Some Aspects of SSPE/PSM Modeling for Quantitative Assessment of Disturbed Hydrological Systems [1]

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Abstract

In previous research involving the SSPE/PSM technique it was demonstrated that this procedure could be used to develop longevity estimates for refuse sites with respect to acid effluent. it could also be used to determine the time frame for maximum acid effluent and to evaluate the potential impact upon the localized watershed. The technique evaluates two field parameters: ALPHA, the rate of acid generation, and BETA, the rate constant of acid discharge. Since this initial work was performed and presented, extensive research has been conducted that has allowed the evaluation of the factors that control ALPHA and BETA. **ALPHA** is a micro-diffusion phenomenon controlled by the pyrite grain size as well as pore size distribution. BETA, although a product of innumerable parameters, has been shown to be a 'steady' field parameter that is a resultant of a very large number of microsystems. Additionally, the modeling technique has been modified to handle active refuse sites. The technique was able to estimate within 1% error the amount of new material placed on an active refuse site in a 1 1/2 year period using discharge chemistry, the amount of refuse material on the site at the time that field measurements began to be taken, and the weekly average amount of new material placed on the pile. The ability of the SSPE/PSM technique to make such reliable estimates strongly supports the theoretical concepts used and applied. Presently, the technique is being refined to accurately evaluate the PHC and CHIA requirements of the permit review procedure and to deal with linear properties that BETA may possess in certain situations.

ADDITIONAL KEY WORDS: shrinking core model, mean-lifetime

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Introduction

In 1988 an initial evaluation on a mathematical model that allowed for an acid production-discharge scenario to be simulated for refuse piles and mountain top removal operations was completed This model is called SSPE/PSM (Simultaneous Species Production-Elimination using Probability simulation Modeling) (Rymer et al. 1988). This model generates two field variables known as ALPHA (the first order reaction rate at which pyrite oxidizes) and BETA (the first order physical rate constant at which mobile ionic species are leached from a site). The model utilizes one form of the "Bateman Equation" as its scientific and mathematical foundation. This equation is widely used in areas such as radioactivity (intermediate daughter isotope) and chemical kinetics (ammonia cycle). Probability simulation employs the use of data distributions rather than discrete data, and dispenses with deterministic formulas due to the numerical randomness of field (input) data. The complex assortment of chemical and physical processes by which acid is produced and discharged can then be reduced to the two field parameters, ALPHA and BETA.

Two types of graphs are output from SSPE/PSM. The first type of graph contains three species-time curves as shown in Figure 1. The curves represent the mass of pyrite remaining unreacted, the mass of sulfate ion that has been discharged to the environment, and the mass of sulfate remaining in the site (undischarged). To illustrate a scientific parallel a graph of the ammonia cycle is shown in Figure 2 (Sawyer 1978), showing the mass of ammonia unoxidized, the amount of nitrate that has been produced over time, and the amount of nitrite that has not, as yet, been oxidized to nitrate. The second type of graph output from the modeling is called a "longevity curve', as shown in Figure 3. This shows the concentration of sulfate ion that can be expected over time. This curve is actually the most probable mean value of the sulfate ion concentration at the most frequent discharge flow value.

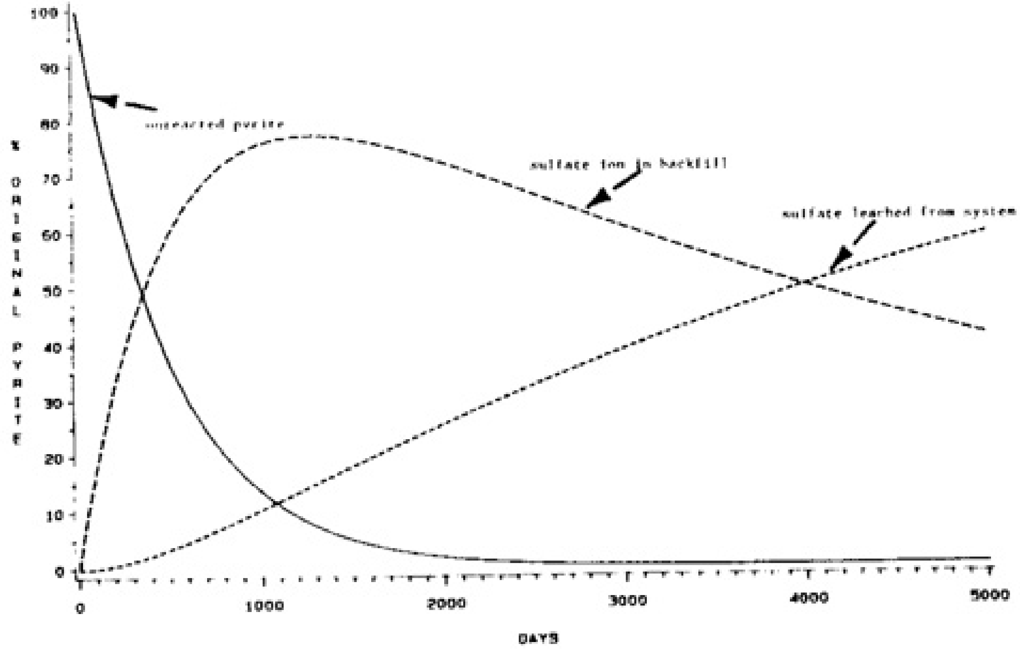

Figure 1.

