WEATHERING OF PYRITE IN MINESOILS AT GIBBONS CREEK LIGNITE MINE, TEXAS[1]

by

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Abstract

This paper discusses the weathering of pyrite in reconstructed minesoils at Gibbons Creek lignite mine in east-central Texas. It is based on data from 68 locations that were sampled in 1987 and re-sampled ten years later. On each occasion samples were collected from four 1-ft depth increments to a total depth of four feet yielding 272 samples, and a total of 544 samples for the two sampling periods. The results indicate that pyrite decomposes rapidly in the sub-tropical conditions of this area. Significant reductions in pyrite content occurred within ten years in all four depth intervals. Projections indicate that pyrite content will be reduced to insignificant levels within 20 years even in the 3-4 ft depth interval. The rapid decomposition of pyrite is due to its structure. The framboidal pyrite nodules have a radial structure and are composed of microcrystals. Physical disintegration proceeds rapidly along the radial planes of weakness to the core of the nodule. The exposed microcrystals decompose rapidly owing to their high surface area. The weathering rates observed in the minesoil chemistry data are supported by field observations and data from groundwater studies.

Introduction

This paper discusses the weathering rate of pyrite in reconstructed minesoils at Gibbons Creek lignite mine in east-central Texas. The mine is located approximately 16 miles east of Bryan-College Station and 70 miles north-west of Houston. It is owned by the Texas Municipal Power Agency (TMPA), a municipal corporation, which provides electricity to its member cities – Bryan, Denton, Garland, and Greenville – from its power plant located near the mine. The mine was active from 1982 to 1996 when it was permanently closed after TMPA switched to sub-bituminous coal from the Powder River Basin in Wyoming.

The longevity of pyrite in minesoils has always been of interest because of its potential to generate acid drainage. There have been many predictive studies based on the weathering of pyrite under controlled laboratory conditions but extrapolations to the field have always been problematical. The main problem has been with the simulation of the kinetics. However, there is now sufficient historical field data to derive a true field weathering rate.

Pyrite weathering rates at Gibbons Creek mine have been evaluated using three sources. The first is visual observation of pyrite weathering in the field. The second is analysis of chemical data from reconstructed

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minesoils. The third is analysis of chemical data from groundwater associated with reclaimed mine blocks. Each of these is discussed in the next section.

Throughout this paper the tem pyrite is used as a generic name for metal sulfides that will produce acid on oxidation. The name comes from the most common mineral – pyrite or iron disulfide (FeS_2). There are a number of other metal sulfides that may also lead to acid formation, such as arsenopyrite ($FeAsS$), chalcopyrite ($CuFeS$), and pyrrhotite ($Fe_{1-x}S$) (Soil Working Group, 1998, p. 3). Pyrite, as found at Gibbons Creek mine, never exhibits the classic cubic crystal habit or the orthorhombic habit of its polymorph, marcasite. It is most often disseminated and not readily visible to the naked eye. Occasionally it is found in the form of rounded or elongated nodules. The rounded nodules are usually embedded along bedding planes in stratigraphic units (Figure 1). The elongated nodules have a vertical or sub-vertical orientation and appear to follow former plant roots (Figure 2). Both types of nodules generally have a surface of rounded protuberances. The rounded nodules resemble raspberries (Old French *framboise*) – hence the term "framboidal pyrite."

Figure 1 – rounded framboidal pyrite nodules *in situ* in highwall

Figure 2 – elongated pyrite nodules *in situ* in paleosol in highwall (stereophoto)

Field observation of pyrite weathering

The first source of information on the weathering rate of pyrite is direct observation of nodules in the field. Visual inspection reveals that the nodules have a radial structure with a focus at the center. This is particularly evident in partially decomposed nodules (Figure 3). In spherical nodules the focus is at the center of the nodule. In elongated nodules the focus is linear and appears to represent the original plant root. In addition, the pyrite in both types of nodule appears to be composed of numerous microcrystals. A determination of the size of the microcrystals occurred by chance in the author's garage. A fresh 1-inch diameter pyrite nodule from Gibbons Creek mine (similar to the one shown in Figure 4) was left inadvertently on a shelf in the garage. After two years, the nodule had disintegrated to a loose pile of particles of a fine sand texture (approximately 50 μm). The particles still exhibited a typical pyrite metallic color. The disintegration had occurred without any mechanical assistance and without any wetting. It is attributed to the temperature and humidity fluctuations typical of east-central Texas. The microcrystalline nature of framboidal pyrite in Texas lignites and elsewhere has been previously reported in the scientific literature (e.g., Dixon et al., 1982; Butler et al., 2000).

