

Lessons Learned from Long-Term and Large-Batch Humidity Cells

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ABSTRACT

The Sobek humidity cell has been in use with minor modification for more than 30 years to determine bulk primary-mineral reaction rates. As a result, it has become a key tool for predicting the bulk rate of sulphide oxidation, the Carbonate Mole Ratio (CMR) of neutralization-potential (NP) consumption to sulphide oxidation, and the rates of metal leaching.

Most humidity cells are operated for less than a year, with the resulting rates extrapolated into the future for years or decades. The validity of these extrapolations was tested by examining longer trends from cells that have operated for three to seven years, as found in the International Kinetic Database (IKD). Additionally, large batches of cells for two minesites in the IKD (45 and 46 cells each) were examined to determine if regular, predictable trends were obtained across ranges of geochemistry at a minesite.

The long-term cells show that the rates of sulphide oxidation and acid generation, based on sulphate production, have a 50% chance of stabilizing within one year, with the remainder fluctuating significantly throughout their test periods. Despite the fluctuations, the CMR, which is critical for defining site-specific or rock-unit-specific ABA criteria, remains relatively steady in many cases between 1.0 and 2.0 as expected from principles of aqueous geochemistry. However, if the sulphate-production rate falls below 10-30 mg/kg/wk, the CMR value can increase significantly. At and below these low rates, physical factors like flow rates of surface waters and groundwaters will determine the rate of NP consumption, rather than geochemical factors. Also, if weekly rinse pH falls to acidic values, the CMR will decrease below 1.0, reflecting the exhaustion of fast-neutralizing minerals. The two batches of multiple cells also confirm these trends across a range of geochemistry.

The long-term cells show that copper leaching often stabilizes within a narrow range as long as rinse pH remains relatively constant. Also, there is no strong dependence of leaching on the sulphate rate. However, the rate of copper production often increases sharply if rinse pH falls to acidic values. This suggests the measured copper-production rate in some cases is not a true primary rate, but a lower secondary rate after secondary-mineral precipitation within Sobek cells. As with the long-term cells, the batches of multiple cells show that copper production often increases gradually with decreasing rinse pH, with no clear dependence on sulphate production. However, high rates can also occur at near-neutral pH, so secondary-mineral precipitation of copper is not necessarily common.

INTRODUCTION

The humidity cell, based on the technique adapted by Sobek et al. (1978), has been in use for more than 30 years with minor modifications (e.g., Appendix C of Morin and Hutt, 1997). This technique involves the placement of a sample, typically several hundreds of grams to a few kilograms, into an enclosed chamber (Figure 1). Air is pumped continuously through the cell, and it may be ambient air or alternating dry and moist air. On a regular interval, usually weekly, excess water of known chemistry is poured into the cell and allowed to stand for at least an hour. If the sample is fine grained, then the sample is gently stirred to ensure all particle surfaces are rinsed by the water. This rinse water is then drained and analyzed.

The purpose of this technique is to obtain reaction rates of primary minerals, like sulphide and acid-neutralizing minerals, that have existed in the sample for at least millennia. The major complication is that aqueous concentrations under field conditions at most minesites are limited by secondary-mineral precipitation (Morin and Hutt, 1997) and thus secondary minerals actively accumulate through time. As explained below, this could overestimate the risk of acidic drainage. As a result, Sobek humidity cells employ excess water, and stirring if necessary, to remove and minimize secondary-mineral accumulation. This leads to two important observations. First, rinse aqueous concentrations from humidity cells cannot often be used directly for

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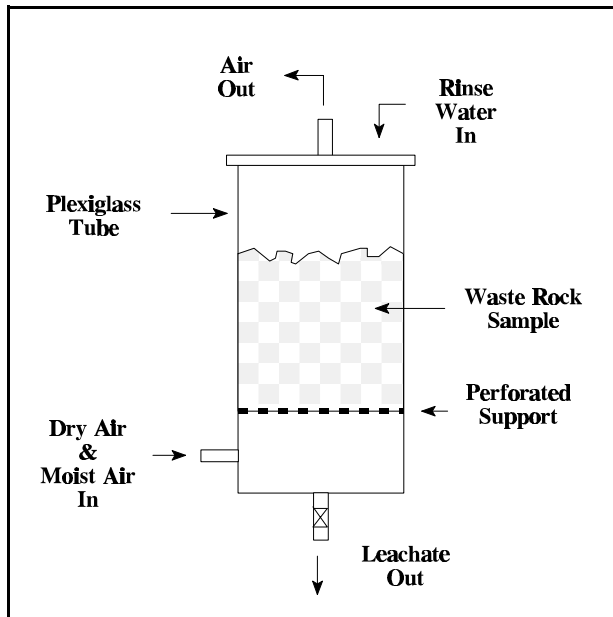


Figure 1 Schematic diagram of a humidity cell.

predictions under field conditions since they are purposely diluted. Instead, aqueous concentrations from Sobek cells are converted to bulk reaction rates for predictions and scaling:

$$\text{Production Rate (mg of parameter/kg of sample/week)} = \frac{\{\text{measured aqueous rinse concentration (mg/L)} * \text{volume of rinse water recovered (L)}\}}{\{\text{weight of sample (kg)} * \text{number of weeks since last rinse (wk)}\}} \quad (1)$$

The second important observation is that cells which are not operated according to the Sobek concept, like the U.S. ASTM standard for humidity cells and low-flush columns, do not necessarily provide primary-mineral rates. Instead, the calculated rates could be much lower than actual rates due to secondary-mineral precipitation. As a result, predictions such as lag time to net acidity and site-specific net-potential-ratio criteria (NPR = neutralization potential/acid potential), based on rates affected by secondary-mineral precipitation, can be wrong and can lead to erroneous estimates of ARD risk (Morin and Hutt, 1998a).

