



Concentrated iron pyrite mine waste as an amendment for alkaline soils
by Troy C Smith

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Soils
Montana State University
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Abstract:

Many agricultural-soils in the western U.S. are alkaline. Soil pH's above 7.0 cause several essential plant nutrients, including iron and sulfur, to become unavailable to plants. These soils often require additional fertilizer, and can be very difficult to correct for agricultural purposes. Sulfur has been identified as one of the best amendments for highly alkaline soils. Many forms of sulfur have been used to amend these soils. Most forms are either only moderately effective, or are expensive to apply.

The mining industry commonly extracts sulfur rich minerals as a waste product. Although other countries have tried these waste products, very little research has been done in the United States to test these materials as an alternative soil amendment to alleviate iron and sulfur deficiencies on alkaline soils.

The Golden Sunlight gold mine in Montana produces a high sulfur by-product. The material contains approximately 55 % finely ground pyrite. Pyrite is composed of iron and sulfur and when allowed to oxidize will acidify, releasing these elements. It was felt this pyrite material would be a good amendment for alkaline soils.

A study was designed to test the benefit of applying finely ground pyrite to several soils varying in alkalinity. The research included a laboratory and field study. In the laboratory, samples of the pyrite, and five soils amended with the pyrite, were kept moist and monitored for chemical parameters that would measure the rate of pyrite oxidation. The samples were monitored for one year. Field test plots were also constructed on one of the alkaline soils tested in the laboratory to evaluate the effect of pyrite applications on a sulfur demanding crop.

The results indicated that applications of finely ground pyrite were very effective at lowering soil pH and increasing plant available iron and sulfur. The results also showed that due to the relatively slow oxidation of the pyrite, successful application rates for very alkaline soils may often exceed 10,000 kg/hectare.

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of

Master of Science

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Bozeman, Montana**

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APPROVAL

of a thesis submitted by

Troy C. Smith

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

4/20/94
Date

Earl. Shogley
Chairperson, Graduate Committee

Approved for the Major Department

4/21/94
Date

[Signature]
Head, Major Department

Approved for the College of Graduate Studies

5/25/94
Date

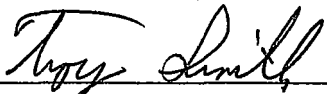
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ABSTRACT

Many agricultural soils in the western U.S. are alkaline. Soil pH's above 7.0 cause several essential plant nutrients, including iron and sulfur, to become unavailable to plants. These soils often require additional fertilizer, and can be very difficult to correct for agricultural purposes. Sulfur has been identified as one of the best amendments for highly alkaline soils. Many forms of sulfur have been used to amend these soils. Most forms are either only moderately effective, or are expensive to apply.

The mining industry commonly extracts sulfur rich minerals as a waste product. Although other countries have tried these waste products, very little research has been done in the United States to test these materials as an alternative soil amendment to alleviate iron and sulfur deficiencies on alkaline soils.

The Golden Sunlight gold mine in Montana produces a high sulfur by-product. The material contains approximately 55% finely ground pyrite. Pyrite is composed of iron and sulfur and when allowed to oxidize will acidify, releasing these elements. It was felt this pyrite material would be a good amendment for alkaline soils.

A study was designed to test the benefit of applying finely ground pyrite to several soils varying in alkalinity. The research included a laboratory and field study. In the laboratory, samples of the pyrite, and five soils amended with the pyrite, were kept moist and monitored for chemical parameters that would measure the rate of pyrite oxidation. The samples were monitored for one year. Field test plots were also constructed on one of the alkaline soils tested in the laboratory to evaluate the effect of pyrite applications on a sulfur demanding crop.

The results indicated that applications of finely ground pyrite were very effective at lowering soil pH and increasing plant available iron and sulfur. The results also showed that due to the relatively slow oxidation of the pyrite, successful application rates for very alkaline soils may often exceed 10,000 kg/hectare.

INTRODUCTION

Calcareous and high pH agricultural soils often produce lower crop yields than neutral soils. The lower yields are usually a result of alkaline induced nutrient deficiencies, increased salt content, or poor soil structure. Consequently, alkaline agricultural soils typically require greater amounts of fertilizer, and often micronutrient applications such as iron. These soil problems can be expensive to correct. Many high sulfur materials have been used to amend alkaline soils. Elemental sulfur has been shown to be an effective amendment because of its ability to produce acid and neutralize soil alkalinity (Follett et al., 1981). Sulfide minerals such as iron pyrite have been tried worldwide as amendments for alkaline soils. Very little research has been conducted in the U.S., partially because sulfide minerals are often associated with unwanted heavy metals.

