APPENDIX 8

Assessment of Acid Sulfate Soils

Occurrence

Acid sulfate soils have been identified in coastal environments for three or four decades (van Breemen, 1973; van Breemen, 1982), but it is only in recent years that serious environmental problems, similar to acid mine drainage, have been recognized. These soils have been thoroughly investigated along the coastlines of Australia, Southeast Asia and West Africa. They have also been documented on the coastal plain in the eastern United States within the past ten years.

Acid sulfate soils are produced by the weathering of sulfide minerals in sediments exposed by human activities or lower water levels in coastal regions. The soils are characterized by low pH and the presence of sulfuric acid. Groundwater and surface water in acid sulfate environments have been affected by increased concentrations of metals, among other factors.

Acid sulfate conditions are of special concern in Australia because the soils of that continent are among the most fragile in the world due to salinization, low nutrient levels and climatic factors (Diamond, 2005). Added loss of soil productivity due to acidification may not be easily reversible under those conditions, and consequences may persist for generations. It has been estimated that acid sulfate soil covers 40,000 square kilometers in Australia. For those reasons, research literature and environmental regulations are more comprehensive there than elsewhere.

Coastal acid sulfate soils appear to be more widely distributed than is commonly appreciated. They have recently been recognized in the tidal marsh environments around the Chesapeake Bay, and in uplands where Cretaceous and Tertiary sediments have been exposed by the building of highways and other construction activities (Fanning, 2006; Hussein and Rabenhorst, 1999). Similar occurrences have been observed on the Virginia coastal plain (Orndorff and Daniels, 2002). The latter authors state that:

> "Excavation through sulfidic geologic materials during road construction has resulted in acid drainage related problems at numerous discrete locations…Acid sulfate weathering problems in the Coastal Plain primarily result from exposure of unconsolidated Tertiary marine sediments, particularly those mapped as the Chesapeake Group and Lower Tertiary deposits."

Similar environmental impacts have been known from mining environments for a long time (Hammarstrom and Smith, 2002). A widely recognized impact is the liberation of heavy metal species that have been adsorbed onto clay particles or fixed in relatively stable complexes. Depending on the metals species, adsorption frequently changes from nearly total to less than 10% with a decrease of one or two pH units (Salomons and Förstner, Chapter 2.5, 1984). The threshold range depends on the cation involved and clay characteristics, but even a temporary drop in pH can release quantities of metals that may enter the ground water and persist for some time.

In coastal acid sulfate soils, the concentrations of inorganic sulfur are generally higher in sediments with more clay. The consequences to groundwater and surface water can be

greater in the case of sandy sediments, however, because exposure to water can rapidly produce acid and release metals, as noted in numerous Australian publications. Orndorff and Daniels (2002) note that:

> "Many of the Virginia coastal plain observations in this publication correspond to those in the Australian literature, including very low pH (2.5 to 3.5) of exposed soils, the presence of yellow jarosite and red redoximorphic features in oxidized sediments, and high levels of iron, aluminum and manganese in groundwater."

It is very likely that acid sulfate soils, or those with a potential to develop such conditions, are present in many coastal plain locations where they have yet to be recognized. It is also possible that impacts from acid sulfate conditions have not been recognized because drainage leading to acidification has not been extensive, or because a loss of soil productivity was ascribed to other causes. The release of trace metals is likely to go unnoticed except for those exceptional cases where potential acid sulfate conditions exist, site drainage or other conditions have locally depressed the water table, and groundwater monitoring is ongoing.

There are two steps involved in the development of acid sulfate conditions in coastal settings. The first involves the formation of pyrite in reducing environments, leading to potential acid sulfate soil (PASS). The second step, which may occur much later, is associated with the exposure and oxidation of the pyrite, producing actual acid sulfate soil (AASS). These aspects will be considered in turn.