This paper discusses lessons learned from Sobek cells, particularly from those operated for several years and from two batches of cells (45-46 cells each from individual minesites). The information for these cells is derived from the International Kinetic Database (IKD), Version 99.1 (MDAG Publishing, 1999).

Initial lessons, based only on rates of sulphide oxidation derived from sulphate production, were presented earlier (Morin and Hutt, 1999). Conclusions from that work were:

- 1) 10 cells that operated for three to seven years indicated that there was roughly a 50% chance that the oxidation rate of a sample will stabilize geochemically within the first year, where geochemical stability was defined as fluctuations of less than a factor of two between the last-five-week-average rate and the long-term average rate;
- 2) there were no pretest or early indications of which cells would stabilize;
- 3) seven batches of cells, with at least 12 cells each, indicated that at least 12 cells were sufficient to show whether oxidation rates were clustering around the lower portion of the range, which was typical; and,
- 4) the batches indicated more than 40 cells would be needed to delineate a reliable statistical distribution such as lognormal or normal.

This paper continues the study by making additional observations about (1) the Carbonate Mole Ratio of neutralization-potential (NP) consumption to sulphate production, and (2) copper leaching.

OBSERVATIONS ABOUT THE CARBONATE MOLE RATIO

For samples with the fast-reacting carbonate minerals of calcite and dolomite, the consumption rate of NP can be defined through the production rate of calcium plus magnesium, converted to units of mg CaCO₃/ kg/wk. Carbonate-based NP is common in rock and tailings (Morin and Hutt, 1997; Hutt and Morin, 2000, these

proceedings) and thus its consumption rate is important for predictions of whether NP is exhausted before sulphide (no net acidity), or for predictions of when NP will be exhausted in the presence of excess sulphide (lag time to net acidity).

The Carbonate Mole Ratio (CMR) is defined as the mole ratio of: the rate of NP consumption to the rate of total-acid generation as delineated by sulphate production. Based on principles of aqueous geochemistry, the value of the CMR should lie between 1.0 and 2.0 in carbonate-bearing rock and tailings that are actively and effectively neutralizing acidity created by sulphide oxidation (Morin and Hutt, 1997). The exact value can be critical because it is the only indication of a site's or rock unit's criterion NPR (= NP/AP) from acid-base accounting (ABA). In other words, if a site's CMR from Sobek cells is around 1.2, then all samples with NPR < 1.2 based on ABA (after adjustment for unavailable NP) are predicted to generate net acidity at some point. If a rock unit's CMR is 1.8, then all ABA analyses with NPR > 1.8 (after adjustment for unavailable NP) are predicted to remain near neutral pH.

However, the CMR can fall below 1.0 when effective neutralization falters and rinse pH decreases below 5-6. This is because the effective and fast-neutralizing carbonate has been exhausted. Additionally, the CMR can rise to high values, sometimes above 10, when the rate of sulphide oxidation is negligible. This is due to the consumption of NP from the simple addition of rinse water to a cell, which naturally dissolves carbonate. The resulting consumption rate is typically much higher than the negligible rate of sulphide oxidation.

To examine the behaviour of the CMR further, trends from long-term cells and in batches of cells were examined. Long-term cells showed a number of trends.

One typical trend, which is consistent with principles of aqueous geochemistry, involves a consistently near-neutral rinse pH throughout the test period (e.g., Figure 2). The measurable sulphate-production rate demonstrates that oxidation of sulphide and generation of acidity are occurring. However, the sulphate rate decreases through time to some negligible level. In the initial weeks, the rate of NP consumption also falls with sulphate production, so that the CMR value remains around 1.0-2.0 as expected for geochemical reasons. However, at some point below a sulphate rate of approximately 20 mg/kg/wk, the rate of NP consumption no longer decreases proportionally, but stays relatively constant due to the solubility of carbonate minerals in the weekly rinse water. Therefore, as the sulphate rate decreases further, the rate of NP consumption remains the same and the CMR increases (Figure 2).

This increase in the CMR below a certain threshold of sulphate leads to two observations. First, if the CMR is 7.4 for example, then any sample with an NPR < 7.4 from acid-base accounting would be expected to lose its effective NP before sulphide is depleted and thus generate net acidity at some point. However, this is rendered invalid by the next observation. Second, NP consumption is no longer driven by geochemical acid generation and thus, under site conditions, the physical flow rates of surface water and groundwater will determine which rock or tailings produces net acidity. This observation is tempered by the fact that acid generation in this situation may be so low that background alkalinity may be sufficient to offset the minimal acid generation.