Iron pyrite has the chemical formula FeS_2 , and when exposed to oxygen and water produces plant available ferrous iron (Fe^{2+}) and sulfate (SO_4^{2-}). Sulfuric acid is also produced as one of the by-products from the decomposition of iron pyrites. The reaction rate for the decomposition of iron pyrites is dependent on particle size, surface area, the composition of the matrix encompassing the pyrite, and surrounding environmental factors.

Golden Sunlight Mines, Inc. is a large gold mine located near Whitehall, Montana which produces a concentrated iron pyrite by-product. This by-product is relatively low in heavy metals other than iron. Since it was known that crop yields from alkaline soils could theoretically increase with iron pyrite additions, it was of interest to learn how the iron pyrite by-product could affect these soils. This study was conducted to identify beneficial agricultural uses for the iron pyrite by-product that could lead to an alternative means of eliminating iron and sulfur deficiencies in calcareous and high pH soils.

Thesis Objectives

- To determine the rate of soil acidification and related iron and sulfur release during a one-year period from the oxidation of pyrite added to five different soils.
- To determine the effects of pyrite applications on alkaline Montana soils in relation to pH and plant available iron and sulfur levels.

BACKGROUND

Soil Chemistry

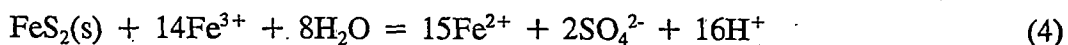
Alkaline soils (soil pH above 7.0) are common in semi-arid agricultural environments. It is known that soil alkalinity affects plant nutrient availability. Many essential plant nutrients in the soil such as phosphorus, sulfur, and iron become less available to the plant as the soil pH is elevated above 7.0 (Follet et al., 1981).

Nutrient requirements vary between agricultural crops, consequently, specific nutrient deficiencies due to soil alkalinity also vary. Plant available iron deficiencies are one of the more common problems associated with alkaline soils (Follet et. al., 1981).

Alkaline soil problems are often corrected with commercially available products which contain either sulfur or acid. Commercially available products include the chemicals ammonium sulfate, gypsum, elemental sulfur, and sulfuric acid. These products are either low acid producers, or are hazardous to handle.

Iron Pyrite

Iron pyrite (referred to as pyrite) is a naturally occurring mineral often found as a by-product of metal and coal mining. Pyrite exposed to water and oxygen will weather according to the following reactions (Hossner, 1988):



The oxidation of pyrite does not always include equation number 4, due to the large amounts of ferric iron required. The rate of reaction is dependent on particle size, surface area, oxygen, moisture and temperature. These reactions can also be catalyzed by thiobacillus bacteria. Thiobacillus ferrooxidans can play an important role in the oxidation rate of pyrite (NTIS, 1991). The conversion of ferrous iron to ferric iron is the rate-limiting step in the oxidation of pyrite (equation 2). Iron-oxidizing bacteria can catalyze this step, thus accelerating this conversion and the oxidation of pyrite (Stumm and Morgan, 1981).

Pyrite oxidation is directly related to surface area (Vlek and Lindsay, 1978). Finely disseminated "framboidal" pyrite will oxidize much more rapidly than larger crystalline pyrites (Caruccio and Ferm, 1974). Crystalline pyrite, if finely ground, may also oxidize rapidly.

Oxygen and water are shown to be essential to pyrite oxidation in the above reactions. In air-dried soils, pyrite oxidation practically ceases (Barrau and Berg, 1977). Oxygen diffusion through certain materials can also limit pyrite oxidation.

Temperature has been shown to have a significant effect on the rate of pyrite oxidation. A 10° C increase in temperature can produce a two-fold increase in the rate of pyrite oxidation (Smith and Shumate, 1970). This is partially a result of biological activity.

Smith and Shumate (1970) have shown that pH affects the rate at which ferrous iron is converted to ferric iron, thus affecting the rate of pyrite oxidation. In the absence of iron-oxidizing bacteria, the ferrous to ferric iron conversion occurs rapidly at a pH above 6.0. In the presence of iron-oxidizing bacteria, the ferrous to ferric iron conversion occurs most rapidly between pH 2.4 and 3.6 (NTIS, 1991). Acidic micro-environments are sufficient for bacterial iron oxidation (Barrau and Berg, 1975). The presence of calcium carbonate can slow the oxidation of pyrite by inhibiting bacterial interaction and creating less soluble iron hydroxides (Caruccio et al., 1981).

