

**THE INTERNATIONAL KINETIC DATABASE: RATES OF ACID GENERATION,
NEUTRALIZATION, AND METAL LEACHING FROM MINES AROUND THE
WORLD**

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INTRODUCTION

An important factor in designing and opening new mines, and closing current mines, is the prediction of drainage chemistry from each minesite component, like mine walls, waste-rock dumps, ore stockpiles, and tailings impoundments. In some countries, simple predictions of whether drainage will be acidic, near neutral, or alkaline are no longer sufficient. More detailed estimates of concentrations for various elements and pH are now required. These detailed predictions allow site-specific evaluations of various treatment or control options, leading to the most cost-effective environmental maintenance.

The first step in predicting drainage concentrations is the determination of reaction rates for primary minerals, like sulfides and oxides (Rate1, Figure 1). When combined with equilibrium chemistry of secondary minerals, concentrations through time can be predicted (Morin, in preparation). This paper focusses on the first step of primary-mineral reaction rates, particularly on the estimation of reaction rates from pre-test parameters.

A standard laboratory method for measuring reaction rates is through a Sobek humidity cell (Sobek et al., 1978), which has been in use and undergone little modification over 30 years (Figure 2). This technique has been compared and calibrated to in-field drainage chemistry for about three decades, and therefore it now has an established validity not equalled by any other reaction-rate method. The International Kinetic Database is based primarily on Sobek humidity cells.

In some places in Australia, a "humidity cell" is reportedly different from a Sobek humidity cell, involving oxygen consumption in a sealed chamber. This type of cell is not included in this paper.

Another established laboratory method is a "leach column", typically holding 1 kg to 1 t of sample onto which water is dripped or trickled. These columns often suffer from insufficient rinsing of particle surfaces, so that secondary minerals precipitate within them and thus primary-mineral rates are not obtained. In these cases, columns provide a laboratory estimate of Rate2 (Figure 1) rather than the intended Rate1, but Rate2 should only be determined under site-specific in-field conditions (Morin, in prep). Therefore, the reaction rates from columns may represent neither primary-mineral rates nor realistic secondary-mineral rates. In spite of the ambiguous value of columns, the results of a few dozen columns are included in this paper because of their wide usage.

One disagreement over humidity cells and columns is that the excess water used in the weekly rinses of cells may interfere with geochemical processes within the sample. As explained above, the intent of cells is to avoid geochemical retention, unlike columns, in order to obtain primary-mineral rates (Rate1, Figure 1). This may

be incorrectly construed as “interference”. In any case, the amount of excess water should not significantly affect predictions for two reasons. First, reaction products presumably accumulate mostly on particle surfaces and their water films. The intent of weekly rinses is to remove as much of these products and any accompanying secondary minerals as possible to define the primary-mineral rates free from interferences. This is an original, primary objective of a Sobek cell (Sobek et al., 1978). Second, concentrations of cells are converted to rates as mg/kg/wk, independent of the amount of water, because it is unrealistic to believe that cells (and columns) can necessarily provide actual concentrations representative of multi-million-tonne minesite components. If the volume of rinse water drained through a cell each week affects the calculated weekly reaction rate, then the amount of water is insufficient to remove all weekly reaction products.

THE INTERNATIONAL KINETIC DATABASE

In order to understand better primary-mineral reaction rates at minesites and factors affecting those rates, the International Kinetic Database (IKD) was initiated as a voluntary effort by the authors. The IKD contains summary statistics for (1) pre-test characterization of samples like acid-base accounting, total-metal contents, and particle surface areas, (2) average reaction rates of metal leaching, acidity generation, and acidity neutralization over the entire duration of each laboratory kinetic test, and (3) average reaction rates over the last few weeks, typically five weeks, representing stable long-term conditions. Reaction rates are expressed as mg of a parameter/kg of sample/week ($\text{mg kg}^{-1} \text{wk}^{-1}$).

For example, the sulfate-production rate, which is synonymous with sulfide-oxidation and acid-generation rates after pre-existing soluble sulfate is removed, is expressed as $\text{mg SO}_4/\text{kg/wk}$. Sulfate production can be converted mathematically to other units like $\text{kg O}_2/\text{m}^3/\text{s}$ and $\text{t acidity/t material/yr}$ based on mineralogy and physical characteristics.

There have been previous papers on the IKD when it was smaller (Morin et al., 1995a and b). However, the IKD now contains 457 kinetic tests from 63 mines and mining projects, and there are new lessons to be learned on estimating test results from pre-test data. The durations of the tests in the IKD range from 10 to 286 weeks (5.5 years), with an average of 35 weeks. For confidentiality, the names of mines in the database are not provided. Most of the mines are located across North America, with several in South and Central America and Australasia. The IKD continues to grow and contributions of data from other mines are gratefully received and kept confidential. We would particularly like to expand the database with Australasia mines.

FACTORS DETERMINING REACTION RATES

There are dozens of physical, chemical, and biological factors that influence the reaction rates of minerals exposed to near-surface environmental conditions. However, many of the factors or processes have not been studied in detail, and several have probably not yet been identified. Therefore, in an open environmental system like a minesite, it is not possible to accurately assess or predict mineral reaction rates within an entire minesite component, although published papers have claimed to do so on the basis of one factor like oxygen diffusion or heat generation. Nevertheless, for predictions of drainage chemistry, which is typically the focus of most environmental studies at mines, only approximate rates are needed for the first several decades to centuries due to the dominant control by secondary minerals (Figure 1). The primary-minerals rates are critical for (1) ensuring secondary-mineral solubility is attained and (2) estimating the time frame for changes in drainage concentrations.

To gain insights into some pre-test factors influencing reaction rates, data in the IKD are plotted to visually reveal relationships and correlations. Particular emphasis is placed on the influences that pre-test parameters have on test results so that rates can be roughly estimated in advance.

TWO-DIMENSIONAL CORRELATIONS OF PARAMETERS IN THE IKD

Earlier papers on the IKD used two-dimensional scatterplots which showed general correlations at best (Morin et al., 1995a and b). For example, a two-dimensional plot of sulfate production rate measured during the kinetic tests against pre-test solid-phase sulfur content as %S showed that rates in the IKD spanned five orders of magnitude, ranging qualitatively from “very high” to “very low” (Figure 3a, top). However, the sulfate production rate generally increased as pre-test sulfur increased, so pre-test sulfur obviously had some influence on sulfate production. A least-linear best-fit line relating the two parameters showed that the distribution of logarithmic values about the line resembled a normal distribution with a standard deviation of 0.753 log cycles (Figure 3a, bottom). According to standard probabilities, approximately two-thirds of the datapoints should lie within one standard deviation above and below the best-fit line, for a total factor of 32 (1.506 log cycles), about the best-fit line. The prediction of sulfate production from pre-test sulfur within a factor of 32 is better than five orders of magnitude, but is still relatively inaccurate. If the influence of other factors could be determined, sulfate production might be more accurately predicted.

Another two-dimensional plot examined the Carbonate Molar Ratio from the kinetic tests. A value for this Ratio of 2.5 from a kinetic test, for example, means the calcium-magnesium-based neutralization potential (NP) in a sample was dissolving 2.5 times faster than acidity was generated by sulfide oxidation. This proportionally faster dissolution rate for NP often indicated by the Carbonate Molar Ratio, or Feldspar Molar Ratio if more applicable, is well known and documented (e.g., Morin and Hutt, 1994). The plot of the Carbonate Ratio with initial, pre-test NP showed that pre-test NP levels below 7-10 t CaCO₃ equivalent/1000 t of sample (or 7-10 ppt) from Sobek ABA were relatively unreactive or unavailable for neutralization (Figure 3b, top).