Classical SSPE system for pyrite oxidation. Curves represented are % of original pyrite remaining (solid line), % of original pyrite that exists in the backfill as sulfate ion (bold dashed line), and the % of original pyrite that has discharged into the environment as sulfate ion.

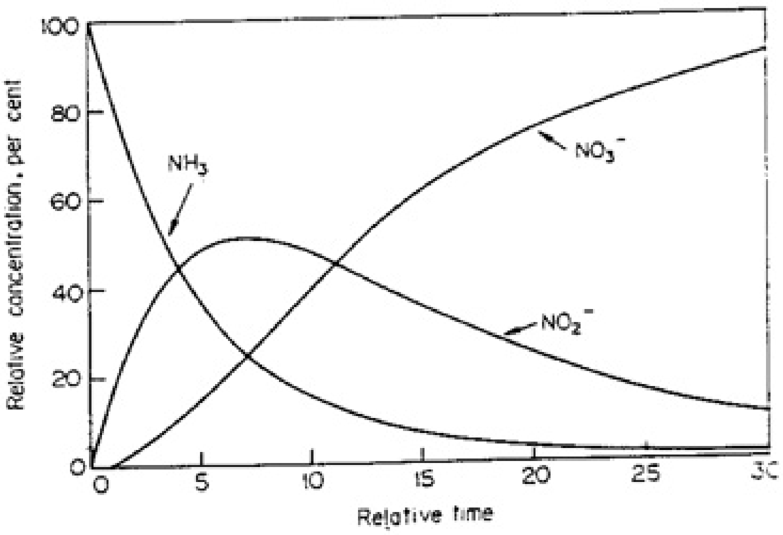

Figure 2.

The Nitrogen Cycle as a classical SSPE system. (after Sawyer, 1876)

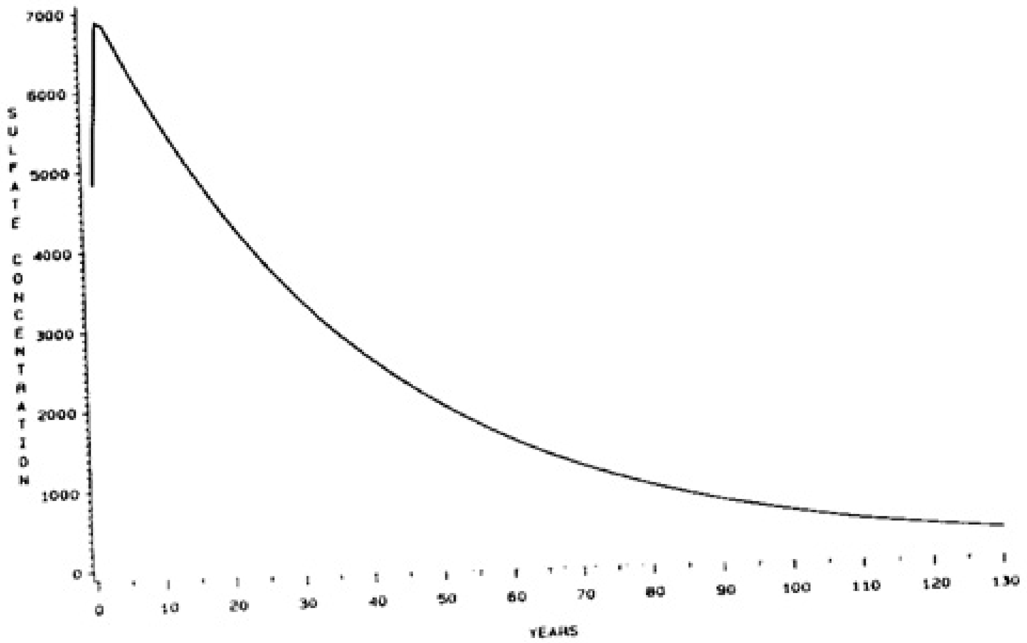

Figure 3.

A longevity curve for a typical refuse site expressed as the concentration of sulfate ion. The curve represents the average of a "window" of probable concentration values.