A second trend noted in the long-term cells is similar to the first. As before, sulphate production begins relatively high and pH is near neutral, so the CMR is generally around 1.0-2.0 (e.g., Figure 3). Sulphate production then falls below 10-20 mg/kg/wk, and the CMR rises above 2.0. However, sulphate production then increases late in the test, so the CMR decreases towards 1.0. In some cells, sulphate production repeatedly fluctuates between relatively high and low values, so the CMR repeatedly falls below, and rises above, 2.0. For this trend, the predictions of NP consumption and net acidity (1) are complicated, (2) depend on varying geochemical and physical controls through time, and (3) require frequent (weekly) analyses to properly monitor weekly changes in the mass balances.

Other trends noted in the long-term cells involve rinse pH decreasing during the test from near-neutral values to acidic values (Figures 4 and 5). In these cases, the CMR correctly falls below 1.0 reflecting the exhaustion of fast-neutralizing minerals. However, contrary to some beliefs, the onset of acidic conditions is not always accompanied by increasing rates of acid generation, sulphide oxidation, and sulphate production. Instead, sulphate production can fall with pH (Figure 4) or fluctuate within a relatively narrow range (Figure 5) without a clear trend. This lack of accelerated sulphide oxidation is actually common in humidity cell tests. It can reflect, for example, the relative insensitivity of sulphide-oxidation rates to pH or the lack of changes in sulphide microenvironments during the onset of macroscopic net acidity (Morin and Hutt, 1997 and 1998b).

Two large batches of cells from the IKD were also used to examine trends in the CMR with changes in rinse pH and sulphate-production rate. These batches, with 45 and 46 cells each, allowed the creation of three-dimensional surfaces across a range of rinse pH and sulphate production (Figures 6 and 7), which is an important, different perspective than examining one cell over a long period. Like the long-term trends within individual cells above, they confirm that the CMR rises significantly above 2.0 at near-neutral pH and low sulphate rates. For both batches, an occasional CMR value notably above 2.0 was obtained at sulphate rates as high as roughly 30 mg/kg/wk, although the IKD as a whole indicates 5-20 mg/kg/wk is a more typical limit for elevated CMR values.

OBSERVATIONS ABOUT COPPER LEACHING

For brevity, observations are made here about metal leaching using copper, although leaching behaviour can be different between metals and between sites. The typical trend observed in long-term cells is that the copper-production rate eventually stabilizes within a certain range, despite steady decreases in sulphate and small changes of roughly one unit in rinse pH (e.g., Figure 8; same cell as Figure 2), or fluctuations in sulphate production (not shown).

When rinse pH begins to decrease significantly, the rate of copper production often increases either gradually (Figure 9; same cell as Figure 4) or sharply (Figure 10; same cell as Figure 5), and then establishes a new steady-state rate. This behaviour indicates (1) the primary rate of copper leaching increases with decreasing pH or (2) copper was accumulating as a secondary mineral within the near-neutral cells so that the near-neutral rates underestimated the true primary-copper rate. Calculations with MINTEQA2 (Allison et al., 1990) for some cells not shown here have indicated that tenorite (CuO) and $\text{Cu}(\text{OH})_2$ are sometimes close to equilibrium. In this case, the rate of copper production (Equation 1, mg/kg/wk) is not relevant, but instead the actual aqueous concentration from the cell becomes a predictor of on-site drainage chemistry.

Less predictable and less common, there are observed trends for metals, like copper, molybdenum, and manganese, where the production rate is steady for at least a year and then the rate rises sharply (e.g., Figure 11). There are no clear explanations for this, but it could be related to the sudden exposure of abundant fresh mineral surfaces during ongoing weathering.

For the large cell batches containing 45 and 46 cells each, three-dimensional surface plots with late-stage copper production (average of rates over the last five weeks of testing) on the z-axis show that copper leaching tends to increase with decreasing rinse pH and with increasing sulphate production (Figures 12 and 13). However, accelerated copper production in one batch (Figure 13) also occurs at lower sulphate-production rates and at near-neutral pH for one cell. This lack of clear, consistent trends, particularly in Batch 2, suggests the observation above on secondary precipitation of copper in Sobek cells may not be common.

CONCLUSIONS

In conclusion, the long-term cells showed that the Carbonate Molar Ratio (CMR), which is critical for defining ABA criteria for a rock unit or minesite, remains relatively steady in many cases between 1.0 and 2.0 as expected from principles of aqueous geochemistry, even when the rates were fluctuating significantly. However, if the sulphate-production rate falls below 30 mg/kg/wk, the CMR value can increase sharply. According to the entire IKD database, such increases typically occur only below 5-20 mg/kg/wk which probably reflects site-specific mineralogy and environmental conditions. In any case, an elevated CMR accompanied by a low sulphate-production rate often indicates physical factors, like flow rates of surface waters and groundwaters, will determine the rate of NP consumption, rather than geochemical factors. Also, if rinse pH falls to acidic values, the CMR will decrease below 1.0, reflecting the exhaustion of fast-neutralizing minerals. The two batches of cells also confirm these trends across a range of geochemistry.

