

HUMIDITY CELLS: HOW LONG? HOW MANY?

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Abstract

The humidity cell is a standard technique for obtaining bulk reaction rates that has been used for more than 30 years. This paper examines rates of sulphide oxidation, based on sulphate-production rates, from several long-term cells and batches of cells in the International Kinetic Database (IKD). The objective of this study is to address how long cells should be operated to obtain long-term stable oxidation rates, and how many should be used to define the range of reaction rates at a site.

How long? Data from 10 cells that operated from 3 to 7 years indicated there is roughly a 50% chance that a cell will geochemically stabilize after the first year and that this stability will persist for at least several years. Geochemical stability is defined here as fluctuations in the last-five-week average of less than a factor of two above and below the long-term average. Thus, on average, 50% of cells can be terminated shortly after the first year of operation. The remaining 50% must be operated for more than 3-5 years to obtain long-term stable rates. There are no factors identified to date that provide an early indication of which samples require many years to stabilize.

How many? Seven batches of cells, each containing at least 12 cells, were obtained from the IKD. The results showed that at least 12 cells will provide a good indication if the average rate is biased towards the lowest measured values, which is apparently typical. However, 40 or more cells may be needed to obtain a reasonable distribution pattern of values, like normal or lognormal distributions.

Key Words: Sulphide oxidation, bulk reaction rates, humidity cells, International Kinetic Database

Introduction

The humidity cell is a widely recognized geochemical kinetic test for obtaining bulk mineral reaction rates under controlled laboratory conditions.^{1,2} It is basically an enclosed chamber through which air is passed (Fig. 1) and, after specified periods of time, the chamber is opened and the sample is rinsed with water of known chemical characteristics. The purpose of the periodic rinse is to remove all reaction products that accumulated since the previous rinse. From the chemical analysis of the rinse water, bulk reaction rates can be calculated:

$$\text{Rate (mg/kg/wk)} = \frac{\text{rinse concentration (mg/L)} * \text{volume of rinse water recovered (L)}}{[\text{weight of sample (kg)} * \text{number of weeks since last rinse (wk)}]}$$

For example, the bulk rate of sulphide oxidation is often

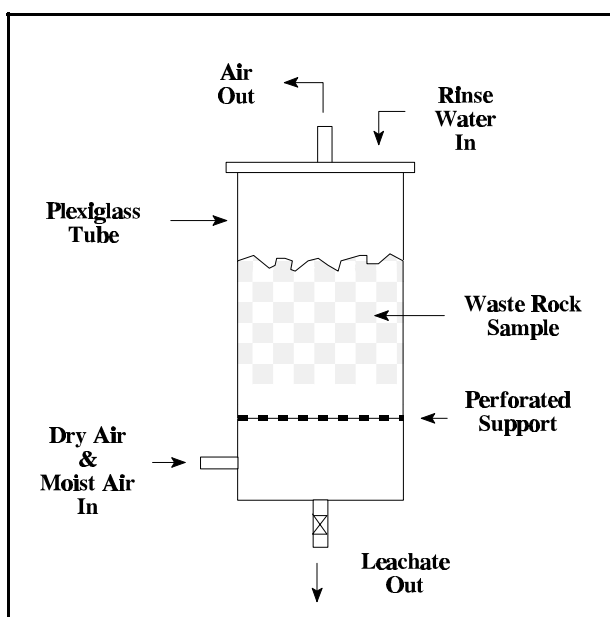


Fig. 1. Schematic Diagram of a Humidity Cell.

expressed as mg SO₄/kg of sample/week, and cell-measured sulphide-oxidation rates from around the world in the International Kinetic Database^{1,3} (IKD) span approximately five orders of magnitude.

The history of the humidity cell can be traced to its origin more than 30 years ago as a plastic shoe box or Bell jar^{4,5}. The primary objective of these tests was, and still is, to remove all accumulated reaction products in order to calculate rates. Interestingly, this basic objective has been overlooked at times. For example, the Association for Standardized Testing of Materials has proposed a standard procedure for humidity cells⁶ that involves trickle leaching of a sample and other steps that would preclude the reliable removal of accumulated reaction products. Also, many column tests are operated and interpreted like cells, where the ongoing retention of reaction products as secondary minerals through these tests actually yields unrealistically low bulk rates¹. This retention in columns and improperly operated cells can result in serious misinterpretations and erroneous predictions⁷. For clarity, cells which are operated with the intention of removing all reaction products, with minimal interference by secondary-mineral precipitation, are referred to here as "Sobek cells". This name reflects an early primary reference for humidity cells⁵, with the understanding that cell-like tests existed for at least a decade prior to that time.

