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### Bimodal Distribution of pH at Minesites with Acid Rock Drainage

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#### Abstract

Aqueous pH at minesites with acid rock drainage (ARD) can span several pH units, from acidic to near-neutral values. We compiled databases for individual minesites containing many hundreds to thousands of pH measurements, spanning decades and many monitoring locations. This showed that site-wide pH displayed a bimodal distribution. In other words, pH values clustered around a preferred near-neutral and preferred acidic value. Intermediate values were measured, but were less common.

This pattern was also seen in compilations of hundreds of drainages from coal minesites. Thus, bimodal pH distributions are seen within and among minesites with ARD.

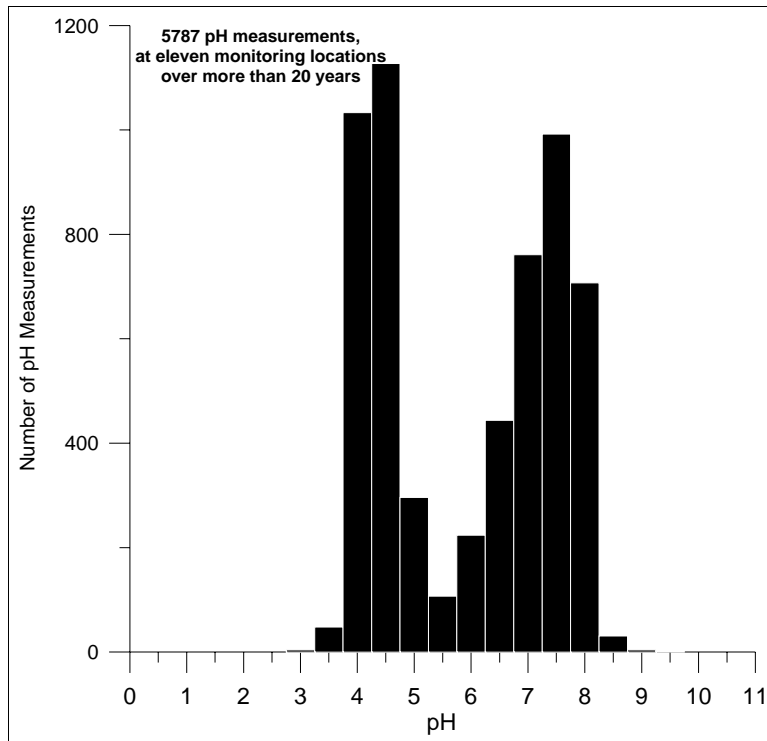
The explanation for the bimodal distribution lies in the step-wise acidification of near-neutral conditions. This step-wise process creates shorter-lived secondary minerals and intermediate pH values. The reasons for the two preferred pH ranges are more complicated.

#### 1. Introduction

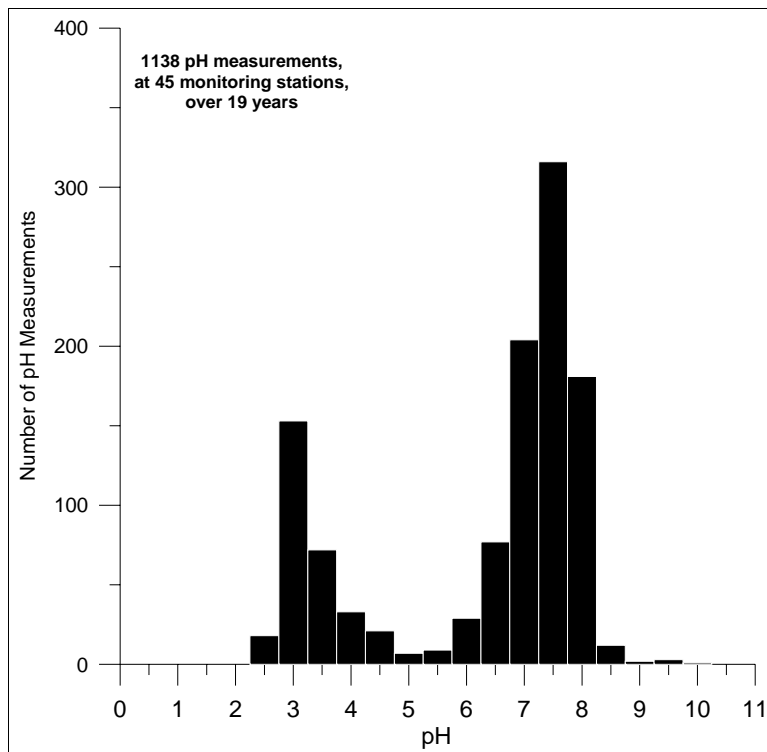
We are not the first to notice this, but the question warrants further discussion. Why do minesites with acid rock drainage (ARD) often display a bimodal distribution in aqueous pH, with “clusters” of datapoints around certain acidic and near-neutral values? Also, what are the explanations for this distribution?