Based on this, pre-test Net Potential Ratios (NPR = Neutralization Potential / Acid Potential) can be adjusted by subtracting 10 ppt CaCO₃ from the measured NP and recalculating adjusted NPRs. If this adjusted value is between 1.0 and 4.0 and is exceeded by the average carbonate molar ratio during the kinetic testwork, acidic conditions should be expected at some point. For most samples with adjusted pre-test NPR values less than 1.0, net acidity is often inevitable and molar ratios are only helpful for calculating when the onset of acidification may begin. Also, most samples with adjusted pre-test NPR values above 4.0 can be expected to remain indefinitely near neutral or alkaline, and thus molar ratios are not particularly valuable for detailed predictions of pH values.

Exceptions to the preceding guidelines for the Carbonate Ratio and adjusted NPR are known and documented under laboratory and field conditions (summarized in Morin and Hutt, in prep). Therefore, long-term kinetic tests operated for at least a year are warranted for all minesites and mining projects. These tests also provide data for predicting concentrations of metals, acidity, and alkalinity under the applicable pH regime. For example, pH-neutral drainage with a zinc concentration of 20 mg/L is not acidic, but is toxic to aquatic life and may require treatment or control.

A two-dimensional plot of adjusted NPR with the lowest pH measured during each kinetic test in the IKD showed a general trend (Figure 3c, top). Obviously, at lower values of adjusted NPR, acidic pH can be expected. A least-linear best-fit line and a normal distribution of logarithmic data about the line with a standard deviation of 1.47 (Figure 3c, bottom) indicated that the lowest pH can only be predicted accurately within 2.94 pH units, two out of three times. Similar general trends and weak correlations were also noted in two-dimensional diagrams for copper and zinc (Morin et al., 1995b).

THREE-DIMENSIONAL CORRELATIONS OF PARAMETERS IN THE IKD

To more accurately assess and predict reaction rates through correlations with other parameters, particularly easily measured pre-test parameters, three-dimensional (3-D) plots were created (Figures 4 to 13). The geostatistical method known as kriging was employed for interpolation and smoothing the 3-D surfaces, using

linear isotropic variograms as provided by Surfer Version 6.01 (Golden Software, 1995).

There are certain commonsense 3-D relationships that can be expected and have been used to determine if the IKD contains reasonable data. For example, because aqueous alkalinity is typically defined as zero at and below pH 4.5, the production rate of alkalinity (mg CaCO₃/kg/wk) should fall below detection around pH 4.5. A plot of alkalinity production against the lowest pH measured during each test (x axis, Figure 4) and the rate of consumption/production of neutralization potential (NP) shows the expected decrease in alkalinity with pH. However, some peaks of alkalinity production are noted near pH 4.5 at very high levels of NP consumption, which is reasonable since alkalinity is derived from NP dissolution. Similarly, acidity production can be expected to correlate with lowest measured pH as well as sulfate production which generates the acidity, and these trends can be seen in Figure 5. Therefore, data in the IKD meet reasonable expectations of basic aqueous geochemistry and are thus considered relatively normal and representative.

Numerous 3-D plots were made of many pre-test and test parameters. Only the plots that showed the best trends for lowest pH and reaction rates are discussed below. Emphasis was placed on using pre-test parameters on the x and y axes as predictors of a parameter on the z axis from the kinetic tests.

Figure 6 shows the 3-D comparison of lowest pH measured during each test (z axis) against initial paste pH (x axis) and log NPR (NP/AP, y axis). The heavy contour line represents a pH of 6, so the portion of the 3-D surface above that line remained near neutral or alkaline throughout the test period. The surface indicates that combinations of (1) paste pH down to nearly 4.5 with very high NPR and (2) high paste pH with low-to-high NPR typically remained neutral to alkaline. This can be used to estimate whether acidic conditions will develop during a kinetic test lasting approximately one year.

The rate of sulfate production (sulfide oxidation) is mostly independent of NP values, but dependent on initial sulfur (Figure 7). However, as shown in Figure 3a, there are parameters in addition to initial sulfur that affect sulfate production, but these are other kinetic-test parameters such as aqueous pH which cannot be predicted well prior to a test (Figures 3c and 8).

The Carbonate Molar Ratio (ratio of calcium-magnesium-based NP dissolution to sulfate production in a kinetic test discussed above) shows a good 3-D trend with initial sulfur and initial NP (Figure 9). Normally, a Ratio greater than 1.0 is needed to prevent acidic conditions (see heavy contour in Figure 9).

For copper leaching, the initial solid-phase copper level is a minor factor, whereas initial sulfur content is a strong influence (Figure 10). The initial copper content, however, does play a more detectible role (Figure 11) when plotted with lowest pH measured during each kinetic test. However, lowest pH cannot be accurately predicted in advance of a kinetic test.

In contrast to copper, initial zinc content has a major influence on zinc leaching in combination with initial sulfur content (Figure 12). Good correlations with test parameters were also noted, particularly lowest pH (Figure 13), sulfate production rate, and NP consumption rate. Therefore, zinc leaching is more regular and predictable from pre-test and test parameters than copper leaching.

CONCLUSION

The two-dimensional and three-dimensional diagrams provide some predictive capability for estimating pH and reaction rates during a kinetic test based on data from other mines. However, the estimates for pH are no better than several pH units and the estimates for rates have uncertainties of at least a factor of 10. Therefore, preliminary site-specific predictions can be made from these generic data, but long-term kinetic tests are required to confirm and refine the preliminary predictions for each minesite.

Ideally, the three-dimensional diagrams in this paper show that the ultimate method for interpreting and predicting primary-mineral reaction rates is a nonlinear, multidimensional analysis of dozens of factors. However, this difficult and complex task may ultimately not be possible anyway because all potentially relevant parameters like sample temperature, infrared flux, and barometric pressure are rarely measured during laboratory and field tests.

Sobek humidity cells remain valuable, time-established tools for estimating primary-mineral reaction rates. When combined with site-specific effects of secondary minerals, they allow detailed predictions of many aqueous parameters through the various stages of minesite drainage (Figure 1).

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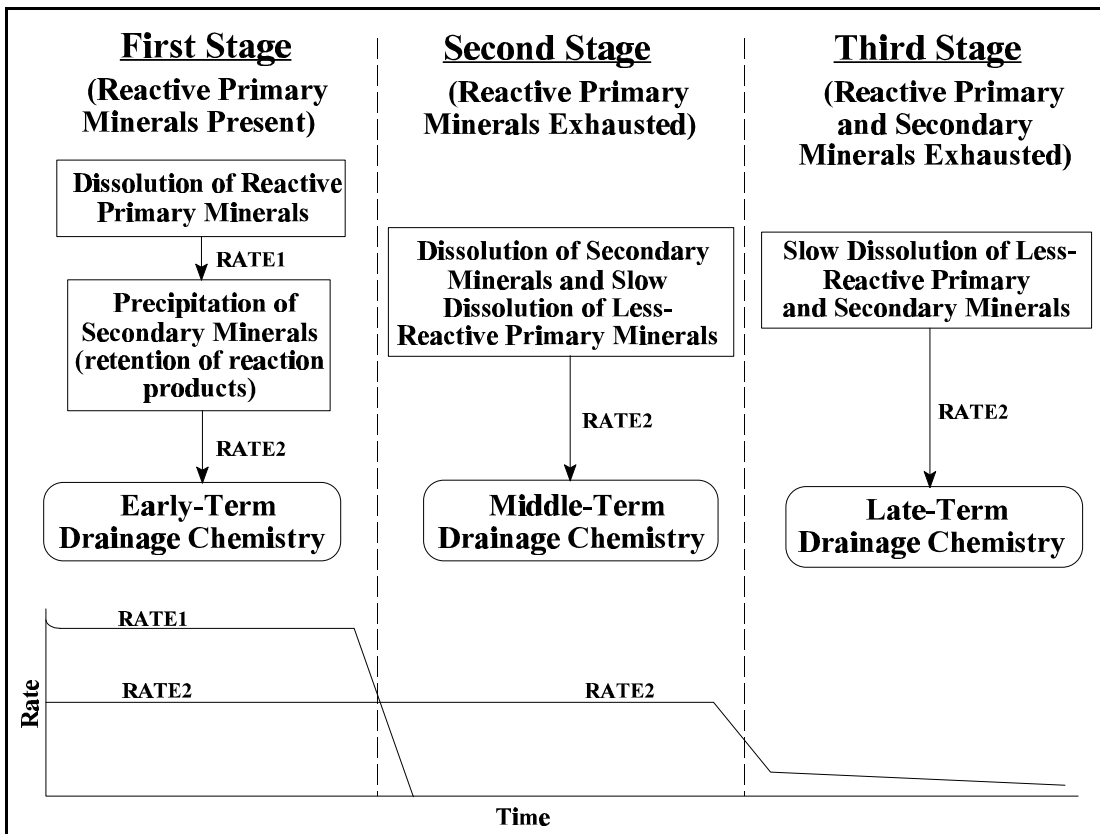


FIGURE 1. Three Stages in Minesite Drainage Chemistry (from Morin, in preparation).