The objectives of this paper are to answer two questions pertaining to rates of sulphide oxidation based on rates of sulphate production in Sobek cells. First, how long should Sobek cells be operated until information is obtained for reliable long-term predictions of sulphide-oxidation rates? Second, how many Sobek cells should be operated for a particular minesite component in order to obtain a reliable and representative range of sulphide-oxidation rates?

How Long Should Sobek Cells Be Operated?

This question has been discussed for many years based on guesswork, speculation, and intuition. Approximately ten to fifteen years ago, many cells were operated for only 10 to 20 weeks and this was thought to be sufficient to obtain rates that would be stable for many years or decades. As cells were operated for additional weeks, it became apparent that 10-20 weeks was not sufficient to obtain stable rates, and the time increased to 30-40 weeks. In recent years, a specific time is usually not set in advance. The typical criterion now requires running a cell until stable rates are obtained based on comparison to previous weeks' rates. If the weekly rates are not fluctuating widely, then the average rate is declared stable. It is worthwhile to examine even this general criterion.

In order to discuss how long a cell should be operated, the International Kinetic Database (IKD)^{1,3} was searched for cells that were operated for more than two years and ten such cells were identified. The weekly sulphate-production data for these cells were then obtained and plotted. Each plot consists of:

- the measured weekly data for sulphate production to represent the bulk rate of sulphide oxidation,
- a running average using the previous five-weeks' data,
- a running average using the previous 53-weeks' (one-year) data, and
- a single-value "long-term" average calculated from all weekly data excluding the first year (Weeks 0 to 52).

Good examples of ideally behaved cells show that early concentrations decrease sharply (or rise sharply), but then stabilize for at least two years after roughly 40 weeks of operation (Figs. 2 and 3). In this case, "stable" is defined here as the five-week running average generally remaining within a factor of two above and below the long-term single-value average. Even a cell that has operated for more than six years meets this definition of stable (Fig. 4) after the first year, although there is some oscillation within a factor of two through the remaining years. These three examples indicate that stability within a factor of two can be obtained after the first year and can persist for several years.

Not all cells behave as ideally as the preceding cells. Some require longer times for stability (Fig. 5) and some display oscillations that are greater than a factor of two around the long-term average (Fig. 6), although additional years of operation are needed to determine this. Interestingly, the cell of Fig. 6 became acidic during testing, with pH generally falling below 6 by Week 70 and generally below 5 by Week 90, eventually reaching a low of 2.8. This may account for the increase in rates after Week 130. Nevertheless, these two cells of Figs. 5 and 6 still display generally stable rates over a period of years, even with changing cell-rinse pH.

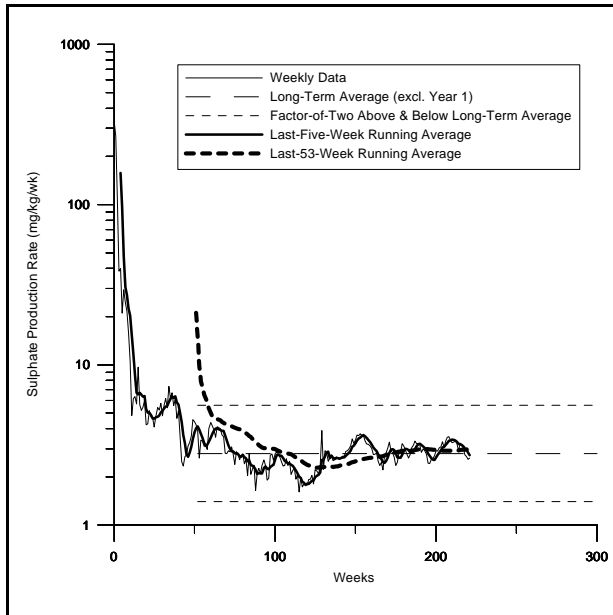


Fig. 2. Cell 1 with Good, Long-Term Stability.

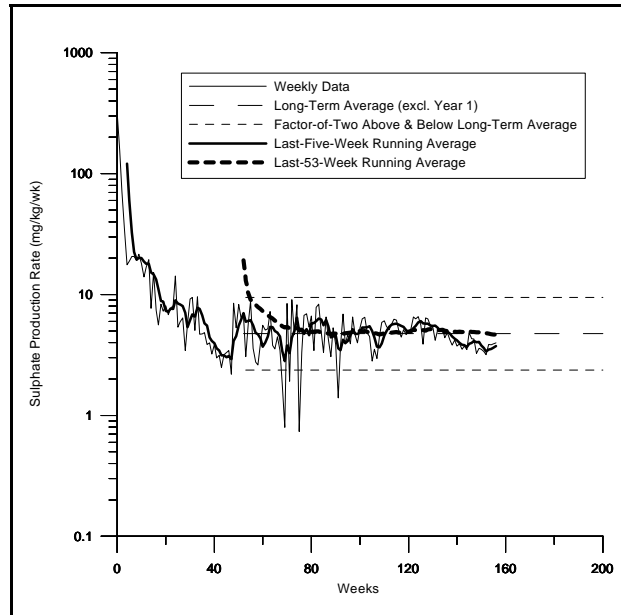


Fig. 3. Cell 2 with Good, Long-Term Stability.