Compilations of drainage-chemistry databases show the bimodal distribution of pH (e.g., Figures 1 to 3). Even leach-column testwork using limestone added to acidic rock showed this distribution, although the peak values did not match the on-site peaks (compared Figures 3 and 4).

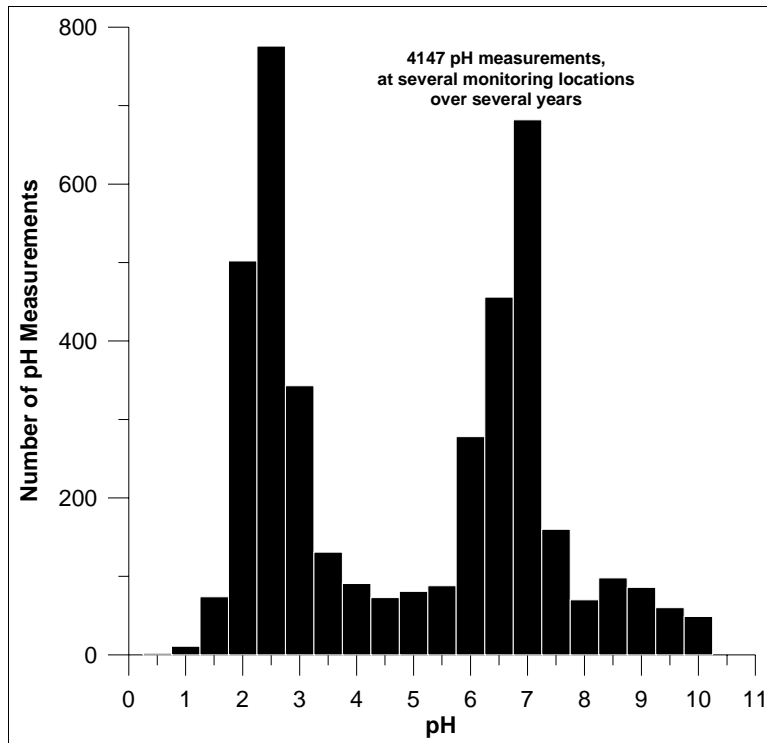
Furthermore, Lehigh Earth Observatory (2004) showed pH values for hundreds of coal-mine discharges in Pennsylvania, USA. Although the text is not clear, presumably each value represents one minesite. Hundreds of discharges, from both bituminous and anthracite coal minesites, showed the bimodal distributions (Figures 5 and 6) also seen within individual minesites (Figures 1 to 3).



