated. Fluid inclusions in the quartz are filled with concentrated chloride brines and indicate temperatures of quartz precipitation at 150 to 300^{o}C (Gold et al., 2006). The larger veins strike about N60W and dip steeply SW. The presence of the hydrothermal sulfides may be related to a NW-striking tear fault passing through the gap in the Bald Eagle Formation. This fault offsets the units about 50 m. Pyrite is known to occur at several other localities along Bald Eagle Mountain, and was probably introduced hydrothermally at these localities as well.

In the near-surface sections of the road cut, the pyrite has been weathered to limonite. An estimated 50% of the rock excavated from the cut was sulfide-bearing, the remainder being weathered to limonitic gossan. Some Reedsville shale was also excavated and moved to the same disposal sites.

Table 1 shows average contents of a range of elements in the composite rock samples from the bottom of the cut, and the maximum values found. Note the significant concentrations of Zn, Cd, As and other heavy metals in a few samples.

A year or more after recognition of the pyrite problem, additional veins and zones of pyrite-bearing rock were recognized a few hundred meters west of the large cut. These veins and zones cut the Juniata redbeds and are noticeable as zones of bleached and reduced sandstone many meters in width. Passage of the reducing, sulfide-depositing fluids evidently reduced hematite and other ferric minerals of the host rock to form chlorite and pyrite.

Table 1. Concentrations in 17 rock sample composites from the Skytop cut.

Element	Units	Average	Maximum
Al	%	2.1	3.4
Fe	%	2.9	5.4
Mg	%	0.4	0.83
Ca	%	0.1	0.28
Na	%	0.04	0.012
K	%	1.7	2.3
Ti	%	0.4	0.54
Si	%	2.4	4.8
P	%	0.02	0.026
As	ppm	7.8	19
Cd	ppm	0.9	2.1
Cu	ppm	11	18
Ni	ppm	21	44
Pb	ppm	167	1450
Zn	ppm	135	867

Analyses by ACTLABS Inc., Ancaster, ON

Results - Lime Addition to Pyritic Rock

High purity limestone is mined underground near Bellefonte and Pleasant Gap about 15 km to the NE of Skytop. Part of this limestone is converted to “lime” in coal- or gas-fired kilns and sold mainly to power plants and the steel-making industry. Waste material from lime production, mainly the fines collected in a bag house, has been placed in large piles near the lime plants. This bag house lime (BHL) is available at low cost and was added to the piles of pyritic rock in an attempt to neutralize any acidity. Most of the "lime" is fine-grained to powdery, but coherent and semi-plastic if damp. Some occurs as lumps of fines up to several tens of cm in size.

Pure lime would be CaO, which commonly absorbs moisture from the air to become $Ca(OH)_2$ (portlandite). Further reaction can lead to partial conversion to $CaCO_3$ by absorption of CO_2 from the air. $CaCO_3$ can also be present as un-reacted limestone.

Analyses of the "lime" indicate that much of it is not simple lime, but contains large erratic amounts of $CaCO_3$ and detectable amounts of SiO_2, SO_3, Al_2O_3 and other components. In a set of 15 samples, the content of portlandite ($Ca(OH)_2$) from quantitative X-ray diffraction averages 37 wt % and ranges from 1 to 58%. Calcite ($CaCO_3$) averages 60% with a range of 38 to 96%. Quartz and gypsum ($CaSO_4{\cdot}2H_2O$) are typically at 1 to 2 % with minor amounts of clay. X-ray diffraction patterns also reveal muscovite and other phases. Clearly the neutralization potential and other characteristics of "lime" added to the spoil piles cannot be considered as fixed, but must be determined by analysis of representative samples.

Table 2 lists the estimated amounts of "lime" added to the various piles. These amounts are based on the ratios of lime to rock and on the total tonnage of lime recorded from the scalehouse weight bills for the lime brought to the site. At many of the piles, lime was added in amounts of 76 to 650 kg/m^3 (128 to 1100 $pounds/yd^3$), equivalent to about 4 to 25% "lime" by weight (assuming 3300 lb/yd^3 for broken rock). Clearly, large amounts of lime were added, in many cases far in excess of the amounts needed stoichiometrically to neutralize the potential acidity (Barnes, 2006).

Despite the large amounts of lime added to the piles, the water seeping from the piles or entering groundwater was extremely acid. Table 3 lists analyses of water from the Skytop, Seibert and Buttress areas. All have pH less than 2.8, acidity exceeding 2100 mg/L, Fe exceeding 90 mg/L and very high Al and SO_4 contents. Values of As and Zn are highly anomalous. The concentrations of several constituents in these waters far exceed standards for drinking water and other uses.

Table 2. Quantity of Lime added to Waste Piles in Skytop Area

Location	Total cubic yds	Pyritic rock cubic yds	Lime Tons
Skytop pile	93,114	93,114	5,959
Seibert pile	349,504	279,361	28,872
3042 fill	137,725	62,100	15,318
Sellers Lane fill	533,000	18,983	1,215
Buttress			(75 kg/m^3)
Bifurcation			(75 kg/m^3)

Figures 5 and 6 illustrate the form of lime in the Skytop spoil pile and the Buttress. The lime occurs as layers up to about 20 cm thick. The lime was evidently spread by a dozer after being dumped on top of previously leveled broken rock. No indication of lime is evident in the underlying or overlying broken rock. The lime is present only in the thin layers. Physically, the lime layers are soft and plastic, or have lithified into a concrete layer, but both appear completely impermeable.

Figures 6 to 10 show the results of overburden analyses of drillholes through the Skytop, Seibert and Buttress areas. The overburden samples were analyzed by the method of Sobek, et al. (1978) as described by Kania (1998). The rock chips were analyzed as samples over at least0.6 m intervals. The %S values have been converted to Maximum Potential Acidity (MPA) in % $CaCO_3$ equivalents by multiplying by 3.125 based on weights of S and $CaCO_3$ in the equation:

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O = Fe(OH)_3 + 2\ SO_4^{2-} + 2\ Ca^{2+} + 2\ CO_2\,(g) \quad (1)$$

The original Neutralization Potential (NP) values in Tons/1000 Tons have been divided by 10 to be in % $CaCO_3$ equivalent. The MPA and NP values are thus in comparable units (though note that if outflow pH exceeds about 6 without loss of CO_2, more $CaCO_3$ may be required, Cravotta, et al., 1990). Note also that only about half or less of the rock removed from the large cut was pyrite-bearing, because the top section was weathered, and the Reedsville shale to the east has only low sulfide contents but does contain some carbonate.