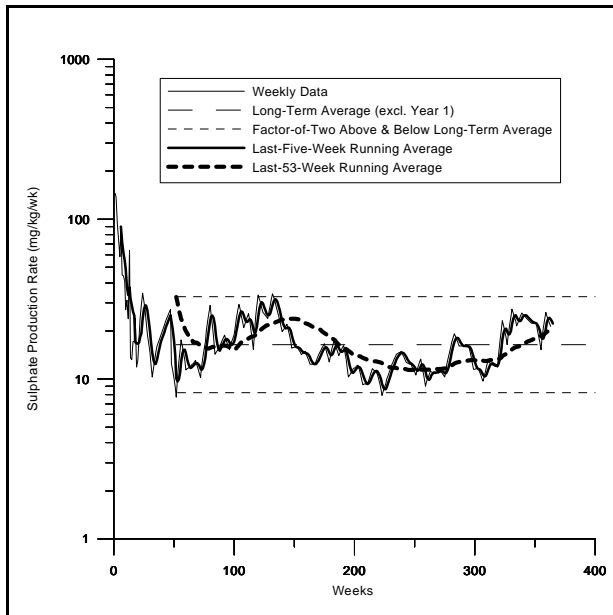


Fig. 4. Cell 3 with Reasonable Long-Term Stability.

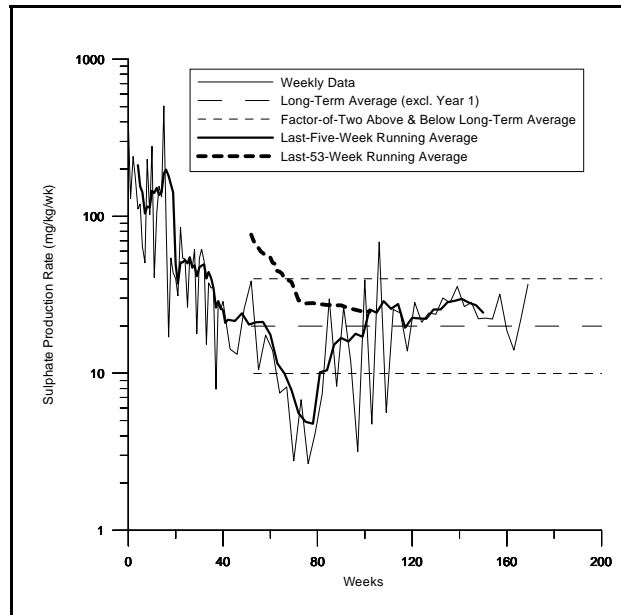


Fig. 5. Cell 4 Requiring More Than a Year for Reach Stability.

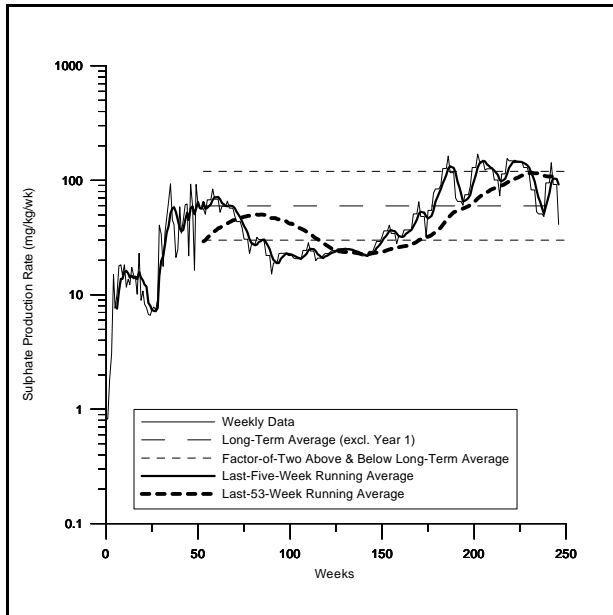


Fig. 6. Cell 5 Showing Some Instability Over Several Years.