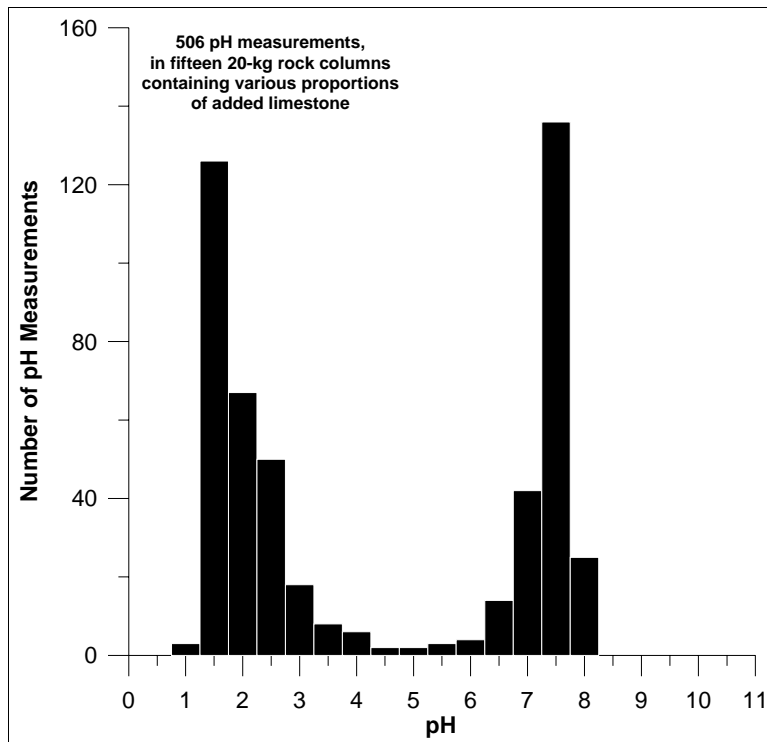
**Figure 1. Aqueous pH Measurements at Minesite A (5787 pH measurements at eleven monitoring stations over more than 20 years).**



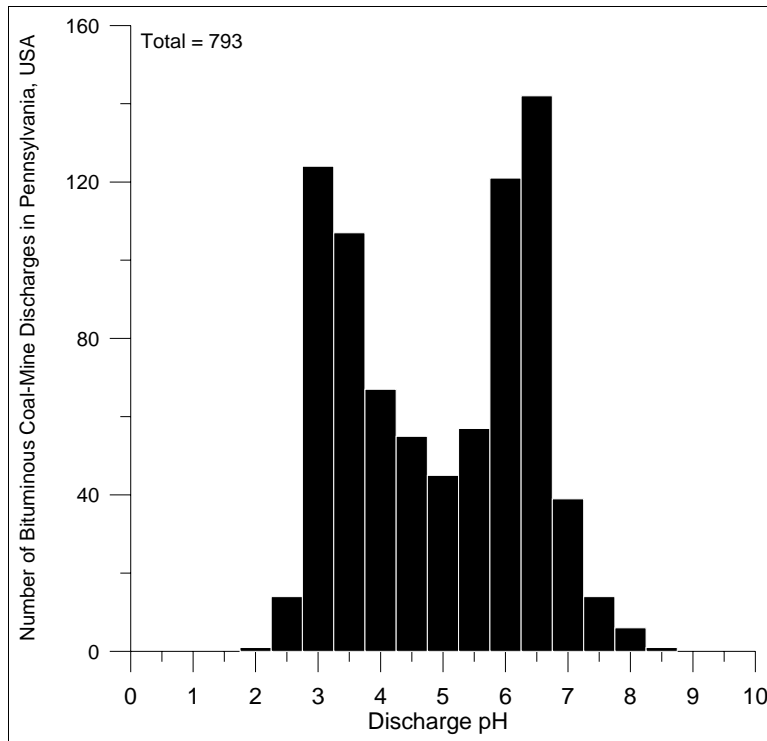
**Figure 2. Aqueous pH Measurements at Minesite B (1138 pH measurements at 45 monitoring stations over 19 years).**