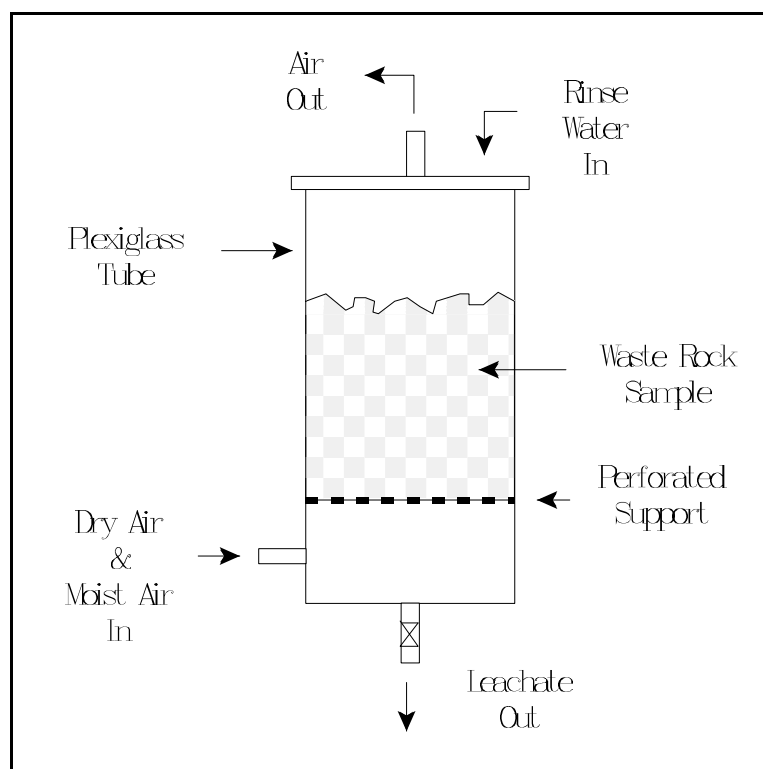


FIGURE 2. Example of a modified Sobek Humidity Cell.

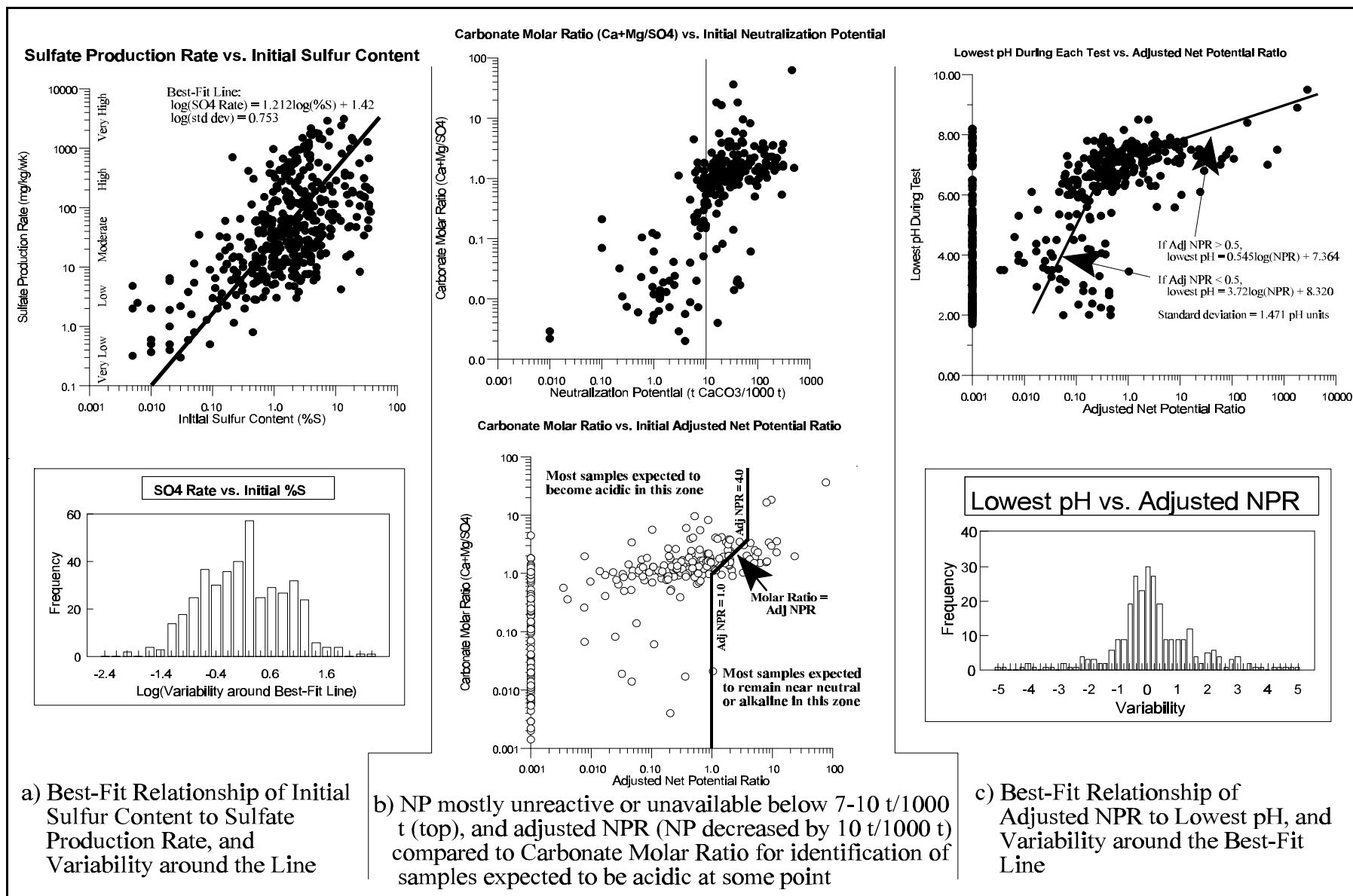


FIGURE 3. Examples of Two-Dimensional Plots of IKD Data (adapted from Morin, in prep).