Table 3. Chemistry of seepages from pyritic rock

	Units	Skytop Seeps[1]	Seibert[2]	Bifurcation[3]
pH		2.4	2.0	2.7
Alkalinity	mg/L as CaCO3	0	0	0
Acidity	"	9545	2126	2896
Fe	mg/L	1532	283	91
Mn	"	18.9	19	15
Al	"	636	152	412
Ca	"	354	149	256
SO4	"	8973	2519	4473
As	"	0.56	ND	0.03
Zn	"	39.5	13	5

[1] Median of 15 samples collected 11/03 to7/04

[2] Sample from base at pond, 4/2/04, PA DEP

[3] Median of 13 samples from MW 45D, 1/05 to 4/06

Figure 4. Photograph of face near top of Skytop pile showing two lime layers in the pyritic rock pile.

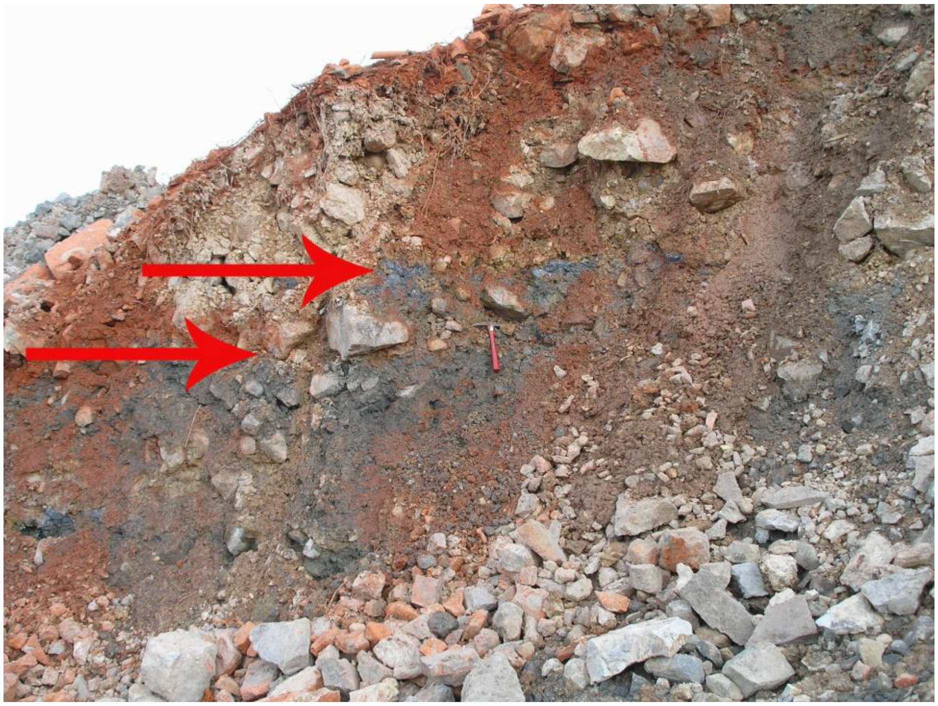

Figure 5. Photo of trench wall cut into the Buttress after Bauxsol slurry was sprayed onto the surface. Gray layer just above hammer is a lime layer; another is just at the level of the hammer. Red stain is from Bauxsol, but below the lower lime layer it has fallen onto the face from above after the trench was cut. Nearly all Bauxsol is above the lime layers

Discussions with PENNDOT personnel indicate that the overburden analyses may underestimate the amount of lime and sulfur present. The holes were drilled by air-rotary methods, and cuttings were captured in a coarse sieve, which probably failed to collect some dust-size lime and rock. It is also possible that the lower parts of holes extend into pre-existing soil and colluvium.

In general, the NP shows sporadic high values of 5 to 60 which evidently represent lime-bearing layers (pure $CaCO_3$ would furnish a value of 100 but is expected to be diluted in the 0.6 m samples). Most of the remaining NP values are less than 1, and may represent minor neutralization by calcareous Reedsville shale included in the broken rock, or reaction with silicates such as chlorite or clay.

In most of the overburden holes, the total amount of NP exceeds the MPA, which means there should be no acid outflow if reactions among the minerals and solutions are complete. Calculations show that in holes OB-1, -2, -3 and -8, the total mass of NP exceeds the MPA by a large margin, and ratios of NP/MPA are 3.71, 1.29, 3.98 and 2.65, respectively. Only hole OB-3 has a deficiency of NP when the entire hole is considered (NP/MPA = 0.75).

Despite the large excess of lime, all three piles generated extremely acid water, as indicated in Table 3. This behavior is attributed to the lack of NP in rock layers up to 3 m thick, as shown by the layering of lime addition and observations of lime layers when the Skytop pile was removed (Fig. 4) and the Buttress was trenched (Fig. 5). In these zones of broken pyritic rock lacking NP, acid metal-rich solutions can be generated and flow downward in the pile. If the solutions encounter lime, there will be some initial neutralization, causing precipitation of Fe oxyhydroxide and gypsum on the surface of the lime layer. However, because the lime layers are impermeable, there is little or no flow through the layers. The lime is armored from any later acid solutions by the Fe and gypsum coatings, so the lime is ineffective. As discussed later, lime in layers is much less effective than lime mixed thoroughly with the pyritic rock.