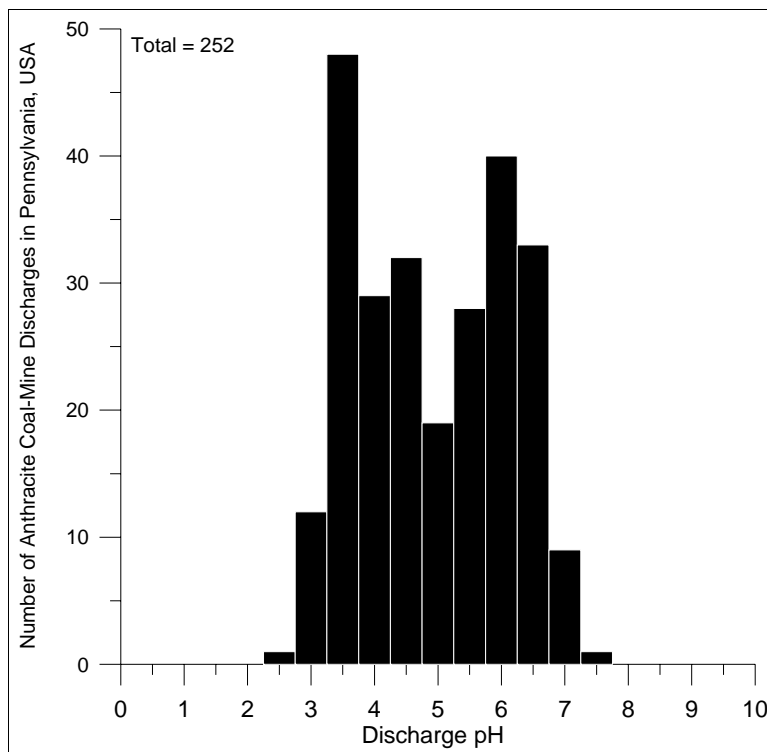
**Figure 3. Aqueous pH Measurements at Minesite C (4147 pH measurements at several monitoring stations over several years).**



**Figure 4. Aqueous pH Measurements at Minesite C (506 pH measurements in fifteen 20-kg rock columns with various proportions of added limestone).**



**Figure 5. Aqueous pH Measurements of Discharges at Bituminous Coal Minesites in Pennsylvania, USA (adapted from Lehigh Earth Observatory, 2004).**



**Figure 6. Aqueous pH Measurements of Discharges at Anthracite Coal Minesites in Pennsylvania, USA (adapted from Lehigh Earth Observatory, 2004).**

## 2. Why?

An easy explanation is that people are fascinated with ARD and, thus, they bias their monitoring with the most acidic and most near-neutral water. However, that is too arbitrary to explain this distribution at so many minesites and among so many minesites (Figures 1 to 6).

A scientific explanation begins with a simple scenario. The initial near-neutral pH at a hypothetical minesite is 7.0. Subsequent ARD from some minesite components has a pH of 3.5. Therefore, simplistically, only pH 3.5 and 7.0 should be measured at this site, with no intermediate values. This is the first step in the bimodal distribution.

The second step in the scientific explanation begins with the recognition that ARD, entering initially near-neutral rock or tailings, is not always completely neutralized to the initial near-neutral pH. It may be only partially neutralized. Thus, intermediate pH values at our hypothetical minesite, between 3.5 and 7.0, would occasionally be measured at certain locations and/or at certain times. However, they would not persist. This explains the distribution seen in Figures 1 to 6.