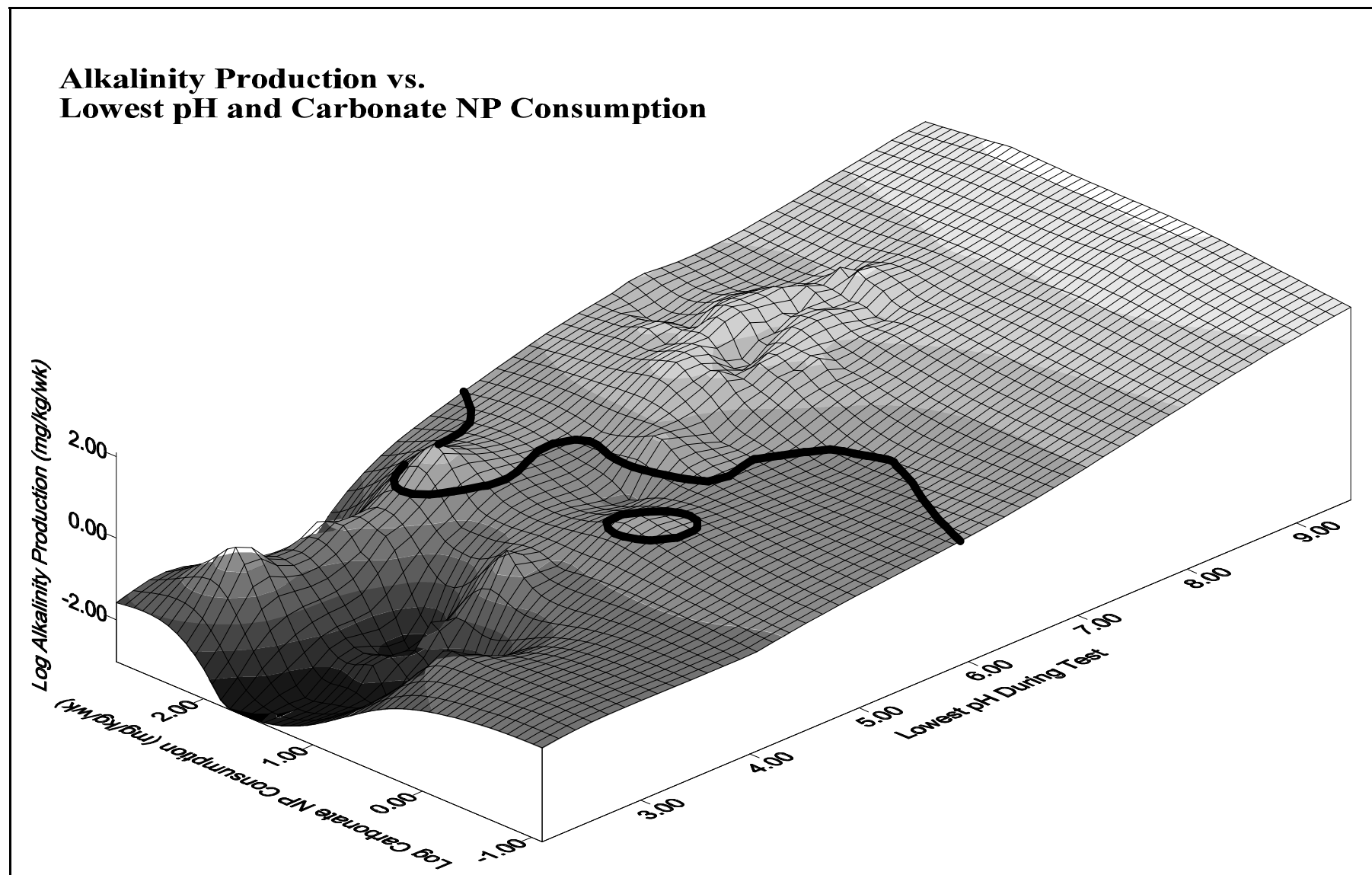


FIGURE 4. Rate of Alkalinity Production (z axis) vs. Lowest pH During Test (x axis) and Rate of Neutralization Potential (NP) Consumption (heavy line = minimal alkalinity production at 1 mg CaCO₃/kg/wk).

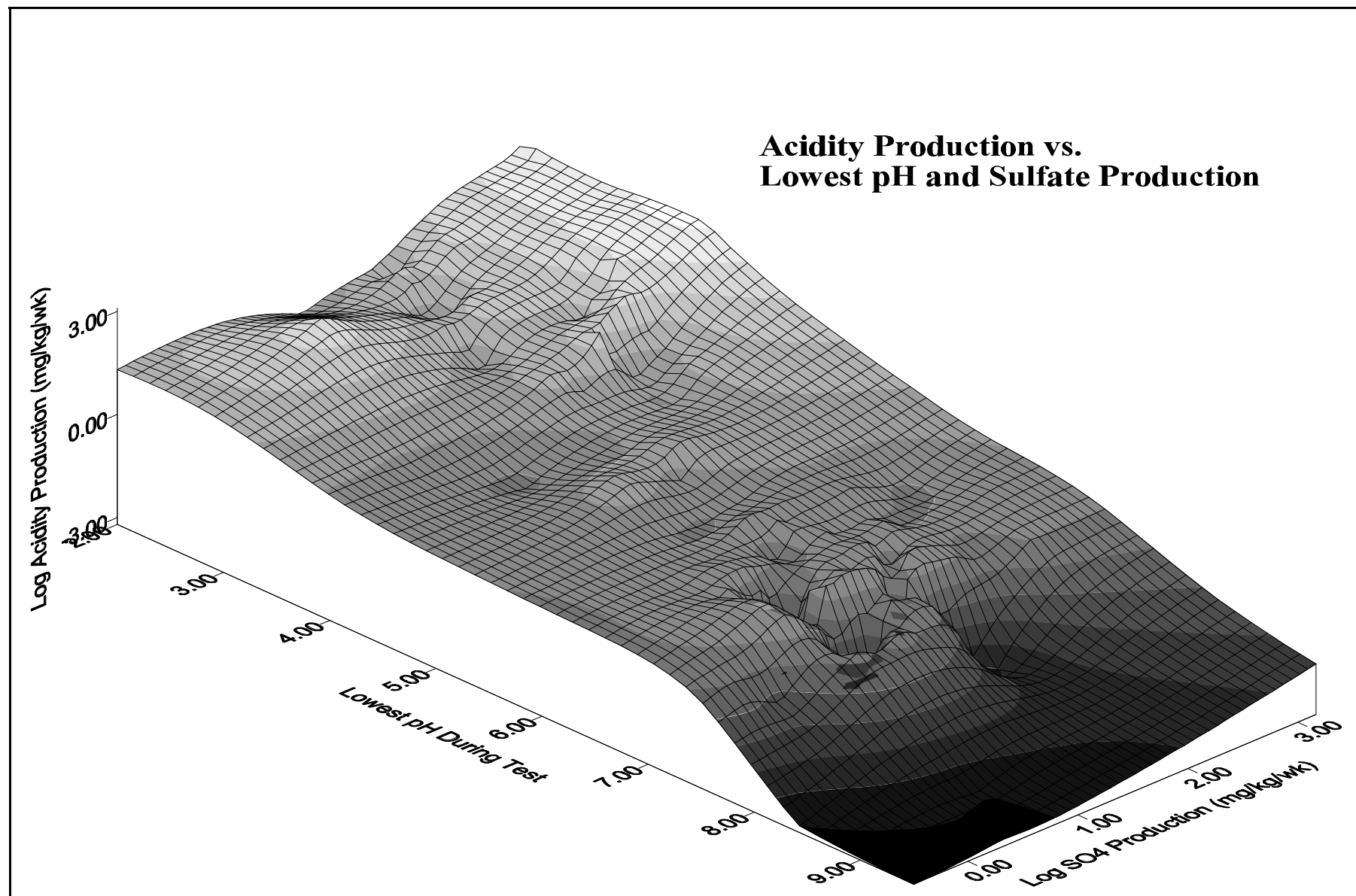


FIGURE 5. Acidity Production vs. Lowest Measured pH and NP Consumption.