The long-term cells show that the rate of copper leaching often stabilizes within a narrow range as long as weekly rinse pH remains relatively constant. Also, there is no strong correlation of copper leaching with sulphate-production rate. However, the rate of copper production often increases sharply if rinse pH falls to acidic values, suggesting the measured copper-production rate in some cases is not a true primary rate, but a lower secondary rate after secondary-mineral precipitation within the cell. The batches of cells show that copper production often increases gradually with decreasing rinse pH, with no clear dependence on sulphate production. However, high rates can also occur at near-neutral pH, suggesting secondary-mineral precipitation of copper in Sobek cells is not necessarily common.

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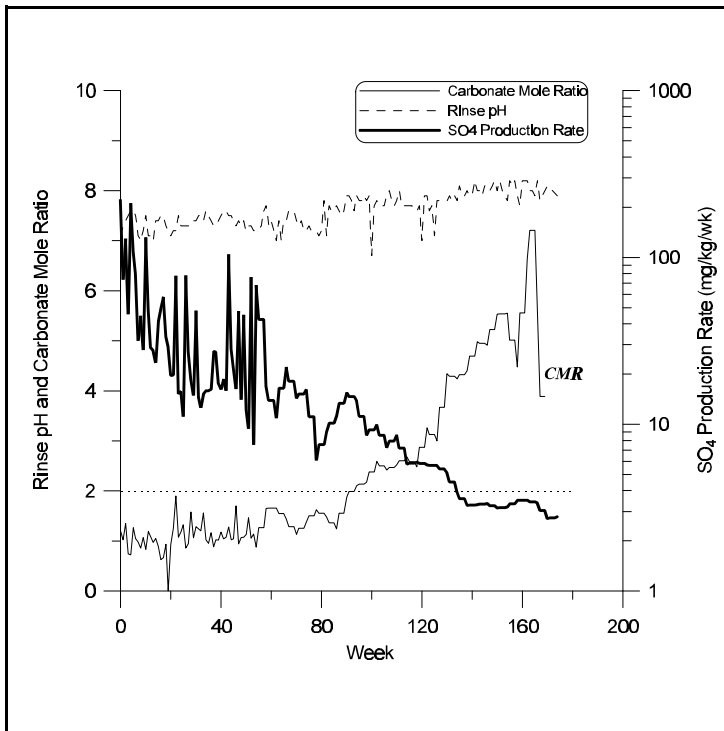


Figure 2 Cell 1: Trend of decreasing sulphate-production rate with increasing Carbonate Mole Ratio (CMR).

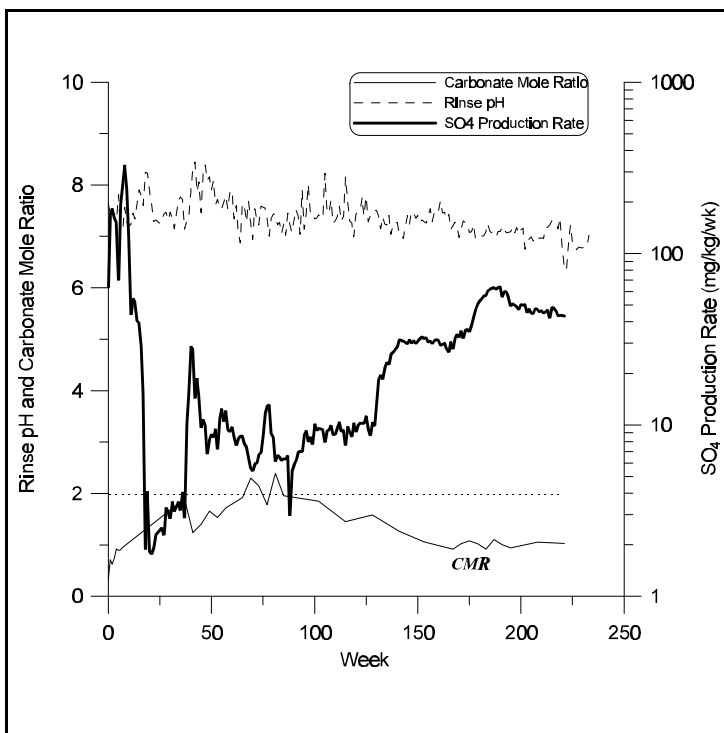


Figure 3 Cell 2: Trend of fluctuating sulphate-production rate and Carbonate Mole Ratio (CMR).