The preponderance of evidence seems to support the model. First, field evidence shows that a peak sulfate concentration can occur during the first 1 to 12 years. Longevity curves exhibit the same time window for peak sulfate concentration. Second, it is commonly accepted that the oxidation process is rapid and the discharge process (or flushing of oxidation products from a site) is slow (Rymer et al. 1988; Skousen 1989; Ziemkiewicz 1989; Hall 1989).. SSPE/PSM shows ALPHA to be greater than BETA by a magnitude of ten (Rymer et al. 1988). Third, some of the longevity curves show AMD to be discharging over a prolonged period of time, often in excess of 100 years. Seventy to eighty year old discharges are not uncommon in the field (Hall 1989). Fourth, the model relies on data distributions of total sulfur to evaluate the amount of pyrite available at the commencement of site operations. Ample evidence exists to show that AMD occurs in areas where the total sulfur content of overburden materials is low (Skousen 1989). Drawing values from distributions rather than a reliance on discrete analytical data seems to be a logical choice in view of the strong evidence that a high probability exists for sampling error and total sulfur underestimation (Rymer et al. 1989). This choice, however, becomes a moot point in SSPE/PSM modeling as will be demonstrated later. Finally, the model was revised and utilized in an acid rain-limestone treatment project in the headwaters of Shavers Fork (Cheat River) in West Virginia . The model correctly projected the calcium ion concentration and pH over time of the tributary under study (Ivahnenko 1988).

Since the introduction of the original model, research has continued that addresses five vital questions:

1. Are the "Bateman Series Equations" really applicable in a situation where ALPHA is a chemical phenomenon and BETA is a physical phenomenon?
2. Does all of the pyritic material react ? If not, how much does react and what factors affect the amount reacted?
3. How sensitive is a BETA value to the original amount of pyrite in the site material ?
4. Since the longevity curves sometimes show a period of AMD discharge, exceeding human life expectancy, how can the model be proven viable in present time? Can enough experimental evidence be amassed to support the model without having to wait to the latter part of the 21st century ?
5. What factors control ALPHA and BETA? Which of these factors are significant and which can aid in the quantification of BETA ?

Results and Conclusions

The oxidation of pyrite has been determined to be an intrinsic "pseudo" first order (behaves as such for quantitative purposes) by a variety of research endeavors. Predominant is the work of Stumm and Singer (1970) in which the rate determining step for pyrite oxidation was determined on a laboratory scale. Later work of Renton et al. (1987) showed the first order behavior of pyrite oxidation to exist not only in the laboratory but also on a small field scale (350 pound fixed-bed plug-flow reactor), as well as on a larger field scale (350 ton test refuse piles).

The determination of the first order behavior of the physical leaching process, prior to this research, had never been discussed or attempted. At the onset of the development of the SSPE/PSM modeling research, three equations (including Bateman's) were studied.

$$dS/dt = aS - bS \qquad (1)$$

is the differential form of Bateman's Equation which demands that BOTH the Oxidation rates and the leach rates be FIRST ORDER (Wehr 1972).

$$dS/dt = aS - b \qquad (2)$$

implies that the oxidation process is FIRST ORDER and the leach rate is a LINEAR CONSTANT.

$$dS/dt = a - b \qquad (3)$$

implies that BOTH the oxidation process and the leach process are LINEAR CONSTANTS.

The resulting curves for each equation can be seen in Figure 4.

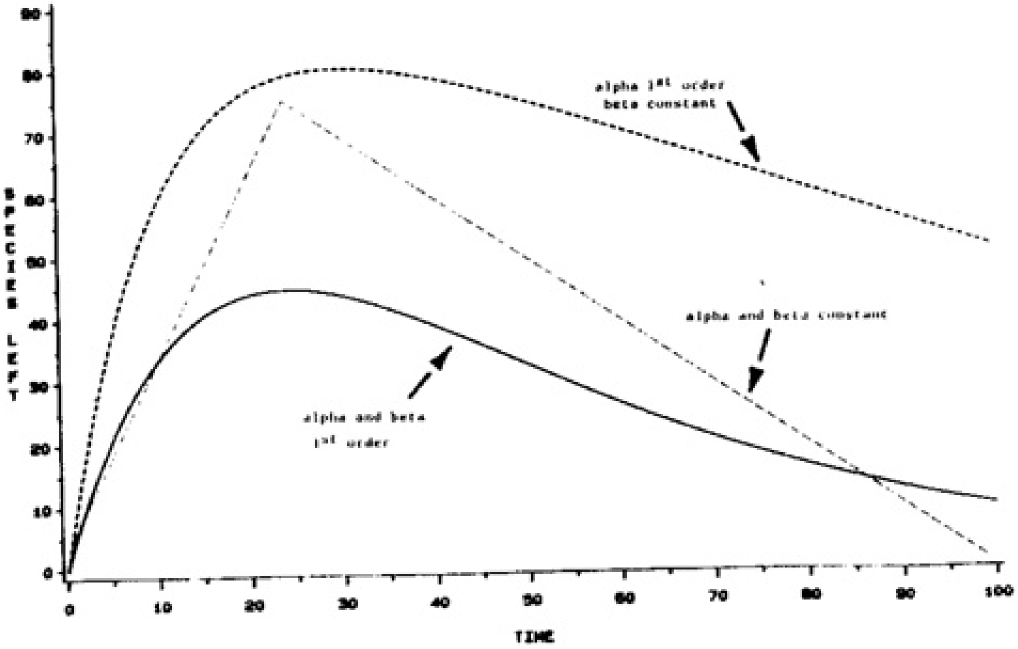

Figure 4.