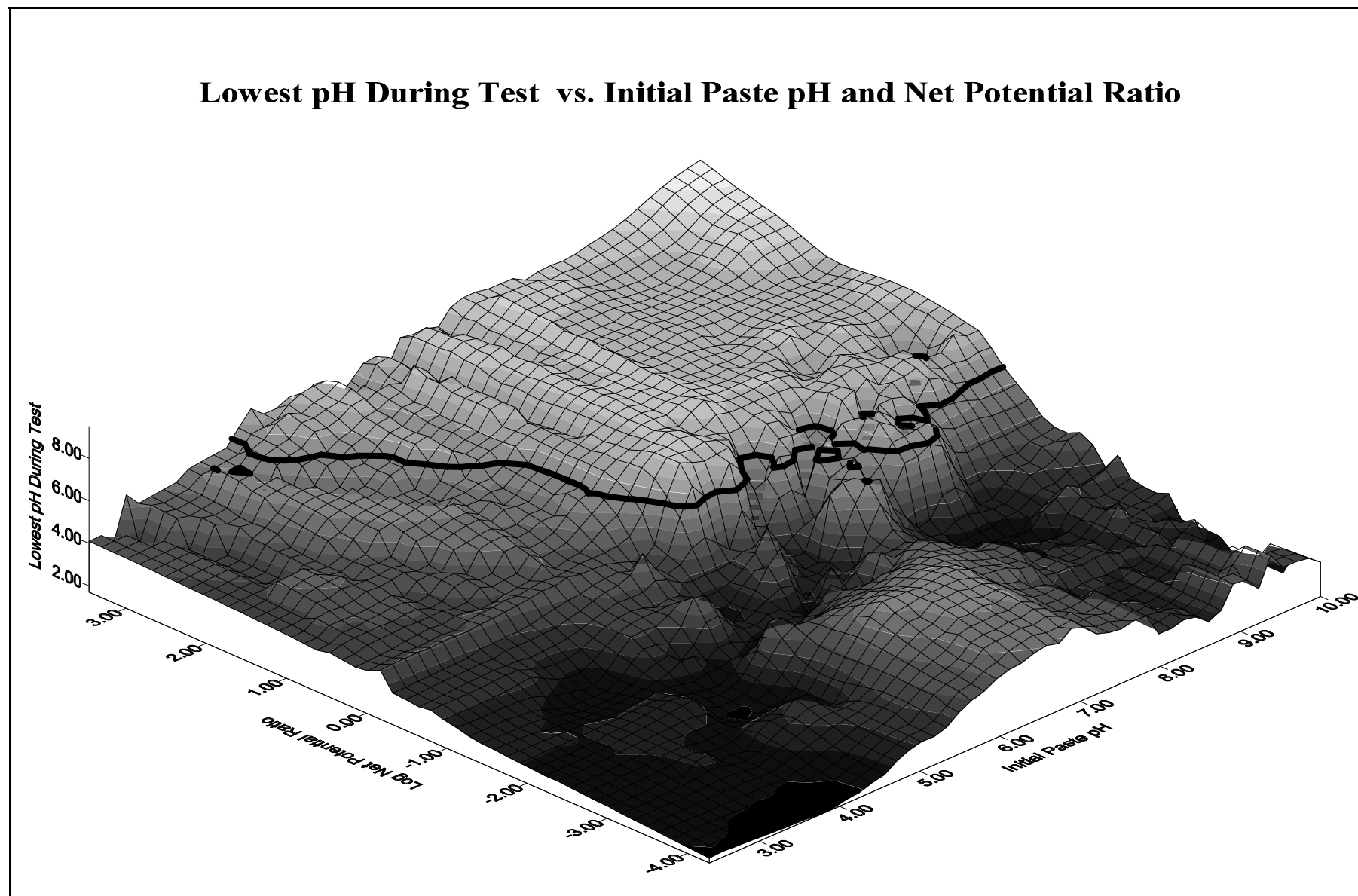


FIGURE 6. Lowest pH vs. Initial Paste pH and Initial Net Potential Ratio (heavy line marks lowest pH of 6.0).

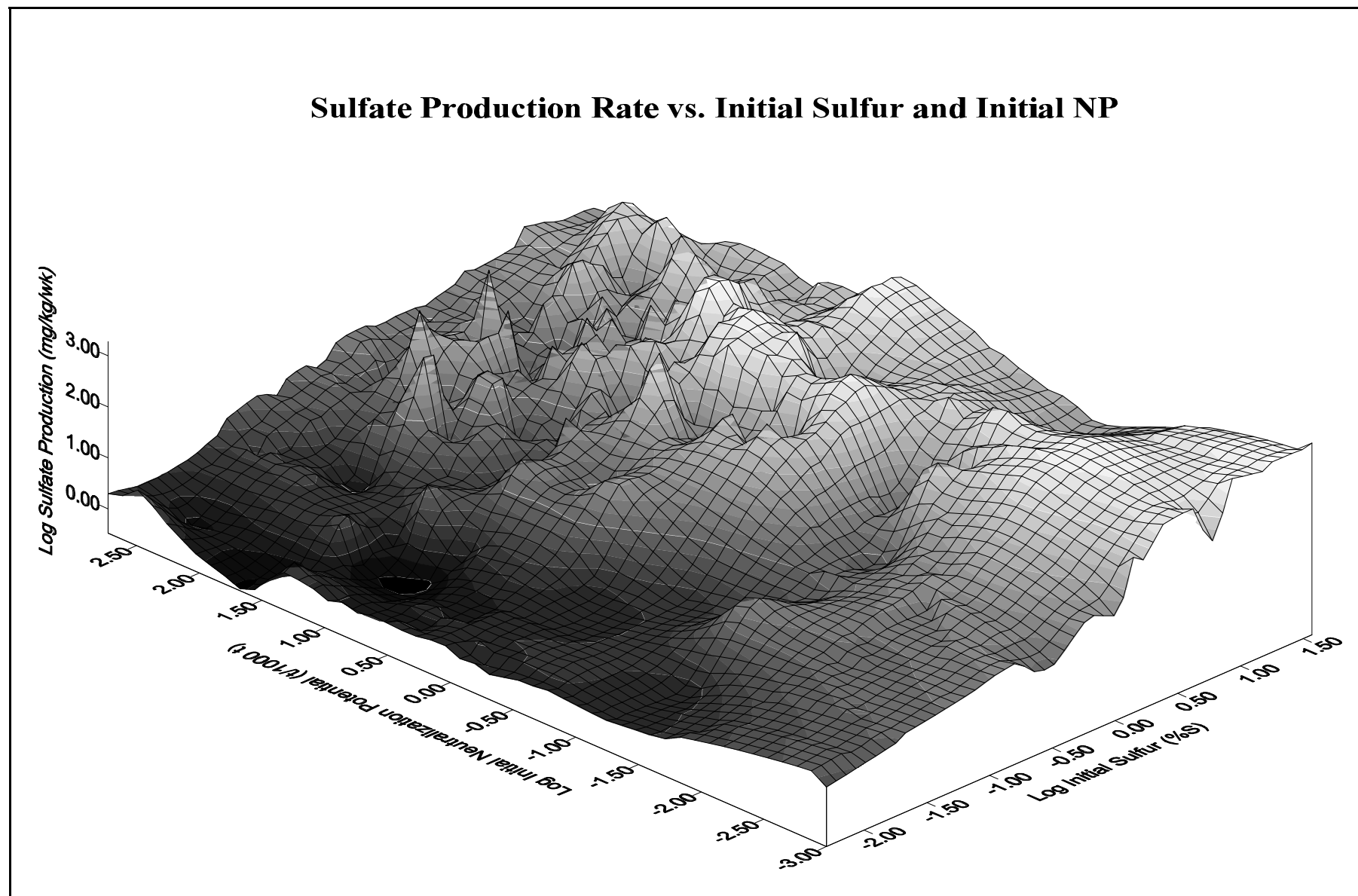


FIGURE 7. Sulfate Production Rate vs. Initial Sulfur and Initial NP.