Under field conditions, where water is also available, the physical disintegration is accompanied by chemical decomposition. East-central Texas has a sub-tropical climate with an average annual rainfall of 40 inches. Under the definitions of the "Soil Taxonomy" (U.S. Dept. of Agriculture, 1975), the local soils have a "thermic" soil temperature regime (mean annual soil temperature between 15º C and 22º C) and an "ustic" soil moisture regime (soil dry for 90 cumulative days in most years). These warm conditions, with many cycles of wetting and drying, are very conducive to chemical decomposition. One of the first visible products of this weathering is jarosite [$KFe_3(SO_4)_2(OH)_6$]. The Soil Taxonomy defines jarosite as having a "fresh straw" color (hue of 2.5Y or yellower and a chroma of 6 or more). In the field, powdery jarosite coatings of this color are visible on decomposing pyrite nodules (Figures 3 and 5) and as "haloes" around *in situ* nodules in the minesoils (Figure 6). Jarosite appears to be stable only at the low pH values typically attained during active oxidation of pyrite; with time, it can hydrolyze to ferric oxyhydroxides (rust-colored deposits) such as goethite (α-FeOOH) (Soil Working Group, 1998, p. 5). The iron oxyhydroxides, unlike jarosite, may serve as a cement to form a resistant "rind" preserving some of the nodule's original shape (Figure 7). By this stage, the interior of the core is usually rotted out with perhaps a small residue of pyrite microcrystals and clear crystals suggestive of gypsum ($CaSO_4.2H_2O$).

It should be noted that jarosite mottles are not confined to mines. They are also found in some native soils of east-central Texas, such as the Shalba and Lufkin soils (Carson et al., 1982). This suggests that these soils also contained, and may still contain, residual pyrite. In most cases, the jarosite is preserved in the dense argillic horizons (claypans) of these albaqualfs, where there is limited access for water and oxygen.

Figure 3 – radial structure in partially decomposed pyrite nodules

Figure 4 – Unweathered pyrite nodule

Figure 5 – decomposing pyrite nodule

Figure 6 – pyrite nodules weathering *in situ* in minesoil

Figure 7 – weathered pyrite nodule with iron oxyhydroxide "rind"

Chemical analysis of minesoils

The second source of information on pyrite weathering rates comes from chemical analysis of reconstructed minesoils of different ages. At Gibbons Creek mine, such analyses are available for 68 5.7-acre grids that were initially sampled in 1987 and then re-sampled ten years later. The same methodology was followed on both occasions so the data are directly comparable. The minesoils were sampled on one-foot depth increments to a depth of four feet giving a total of 272 samples for each sampling period. The entire data set for the two sampling periods therefore comprises 544 samples.

<u>Changes in mean and median pyritic sulfur contents over 10 years</u>

Changes in mean and median pyritic sulfur contents over the 10-year period are summarized in Table 1.

Table 1 – Changes in pyritic sulfur content in Gibbons Creek minesoils over 10 years

Depth interval	Mean pyritic sulfur content (%)			Median pyritic sulfur content (%)		
	1987	**1997**	**Change**	**1987**	**1997**	**Change**
0-1 ft	0.01	0.00	0.00	0.00	0.00	0.00
1-2 ft	0.05	0.02	-0.03	0.03	0.01	-0.02
2-3 ft	0.06	0.03	-0.03	0.03	0.01	-0.02
3-4 ft	0.07	0.04	-0.03	0.03	0.02	-0.01

*Note: 0-1 ft depth interval is anomalous because non-pyritic native topsoil was replaced on many of the grids.