SSPE curves for the 3 types of systems corresponding to equations 1 through 3. Curve "A" represents the case where both ALPHA and BETA are first-order, Curve "B" represents the case where ALPHA is first-order and BETA is a linear constant, and Curve "C" represents the case where both ALPHA and BETA are linear constants.

Equation 3 from the above selection was immediately eliminated due to the strong evidence that the oxidation process can be quantified in first order kinetic terms (Stumm and Singer 1970; Renton et al. 1987). Left with Equations I and 2, the only remaining factor to be determined was whether the leach rate exhibits similar 1st order kinetic behavior, despite being a purely physical process. If the leaching process exhibits first order behavior, then it will also emulate a "Poisson process" (Devore 1982). The evidence for the leaching process being a Poisson process exists:

(1) It has the properties common to Poisson processes. Other Poisson process examples include the monitoring of a computer system over time with breakdowns constituting the events of interest, recording the number of accidents in an industrial facility over time, answering calls at a telephone switchboard, and observing the number of cosmic-ray showers from a particulate observatory over time (Devore 1982). Flow discharges are functions of independent Poisson events, such as rainfall.

(2) The quantification of the leaching process involves both a chemical and physical parameter, sulfate concentration and flow rate, respectively. Thus, field data could serve as a basis to test whether this process , truly, exhibits first order rate characteristics. The BETA values obtained in the SSPE/PSM simulations have a magnitude of 5 x 10-4 /day. It was decided to compare the distribution functions of the product of sulfate and flow present at a minesite (mine 4, Table 1) over a defined period of time with the disintegrations of a

radioisotope having a known half-life of 1400 days over the same time period. Sodium-22 was the radioisotope chosen due to the fact that it has a decay rate constant nearly equal to the BETA values obtained in this research and the data was readily available from Lawrence-Livermore Labs (Berkeley, CA). comparisons can be drawn by examination of Figure 5. The Poisson nature of the flow-sulfate concentration obtained from actual field data exhibits properties similar to the radioactive disintegrations. Therefore, in the case of a backfill discharge the assumption of first-order emulation is valid and Equation (1) can be applied. it is theorized, however, that the kinetic emulation of the physical discharge process is, in all probability, some combination of Equation (1) and Equation (2) with the latter equation coming into play at very high flows, In fact, the area of the SSPE/PSM technique in need of research is this overlapping boundary between first order rates and linear rates.

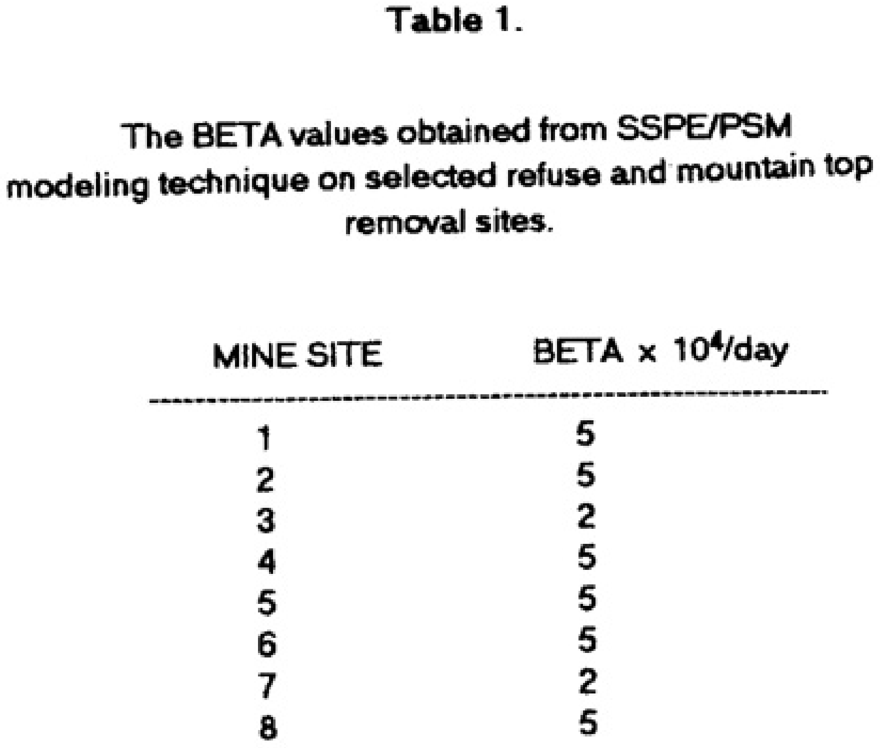

Table 1.