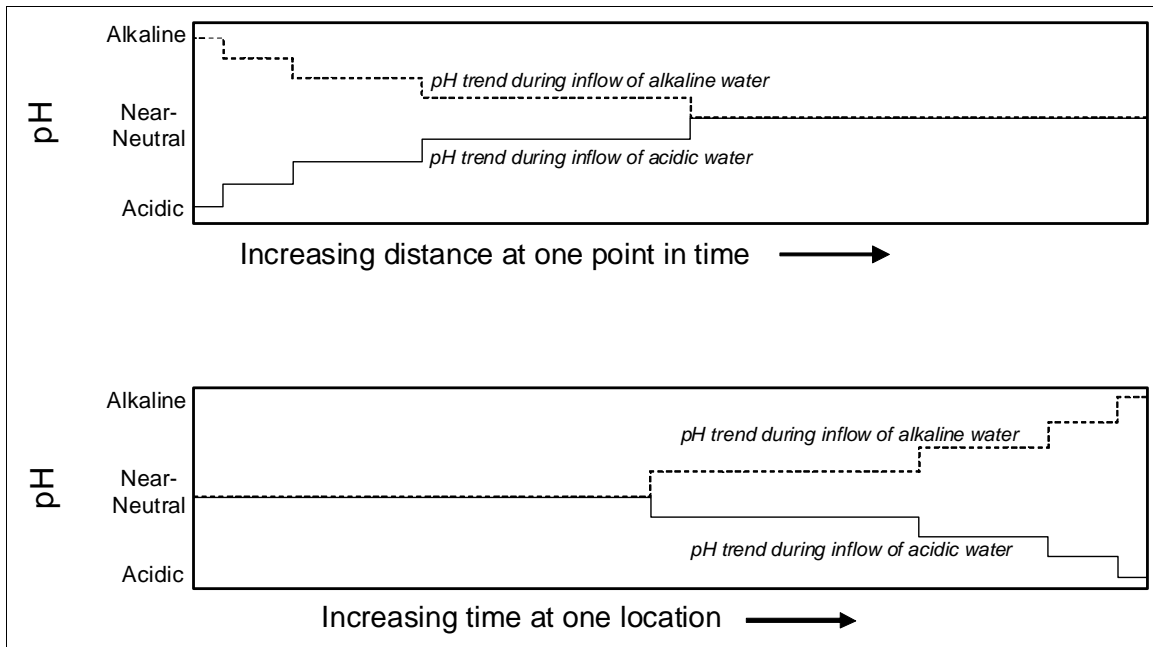
Being more scientific, the story does not end here. The transient intermediate pH values can tell us much about the complex precipitation-dissolution of minerals during the spatial and temporal migration of ARD through initially near-neutral materials. This has actually been studied and simulated for many decades.

Morin et al. (1982) described chromatographic-like, almost step-like intermediate pH values in a ground water plume of ARD moving through a sand aquifer initially containing calcite. These steps were called “sub-regions” of distinct mineral precipitation-dissolution (Figures 7 to 9, and Table 1), reflecting transient equilibrium conditions (Morin et al., 1982; Morin, 1983; Morin et al., 1988a and 1988b; Morin and Cherry 1988). The lowest, persistent, acidic pH represented the “inner core”, which created the downgradient sub-regions.

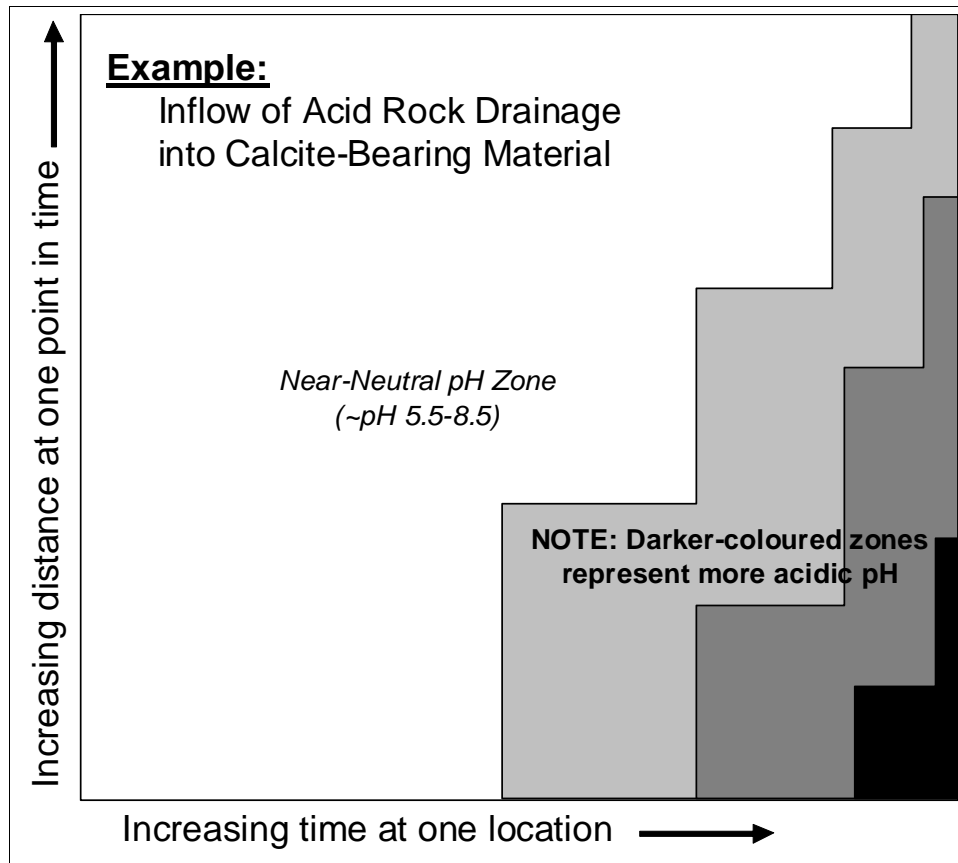
“Equilibrium” here does not automatically imply thermodynamic equilibrium. There are many other types of aqueous equilibrium (e.g., Morin and Hutt, 2007), reflecting site-specific factors like mineralogy, solubility, reaction rates, aqueous concentrations, and climatic factors.