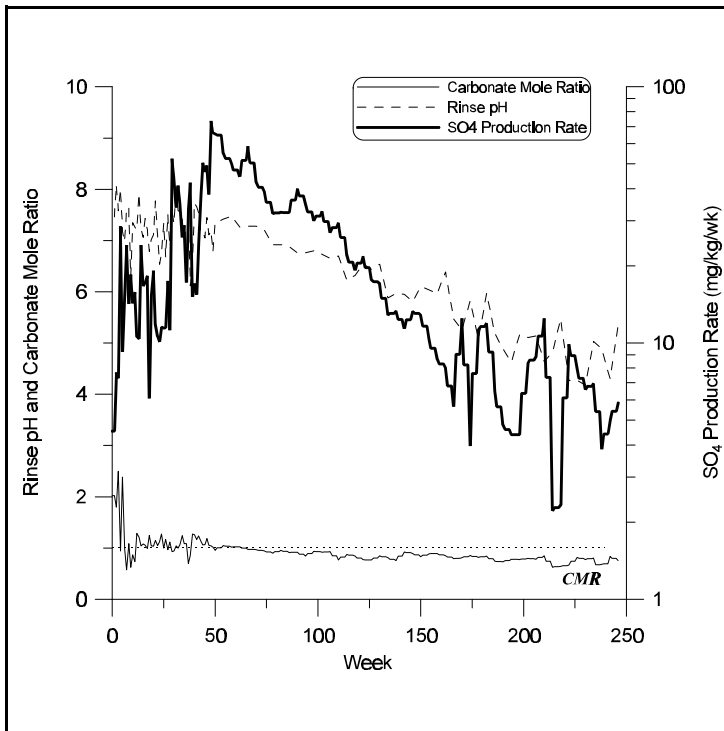


Figure 4 Cell 3: Trend of decreasing rinse pH, Carbonate Mole Ratio (CMR), and sulphate-production rate.

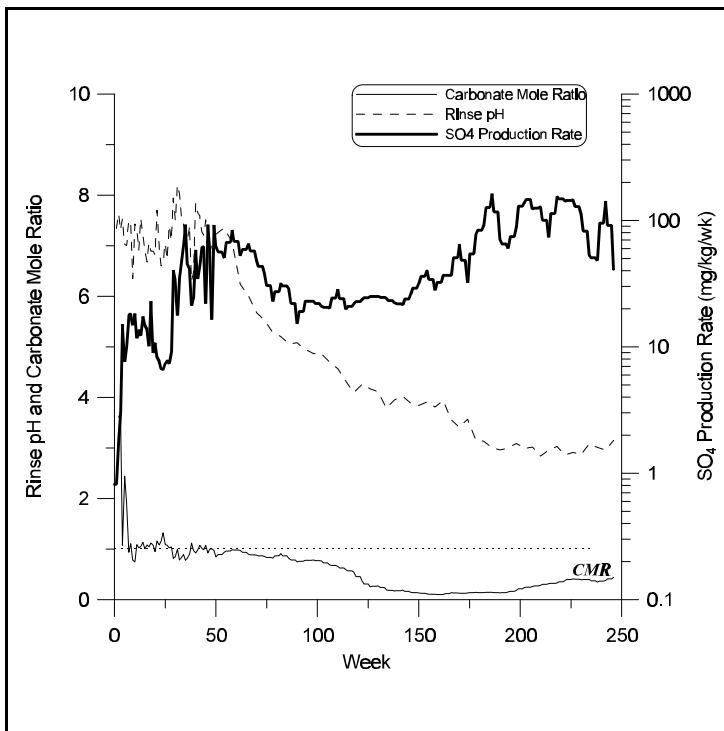


Figure 5 Cell 4: Trend of decreasing rinse pH and Carbonate Mole Ratio (CMR) with relatively steady sulphate-production rate.

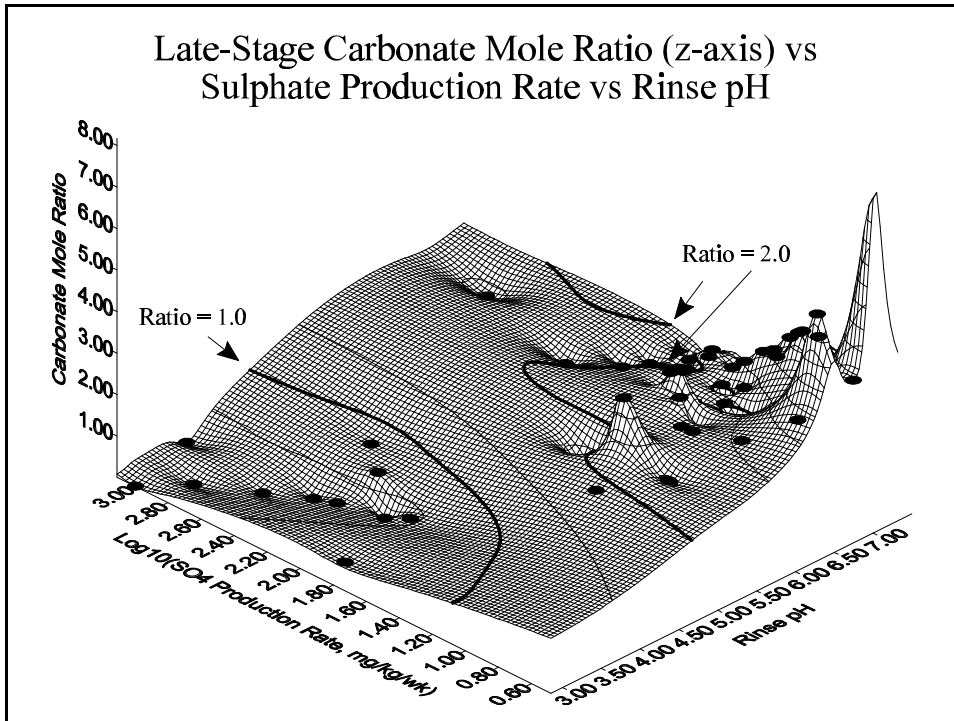


Figure 6 Batch 1: Surface trend of Carbonate Mole Ratio (z-axis) with rinse pH and sulphate-production rate.