Formation of Potential Acid Sulfate Soils

The genesis of potential acid sulfate soils involves the growth of microscopic pyrite framboids in an anoxic or oxygen-poor environment. Framboids are spherical clusters of pyrite grains, with size ranging from 5 to 20 μm, and are formed by bacterial reduction of sulfate to sulfide, partial oxidation of sulfide to elemental sulfur, and interaction between ferrous or ferric iron with sulfide and elemental sulfur.

Therefore, the requisite factors are (1) a sufficient supply of sulfate, (2) a supply of iron, (3) large amounts of metabolizable organic matter, (4) sulfate reducing bacteria (typically Desulfovibrio desulfuricans and Desulfomaculatum species), and (5) an anaerobic environment alternating with limited aeration.

In that context, it is worth noting that the anoxic conditions may prevail in a microenvironment, such as the upper portion of the sedimentary column or lowest portion of the water column. Also, anoxic conditions may form in eutrophic systems (having a large supply and rapid flux of organic material) after the oxygen-consuming bacteria have removed most of the dissolved oxygen.

In addition, several researchers have pointed out that tidal environments not only supply sulfur but also flush away the metabolic byproducts of bacterial action. Tidal action removes a part of the alkalinity in the form of bicarbonates (HCO_3) formed during sulfate reduction. The resulting slightly acidic conditions kinetically favor pyrite formation.

Environments that possess these characteristics are generally coastal lagoons, salt marshes, and estuaries. Seawater provides dissolved sulfate. Terrigenous sediments provide a source of iron. Salt-resistant vegetation within marshes or adjacent to lagoons provides abundant organic matter on which the bacteria feed. Tidal flushing is strong in areas dissected by tidal creeks, commonly found near river mouths and in areas surrounding lagoons.

Hussein and Rabenhorst (1999) present the following connection to transgressive conditions:

> "In areas of transgressing coastlines where the sea level is rising, coastal marshes begin to form as low-lying upland soils become progressively inundated with brackish tidal waters until they become permanently submerged…Among the acquired properties reflecting such a change [are] the formation of organic horizons and the accumulation of S in both organic and mineral forms. Pyrite (FeS_2) is the principal mineral phase and forms through the process of sulfidization. Factors necessary for the formation of pyrite have been described by others (Pons et al., 1982) … and are ideally met in coastal marsh soils."

Where swamps are normally covered with dense stands of Rhizophora and similar plants, sediments with large quantities of clay have accumulated and that can be a source of iron. Those terrains are commonly characterized by extremely high contents (2–6 %) of pyrite. With regard to marshes in the Chesapeake Bay area, Hussein and Rabenhorst (1999) found that:

> "Organic S was the dominant S fraction in the organic horizons. … where high n-value [standard penetration test results] mineral sediment of estuarine origin lay beneath the organic materials, chromium-reducible S [inorganic sulfur, e.g. pyrite] rather than organic S was the dominant S fraction in the mineral sediment, presumably because of the higher levels of sorbed reactive Fe and relatively low organic-C content in these sediments."

Iron availability can be a limiting factor in pyrite formation, not only for organic (peaty) sediments, but also in sand. Less pyrite is also said to accumulate in the permanently reduced zone below the lowest groundwater level. However, PASS can include predominantly sandy sediments. According to the Australian Environment Protection Authority (1999):

> "Most acid sulfate soils were deposited during the Holocene geological age (the last 10,000 years) … However, they may be as old as the Tertiary geological period (more than a million years ago) – for example, some of the sandy formations underlying the south-eastern suburbs of Melbourne such as the Brighton Group. Present-day estuarine and marine sediments may also have acid sulfate properties…"

Speaking of acid sulfate conditions in Tertiary marine deposits on the Virginia coastal plain, Orndorff and Daniels (2002) note that:

> "These sediments occur in drab shades of green, blue and gray, and consist of fine- to coarse-grained, quartzose sand, silt, and clay. … Sulfides occur as abundant dispersed framboids, clusters of microcrystals, and small, weathered, subhedral grains of pyrite."