According to mass-balance simulations, downgradient boundaries of sub-regions migrate faster than the upgradient boundaries (e.g., Figure 9). Thus, the lengths of the sub-regions stretch with increasing time, but downstream pH does not fall immediately to the most acidic input value.

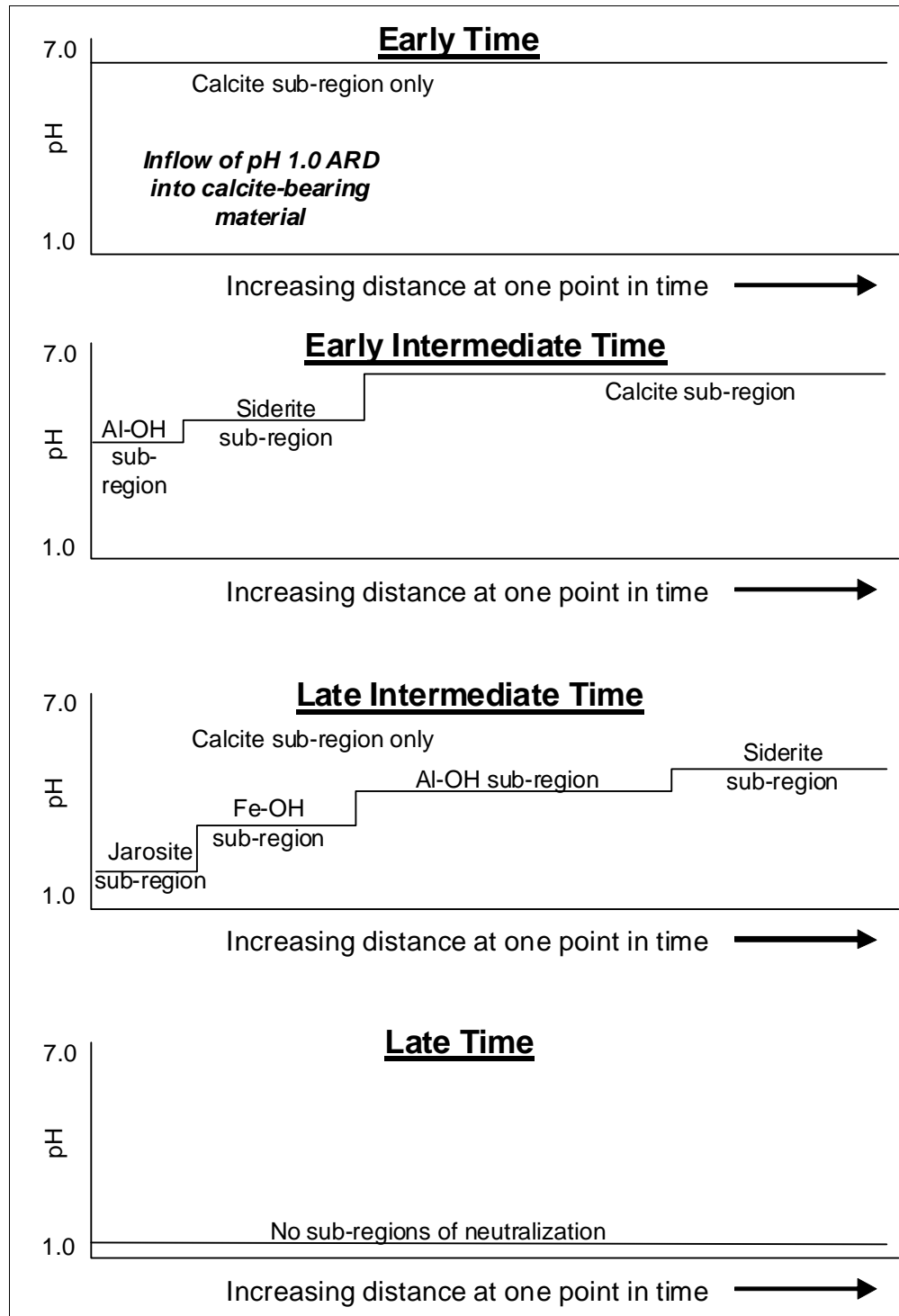
Based on Figures 7 to 9 and Table 1, Minesite A of Figure 1 has a long-term, persistent, preferred acidic pH of 4.0-4.5, probably reflecting Al-OH buffering. Relatively few pH values below that, in the Fe-OH range, were measured over the life of the minesite. Minesite B (Figure 2) had a more acidic preferred range, around pH 3.0-3.5, reflecting Fe-OH buffering. Minesite C (Figure 3) had an even more acidic preference, around pH 2.0-3.0, which did not coincide with any identified sub-region level. For carbonate sub-regions, peak-frequency pH of 7.0 at Minesite C was somewhat lower than Minesites A and B at 7.5.