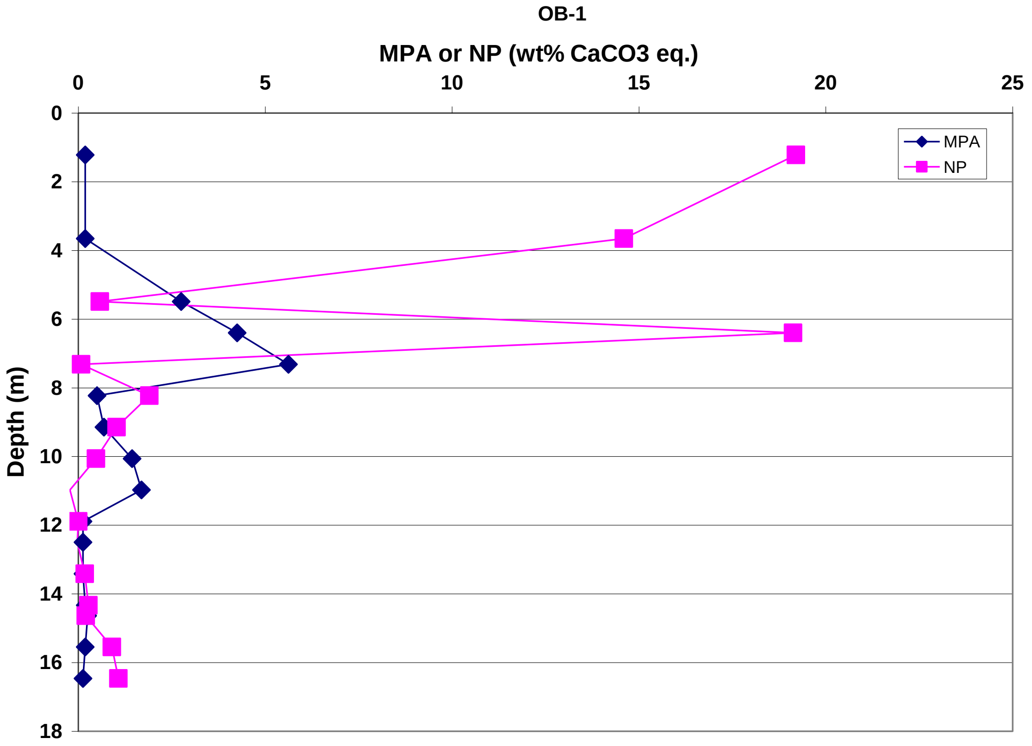

Figure 6. Maximum potential Acidity (MPA) and Neutralization Potential (NP) in overburden hole OB-1 in the Skytop pile .

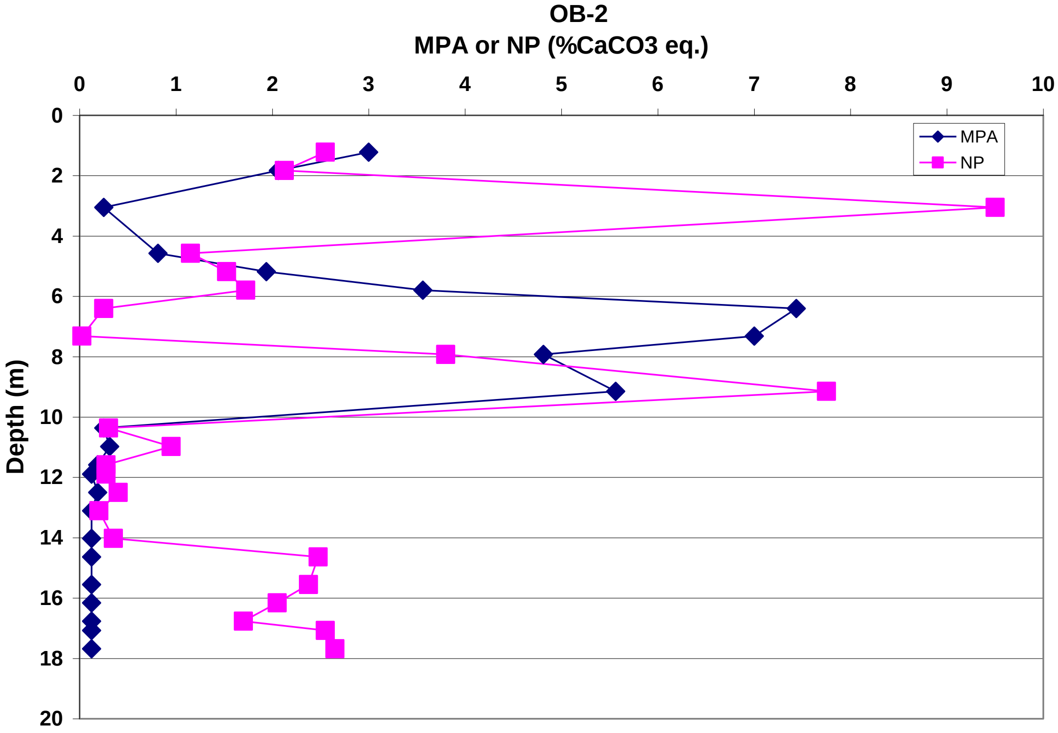

Figure 7. Maximum potential Acidity (MPA) and Neutralization Potential (NP) in overburden hole OB-2 in the Skytop pile .