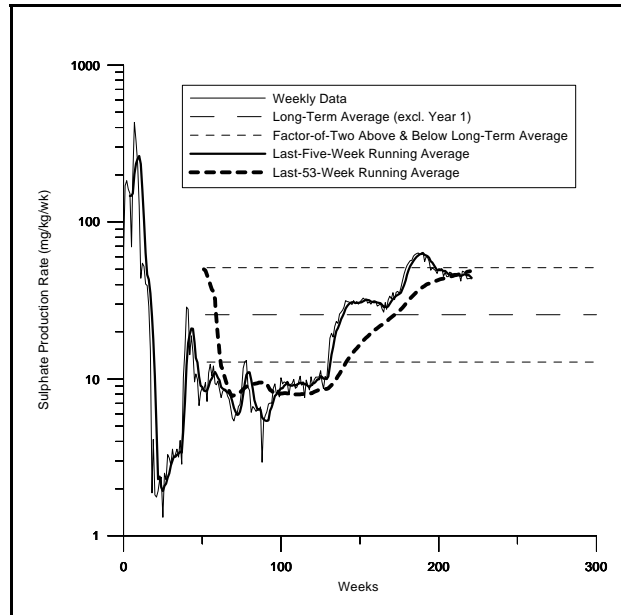


Fig. 7. Cell 6 Showing Instability After Four Years.

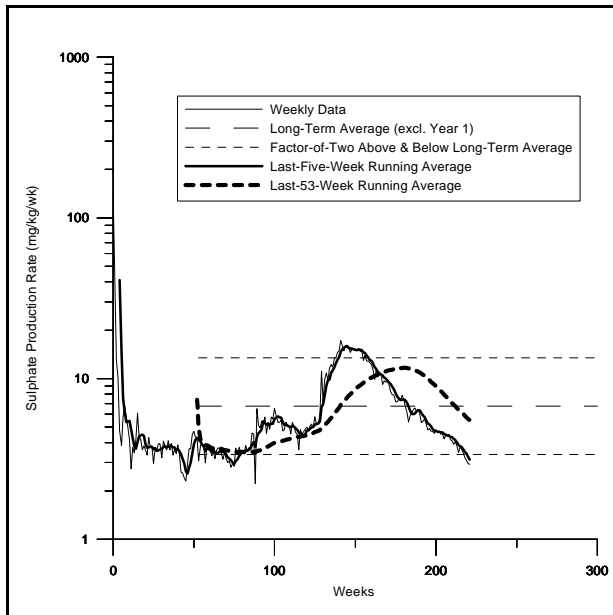


Fig. 8. Cell 7 Showing Some Stability But With Significant Trends That Indicate Long-Term Instability.

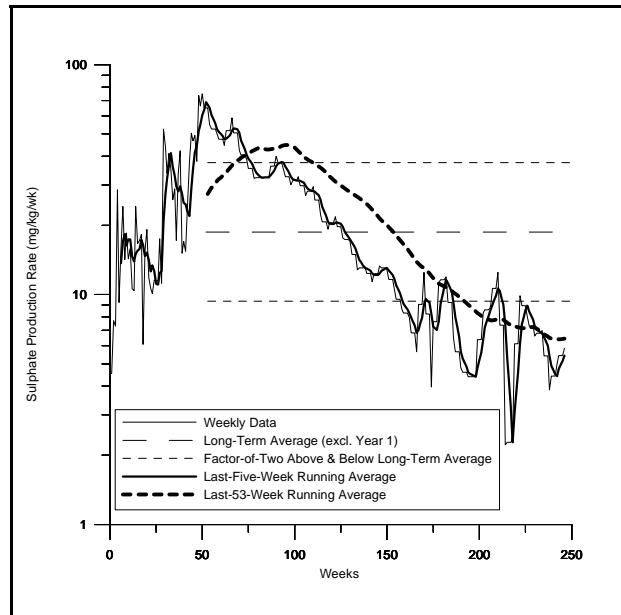


Fig. 9. Cell 8 Showing Instability As Increasing Rates Followed By Decreasing Rates.

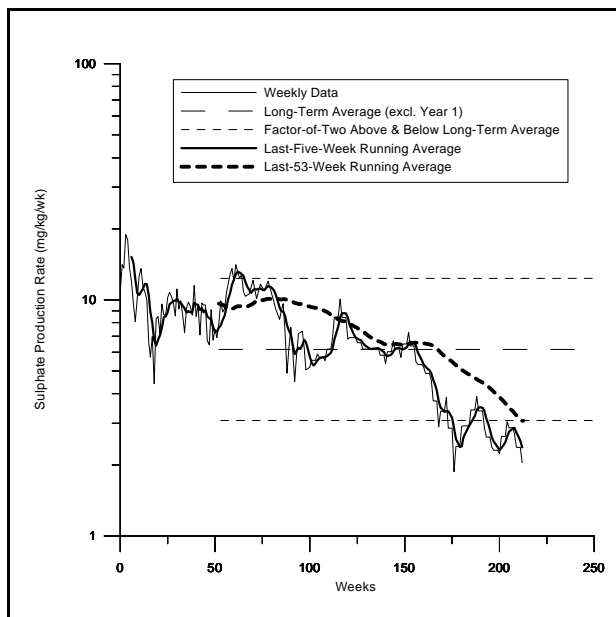


Fig. 10. Cell 9 Showing Instability Through Decreasing Rates.