Potential acid sulfate soils that remain saturated do not become acidic until they are exposed to air. The soils and associated groundwater are generally neutral in pH and may remain so for thousands of years. However, there is no absolute demarcation between potential and actual acid sulfate soils. Partial oxidation of the pyrite may occur in zones that have intermittently or partially dried out, for example due to fluctuations in groundwater levels.

Formation of Actual Acid Sulfate Soils

Actual acid sulfate soils (AASS) form when PASS are exposed to the atmosphere. Oxidation of the pyrite leads to the development of extreme acidity (van Breemen, 1982). Two moles of sulfuric acid and four moles of acidity are produced from each mole of pyrite if iron is completely oxidized and hydrolyzed.

Thomas et al (2003) present a good account of the present state of knowledge about the reactions involved. The overall reaction for oxidation of pyrite is:

$$FeS_2 + 15/4\ O_2\ (g.aq.) + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-}\ (aq.) + 4H^+\ (aq.)$$

In reality, the pyrite oxidation proceeds in stages, a matter of some consequence when soil properties are considered. The first stage results in the formation of ferrous iron, sulfate and acid:

$$FeS_2\ (s) + 7/2\ O_2\ (g.aq.) + H_2O \rightarrow Fe^{2+}\ (aq.) + 2SO_4^{2-}\ (aq.) + 2H^+\ (aq.)$$

The acid can be neutralized to some degree by reaction with soil carbonates (e.g. shell fragments) or by displacing exchangeable cations. Excess acidity reacts with soil minerals, "releasing major constituents such as potassium, magnesium, aluminium and silicon, as well as trace elements such as arsenic, copper, cadmium, chromium, nickel and zinc".

Thomas et al state that the remaining acidity is exported away from the reaction site, and the ferrous iron produced in the reaction may be also. That iron can then produce an additional two moles of acid according to this equation:

$$Fe^{2+}\ (aq) + ¼\ O_2\ (g.aq.) + 3/2\ H_2O \rightarrow FeO{\bullet}OH(s) + 2H^+$$

That reaction is responsible for the frequently observed lowering of dissolved oxygen concentration in drainage waters.

But this does not exhaust the possibilities for acidification. When the pH drops below 4, the rate of pyrite oxidation is increased by the agency of the bacterium Thiobacillus ferroxidans. That organism causes catalytic oxidation of ferrous iron to ferric iron:

$$Fe^{2+}\ (aq) + \tfrac{1}{4}O_2\ (g.aq.) + H^+\ T.ferroxidans \rightarrow Fe^{3+}\ (aq.) + \tfrac{1}{2}H_2O$$

The ferric iron in turn acts as a pyrite oxidant via a very rapid electron-transfer mechanism that does not involve oxygen, but regenerates ferrous iron:

$$FeS_2\ (s) + 14Fe^{3+}\ (aq) + 8H_2O \rightarrow 15Fe^{2+}\ (aq) + 2SO_4^{2-} + 16H^+(aq)$$

Thomas et al also explain that the aluminum released from the soil matrix can produce three additional moles of acidity through hydrolysis. The details will be omitted here, but they further state that aluminum ions (Al^{3+}) do exist at low pH and are very toxic to plants and marine organisms.

Australian publications present a consistent list of field characteristics that are indicators of active acid sulfate soils. These include:

- Soil pH is less than 4.0 units.
- Water in streams, drains and groundwater has a pH of less than 5.5, often less than 4.5, and sometimes as low as 2.0 units.
- Drain waters are unusually clear or may present a milky blue-green appearance. This is produced by a high concentration of aluminum which causes flocculation of fine suspended material.
- Extensive iron stains form on drain or pond surfaces; iron-stained water and ochre deposits are present. These result from precipitation of iron when low-pH water contacts more neutral waters, or the rapid oxidation of mobilized iron at seepage locations.
- Straw-yellow jarosite horizons or iron oxide mottling are seen in auger holes or recently excavated surfaces. Where the water table fluctuates, jarosite may appear along root holes & cracks.
- Jarosite appears as surface encrustations on excavated soil that is left exposed.