The BETA values obtained from SSPE/PSM modeling technique on selected refuse and mountain top removal sites.

MINE SITE	BETA × 10^4/day
1	5
2	5
3	2
4	5
5	5
6	5
7	2
8	5

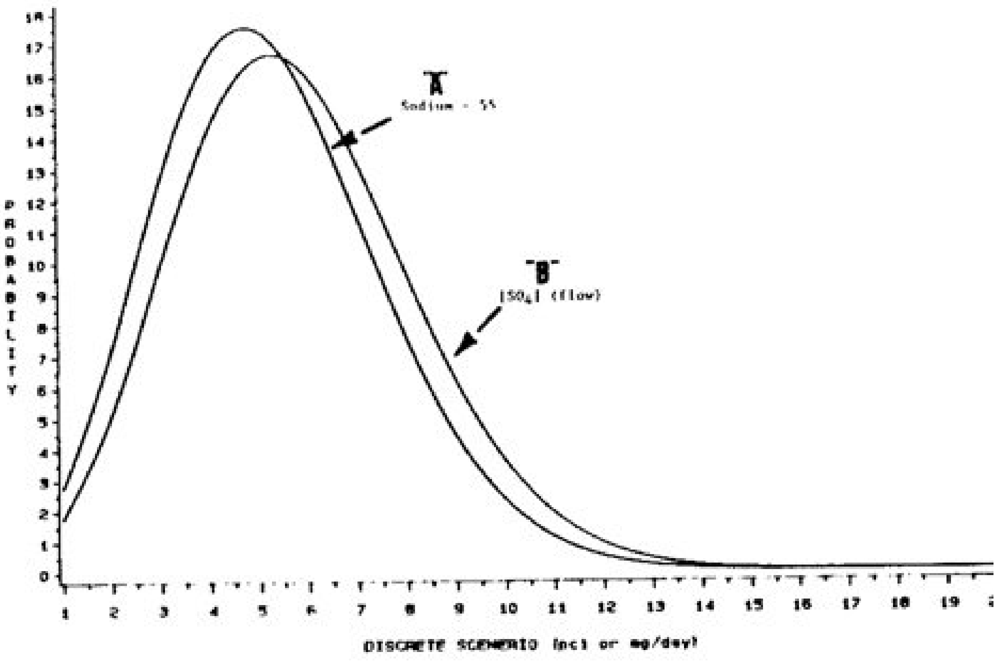

Figure 5.

Comparison of two systems exhibiting Poisson Properties. Curve "A" represents the disintegrations per day of sodium-22 which has a half-life of approximately 1400 days. Curve "B" represents the product of sulfate ion concentration and flow (milligrams of sulfate per day). Sodium-22 data courtesy of Lawrence-Livermore Labs, Berkeley, California. The discharge data courtesy of WV DOE and US Dept of the Interior OSMRE.

The amount of pyritic material that actually undergoes oxidation has been a subject of much recent speculation. To resolve whether an entire pyrite grain oxidizes, a mathematical model (Batarseh et al , 1988). was developed and tested experimentally (Batarseh 1987). The model is based on as the "shrinking core model" with a moving boundary and quantifies the reaction zone of a pyrite grain.

Classical rate kinetics predict that an average of 63% of all pyritic material will react (Appendix 1). This was borne out in the work of Baker (1983) and McConihey (1985) in which three untreated 1 350 -pound waste rocks were allowed to naturally weather in a "fixed bed-plug flow" reactor. Using a measured total pyritic sulfur value of 3.14%, an average of 35% pyrite remained unreacted after 256 days. This is in excellent agreement with the amount of unreacted pyritic material predicted from reaction kinetics.

APPENDIX 1

The proof that 63% of a reactive substance will remain after the "mean lifetime" in a 1st order kinetic process.

the 1st order rate equation states that:

$$\%S_u = 100\ e^{-at}$$

where: $\%S_u$ = % unreacted pyritic sulfur
a = rate constant (ALPHA)
t_m = time

the mean lifetime $t_m = 1/a$ (Van Nostrands 1976)

then: $\%S_u = 100\ e^{-a(t_m)} = 100\ e^{-a(1/a)}$

and: $\%S_u = 100^{e-1} = 100\ (1/e) = 100(0.63) = 37\%$

then the %S (reacted) = **63%**

Batarseh et al. (1987) showed, however, that the amount of sulfate ion produced in a weathering process relates directly to the pore size distribution and pyrite grain size. He also demonstrated that the average pyrite grain will reduce in size about 20%. Therefore, the amount of unreacted pyrite should be 80%, much higher than predicted by rate kinetic theory. This non-agreement is expected since rate kinetic theory does not take into account such parameters as pyrite grain size and pore size distribution. However, to account for the discrepancy in the Baker data from 1983, which showed 35% of pyrite unreacted, another phenomenon must be taking place -- postulated to be neither a purely chemical nor physical process, but biochemically induced. It is speculated that when the role of iron oxidizing bacteria such as thiobacillus ferrooxidans is illuminated and compared to and integrated with existing data then this discrepancy will be solved. Such an investigation has commenced. Another potential contributor to this discrepancy is analytical -- the total pyritic sulfur measured by Baker could have been underestimated. This brings the Baker data and the Batarseh data slightly closer but will not account for the gap.