The data show a consistent decline in both the mean and the median pyritic sulfur contents in all depth intervals. This suggests that the sample size is large enough (68 samples per depth interval) to reveal a real trend in spite of the high spatial variability normally associated with spoil materials. These summary data suggest that the decline in pyritic sulfur content occurs at a constant rate regardless of depth. The decline is 0.03% for the mean value and 0.02% for the median value (median values are lower because they are not as biased by outliers, "nugget" effects, as mean values). The similarity in weathering rate among the four depth intervals suggests that weathering probably extends to depths significantly greater than four feet.

<u>Changes in absolute content of pyritic sulfur over 10 years</u>

The number of samples with pyritic sulfur contents smaller than 0.05% and 0.1% at the beginning and at the end of the 10-year monitoring period are summarized in Table 2.

Table 2 – Changes in absolute pyritic sulfur content in Gibbons Creek minesoils over 10 years

	Number of samples with pyritic sulfur content < 0.10%		Number of samples with pyritic sulfur content < 0.05%	
	Initial	**Final**	**Initial**	**Final**
0-1 ft	66 (97%)	68 (100%)	63 (93%)	68 (100%)
1-2 ft	55 (81%)	63 (93%)	43 (63%)	61 (90%)
2-3 ft	49 (72%)	64 (94%)	39 (57%)	52 (76%)
3-4 ft	48 (71%)	57 (84%)	39 (57%)	47 (69%)

The absolute pyritic sulfur contents show clear and consistent declines over ten years. It should be noted that the threshold values employed for this assessment content are very low. For reference, a 0.1% pyritic sulfur content equates to a lime requirement of 3.125 tons per 1000 tons of spoil (Soil Working Group, 1998, p. 5). A thousand tons of spoil represents an acre-furrow slice so this lime requirement is equivalent to 3 tons of lime per acre, a routine agricultural application rate. A 0.05% pyritic sulfur content is even smaller and essentially represents complete depletion of pyrite.

<u>Changes in frequency distributions of pyritic sulfur content over 10 years</u>

A more detailed assessment of weathering rates may be made by examining the entire dataset instead of summary statistics. This can be done by comparing changes in the cumulative frequency distributions of pyritic sulfur content in each depth interval over the ten year period. The initial sampling data (Figure 8) show a fairly close alignment of the lines representing the three depth intervals below the top foot (the top foot is anomalous because native pyrite-free topsoil was replaced in a number of the grids). In theory, the lines should be congruent because the spoil material at time zero would be expected to be homogenous and therefore have the same pyritic sulfur content in all three intervals. However, the initial sampling was not always done at a true time "zero." In practice, some minesoils had been reclaimed two or three years before the initial sampling was performed in 1987 and therefore had already partially weathered. The second graph (Figure 9) shows frequency distributions ten years after the initial sampling. The different depth intervals have separated with the deepest intervals showing the least reduction in pyritic sulfur. The inference is that the rate of weathering decreases with depth. This is consistent with our understanding of weathering processes and underlines the limitations of summary statistics (such as the mean and median values of Table 1) which had suggested that the rates were the same in all four depth intervals.