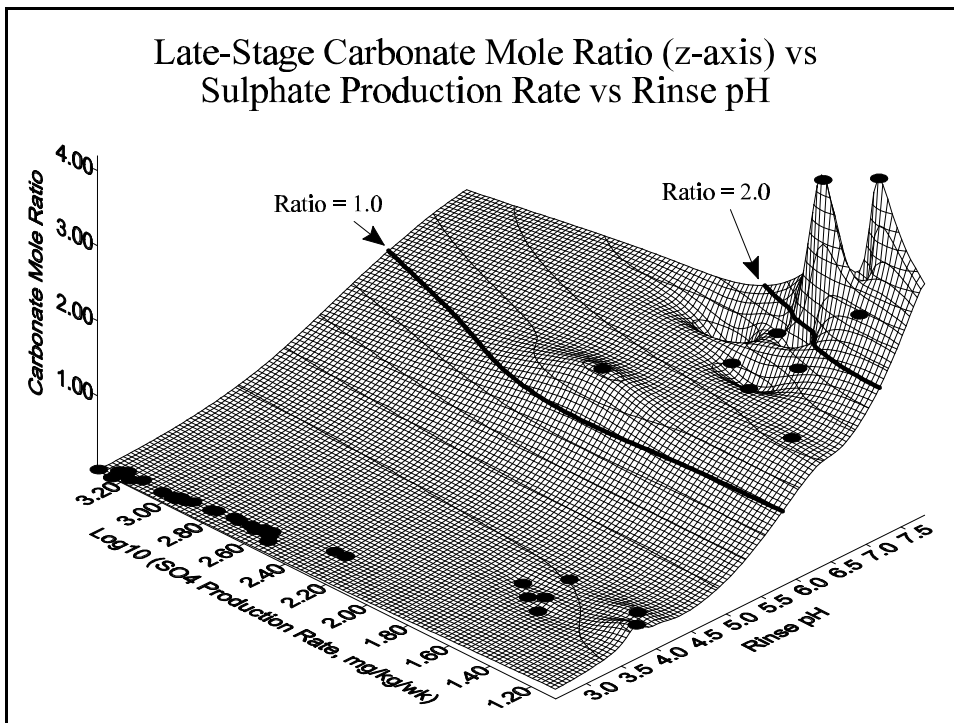


Figure 7 Batch 2: Surface trend of Carbonate Mole Ratio (z-axis) with rinse pH and sulphate-production rate.

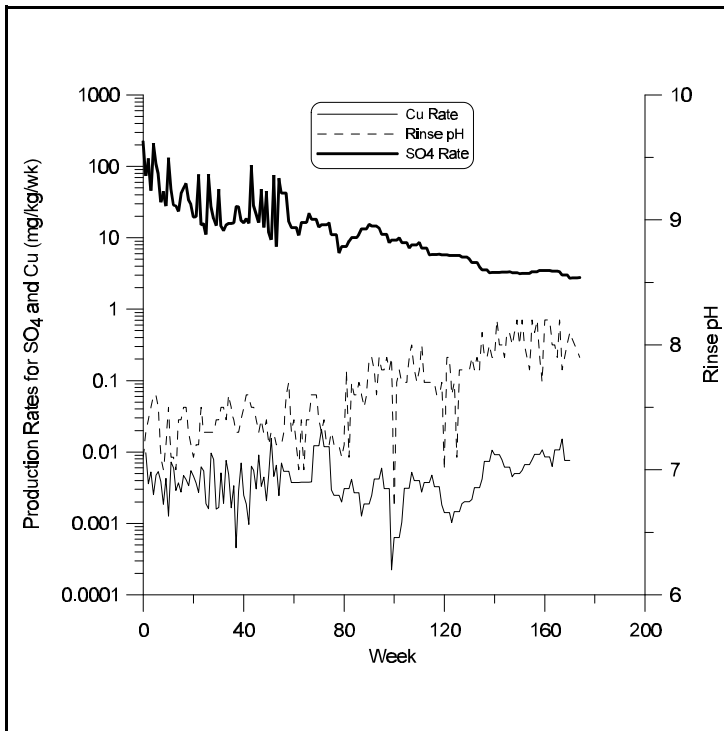


Figure 8 Cell 1: Trend of steady copper-production rate with decreasing sulphate and increasing pH.