The underestimation of total pyritic sulfur brings up another problem in need of resolution. since the SSPE/PSM technique involves the calculation of some original amount of pyritic sulfur present in a minesite prior to mining, and this number may be too low, how is the final calculation of "BETA" affected? To answer this, a computer was programmed to analyze a typical flow-sulfate discharge scenario from actual field data. Instead of looking through various rock type sulfur distributions and adjusting for the area and volume of material present to obtain a value for the original amount of pyrite present prior to mining, the computer was programmed to set this original pyrite amount at certain tonnages. A "BETA" value was then calculated for any given size and corresponding sulfur tonnage. Hence, the sensitivity of "BETA" to this original amount could be studied. The results of this response of a calculated "BETA" value to the original amount of pyritic sulfur can be seen in Figure 6. It can be seen from Figure 6 that the amount of pyrite originally present ceases to exert influence on a calculated "BETA" value after a certain point (a point well above the amounts actually present in typical minesites). This adds credence to the use of distributions in the SSPE/PSM modeling technique. This also opens the door to use this technique on deep mines as well as surface operations other than refuse disposal and mountain top removal sites (for which the model was originally developed). This also lends support to another contention -- that "BETA" is some summation of innumerable dissolution and physical microprocesses and that at some point these microprocesses begin to take on a single macroprocess emulation. Nature has conveniently sorted out these processes into a single quantifiable number -- BETA.

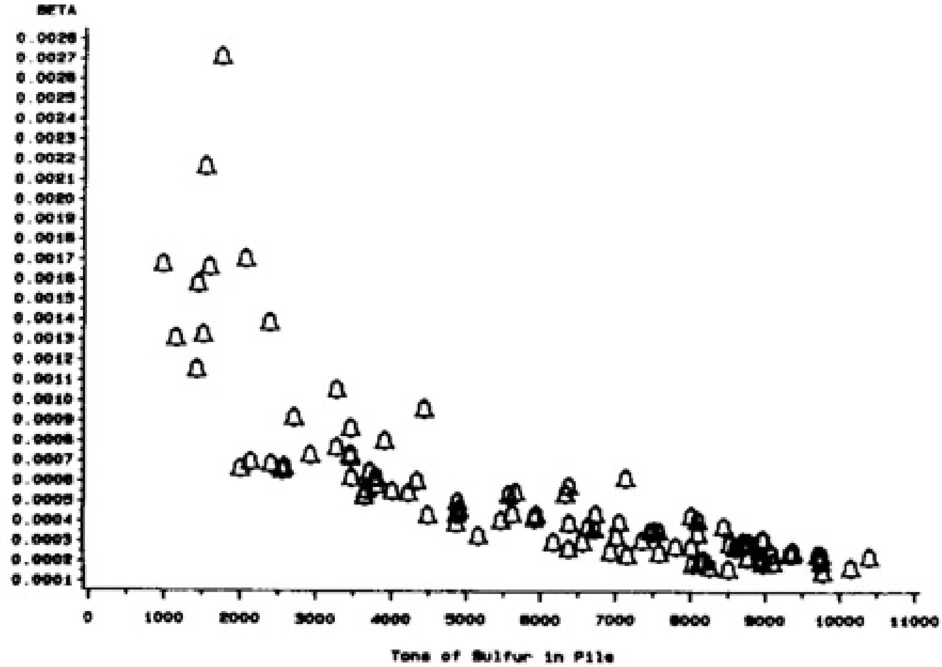

Figure 6.

Shows the sensitivity of a BETA value generated via SSPE/PSM to the mass of pyrite originally present in a system. For a given discharge scenario the BETA value will become constant after a certain point.

Since the inception of this model, an actual field proof for a coal mining scenario has been sought. The model was successfully applied to the addition of limestone into a pristine mountain stream, but AMD is not quite so pure. The unfortunate fact that verification of the model for large systems requires moving forward to the latter part of the 21st century has made direct proof impossible at the present time. However, - - support did emerge from research which appeared to be, at first, a situation where the model did not appear to work. The minesites studied in the development of the SSPE/PSM modeling technique were coded by the field hydrogeologist. Since refuse piles were being used, it was postulated that all of the "BETA" values would be of comparable magnitude. indeed, as seen in Table 1, they are.