Golden Sunlight Pyrite Material

Golden Sunlight Mine produces a concentrated tailing material that is primarily pyrite and has no appreciable heavy metal content other than iron. Golden Sunlight's gold ore contains approximately 4 to 7% pyrite. In the milling process about 40% of this pyrite is removed in a gravity circuit to increase gold recovery. The pyrite material removed in the gravity circuit is composed of approximately 55% pyrite by weight. The remaining 45% is composed primarily of feldspars and silica. After the gold is removed this material becomes a by-product. Approximately 400 tons of pyrite enriched tailing is produced per day.

A concentrated pyrite tailing composite sample was created by blending equal weights of monthly samples from July, 1989 to January, 1990. The sample was submitted to Chen Northern Laboratories, Inc. in Billings for heavy metal analysis.

Tests were conducted in accordance with the U.S. Environmental Protection Agency Manual SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition, November, 1986 and Method 1311 published June 29, 1990 in 40 CFR Part 302. The results of the analysis for the Toxicity Characteristics Leaching Procedure (TCLP) have been adjusted for spike recovery and are summarized in Table 1.

Table 1. Pyrite material TCLP Metal Concentration Data (ppm).

Metal	Test Extract	EPA Extract Limit
Ag	<0.040	5.0
As	0.020	5.0
Ba	<0.200	100
Cd	0.145	1.0
Cr	0.150	5.0
Hg	0.0006	0.2
Pb	<0.040	5.0
Se	0.006	1.0

Since all the test extracts were less than the EPA extract limits, the pyrite material is deemed non-hazardous by the EPA method based on heavy metal content.

Table 2 summarizes total metal analyses for monthly composite samples from July, 1989 through January, 1990 (Rhoades, 1982).

Table 2. ICP multielement concentrations of pyrite material composite samples.

Month	Year	Ag (oz/ton)	Al (%)	As (ppm)	Au (oz/ton)	Ba (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cu (ppm)	Li (ppm)	Cr (ppm)	Hg (ppm)
July	1989	0.0496	2.21	128	0.0223	>2000	32	0.87	1	40	53	410	11	79	0.604
August	1989	0.0204	2.85	96	0.0186	1558	24	0.19	1	33	46	217	10	64	0.617
September	1989	0.0496	2.62	96	0.0212	1891	29	0.19	<1	42	58	225	15	97	0.478
October	1989	0.0408	2.62	99	0.0215	1971	40	0.15	<1	44	57	209	10	69	0.448
November	1989	0.0467	2.49	106	0.0207	1745	38	0.14	<1	46	54	208	10	55	0.449
December	1989	0.0525	2.78	115	0.0207	>2000	39	0.22	<1	37	50	354	15	88	0.798
January	1990	0.0321	2.97	89	0.0206	>2000	32	0.23	<1	37	53	271	11	76	0.667
Maximum		0.0525	2.97	128	0.0223	>2000	40	0.87	1	46	58	410	15	97	0.798
Average		0.0418	2.64	104	0.0208		33	0.28		40	53	268	12	75	0.580
Std. Dev.		26	9	12	5		16	85		10	7	28	18	13	0.121

Table 2 continued.

Month	Year	Mg (%)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)	Pb (ppm)	Sc (ppm)	Sr (ppm)	Te (ppm)	Ti (%)	V (ppm)	Zr (ppm)	Se (ppm)
July	1989	0.25	48	0.37	18	73	56	4	215	3.7	0.08	41	47	2.2
August	1989	0.19	46	0.66	21	59	65	4	182	2.8	0.08	40	46	2.7
September	1989	0.32	52	0.32	15	83	109	5	178	4.0	0.09	51	50	3.0
October	1989	0.22	57	0.55	21	69	115	4	188	4.6	0.07	40	40	3.8
November	1989	0.20	56	0.41	17	73	112	4	158	4.1	0.07	37	41	3.3
December	1989	0.24	62	0.48	18	71	213	4	183	5.0	0.08	47	48	3.2
January	1990	0.25	55	0.74	20	60	78	4	191	3.6	0.08	41	44	3.5
Maximum		0.32	62	0.74	21	83	213	5	215	5.0	0.09	51	50	3.8
Average		0.24	54	0.50	19	70	106	4	185	4.0	0.08	43	45	3.1
Std. Dev.		17	10	29	11	11	46	8	9	17	8	10	8	.49