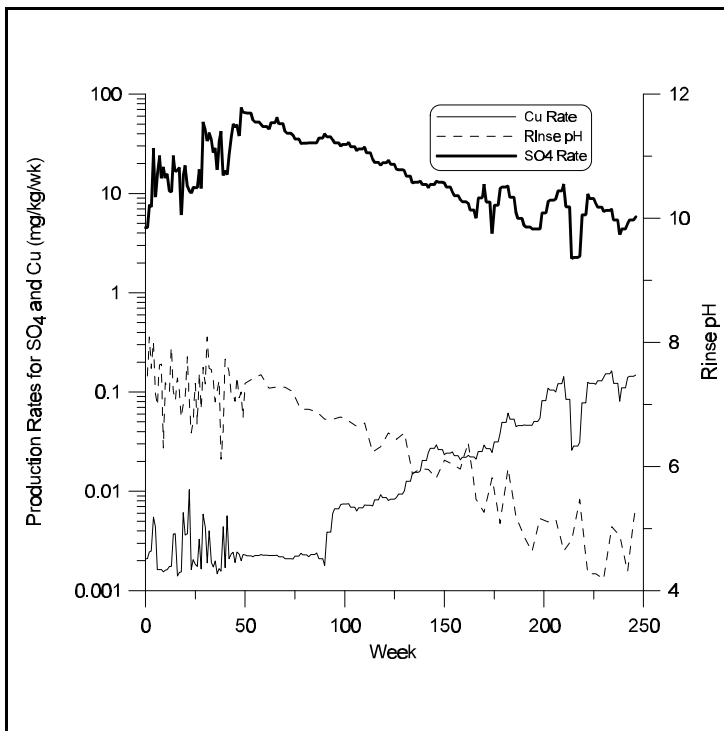


Figure 9 Cell 3: Trend of increasing copper-production rate with decreasing pH.

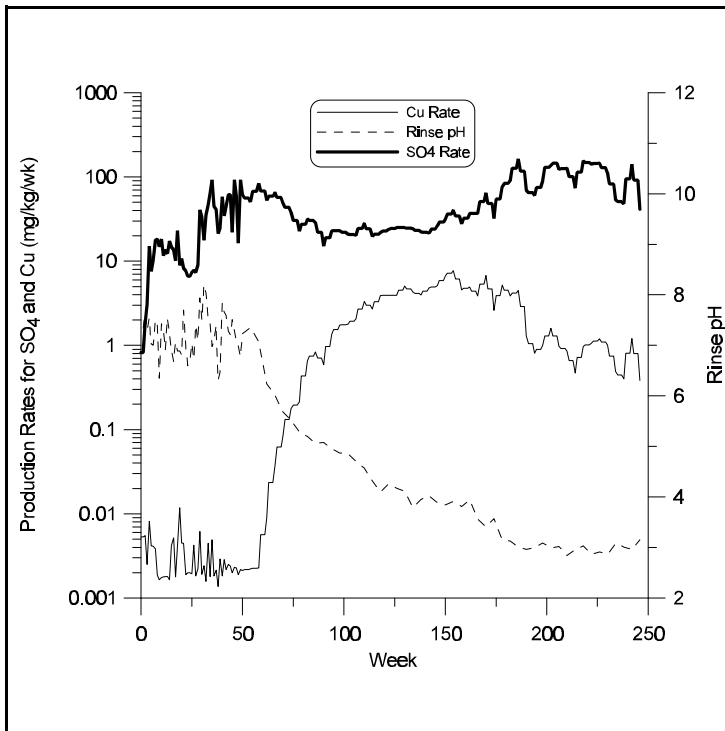


Figure 10 Cell 4: Trend of sharply rising copper-production rate with decreasing pH.

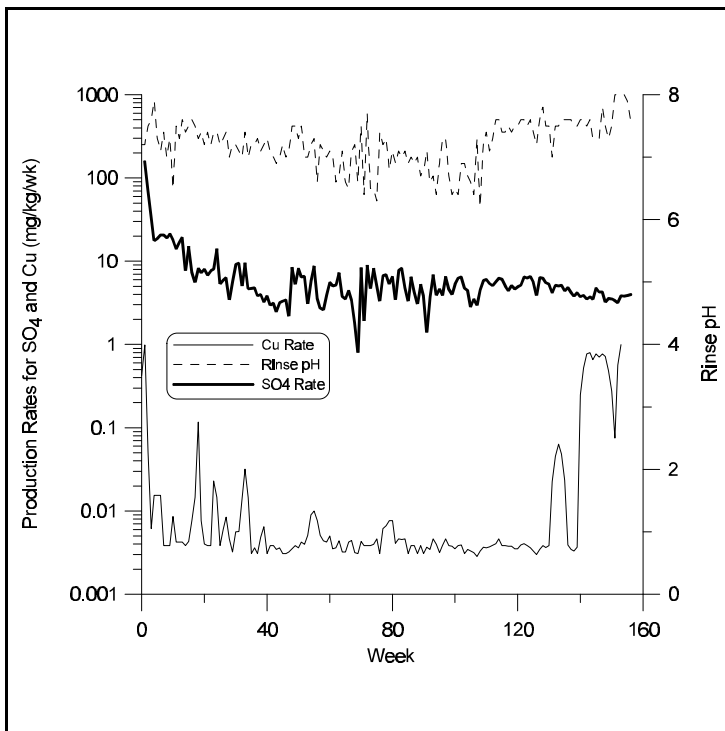


Figure 11 Cell 5: Trend of steady copper-production rate until sharp increase after 2.5 years.