Jarosite deposits, usually forming when pH is less than 4.0, are very characteristic of acid sulfate conditions. Natrojarosite, which may be bright yellow, brown or orange, forms when pH is less than 3.7 and is equally definitive. It is difficult to distinguish jarosite [$KFe_3(SO_4)_2{\bullet}(OH)_6$, i.e. potassium iron sulfate hydroxide] from natrojarosite [$NaFe_3(SO_4)_2{\bullet}(OH)_6$] without chemical testing. Both are relatively insoluble and are most stable at pH 3 to 4, but can be stable at higher pH if conditions are dry.

In addition to these, schwertmannite [$Fe_8{\bullet}O_8{\bullet}(OH)_6{\bullet}SO_4$] has recently been found to be a major component of iron precipitate accumulations in Australia (Sullivan and Bush, 2004) and in many acid mine drainage sites. It forms within a pH range of 2.8-4.5, and is initially orange in color but can become yellow-brown or reddish-brown, making it

difficult to visually distinguish from other iron precipitates. Schwertmannite is important because it stores large quantities of heavy metals in the form of anions, e.g. arsenate and chromate. Rüde et al (1997) found that:

> "Minerals like ferrihydrite or schwertmannite contribute only a few percent to the total iron concentrations. In contrary to this they are very important for the fixation of trace elements due to their high specific surface. Up to 50 % of the total arsenic concentrations are mainly sorbed by these minerals."

Schwertmannite is metastable and eventually degrades in contact with acidic water to goethite and jarosite. During that degradation, sulfate is released and acidity increases. Of interest is what happens to the trace metals. Arsenic and iron are released, but many other metals are apparently incorporated into the replacement structure (Acero et al, 2005).

The remaining question is, what happens to the trace metals that are left in jarosite and other deposits if the pH changes? The pH of groundwater may vary, in part due to infiltrating rainfall and changes in the water table. Hudson-Edwards et al (2005) investigated that issue and reached the following conclusions:

> "Jarosites are commonly found in ferric-rich, acidic (pH < 3), oxic, acid mine drainage (AMD) environments, where they are important stores of SO4 and of potentially toxic elements such as Pb and As….. The alkaline (pH 8) dissolutions all yield secondary phases…There is evidence for some co-precipitation and resorption of the Pb and As in and onto the newly-formed phases, suggesting that the remainder of these potentially toxic elements may be released back to AMD waters."

The reactions and observations presented above could be applied to the situation of a coastal soil with potential acid sulfate characteristics under drought conditions and/or dewatering. That knowledge provides a basis for informed speculation about likely sequences of events as follows:

(1) The *average* water table gradually becomes lower. Natural fluctuations in the water table on top of the general lowering allow areas of unoxidized or partly oxidized PASS to partially dry out at times and become exposed to atmospheric oxygen for longer periods than previously.

(2) The first stage of pyrite oxidation occurs and produces excess acidity. That liberates some metals that were adsorbed on soil particles. Additional oxidation stages may continue to release more acidity over time.

(3) Rainfall events produce temporary rises in the water table. That brings shallow groundwater into contact with oxidized zones. Sulfuric acid, aluminum and trace metals are released into the groundwater as a result, probably as pulses sometime after rain events. Infiltrating water may also wash these constituents downward. Thus,

a decrease in pH and increased metal concentrations may occur at times when groundwater elevations are higher.

(4) As water levels repeatedly rise and fall, deposits of jarosite, natrojarosite, schwertmannite and related minerals form in the subsurface, coating mineral grains and soil fissures. Many heavy metals are incorporated into the schwertmannite structure, which may reduce concentrations in groundwater for some time. The schwertmannite breaks down over time, releasing arsenic and iron. Many other trace elements are incorporated into remaining deposits such as jarosite.

(5) Groundwater pH fluctuates in reaction to complex interactions between punctuated releases of sulfuric acid, the differing geochemistry of layers wet by groundwater at various times, and dilution by infiltrating water. At times when pH is higher, alteration of secondary minerals (e.g. jarosite) may release bound metals. Thus, periods of slightly higher groundwater pH may be accompanied by relatively higher metal concentrations, even though those metals were initially released by low pH conditions.