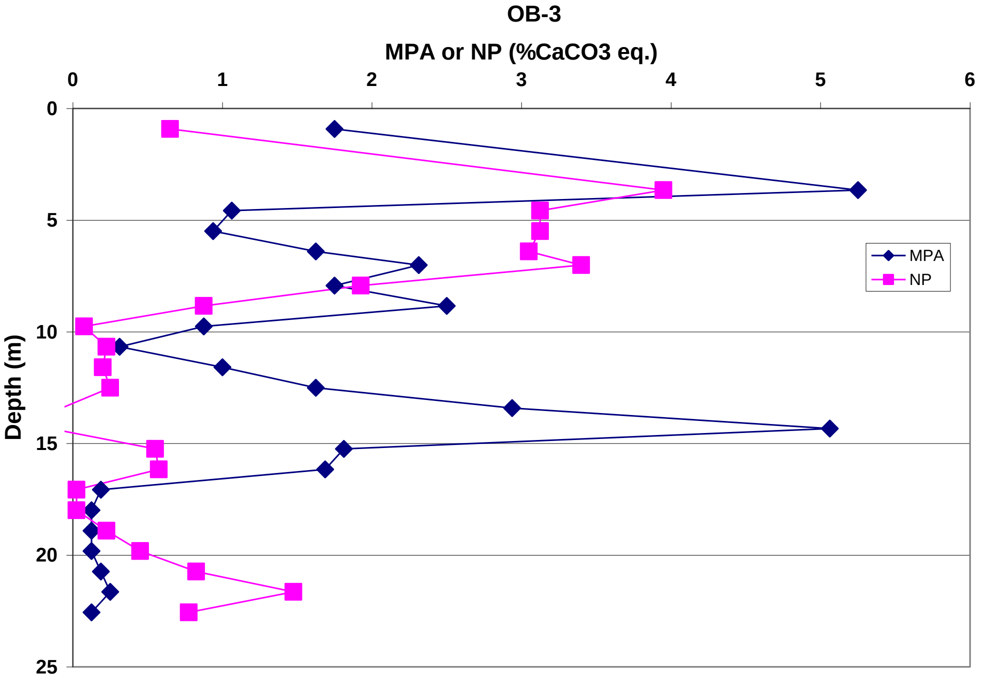

Figure 8. Maximum potential Acidity (MPA) and Neutralization Potential (NP) in overburden hole OB-3 in the Seibert pile .

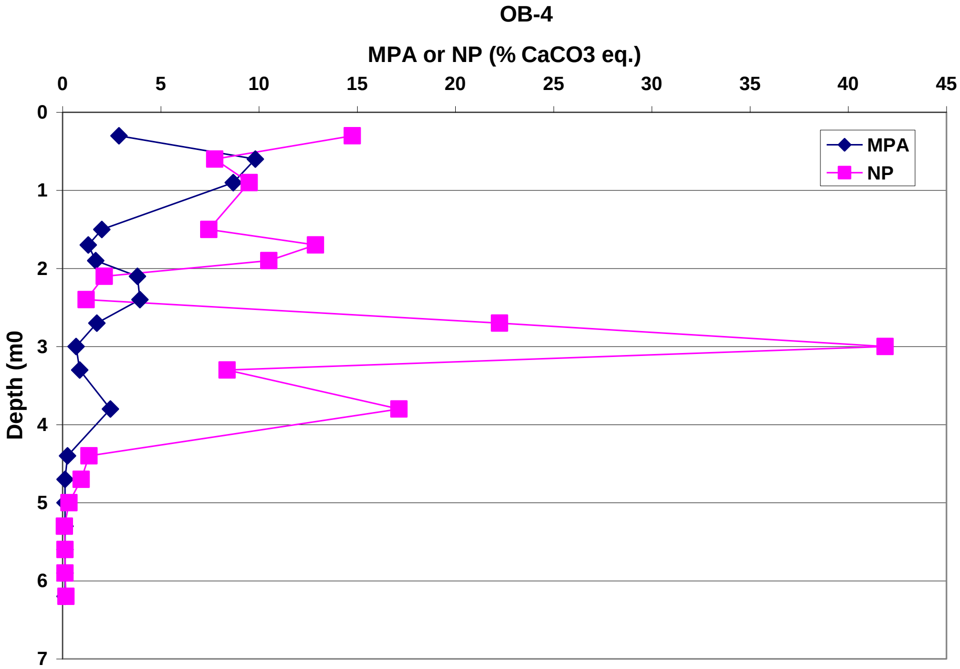

Figure 9. Maximum potential Acidity (MPA) and Neutralization Potential (NP) in overburden hole OB-4 in the Seibert pile .

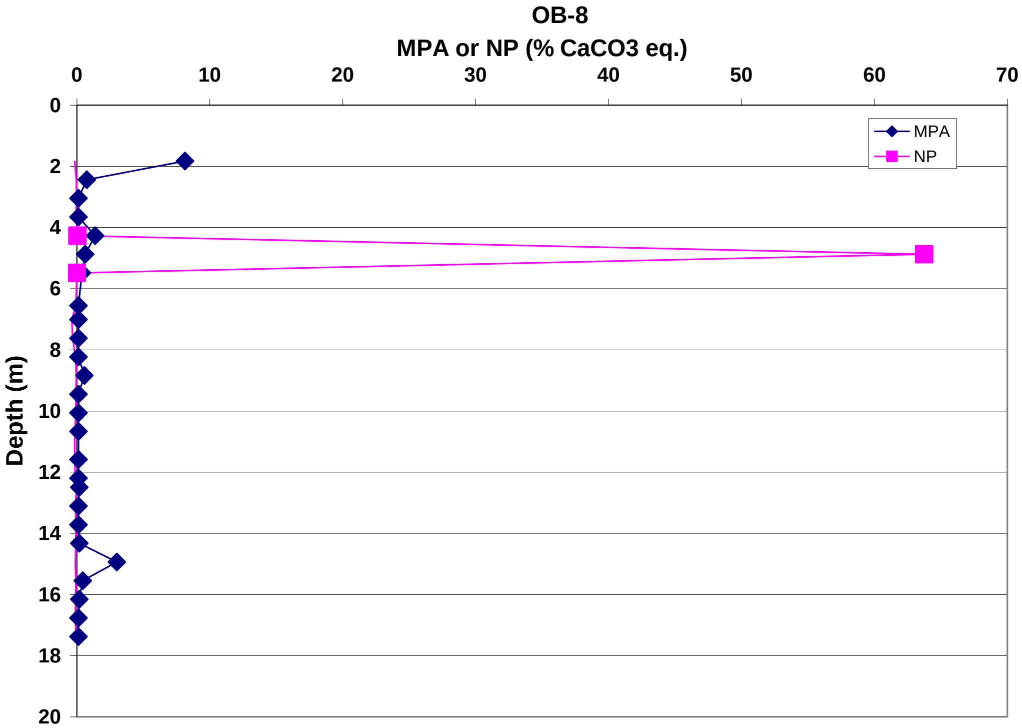

Figure 10. Maximum potential Acidity (MPA) and Neutralization Potential (NP) in overburden hole OB-8 in the Buttress pile .