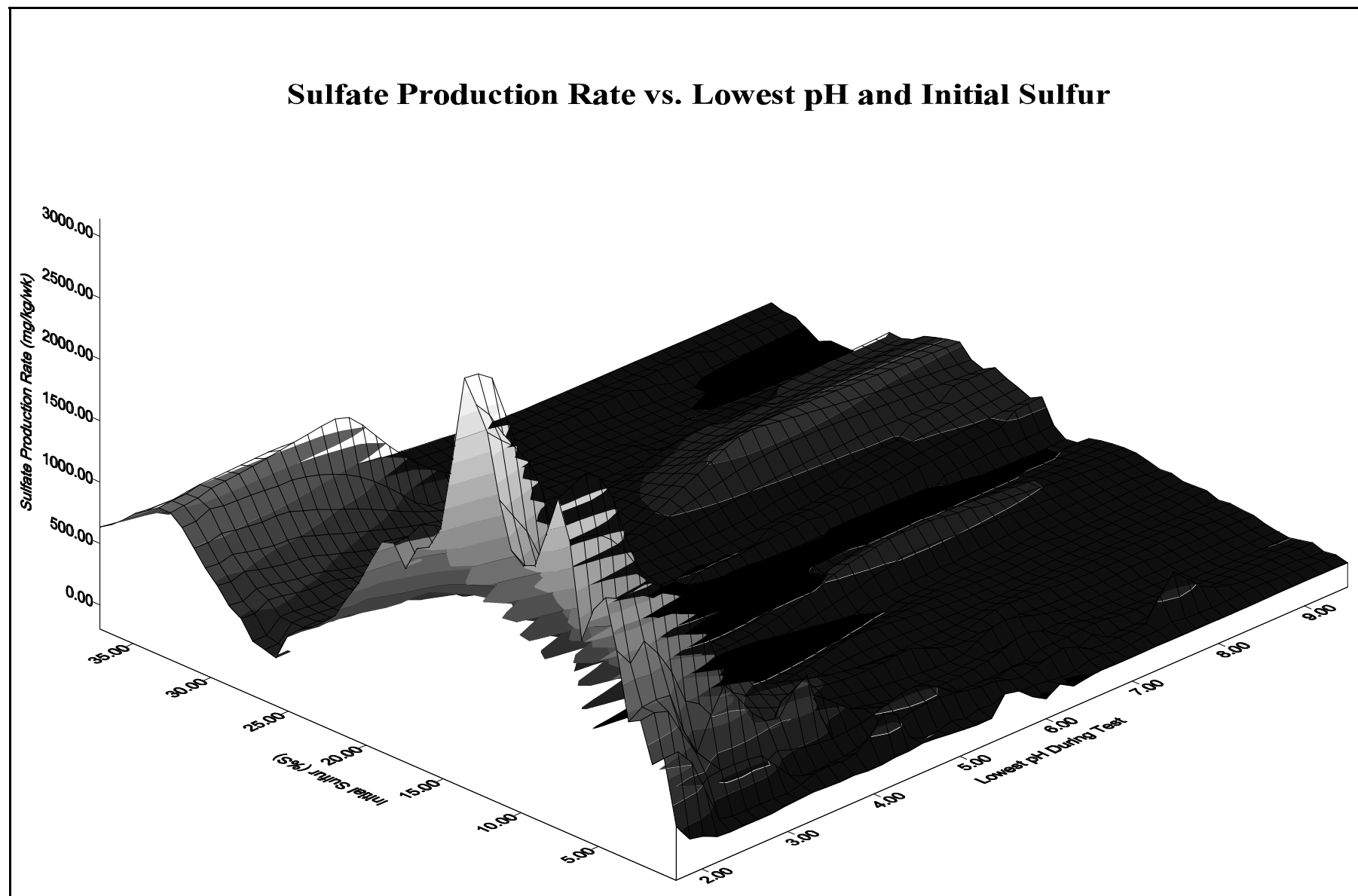


FIGURE 8. Sulfate Production Rate vs. Lowest pH During Test and Initial Sulfur.

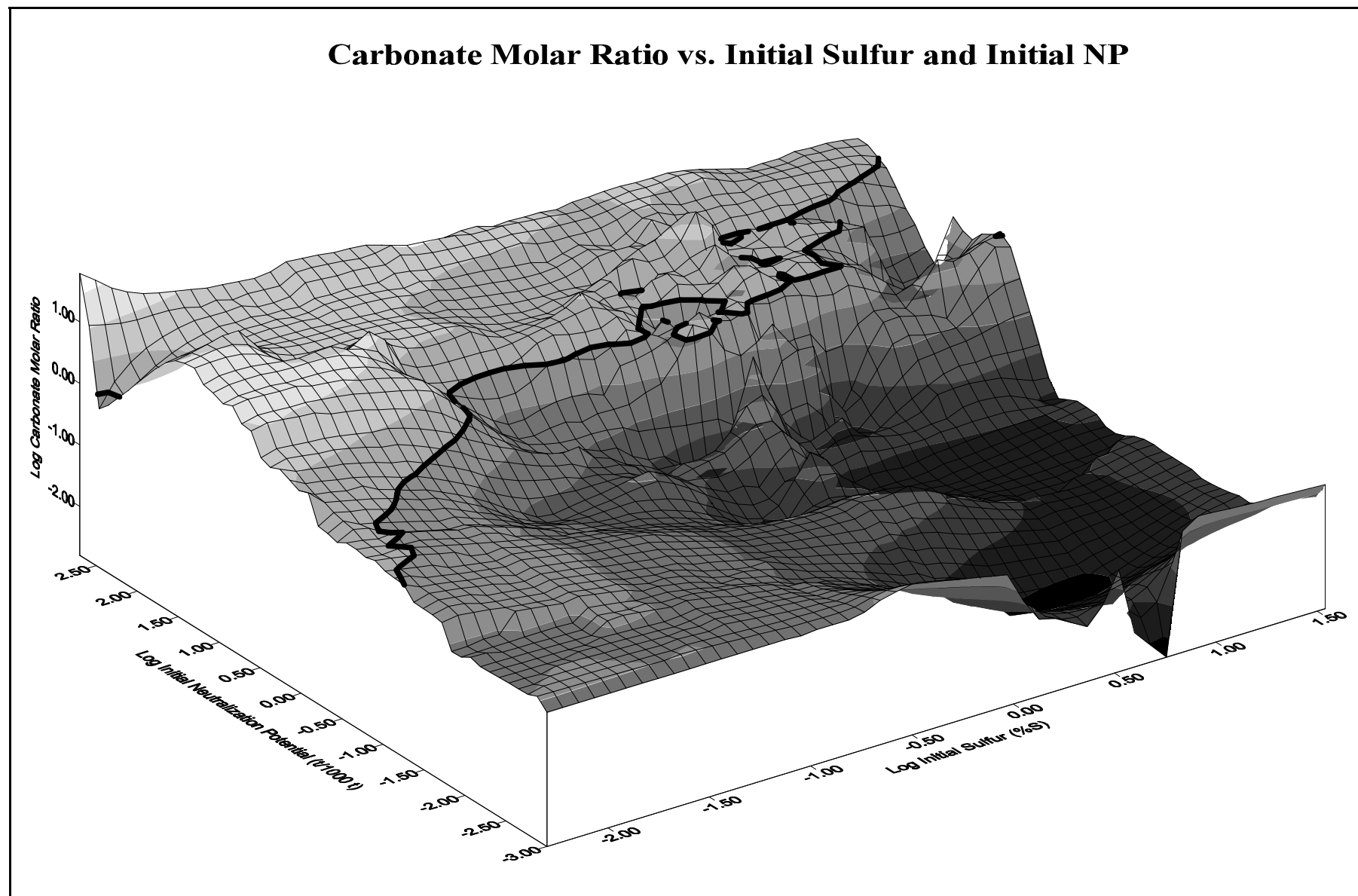


FIGURE 9. Carbonate Molar Ratio vs. Initial Sulfur and Initial NP (heavy lines marks a Ratio of 1.0).