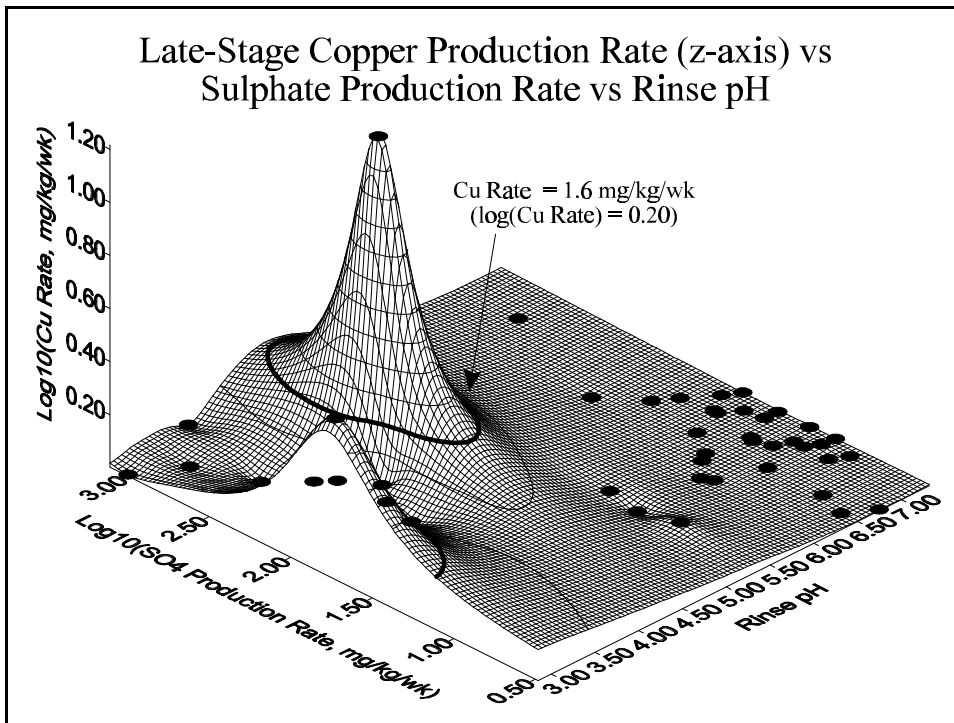


Figure 12 Batch 1: Surface trend of copper-production rate (z-axis) with rinse pH and sulphate-production rate.

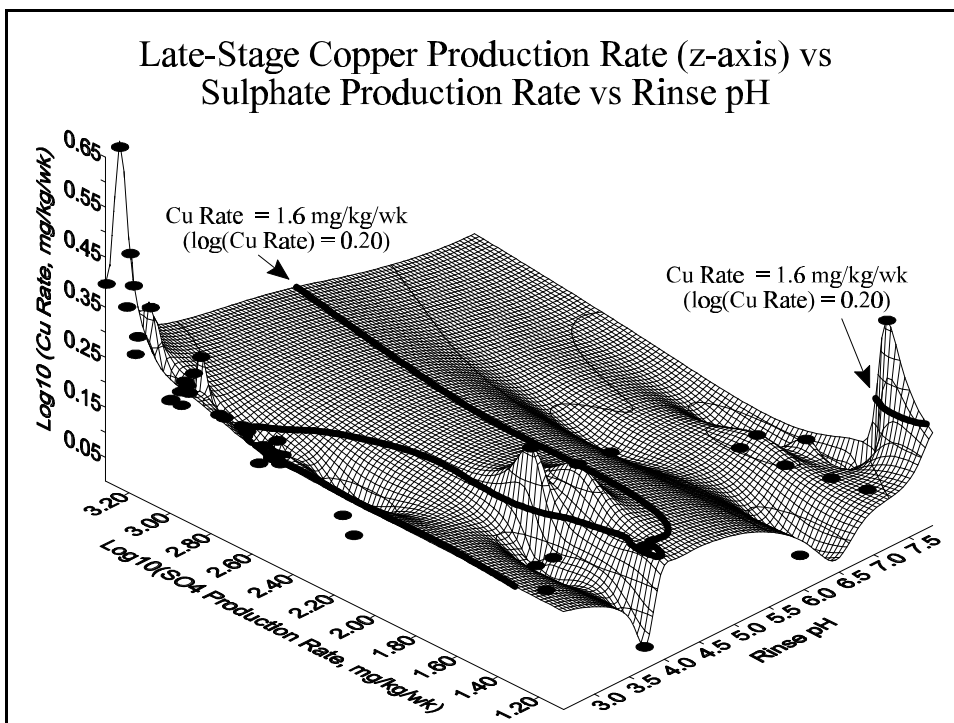


Figure 13. Batch 2: Surface trend of copper-production rate (z-axis) with rinse pH and sulphate-production rate.