(6) During periods of higher pH, some metal cations may be resorbed onto clay particles in the saturated soil. The rate is apt to vary by local pH, and also the metal species and clay species where they intersect, which may be different from the point where they were initially released from clays.

It is apparent that the relationship between water levels, pH and metal concentrations can be far from straightforward. In terms of expected consequences, we may be able to conclude that a lowering of average groundwater elevations in PASS would produce:

- An increase in average concentrations of some trace metals.
- A lowering of average pH, and often fairly low pH values at most times.
- Metal concentrations that are higher after periods of heavy rainfall, when groundwater levels have risen briefly, and persisting for some time thereafter.
- Metal concentrations whose changes may be erratically correlated with groundwater elevations that are observed infrequently, e.g. every six months.
- Either somewhat higher or somewhat lower pH accompanying higher metal concentrations.
- Sharp drops in pH that are accompanied by sharp increases in metals.

Onsite Investigation of Acid Sulfate Soils

To investigate whether acid sulfate soils are present at the Dean Forest Road facility, soils exposed in the borrow area immediately west of the fill and in the southwest landfill quadrant were observed and photographed, and their characteristics compared to known indicators of pyrite-bearing sediments. A total of 32 field peroxide tests were conducted on soil samples collected from the borrow area, and five samples were submitted for laboratory analysis.

Visual Appearance

Soils exposed in the borrow area have exhibited a great many visual characteristics of acid sulfate soils as described in the Australian literature and elsewhere. Site photographs referenced herein are included in Appendix 3. Many of the borrow area exposures are very similar to photographs in the literature. These characteristics include:

- Waterlogged soils with dark greenish-gray color. (Photos 9, 14, 19.)

- Horizons with secondary mineralization, apparently near the former elevations of the water table. (Photos 3, 15.) This is often a dark brown color typical of goetheite in its small-crystal form, and is likely to be the long-term weathering product of various iron precipitates.

- Intense secondary mineralization on the recently exposed surfaces of sediments that are apparently below the former zone of aeration. This often takes the form of pale yellow, bright yellow, brilliant orange and bright red crusts overlying dark grey or greenish grey sediments. (Photos 3, 6, 8, 13, 15 and others.) These are likely to be jarosite, natrojarosite, schwertmannite and other iron sulfates forming on the surface of sediments with appreciable pyrite content.

- Zones within the historic range of aeration that are pale-colored and appear to be partially to completely oxidized and leached (Photos 2, 3, 15, 17, 18 and others.)

- Seeps that stain exposures with bright red and yellow deposits. (Photo 18.) The staining may result from mobilized dissolved iron that forms iron oxides and hydroxides (e.g. hematite, goethite) on exposure to the air.

- Ponded water (pumped into temporary retention basins) that is either very clear or, more commonly, milky blue-green. (Photo 23.) This results from release of aluminum as mentioned previously.

Extraction in the borrow area is ending, and re-grading is now covering many former exposures. The photographs that accompany this report represent a small fraction of the digital images that illustrate the appearance of the borrow area and secondary mineralization. Additional photographs are available upon request.

Deeper (previously unoxidized) sediments throughout the borrow area exhibited the above characteristics to varying degrees. This indicates that, if related to acid sulfate conditions, the potential is present to some extent in most of the soils west of the landfill. Some of the differences may be attributed to varying degrees of dewatering and clay content that can inhibit drying compared to sand-rich and more permeable layers.

Field Tests

Soils containing pyrite will react strongly to oxidizers. A rapid and simple field test, one that can be used to screen for potential acid sulfate soils, involves the addition of hydrogen peroxide and measuring pH changes. Photo 27 shows this reaction being demonstrated during a field trip to acid sulfate soil locations on the Maryland coastal plain, while Photo 28 shows a similar strong reaction in a sample from the Dean Forest Road borrow area.