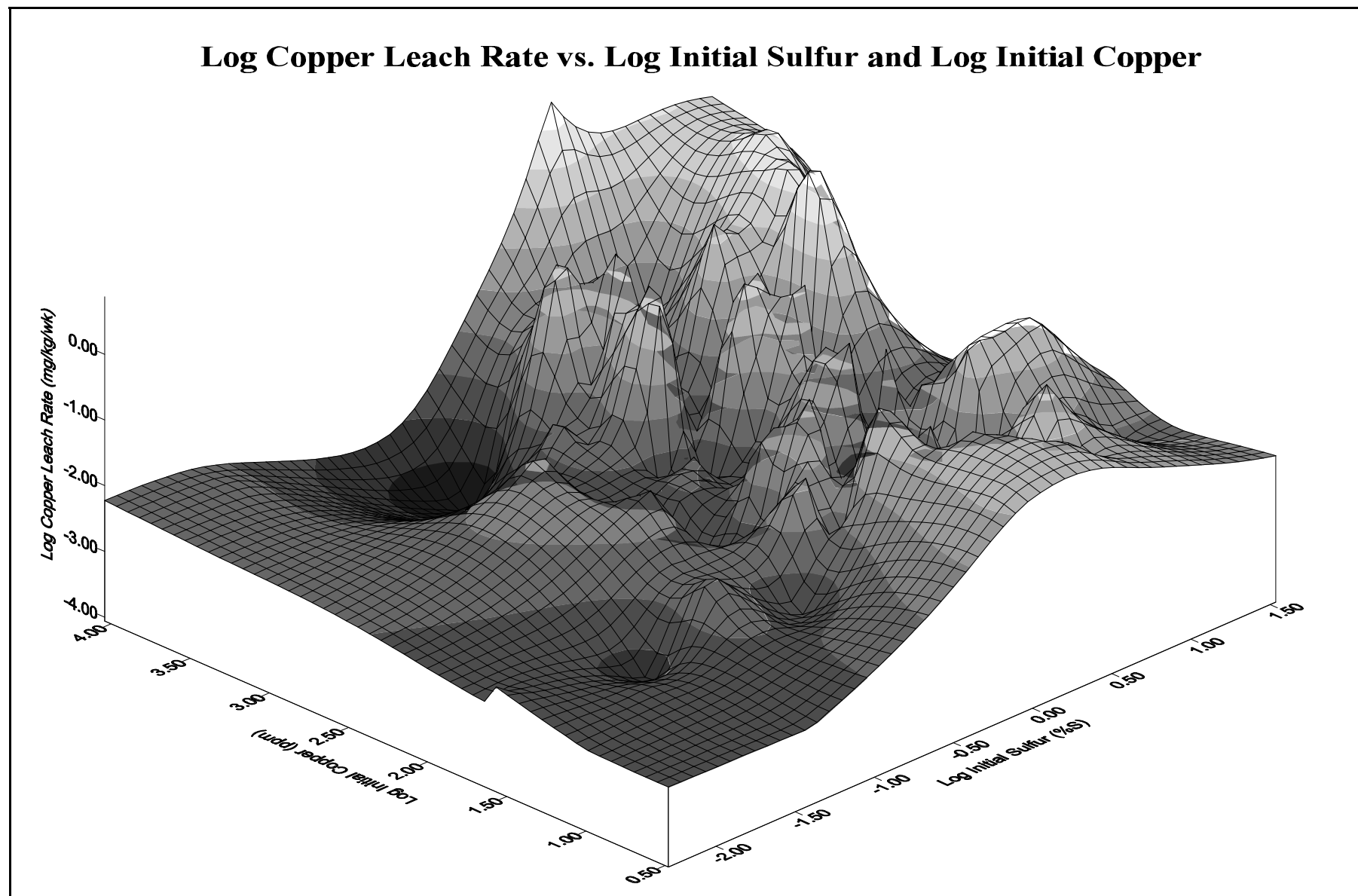


FIGURE 10. Copper Production Rate vs. Initial Sulfur and Initial Copper Content.

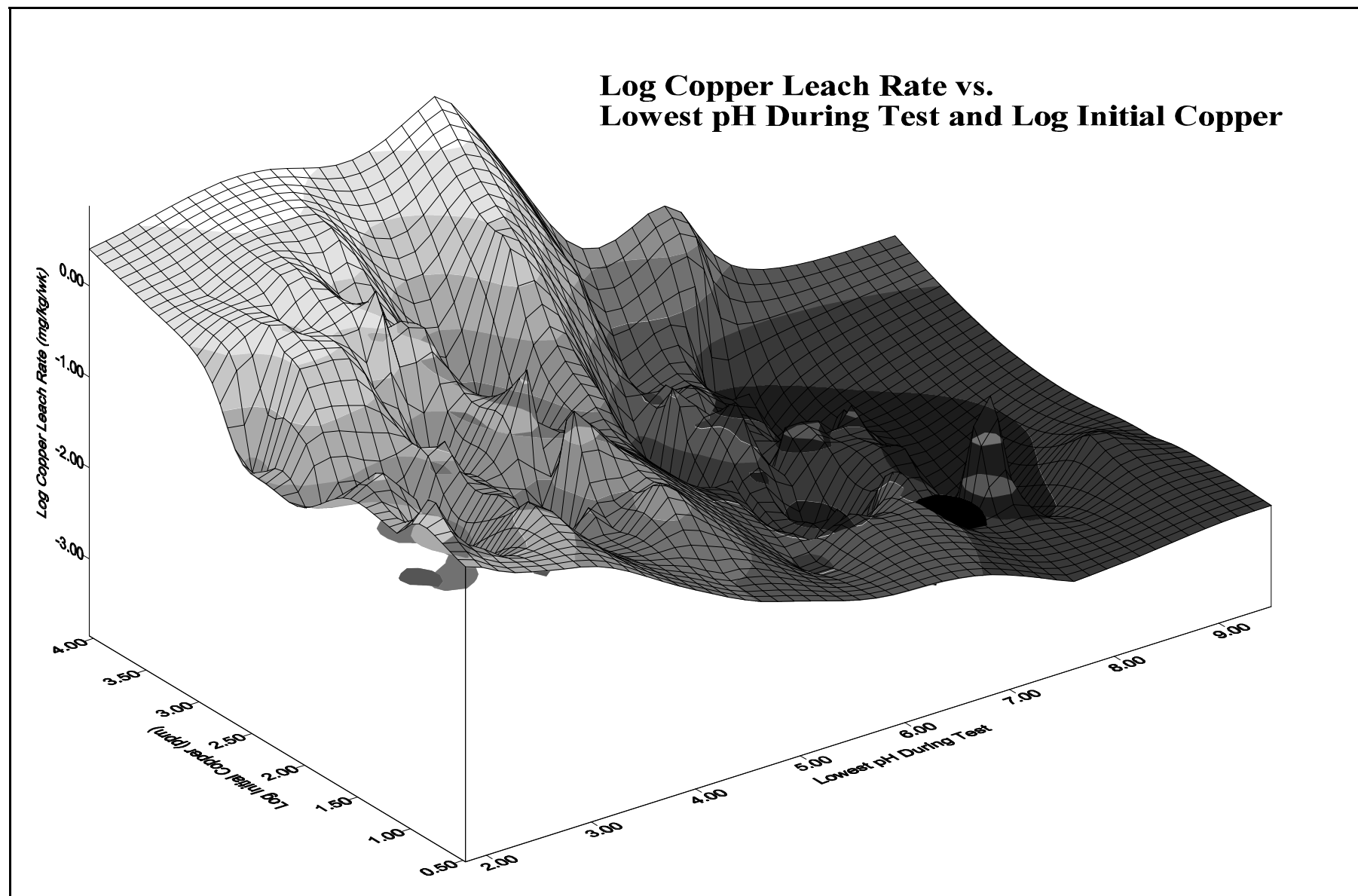


FIGURE 11. Copper Production Rate vs. Lowest pH During Test and Initial Copper Content.