Figure 8 – Frequency distribution of pyritic sulfur at initial sampling
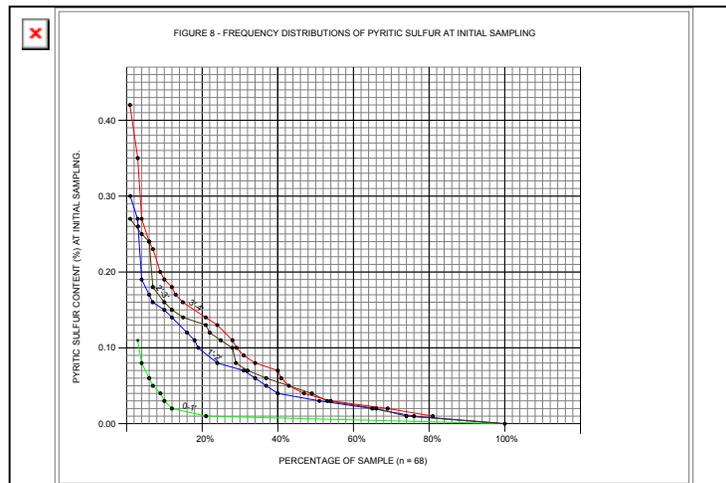
Figure 9 – Frequency distribution of pyritic sulfur 10 years later
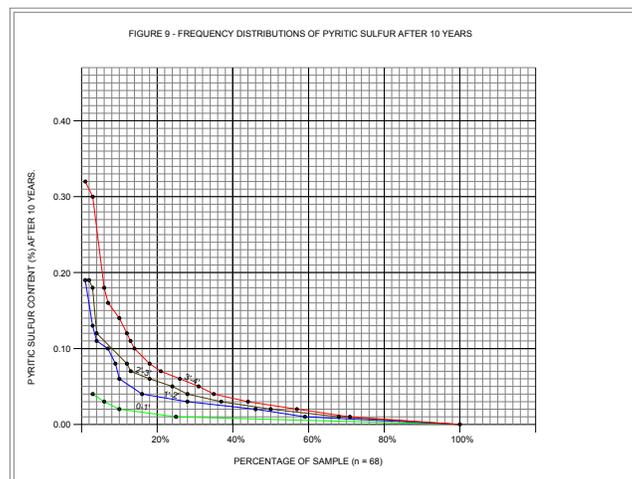
Based on these historical weathering rates, some projections of future weathering rates may be attempted (Figures 10 through 13). The graphs use a straight-line projection. This probably overestimates the weathering time because, as previously discussed, chemical decomposition proceeds rapidly after the nodules have physically disintegrated. Also, the chemical decomposition itself accelerates when the local pH has declined to the point (pH<3.0) at which the ferric ion (Fe^{3+}) can catalyze the oxidation process (Nordstrom, 1982). The graphs are therefore somewhat conservative but suggest that there will be no pyritic sulfur contents greater than 0.1% after about 20 years in the 3-4 ft depth interval, 15 years in the 2-3 ft and the 1-2 ft depth intervals, and 10 years in the 0-1 ft depth interval. Complete exhaustion of all pyrite is shown by the very conservative line for 0.05% pyritic sulfur. The projections indicate that this point will be reached in the deepest, 3-4 ft, interval after about 35 years.

These findings are consistent with the studies of pyrite content in spoil materials ranging up to 35 years in age at an abandoned mine land project in central Texas (Horbaczewski and Van Ryn, 1988). Those studies revealed virtually complete elimination of pyrite to a depth of 10 feet after about 30 years.

