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The Meaning and Complexity of pH "Plateaus", like pH 3.0 to 3.7 for Fe-OH Minerals, during Neutralization along Flowpaths

by K.A. Morin

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Summary

This MDAG Case Study is about pH plateaus (originally called geochemical "sub-regions") during the neutralization of acid rock drainage (ARD) along flowpaths. This Case Study shows how recent documents like the INAP GARD Guide fail to identify the original source of these plateaus and fail to accurately describe the meaning and complexity of the plateaus.

Tracing backwards through earlier documents confirms that the original source of pH plateaus, including the detailed explanation, simulation, and application to full-scale ARD, was Morin (1983). This is the Ph.D. thesis for Dr. Kevin Morin (the author of this MDAG Case Study) under the supervision of Dr. John Cherry at the University of Waterloo. An excerpt of this work published in the Canadian Geotechnical Journal was awarded the 1983 Canadian Geotechnical Society Prize.

Accurate details are then excerpted from Morin (1983). These show that the sub-regions/plateaus are so complex that they cannot be accurately understood and simulated. This is far more complex than suggested by explanations in later documents written by others.

1. Introduction

Today, it is common knowledge that acid rock drainage (ARD) travelling along surface and subsurface flowpaths can display a stepwise, sequential neutralization of pH (e.g., Figure 1-1 below taken from Jurjovic et al., 1995). Each "step" in pH neutralization is typically called a "plateau", although it was originally called a geochemical "sub-region". Similar stepwise neutralization from alkaline pH can also occur, and is illustrated here, but is not a primary focus.

The common explanations for pH plateaus typically lack details on their meaning and complexity, or incorrectly explain them. They are so complex that they exceed the current human capacity to accurately understand and simulate them.

To reveal and understand their detailed meaning and complexity, as best we can at this time, we have to track back information on pH plateaus to the original source. As shown in the subsequent sections of this Case Study, this tracing leads to my (Kevin Morin's) Ph.D. thesis from 1983 under the supervision of Dr. John Cherry at the University of Waterloo (Morin, 1983).

Along the way, we find interesting assumptions and simplifications in various references that are not justified for some cases. Along the way, we see interesting aspects of the complexity, like spatial trends vs. temporal trends. These are demonstrated in the original reference on pH plateaus and geochemical sub-regions: Morin (1983).

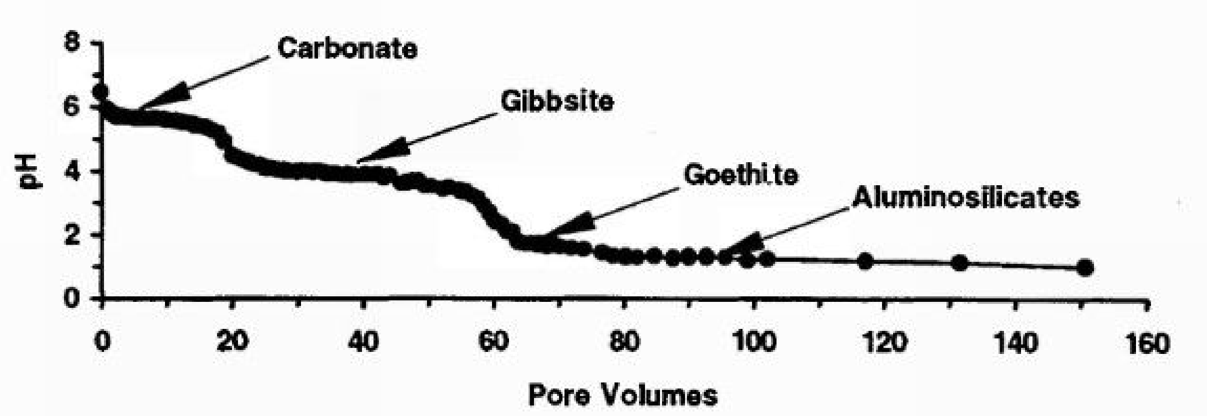

Figure 1-1. An example of pH plateaus, or geochemical sub-regions, during neutralization of acid rock drainage (from Jurjovic et al., 1995).