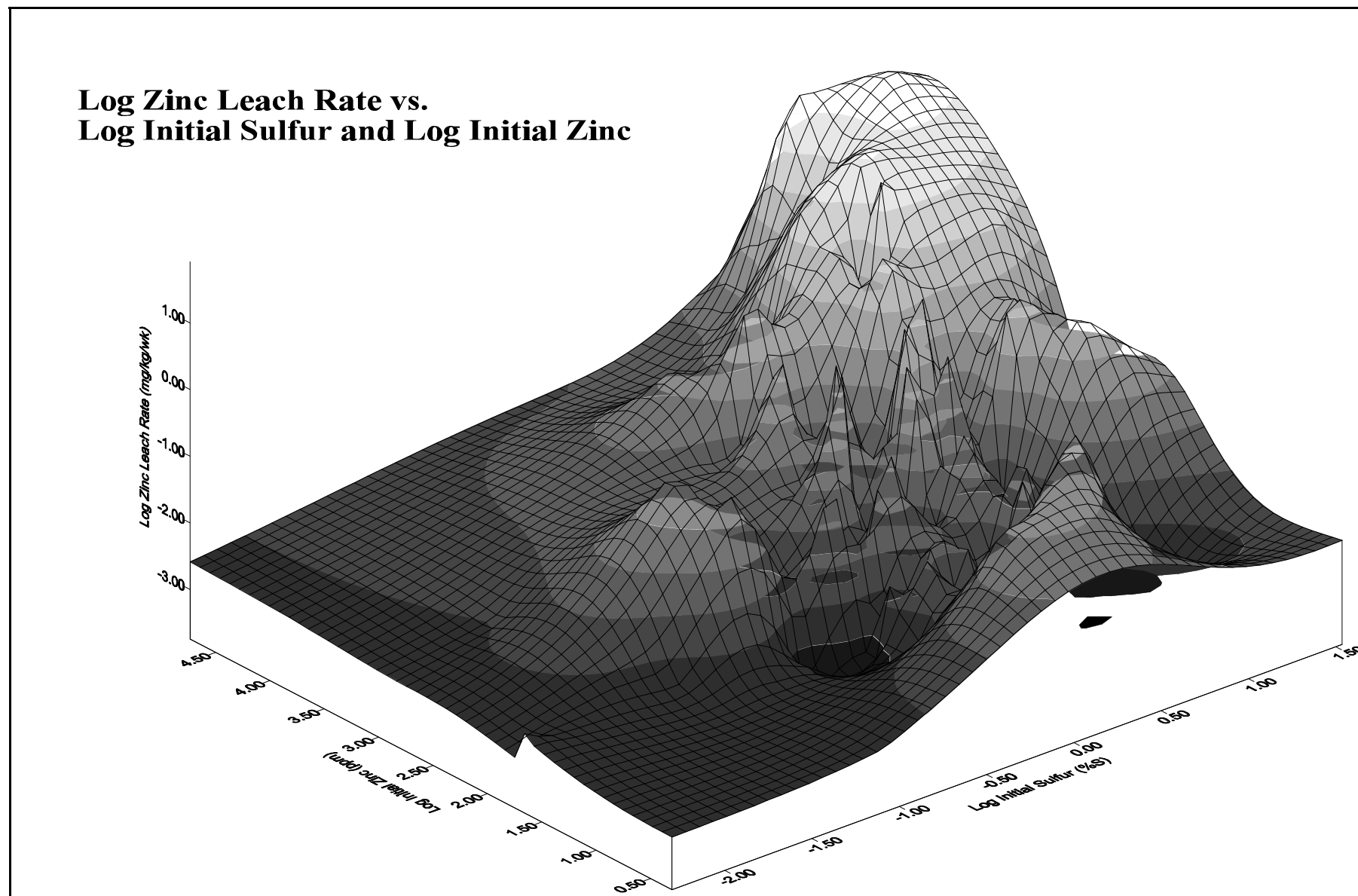


FIGURE 12. Zinc Production Rate vs. Initial Sulfur and Initial Zinc Content.

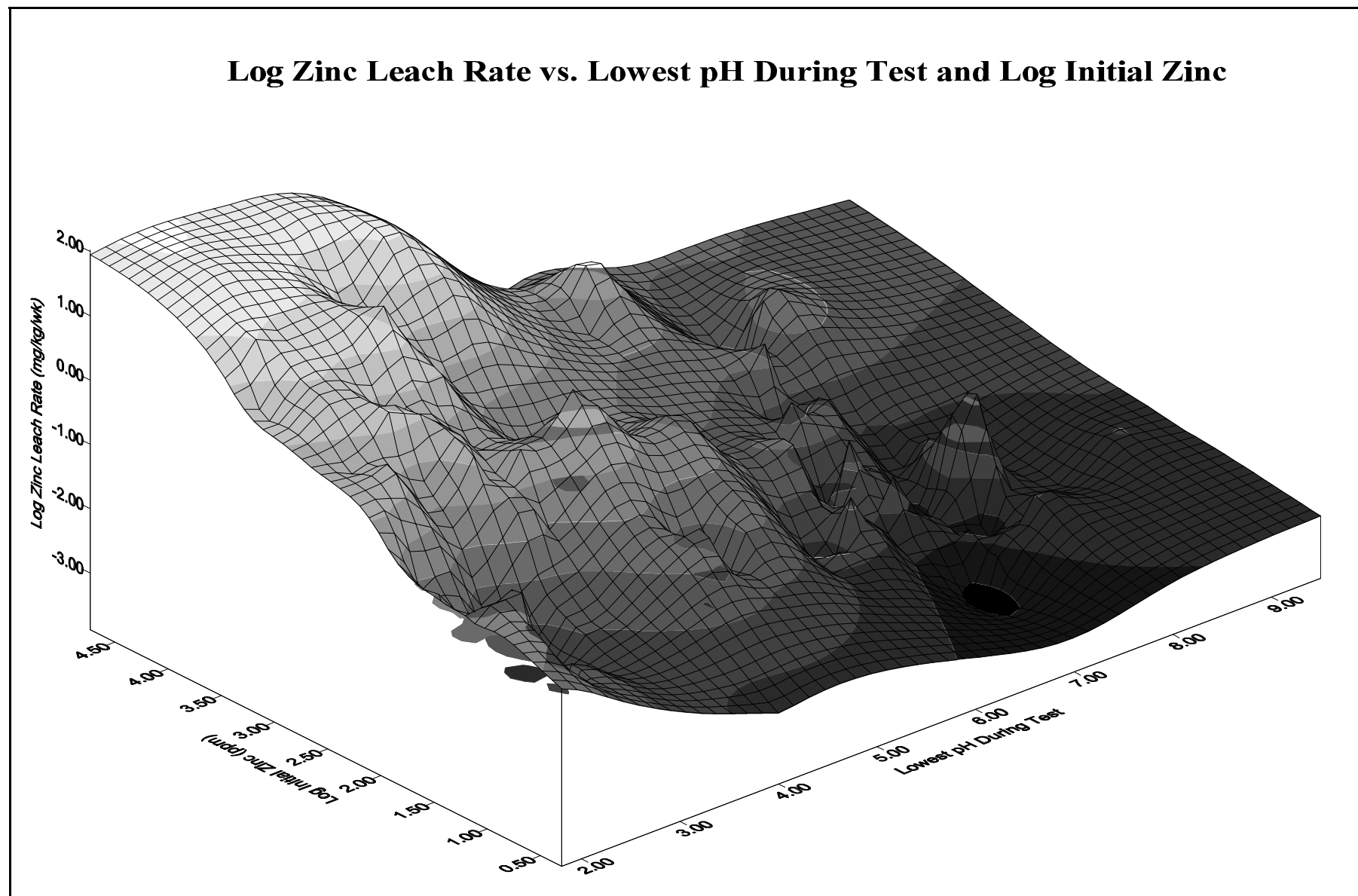


FIGURE 13. Zinc Production Rate vs. Lowest pH During Test and Initial Zinc Content.