However, one minesite listed (known as mine 4), had produced an unusually high "BETA" value and a rapid longevity curve as can be seen in Figure 7. The geometry of this site was comparable to all of the other sites and the size of this site was somewhere in the middle. If this discrepancy could not be explained then a definite fallacy exists in the critical premises used in construction of the model. It became paramount to discover what phenomenon was responsible for such a high "BETA" value. The answer was provided by the field hydrogeologist in that this site was the only one under study that was still an "active" site. The computer made calculations implicitly assuming that the sulfate coming out through the discharge was based on a finite amount of material being present, not an increasing, fluctuating amount of material. It should be noted that although the BETA value will not be significantly affected by the addition of more material beyond a certain value, the sulfate concentrations in the discharge certainly will.

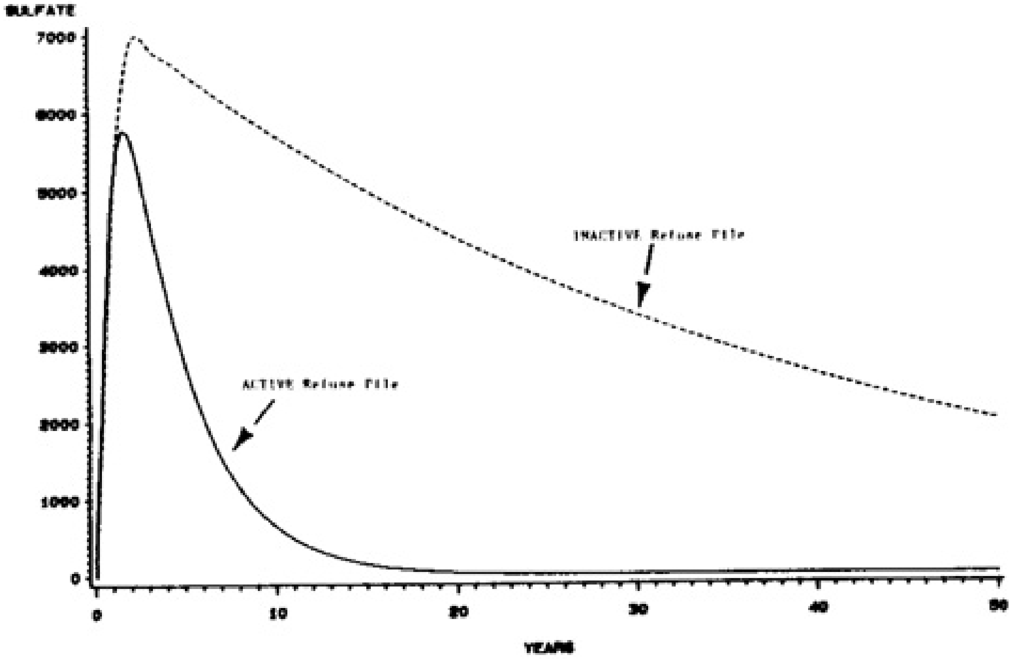

Figure 7.

Shows the curve (solid line) of the "active" refuse site compared to the typical "inactive" refuse site. The BETA value generated was "inflated" due to sulfate ion in the discharge originating in new material being added.

The SSPE/PSM technique was modified to handle new material being added. Using the "BETA" value obtained for the other minesites that were examined (5×10^{-4}/day) and a modified simulation, the computer was reprogrammed to calculate how much new material had been added during the course of the study. The company provided the amount of new material that had actually been added and the two results were compared (17.1 million tons actually added and 17.3 million tons calculated to have been added). This is statistically considered to be excellent agreement. This is also strong verifiable field evidence that the SSPE/PSM model is valid.

An example of the SSPE/PSM curve for an active refuse pile showing the "remaining unreacted pyrite," "sulfate in system," and "sulfate discharged to the environment" curves can be seen in Figure 8 . When the refuse pile becomes inactive the curve representing the "sulfate remaining in the system" will exhibit a first order decay mode with a half-life equal to

$$t_{1/2} = \ln(2) / \mathrm{BETA} \qquad (4)$$

and a mean-lifetime $t_m = 1 / \mathrm{BETA} \qquad (5)$

source: Van Nostrands Scientific Encyclopedia--5th Ed.

This case can be seen in Figure 9.