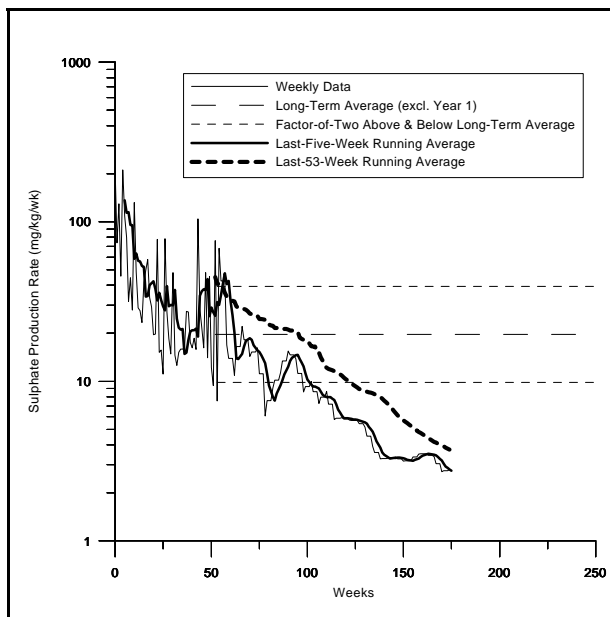


Fig. 11. Cell 10 Showing Instability Through Decreasing Rates.

There are other cells that show some stability for a few years and then oxidation rates rise and/or fall sharply (Figs. 7 and 8). Finally, there are cells that show few signs of stability over three to five years of operation (Figs. 9, 10, and 11). No explanation for this instability could be found in the pre-test characterizations of the samples or in intratest results like cell-rinse pH, although pH from the cell in Fig. 9 fell from greater than 6 to a minimum of 4.2 after Week 140 as the oxidation rate was also decreasing.

In summary, ideally behaved cells yield geochemically stable rates after the first year, which is supported by additional years of operation. “Stable rate” means the last-five-week running average generally remains within a factor of two above and below the long-term average rate, and other studies indicate that this stability may persist for at least five to ten years¹. Three of the ten long-term cells (30%) located in the IKD displayed such stability. Another two cells (20%) showed signs of stability, but more than a year was needed to obtain it or oscillations around the long-term average were significant. The remaining five cells (50%) showed signs of stability at various times, but additional testing showed that rates increased and/or decreased sharply at later times. As a result, this small set of cells indicates that there is a 50% chance of achieving stability within a year or two. For the 50% that do not, and only longer testing will identify them, more than three to five years are needed. No explanation or predictive indicator for instability could be identified in the pre-test characterizations of the samples or the intratest results.

How Many Sobek Cells Should Be Operated?

For any particular project or minesite component, a reasonable question is: How many cells should be operated to obtain a representative range or numerical distribution of sulphide-oxidation rates? This can be important for large-scale predictions. For example, if 15 cells are operated on waste rock from a particular mine-rock pile and the rates resemble a normal or “Bell shaped” distribution, then various predictions can be made using the statistical meanings behind such a distribution.

The International Kinetic Database (IKD)^{1,3} was searched for minesites that provided at least 12 cells for rock or tailings, and this led to seven sites: Minesite H2 (46 cells), H6 (16 cells), H24 (13 cells), H28 (25 cells), H29 (24 cells), H45 (15 cells), and H61 (44 cells). On an arithmetic scale, all seven datasets showed distributions that resembled

a lognormal distribution, with the lowest sulphide-oxidation rates being most abundant and the frequency of rates decreasing as the value of the rate increased (e.g., Figs. 12a-16a). However, when displayed on a logarithmic scale (Figs. 12b-16b), most datasets did not show a clear normal distribution except Site H61 (Fig. 16).

Therefore, at least 12 cells appear sufficient to determine whether relatively low reaction rates tend to be most frequently measured at a site, but more than 12 are typically needed to delineate a reliable distribution. Furthermore, approximately 40 cells may be sufficient (Fig. 16) or insufficient (Fig. 12) to identify a reliable distribution.