In another situation, lime was dumped on top of a pile of rock (mainly Reedsville shale) adjacent to a cut about 1 km east of Skytop (Fig. 11). Seepage from this layering had high pH's, in the range of 8.8 to 12. Examination of the pile suggests that the sampled seeps are water flowing on the surface or very shallow subsurface of the lime, and not penetrating the broken shaly rock. The high pH values from this situation may be as toxic to biota as the ARD from pyrite.

Bauxsol Treatment

In August 2005, PENNDOT accepted a proposal from Virotec USA Inc. to conduct a pilot investigation of their proprietary product Bauxsol™ as a means of remediating the acid generation. The pilot study was conducted at the SW end of the Buttress area, where monitoring wells indicated appreciable acid generation. Occasional boulders of pyritic rock were observed at the surface in this area. The NP distribution in overburden hole OB-8 is probably typical of this area (Fig. 10), but some zones in the larger Buttress probably contain more pyrite.

Figure 11. Photo of pile of rock (mainly Reedsville shale) near Matternville school covered with piles of lime. The seeps along the front of this pile had high pH from flow over the lime.

The main ingredient of Bauxsol is the residue left from leaching alumina out of bauxite ore (McConchie et al., 1999). Bauxite is a highly weathered tropical soil with high contents of Al along with considerable Fe and small amounts of clays and other constituents. The alumina is leached with strong caustic, leaving a highly alkaline mud that is then neutralized with seawater at some processing plants. The seawater converts some of the alkali to various carbonates, hydroxides and alkaline silicates. X-ray diffraction analyses show 31% hematite (Fe_2O_3), 19% gibbsite ($Al(OH)_3$), 14% sodalite ($Na_4Al_3(SiO_4)_3Cl$), 11% goethite (FeOOH), 5% anatase (TiO_2), 4% halite (NaCl), 4% calcite ($CaCO_3$) and 2% quartz (SiO_2) in a sample of Bauxsol from the site (Barnes and Gold, 2008). A neutralization potential of a few % $CaCO_3$ equivalent has been found for some samples, but additional slow neutralization is possible from the alkaline silicates in the Bauxsol. Virotec reportedly added additional alkaline materials, such as MgO, to the neutralized material to provide rapid neutralization of immediately available acidity, but quantitative data on these amounts are not available.

The application of Bauxsol at the I-99 site was conducted between August and November 2005, and monitoring was completed in 2006 (McNally, 2006). Two methods of application were attempted. First, a slurry of about 10% Bauxsol was sprayed onto the surface of the Buttress. The intent was that the slurry would infiltrate the broken rock and provide neutralization of acidity, as well as inhibition of further acid generation. Second, Bauxsol slurry was injected into a series of horizontal drillholes cased with perforated pipes under the raised lane (the “Bifurcation”) to neutralize acidity from the pyrite in the rock used to raise the lane.

During August through November 2005, about 300 tons of Bauxsol in slurry form was sprayed onto the Buttress. Virotec intended to apply about 6 times as much, but much of the Bauxsol accumulated on the surface rather than infiltrating the broken rock. A possible factor contributing to lack of infiltration is that the Bauxsol used contained a considerable proportion of sand-size particles that settled out rapidly and plugged the void space between particles at the surface. Additional slurry flowed over this surface mud-cake and had no effect. Analyses also show that the Bauxsol supplied to the project was relatively low in neutralization potential.

Trenches excavated into the Buttress after the spraying of slurry showed that the red Bauxsol typically penetrated only about 15 cm into the material of the Buttress (Fig. 12). Actually, when first excavated, this zone was green from the development of “green rust”, a ferrous-ferric hydroxysulfate phase. The “green rust” oxidized rapidly to red (Fe oxyhydroxide) with release of acid. At a couple of localities the red Bauxsol had moved down channels until it encountered a layer of lime. Based on red staining, the slurry above the lime layer apparently moved laterally, but beneath the lime layer, there was essentially no indication of any penetration of Bauxsol. The lime layers acted as aquicludes, preventing downward flow of the slurry.

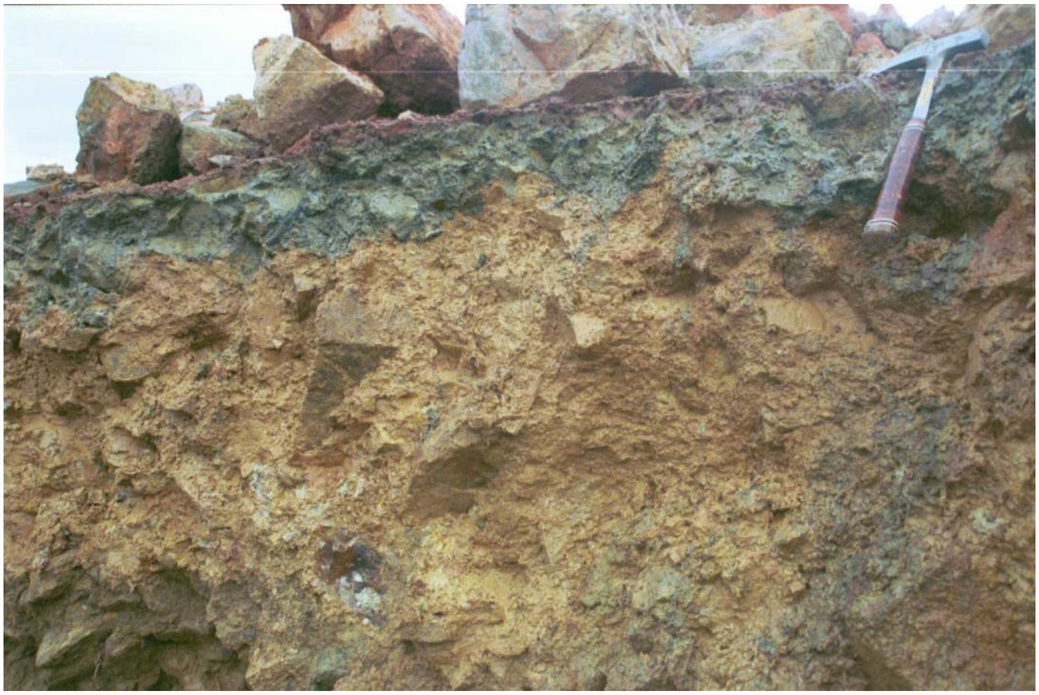

Figure 12. Photo of trench wall excavated in the Buttress area where Bauxsol slurry had been sprayed on the surface. The green zone contains the green rust phase that turned red in a few hours after exposure.