Soil samples from the borrow area were tested for potential acid sulfate characteristics using field test procedures described in the Australian literature, for example in Section H of the "Acid Sulfate Soils Laboratory Methods Guidelines, Version 2.1" (2004) and Appendix 1 of "Identification and Investigation of Acid Sulfate Soils" (2006). These publications are listed under References and included as Appendices 15 and 16, respectively.

The field test employed involves two steps. The first step is addition of water to diaggregated soil and measurement of the resulting pH, which is designated pH_F. The second step, in its simplest and most general form, involves oxidation of the sample by adding laboratory-grade 30% hydrogen peroxide and measurement of the stabilized pH_{FOX}. If pyrite is present in the sample, it will be rapidly oxidized and release sulfuric acid. Interpretation of the test is based on several factors:

- The value of pH_F. If less than 4.0, AASS is possible and oxidation has already occurred. This is not conclusive by itself because other soils, such as peat, may have low pH. If parts of the sample have yellow coloration and pH_F is less than 3.7, indications are stronger as this is the limit for jarosite formation.

- The nature of the reaction to hydrogen peroxide (e.g. mild bubbling, foaming or violent exothermic reaction). A strong reaction may not be diagnostic by itself because organic constituents can react to a strong oxidizer. A very rapid and violent reaction, however, is not likely to be due to organics.

- The value of pH_{FOX}. If less than 3.0 and there was a strong reaction, it strongly indicates PASS. The more pH_{FOX} drops below 3, the stronger is the indication of inorganic sulfides.

- The difference between pH_F and pH_{FOX}. The larger the pH decrease, the stronger is the indication of PASS. If the initial pH is near neutral, a very large drop, several units typically, can be expected.

Detailed interpretive guidelines are included in the cited publications. These references note that the peroxide test, while useful, is qualitative and cannot be used to conclusively establish the presence or absence of acid sulfate soil. One reference (Identification and Investigation of Acid Sulfate Soils, 2006) states that:

> "Recent review of field pH_F and pH_{FOX} tests in Western Australian soils indicates that these tests provide an accurate identification of ASS in only 60% to 80% of cases and are capable of providing both false positives and false negatives (i.e. may underestimate or overestimate acid-generating potential). Underestimation of acid-generating potential appears to be most common in clays and may be due to poor mixing during the field test."

Most of the field tests were not actually performed in the field, but on samples that had been tightly packed and sealed in airtight jars for several days. This was done to maximize the value of field time. Photo 29 shows an example of the bench setup, and Photo 30 shows the appearance of a sample, initially dark greenish gray, after peroxide oxidation.

Figure 25 in Appendix 2 shows the locations where samples were collected. Table 6 (Appendix 1) contains information about the samples, including the location and depth, a summary description, and identification of digital photographs of the location. Also included in this table are samples TP-1 through TP-3 from a force main excavation on the east side of the landfill, near GWC-2. They were used for descriptive purposes only and were not tested because their appearance gave no indications of acid sulfate characteristics.

Table 7 presents estimated elevations for some of the sample locations in Figure 25, based on measurements to the nearest monitoring well with a hand level. This was done to obtain some idea of the dewatered elevation on the date when the samples were collected. Based on these data, it appears that the lowered water table was only a few feet above sea level.

Data and plots for the field peroxide tests are contained in Appendix 14, along with pH meter calibrations and other information. Two of those plots are presented as Figures 26 and 27 in Appendix 2, representing a range of results.

Figure 26 shows the pH response to peroxide oxidation for duplicate analyses on samples that had already undergone some atmospheric oxidation.

AST-10 was collected from saturated sediment near the ground surface, at an elevation of around two feet above sea level. Runs AST-10a through AST-10c were subsamples tested 6 days after collection, while run AST-10d was tested 12 days after collection. The added storage time in the sample jar may have decreased the initial measurement (pH_F) by about one unit. Storage appeared to have less effect on the pH after oxidation, posssibly increasing pH_{FOX} by 0.2 to 0.3 units.