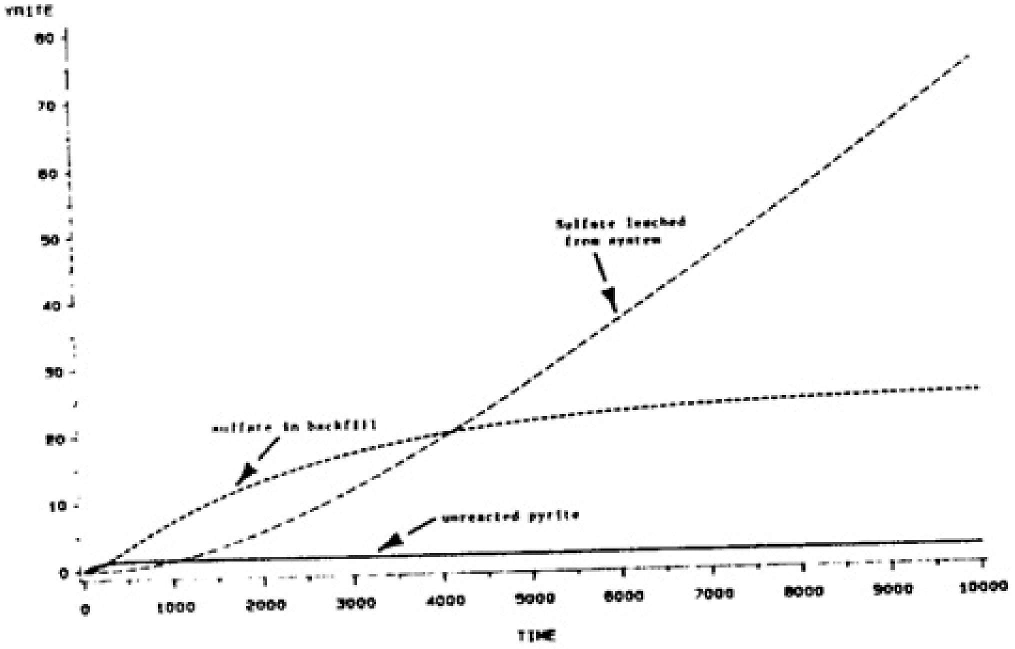

Figure 8.
The SSPE/PSM system curves for an active refuse pile. The vertical axis labelled "pyrite" is expressed as the percentage of the total amount of pyrite that has been placed on the pile. The time axis is in days. The amount of new material added per day was 500 tons per day.

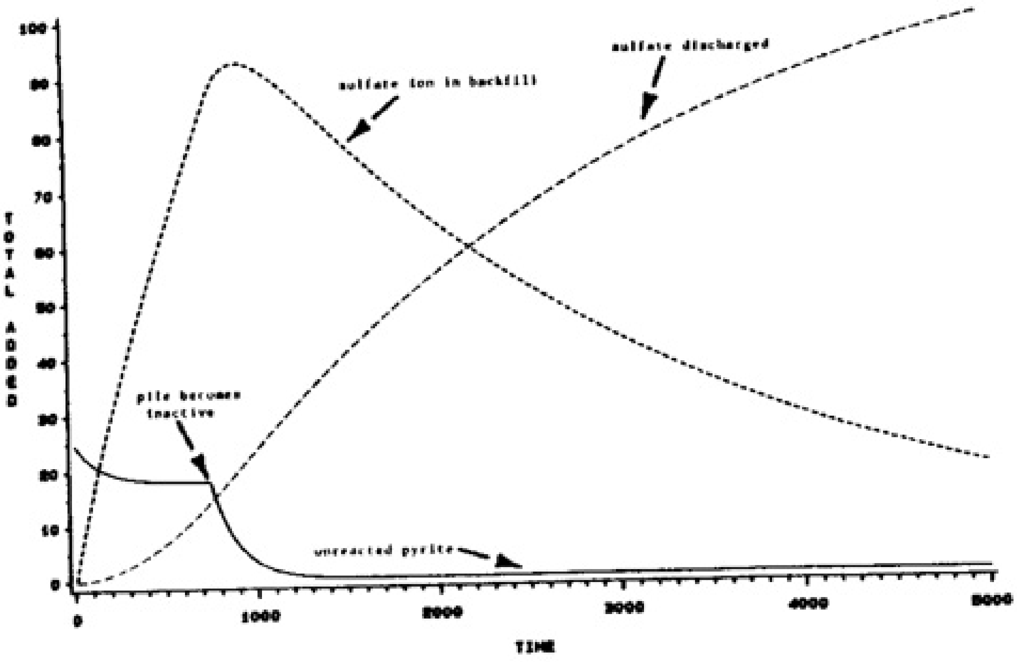

Figure 9.

The SSPE/PSM system curves for an active refuse pile up to 800 days then inactive after 800 days. The vertical axis labelled "pyrite" is expressed as the percentage of the total amount of pyrite that has been placed on the pile. The time axis is in days. The amount of new material added per day was 500 tons per day.

Conclusions

Several conclusions have been drawn from the modeling research:

(1) The chemical and physical processes for pyrite oxidation exhibit first order kinetic behavior;

(2) All of the pyrite present in a minesite does not react and this amount is significantly less than 100%;

(3) The incalculable number of microprocesses responsible for the oxidation product dissolution and physical "flushing" from a minesite are accounted in a single, quantifiable parameter (BETA);

(4) The "BETA" values for refuse piles and mountain top removal operations consistently show a magnitude of 10^{-4}/day;

(5) This "BETA" value may not hold for other mine types, but since "BETA" becomes less and less mass dependent at large volumes of material, unique scenarios involving these other mine types can be simulated.

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