A monitoring well at the base of the Buttress showed strongly acid water prior to the pilot test (pH 2.9 to 3.0; acidity 1100 to 2400 mg/L), followed by slight improvement during late 2005 (pH 3.7-4.3, acidity 190 to 964 mg/L) followed by return to relatively acid conditions in late 2005 and early 2006 (pH 3.1 to 3.2, acidity 900 to 1250 mg/L). All samples had high SO_4 (2500 to 5000 mg/L) indicating continuing oxidation of pyrite. Clearly the Bauxsol spraying had little effect except superficially on the slope surface.

Injection into the horizontal boreholes under the Bifurcation also was ineffective. Water dripping from some boreholes had pH 11 to 12, a few others had pH 6 to 8 and still others had pH 2.5 to 4. The pH 11-12 water is probably due to lime in the road fill, and the pH 2.5 to 4 represents pyrite continuing to generate acid, and the near-neutral pH may represent water treated by Bauxsol containing MgO or by partial neutralization with lime. Again, the Bauxsol injection at best accomplished partial remediation.

In summary, the Bauxsol experiment was judged to be unsuccessful.

Mixing with Alkaline Ash

In 2005-06, the possibility of moving the pyritic rock to a coal refuse site in Indiana County and mixing with alkaline ash from circulating fluidized bed (CFB) combustion was evaluated. Several specialized electric generating plants near Ebensburg and Johnstown produce this ash. The fuel for these plants is abandoned piles of coal refuse containing 40 to 70% coal mixed with rock. The refuse is ground to about 0.5 cm and mixed with limestone. When burned in the CFB, the limestone is decarbonated to CaO which reacts with SO_2 to form Ca sulfites and sulfates. An excess of limestone is provided to ensure fixation of sulfur. The excess CaO (later converted to $Ca(OH)_2$ and $CaCO_3$) provides appreciable neutralizing power in the resulting ash.

To evaluate the ability of the CFB ash to neutralize acidity and inhibit its generation, a series of bucket tests was conducted on mixtures of Skytop rock with CFB ash. The mixtures used had ash/rock ratios of 0.5, 1 and 1.5, plus a control with no added ash. The rock fragments were a maximum of 5 cm in dimension, with an average of 2.5 wt. %S in one set and higher %S in another. The ash had a Neutralization Potential of about 150-200 T/1000T (15-20% $CaCO_3$ equivalent). The ash and rock were thoroughly mixed before placement in the 19 L buckets. On a weekly schedule, the buckets were filled with water to the rock surface and after one day were drained and the moist rock left to oxidize for 6 days. Typically, 3 to 4 liters of water were added and drained each week.

Figure 13 shows the pH of the leachates over a 15 week period. The untreated rock generated pH's near 2 for the entire period. The mixtures generated pH above 10.5, as expected from the presence of CaO and $Ca(OH)_3$, which are capable of producing pH's exceeding 12. These experiments and other previous tests on this material have shown that with at least a 1:1 ash/rock ratio, the leachate is alkaline if the ash and rock are well mixed. However, if mixing is incomplete, some acid leachates are generated.

The conclusion of these tests and other investigations was that a 1:1 mixture of ash and Skytop rock would not generate acid in the placement site, <u>if the ash and rock were well mixed</u>. However, residents of the placement area strongly objected to placing the material in their

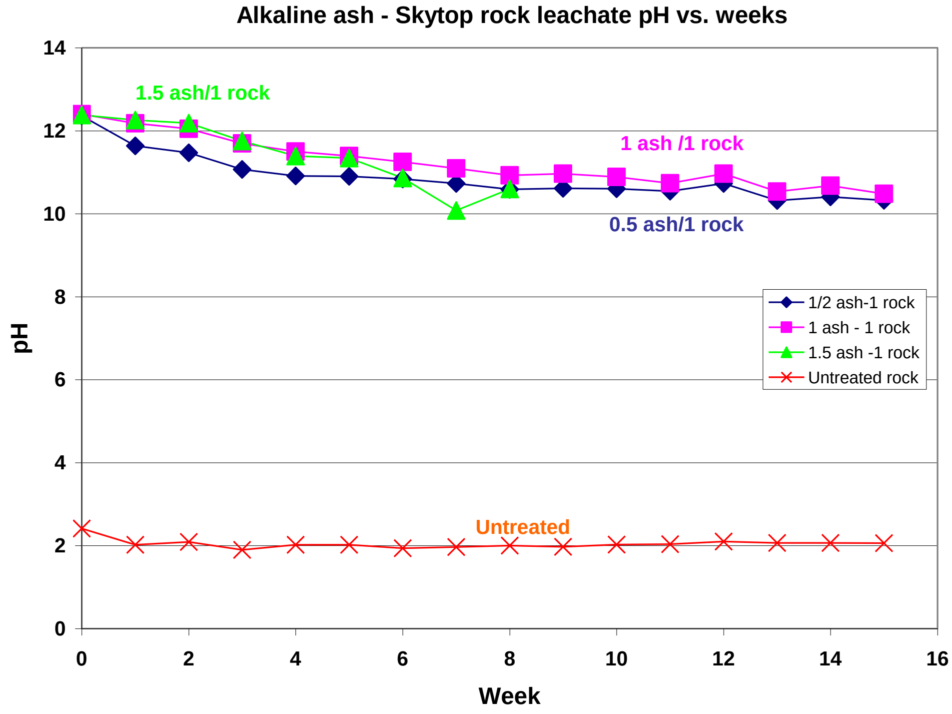

Figure 13. Values of pH in leachates from bucket tests of mixtures of Skytop pyritic rock with alkaline CFB ash, conducted by Meiser and Earlfor Robindale Energy Services, Inc. neighborhood and the traffic that would be generated. As a result, this plan was dropped.