Figures 10-13 – Projections of weathering rates in the four 1-ft depth intervals
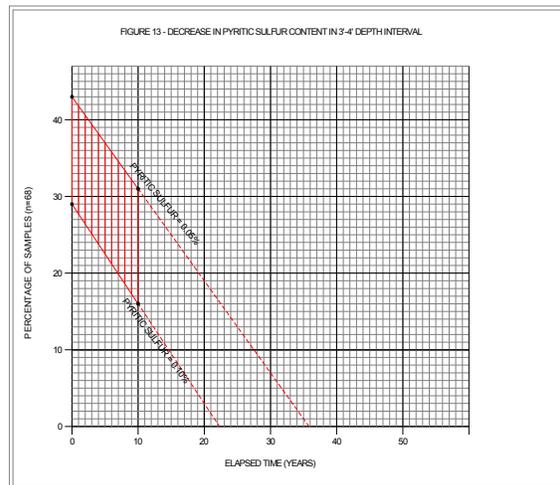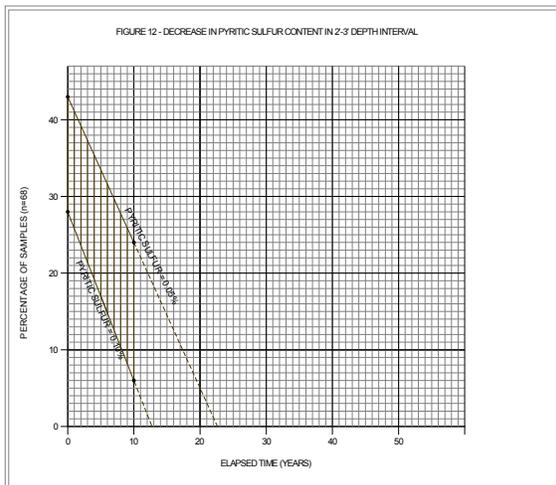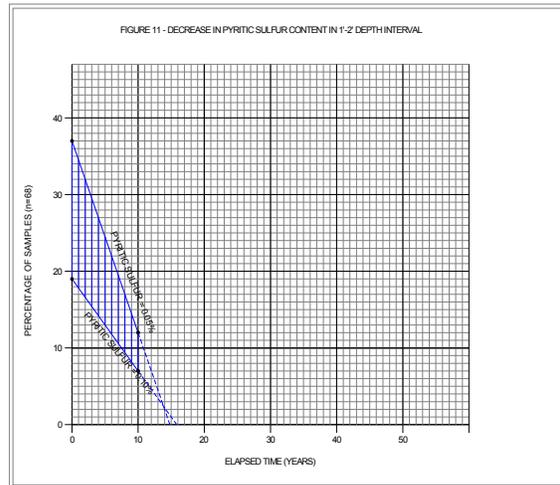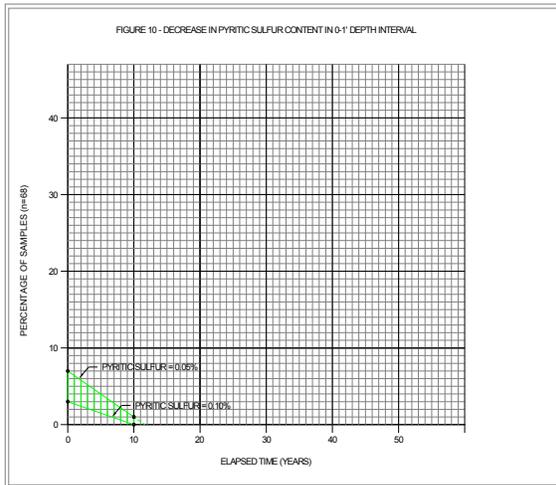
Recharge and chemical evolution of post-mining groundwater

The third source of information on the weathering of pyrite in minesoils comes from groundwater studies. The chemistry of the groundwater that becomes re-established in reclaimed spoil areas reflects the reactions that have occurred in the spoil.

Recent groundwater studies at Gibbons Creek (Marston Environmental, Inc., 2007) show that re-saturation of spoil materials was achieved within five years of completion of mining operations (from 1987 to 1992). Most of the re-saturation came from rainfall. Infiltration and percolation of rain water (and oxygen) appears to be relatively unimpeded by the unconsolidated and uncompacted spoil. Concentrations of sulfate in the spoil groundwater, attributed to the weathering of pyritic materials in the spoil, showed strong increases over a period of about ten years (from 1992 to 2002) followed by a slow decline. The conclusion was that this may indicate a reduction in the rate of pyrite oxidation above the re-established water table. A reduction in the rate is to be expected if the pyrite has become significantly depleted.

Conclusions

The following conclusions may be drawn about the weathering of pyrite at Gibbons Creek mine:

- In spite of their size, framboidal pyrite nodules weather rapidly in the minesoil environment.
- This is primarily due to their radial structure and microcrystalline composition.
- Both of these properties ensure that the nodules disintegrate physically to small particles of pyrite (the size of fine sand [50 μm] or smaller).
- Chemical decomposition then proceeds rapidly because of the high surface area of the particles and the sub-tropical climate of east-central Texas.
- Chemical analyses of the minesoils show substantial declines in the content of pyrite after ten years.
- Projections based on historical data suggest that virtually all the pyrite will be weathered from the top four feet within 20 years.
- These projections are supported by investigations of spoils ranging up to 35 years in age at an abandoned mine land project in central Texas.
- Groundwater studies at Gibbons Creek mine provide separate evidence that pyrite weathering is most intense in the first ten years and that the rate declines afterwards.

Acknowledgments

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