2. The Explanation of pH Plateaus in the INAP GARD Guide

The International Network for Acid Prevention (INAP) has created the Global Acid Rock Drainage (GARD) Guide. This Guide "is intended as a state-of-the-art summary of the best practices and technology to assist mine operators and regulators to address issues related to sulphide mineral oxidation" (INAP, 2025). As a Global Guide, we can turn to it for its "state-of-the-art summary" on pH plateaus.

Chapter 2 of the GARD Guide explains,

> *"The combination of acid generation and acid neutralization reactions typically leads to development of ARD, as illustrated in Figure 2-10 (Broughton and Robertson, 1992). Over time, pH decreases along a series of plateaus governed by the buffering of a range of mineral assemblages. Stage I is characterized by a circumneutral pH range and consumption of acid by carbonate minerals such as calcite according to generic reaction [6]. Reactions [1], [3], and [4] describe the sulphide oxidation process, which results in sulphate release. As this alkalinity is consumed, the pH declines in stages depending on the nature of the neutralizing minerals (Stage II). Generally, at this stage sulphate, acidity, and trace metal levels increase although for some metals (e.g., Cu, Pb), concentrations may be limited by mineral solubility controls. Buffering may be provided by metal hydroxides. At pH values of approximately 4.5 and below, microbially mediated oxidation predominates (reactions [2] and [3]), resulting in a rapid acceleration of acid generation. In Stage 3, final buffering is usually limited to dissolution of silicate minerals (reaction [7]), and solubility controls on trace metal concentrations are largely absent."*

Figure 2-10 of the GARD Guide to which this quotation refers is copied below as MDAG Figure 2-1. Some interesting and unsettling observations about this quotation and its Figure 2-10 include the following.

- The wording of the quotation itself is complex and cryptic in places, and includes discussions of both pH plateaus and Stages.
- There are unfounded and likely wrong explanations such as "microbially mediated oxidation predominates" at approximately pH 4.5 and below (e.g., Morin and Hutt, 2010; Morin, 2021a).
- The text refers to chemical reactions numbered in brackets ([]), such as "generic reaction [6]" and "reaction [7]", although Figure 2-10 and the text contain no such reactions and equations.
- The y-axis is labelled "pH in Micro Environment Around Minerals", which incorrectly restricts the pH plateaus only to microenvironments for some unstated reason.
- The microscale pH is shown to decrease (become more acidic) with increasing time, although the diagram is showing neutralization of pH that should increase with time from acidic values. This is one of the complexities that require careful differentiation of spatial and temporal trends in pH plateaus, and is illustrated in detail below in Section 4 of this Case Study.
- This figure is "after Broughton and Robertson, 1992", which refers to a conference in Manchester, UK that is apparently not available on the internet. Thus, an original source of the pH plateaus, if this conference paper is not the original source, is unidentified in this "state-of-the-art" GARD Guide.
- This figure points to "pH Plateaus Resulting From Minerals Buffering at Various pH Values", with "e.g.," in front of each mineral indicating each plateau may be caused by more than one mineral with no further explanation.

Figure 2-10: Stages in the Formation of ARD (after Broughton and Robertson, 1992).