Experiments with Slurries of $Mg(OH)_2$, Bauxsol and Limestone

While the Bauxsol test was being planned, small-scale alkaline addition tests of three materials were initiated (Barnes and Gold, 2008). A key distinction was the use of $Mg(OH)_2$ slurry in one test. This phase acts as a buffer to pH, controlling the pH initially to about 9. Such a value is more acceptable environmentally than the very caustic pH 11-12 set by lime. The $Mg(OH)_2$ was supplied by Premier Chemicals, Middlebury Hts., OH and contained 96% $Mg(OH)_2$. Other slurries were made from Bauxsol and from limestone powder. The Bauxsol was from the supply stockpiled for the Virotec test, and the limestone powder was from Graymont, Inc., Pleasant Gap, PA (97% $CaCO_3$). All three reagents were nominally <325-mesh material.

The tests were conducted in three 5.4 m^3 concrete septic tanks lined with an impermeable sealant. The tanks were filled with 9.1 metric tons of crushed pyritic rock containing about 1.0% S. The top 0.3 m and the bottom 0.4 m of the tank filling were AASHTO 2A pyritic aggregate (up to 5 cm diam.), and the middle 0.46 m was coarser R3 aggregate (<15 cm). An un-reactive quartz sand layer at the bottom provided drainage to a valve for sampling. The filled tanks were washed initially with spring water, then Bauxsol slurry (4 % by weight in spring water) was added to tank 1, 4% $Mg(OH)_2$ slurry to tank 2, and 4% powdered limestone slurry to tank 3. Samples of leachate were collected daily and the pH measured. On day 19, the pH of effluent from the Bauxsol tank was still very acid, so the added slurry concentrations were doubled, to 8% in all tanks on days 20 and 21. The detailed sequence of activities over 652 days is described by Barnes and Gold (2008).

Figure 14 shows the pH of the effluent from the 3 tanks during this period. Except for brief periods, the effluent from the Bauxsol tank was acid, in the range 3 to 4.5. The effluent from the $Mg(OH)_2$ tank was nearly always above 6, and reached 9 in the later period of the experiment. The effluent pH from the limestone tank was less than 5 much of the time (Fig. 14), but did show values above 6 during slurry addition and from days 37-56 after draining on day 37.

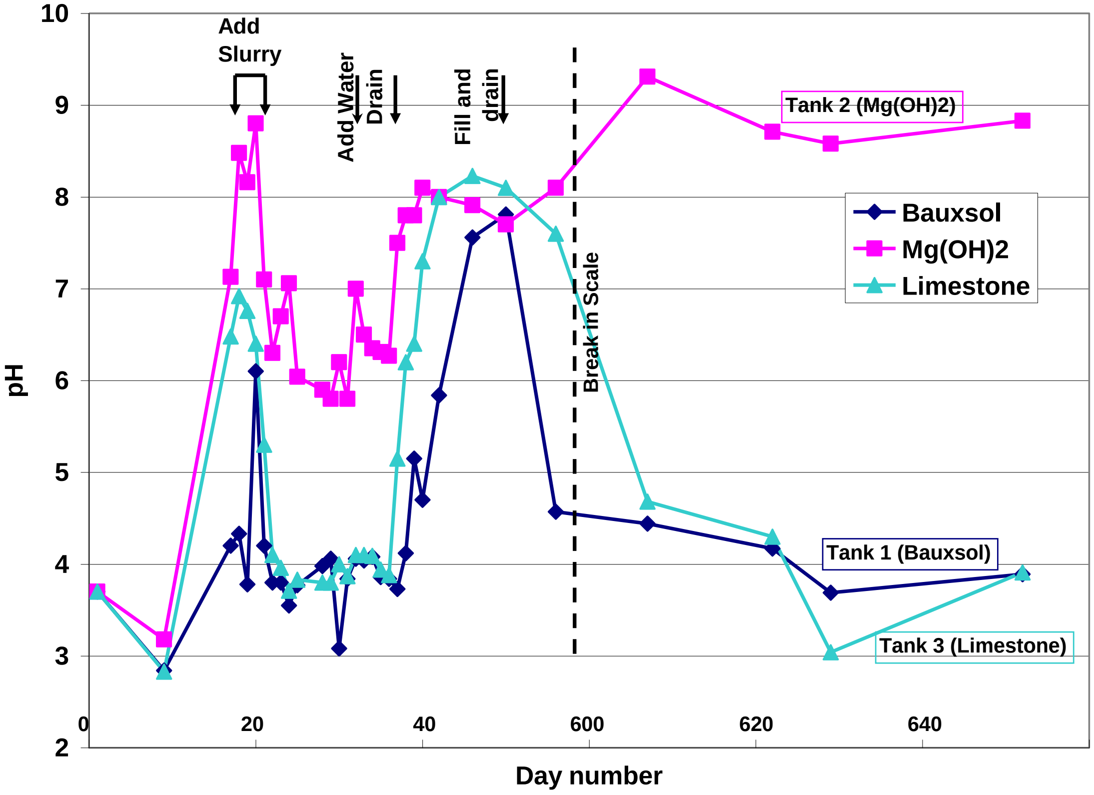

Figure 14. Plot of pH values of effluent from tank experiments, versus day number. Note break in scale at 60 days.

The results indicate that the $Mg(OH)_2$ slurry was considerably more effective in maintaining neutral to alkaline pH than was the limestone slurry. At least part of the reason is that $MgSO_4$ is considerably more soluble than $CaSO_4$, so that coatings are not a problem as with lime and limestone. The Bauxsol slurry was ineffective, probably because it had relatively little rapidly available neutralization potential, and contained too large a proportion of less reactive, coarser particles that plugged the surface. The limestone slurry was also ineffective much of the time, probably in part because of coating with gypsum.