Summary

Based on long-term humidity cells and at least a dozen cells for a particular minesite stored in the IKD, the questions of “How long?” and “How many?” to obtain realistic sulphide-oxidation rates can be addressed. How long: there is a 50% chance that a cell will stabilize after the first year and this stability (factor of two in the last-five-week average above and below the long-term average) will persist for at least several years. The remaining 50% chance points towards running a cell for more than 3-5 years. How many: at least 12 cells will provide an indication if the average rate is biased towards the lowest measured values, but 40 or more cells may be needed to obtain a reasonable distribution pattern of values.

References

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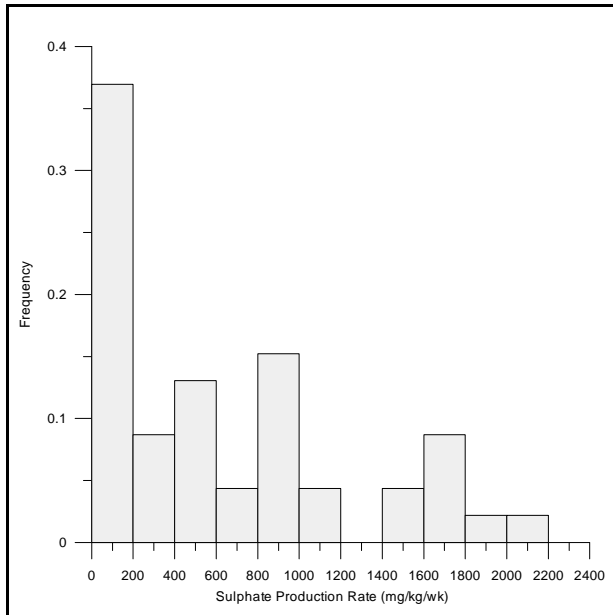


Fig. 12a. Linear Sulphate-Production Histogram for Minesite H2 (Cells = 42).

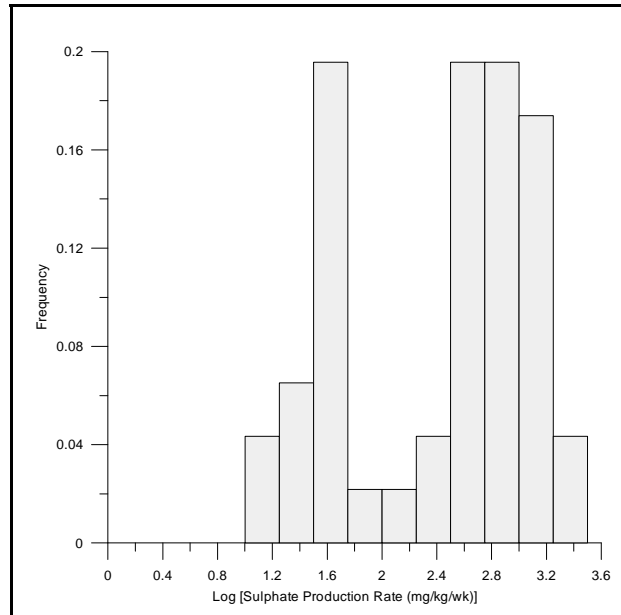


Fig. 12b Logarithmic Sulphate-Production Histogram for Minesite H2 (Cells = 42).

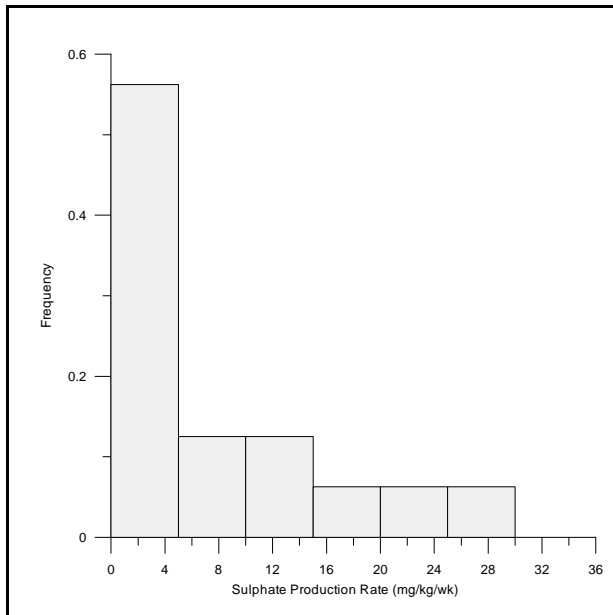


Fig. 13a. Linear Sulphate-Production Histogram for Minesite H6 (Cells = 16).