AST-14a had been stored for 8 days before testing, and AST-14b for 13 days. For this sample there appeared to have been no significant changes during storage, possibly because the sample was from a higher elevation (well above the water table) and was

more thoroughly oxidized at the outset. When the residue from this sample was heated, there was an unmistakable odor of sulfuric acid.

All of the partly oxidized samples began at pH levels around 2.5 - 3.5, and ended with pH in the 0.9 - 1.73 range.

Figure 27 shows the pH response to peroxide oxidation for aliquots from 5 samples (ASL-1 through ASL-5) that were collected at a later date for laboratory analysis. As will be discussed below, these samples were all taken by hand auger from depths of one to three feet below the surface and well into the saturated zone. These samples were similar in most respects to AST-10 and AST-14, except for their greater isolation from the atmosphere. Here the initial pH values are much higher (5.2 – 6.2) than those for the partly oxidized samples, and after oxidation they all ended up around pH 1.5 despite the spread in sample locations. The final pH appears to be generally similar to those for the oxidized samples (AST-10 and AST-14).

The peroxide tests whose results are shown in Figure 27 used a different methodology that was taken from the most recent guidance document (2006). That involved testing pH_F and pH_{FOX} on separate subsamples, so that peroxide was added directly to the dry sample rather than added to the distilled water solution used to measure pH_F. When testing the ASL-series samples, duplicate runs were tested using the older method (peroxide addition to water) and the newer method (pH-adjusted peroxide addition to dry soil). The final pH values did not differ significantly, although the strength and rapidity of the reaction was greater with the newer method. The controlling factor on pH_{FOX} appears to be the pyrite content, provided sufficient peroxide is present to permit full oxidation.

Table 8 in Appendix 1 summarizes the results of all 32 field peroxide tests and provides a brief interpretation of the results. On the second page of that table are a summary of the guidelines for interpretation and a description of test methods.

In general, the samples that appeared oxidized and/or leached (e.g. AST-3, AST-4) showed little response to the peroxide and the pH decrease was one-half unit or less. Some other samples (e.g. AST-6, AST-11) had a pH_F close to 2 but also had little decrease, and thus were probably AASS. Other samples exhibited strong exothermic reactions, as seen in the tabulated temperature rises, and pH dropped by 1 to 2.5 units. These were likely PASS that had undergone partial oxidation.

In the case of the ASL-series, expected to be the least oxidized, the reactions were extremely high or violent, temperature usually rose by 40°C or more, and pH dropped by about 3.7 to 4.7 units. Specific conductance in these samples decreased to very small values (reflecting aluminum release and flocculation), and the settling rate remained extremely rapid when vials of the slurry were shaken. These were considered almost certain to be PASS, even before laboratory results were received.

Laboratory Tests

Laboratory analysis for acid sulfate conditions is not routine in this country, and research along the Atlantic coastal plain is very recent. Australian methods appeared to be the most developed, and a copy of the "Acid Sulfate Soils Laboratory Methods Guidelines, Version 2.1" (2004) was eventually obtained (see Appendix 15). This document exhaustively describes numerous current and obsolescent methodologies, and presents detailed sample handling requirements.

Two methodologies are currently recommended for most circumstances. The Suspension Peroxide Oxidation Combined Acidity and Sulfate (SPOCAS) method is actually a suite of tests, and provides a self-contained acid-base accounting. This is most useful for determining rates of application for soil treatment, but would be overkill in the present situation where quantification of pyrite concentrations is sufficient.

Chromium Reducible Sulfur (S_{CR}) is the preferred method for estimating reduced inorganic sulfur in acid sulfate soils, and has the advantage of being immune to significant interferences from sulfur present in either organic matter or sulfate minerals such as gypsum. The method measures only reduced inorganic sulfur compounds, principally pyrite and other iron disulfides.

Although the S_{CR} methodology is fairly simple, a great deal of difficulty was encountered in finding a laboratory willing and able to perform non-routine analyses within the desired time frame. Neither commercial analytical labs nor university and research facilities within the region were willing to do this. Galbraith Laboratories in Knoxville, Tennessee has performed customized analyses since 1950, and they were able to obtain specialized materials and follow the methodology provided.