Discussion

The addition of large amounts of lime as layers to the Skytop spoil piles was ineffective, despite the fact that the amount of lime was generally several times that necessary to neutralize all acid produced by oxidation of the pyrite in the piles. This outcome is similar to that found by Rose, et al. (1995) in experiments with pyritic rock at a coal mine. In that case, the lime was partially mixed into the pyritic shale, and the acidity of the effluent was considerably reduced, but was still pH <3.

The bucket tests in which the alkaline ash was thoroughly mixed with the pyritic rock were successful in preventing acid effluent. In a full scale project at Seward, PA, alkaline ash was thoroughly mixed with pre-existing piles of pyritic spoil, and acid generation ceased. These results indicate that thorough mixing of alkaline materials with pyritic rock can be effective in preventing acid release. In addition to mixing effects, the cementitious properties of the alkaline ash transform the spoil materials into a solid monolithic mass which greatly reduces permeability and water infiltration.

The success of the tests with $Mg(OH)_2$ slurries indicate that this reagent has promise as an alkaline material for prevention of acid rock drainage. Further tests on mixtures of this compound with limestone and clay indicate superior ability of the mixtures to coat fragments of rock (Barnes, 2007).

Conclusions

1. Excavation of about 900,000 m^3 of sandstone containing about an average pyrite content of about 4.5 wt % caused severe acid rock drainage from the piles and fills into which the rock was placed.

2. Addition of considerable “lime” as layers into the upper parts of the piles was ineffective in neutralizing or inhibiting acid generation. The “lime” acted as impermeable layers which rapidly became armored by Fe oxyhydroxides and gypsum from percolating acid solutions.
3. Attempts to inject a Bauxsol slurry into the rock piles were unsuccessful, because the slurry plugged the surface, and was also diverted by impermeable layers of lime. The test site for this experiment continued to seep acid water.
4. Lab experiments in which the pyritic rock was thoroughly mixed with alkaline CFB ash were successful in producing alkaline leachate. These tests and other case studies indicate that thorough mixing can be successful in preventing acid generation from pyritic rock. However, a large excess can cause caustic, high pH outflows.
5. Tests with $Mg(OH)_2$ indicate that it can be effective when added as a slurry to piles of pyrite-bearing spoil.

Acknowledgements

We are greatly indebted to the Pennsylvania Department of Transportation and to numerous of its managers and employees. In particular, Dr. Tom McNally, Chief Construction Manager with PENNDOT for the I-99 project, was very helpful on many occasions and furnished crucial information on construction and alkaline addition activities. Prof. D.P. Gold of Penn State University collaborated on many aspects of the studies, as did Dr. Ed Meiser of Meiser and Earl, Inc. of State College. Robindale Energy Services, Inc. initiated and funded studies of mixtures with alkaline ash and sampling of the Skytop cut.

References

Barnes, H. L., 2007. US Provisional Patent Application, Serial No. 60/893,508.

Barnes, H. L., 2006. Supplement to a proposal for use of the ERPA disposal site. Report to PENNDOT, June 14, 2006. 10 pp.

Barnes, H. L and D. P. Gold, 2008. Pilot tests of slurries for in situ remediation of pyrite weathering products. Environmental and Engineering Geoscience, v. 14, p. 31-41. http://dx.doi.org/10.2113/gseegeosci.14.1.31.

Centre Daily Times, 2003. Acid from I-99 site leaks into stream. 11/21/03, p. A 1.

Centre Daily Times, 2007. Costs climb again. 11/11/07, p A 1.

Cravotta, C. A., K. B. C. Brady, M. W. Smith and R. L Beam, 1990. Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage: Part I. Geochemical considerations. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Ed. By J. Skousen, J. Sencindiver and D. Samuel, West Virginia University, p. 221-225.
https://doi.org/10.21000/JASMR90010221

Gold, D. P., A. G. Doden, R. Mathur, L. G. Mutti, F. Barra and A. A. Sicree, 2006. Sulfide occurrences in Central Pennsylvania. Geological Society of America, Northeastern Section (41st meeting). Field Trip Guidebook, p. 96-105.

Kania, T., 1998. Laboratory methods for acid-base accounting: An update. In Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, ed. By K.B.C. Brady, M.W. Smith and J. Schueck. PA Department of Environmental Protection, p. 6-1 to 6-9.

McConchie, D., M. Clark, C. Hanahan and R. Fawkes, 1999. The use of seawater-neutralised bauxite refinery residues (red mud) in environmental remediation programs. *In*: I. Gaballah, J. Hager and R. Solozabal (eds.) *Proceedings of the 1999 Global Symposium on Recycling, Waste Treatment and Clean Technology,* San Sebastian, Spain. The Minerals, Metals and Materials Society, **1:** 391-400.

McNally, T., 2006. Report on Virotec USA Inc. Bauxsol pilot test conducted on Interstate 99 construction site, Centre County, Pennsylvania. Unpublished report to PENNDOT. 14 pp.

Rose, A. W., L. B. Phelps, R. R. Parizek and D. R. Evans, 1995. Effectiveness of lime kiln flue dust in preventing acid mine drainage at the Kauffman surface coal mine, Clearfield County, Pennsylvania. Proc. 12th Annual Meeting, American Soc. for Surface Mining and Reclamation, Gillette, WY, June 5-8, 1995, ed. by G. E. Schuman and G. F. Vance, p. 159-171.
https://doi.org/10.21000/JASMR95010159

Sobek, A. A., W. A. Schuller, J. R. Freedman and R. M. Smith, 1978. Field and laboratory methods applicable to overburden and minesoils. U.S. E.P.A. Report EPA-600/2-78-054.

Thompson, A. M., 1970. Geochemistry of color genesis in red bed sequence, Juniata and Bald Eagle formations, Pennsylvania. Journal of Sedimentary Petrology, v. 40, p. 599-615.