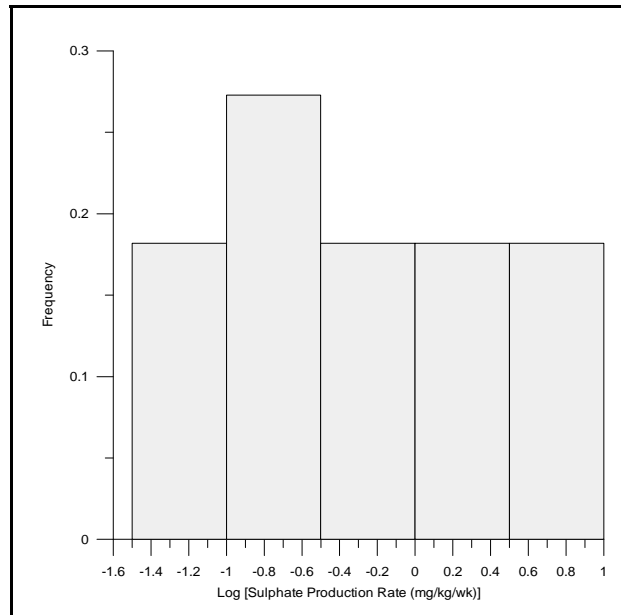


Fig. 13b. Logarithmic Sulphate-Production Histogram for Minesite H6 (Cells = 16).

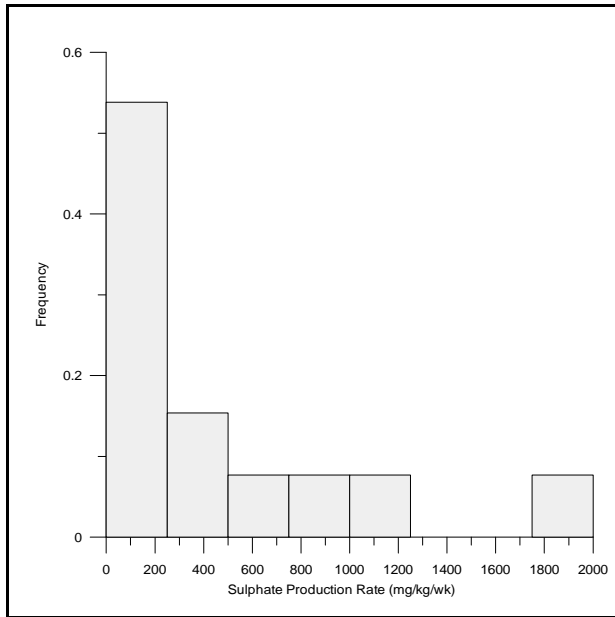


Fig. 14a. Linear Sulphate-Production Histogram for Minesite H24 (Cells = 13).

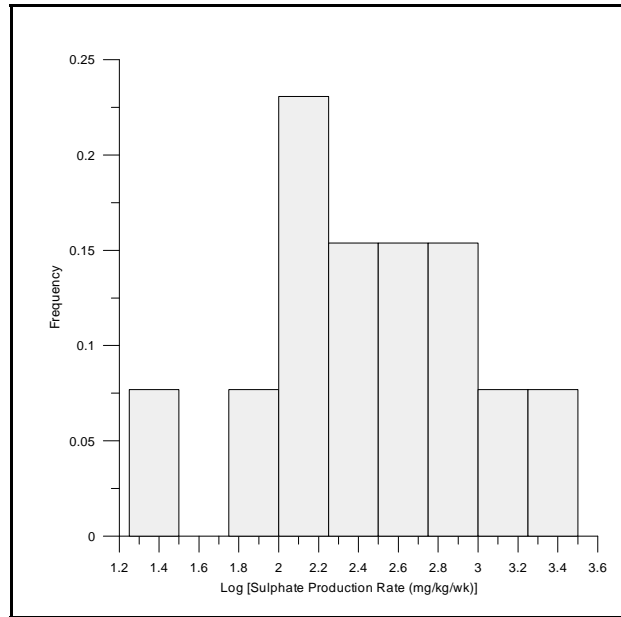


Fig. 14b. Logarithmic Sulphate-Production Histogram for Minesite H24 (Cells = 13).

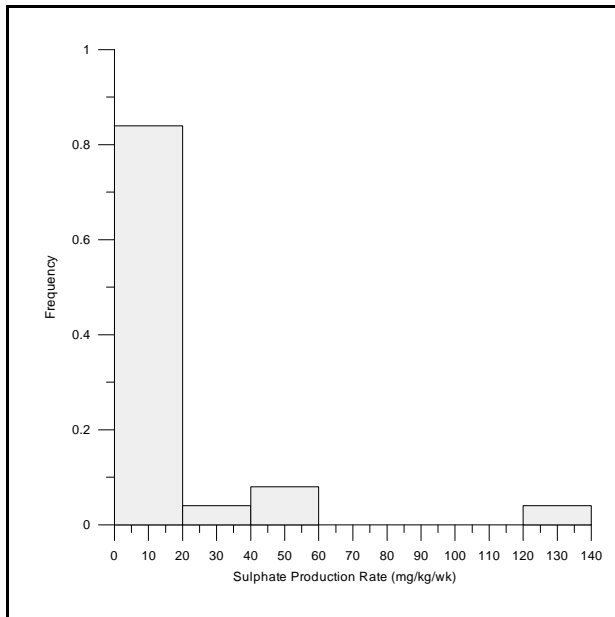


Fig. 15a. Linear Sulphate-Production Histogram for Minesite H28 (Cells = 25).