After laboratory services were secured, personnel returned to the site to obtain the samples. In the intervening month and a half, borrow pit operations appeared to have ended and much re-grading had taken place. A hand auger was used to collect samples, in part to assure that they came from below the water table and were as unoxidized as possible, but partly out of necessity because some previously sampled locations were now covered over. Other locations were difficult to reach because of quicksand conditions. These factors plus weather conditions limited the number of collected samples to five.

Samples ASL-1 through ASL-5 were obtained from locations shown in Figure 25 and described in Table 6. As seen in Photos 13, 14 and 15, a hole was augered and water level measured with a tape, and samples below the water table were carefully extracted and placed in a heavy-gauge polyethylene zip-lock bag. A representative aliquot of the soil was taken from the bag for peroxide testing and examination and placed in a clean, laboratory-supplied jar. Air in the bag was minimized by compression and the bag sealed. That bag was then placed in an outer bag, the air was again expelled, and the second bag sealed.

Samples were placed on dry ice in a cooler for overnight delivery to the lab. However, there were unexpected difficulties in getting the samples delivered on time and analyzed promptly upon receipt at the lab. Therefore, the samples were frozen on arrival and analyzed seven days after collection. Some oxidation and consequent loss of reduced inorganic sulfur might have resulted from the freezing and thawing process along with the time delay. Sample handling procedures emphasize the importance of beginning sample preparation within 24 hours, but keeping them at a cool temperature is recommended if that cannot be done.

The results of Chromium Reducible Sulfur analysis are shown in Table 8. The samples contained between 0.24% and 0.49 % inorganic sulfur, and the average is 0.35%. The laboratory report is contained in Appendix 14.

Implications

To put the S_{CR} results in perspective, it is helpful to consider the current action levels for acid sulfate soils in Australia. A management plan, possibly including soil treatment, is required when action levels are exceeded for a particular soil texture class. Action levels differ depending on whether less or more than 1000 metric tons are to be disturbed. Restrictions on dewatering and drawing down the water table are included under the regulatory requirements.

The action levels are given in terms of Net Acidity expressed as equivalent percent sulfur. The Net Acidity is Potential Sulfidic Acidity (S_{CR}) plus Existing Acidity minus Acid Neutralizing Capacity. The Existing Acidity will be quite low in the case of the ASL-series samples due to near-neutral pH_F. The Acid Neutralizing Capacity is also expected to be very low due to the fairly low apparent clay content and the absence of shell fragments (determined by hydrochloric acid tests). Thus, the Net Acidity should be essentially the same as S_{CR} in this case.

Guidelines state that the average result should not be used for comparison to action levels, but rather the highest value obtained.

For a coarse texture soil (sands and loamy sands with less than 5 percent clay), if less than 1000 metric tons are disturbed, the action level is 0.03% sulfur. For medium texture soil (sandy loams to light clays), the action level is 0.06%. Assuming a medium texture and comparing these values to the highest S_{CR} of 0.49%, the tested soil would be about 8 times the action level. The average S_{CR} value is 5.8 times the action level.

Using an approximate soil density of 100 pounds per cubic foot, 1000 metric tons would be equivalent to lowering the water table by one foot over one-half acre. If we assume a larger volume of soil disturbance, the action level for medium texture soil would be 0.03% sulfur, and the maximum S_{CR} from our analysis is 16 times the criteria. Therefore, the tested materials would certainly be considered potential acid sulfate soils (PASS) in Australia.

The site is not in Australia, of course, and many of the soil productivity concerns faced there are less pertinent in the United States as a whole, and probably not relevant in the immediate vicinity of the landfill in particular. However, the results of laboratory testing of soils from this facility, as compared to the Australian action levels, does indicate a very clear presence of Acid Sulfate Soils and the potential for those soils to cause depressed pH levels and elevated metals levels at the site.