**Figure 7. Schematic Diagrams of the Geochemical Sub-Region Concept at Both Increasing Distances and Increasing Times, for Inputs of Acidic or Alkaline Water.**



**Figure 8. Pseudo-Three-Dimensional Schematic Diagram of the Geochemical Sub-Region Concept for an Input of Acidic Water.**



**Figure 9. Schematic Spatial Movement and Increasing Size of Geochemical Sub-Regions during Input of pH 1.0 ARD into Calcite-Bearing Material.**

<b>Table 1. Examples of Equilibrium pH within Geochemical Sub-Regions (compiled from data and references in Section 4.5 of Morin and Hutt, 1997 and 2001)</b>	
<u>Dominant Mineral Controlling pH</u>	<u>General pH Range</u>
Aluminosilicates	1.3
Jarosites	1.8
Fe-OH (where ferric iron is remobilized and rusty ferric-iron staining can become prominent)	3.0-3.7
Al-OH (white mineral staining can become prominent, but can be confused with gypsum)	4.3-5.0
Siderite (where ferrous iron is stable)	5.1-6.0
Calcite and related carbonates	5.5-8.5
Ion exchange	6.0-8.0
Brucite	10-11
Lime	12-13

Based on the sub-region concept, many acidic drainages from bituminous coal minesites in Pennsylvania (Figure 5) preferred the Fe-OH sub-region (~pH 3.0-3.7), but several also reflected the Al-OH subregion (~pH 4.3-5.0). In comparison, drainages from anthracite coal minesites in Pennsylvania (Figure 6) were less biased in their ranges.

This explains the bimodal distribution of pH. However, a fundamental question remains unanswered: how does a persistent, preferred acidic pH arise at a minesite? Why does ARD at one minesite prefer 2.5 and another 3.5? That is a story for another time, which ultimately may not have a simple answer (e.g., Figure 1 of Morin and Hutt, 2007).

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