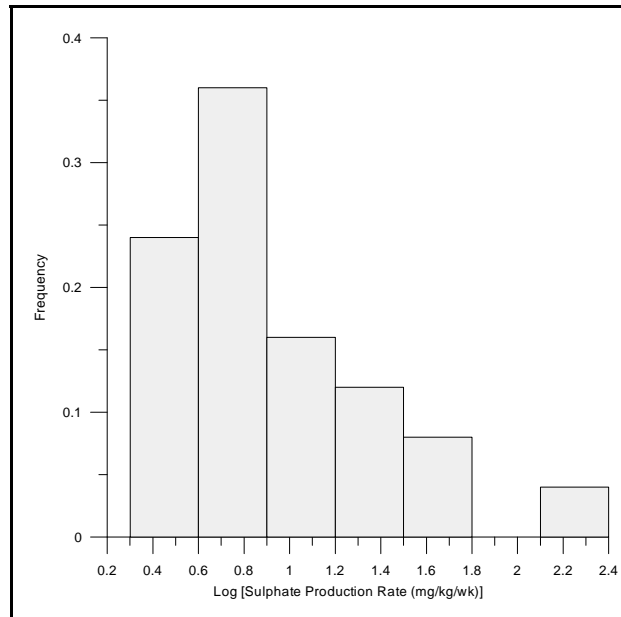


Fig. 15b. Logarithmic Sulphate-Production Histogram for Minesite H28 (Cells = 25).

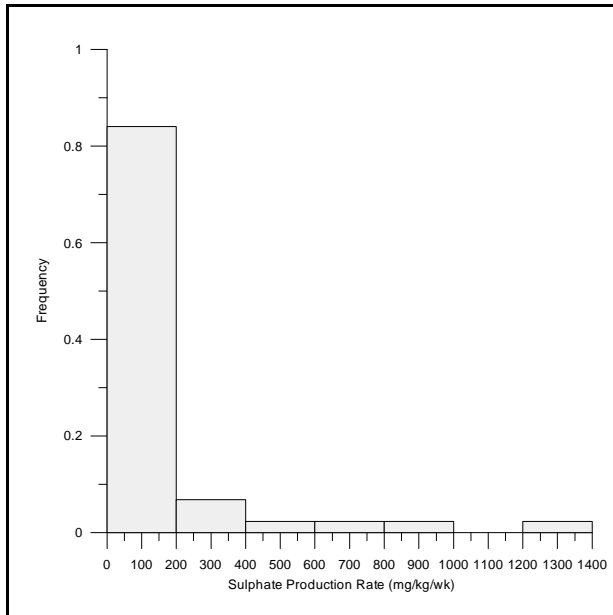


Fig. 16a. Linear Sulphate-Production Histogram for Minesite H61 (Cells = 44).

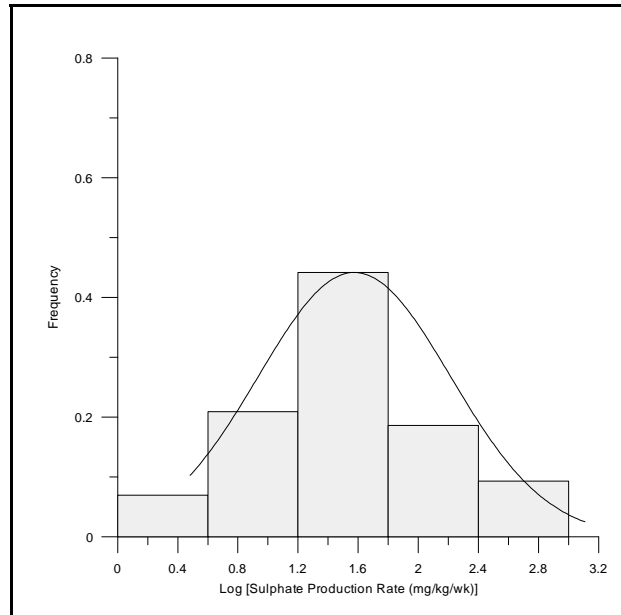


Fig. 16b. Logarithmic Sulphate-Production Histogram for Minesite H61 (Cells = 44).