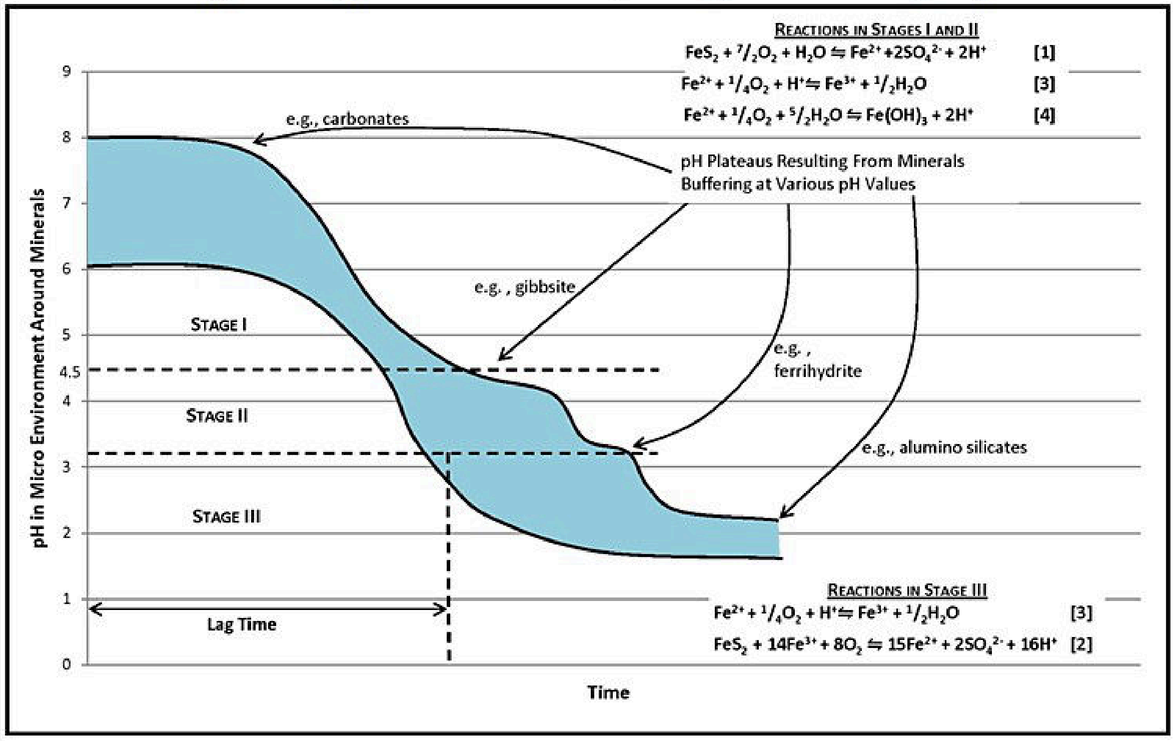

Figure 2-1. A copy of Figure 2-10 from the INAP GARD Guide.

Located immediately above Figure 2-10 and its text in the GARD Guide, the Guide states,

> *"Table 2-2 provides an overview of the ranges of neutralization potential and buffering pH for a number of common minerals. As is immediately obvious, carbonate minerals generate significantly more neutralization potential than silicate minerals, while they also tend to buffer at higher pH values. Effective neutralization, in practice is therefore generally directly related to the abundance of non-Fe/Mn carbonate minerals."*

A screen shot of Table 2-2 mentioned in this quotation is copied below as MDAG Figure 2-2. Some interesting and unsettling observations about this quotation and its Table 2-2 include the following.

- The quotation is wrong. *"As is immediately obvious, carbonate minerals generate significantly more neutralization potential than silicate minerals, while they also tend to buffer at higher pH values."* These observations are not "immediately obvious" at all, and in some cases are wrong! Some silicate minerals, like olivine and brucite and many others, can in fact (1) generate significantly more neutralization potential (NP) than carbonate minerals and (2) buffer at higher pH, like pH 10-11, than carbonate minerals. Even plagioclase minerals that form about 40% of the earth's crust (Wikipedia, 2024) can yield an order of magnitude or more fast-neutralizing NP than carbonates (e.g., Morin, 2024, and Morin et al., 2024a and 2024b).
- *"Effective neutralization, in practice is therefore generally directly related to the abundance of non-Fe/Mn carbonate minerals."* While this might be *"generally"* true with no specified limitations given by INAP, it is interesting that measuring NP using a common correction for Fe/Mn carbonates can result in anomalously higher and wrong Effective NP values (Morin, 2021b).

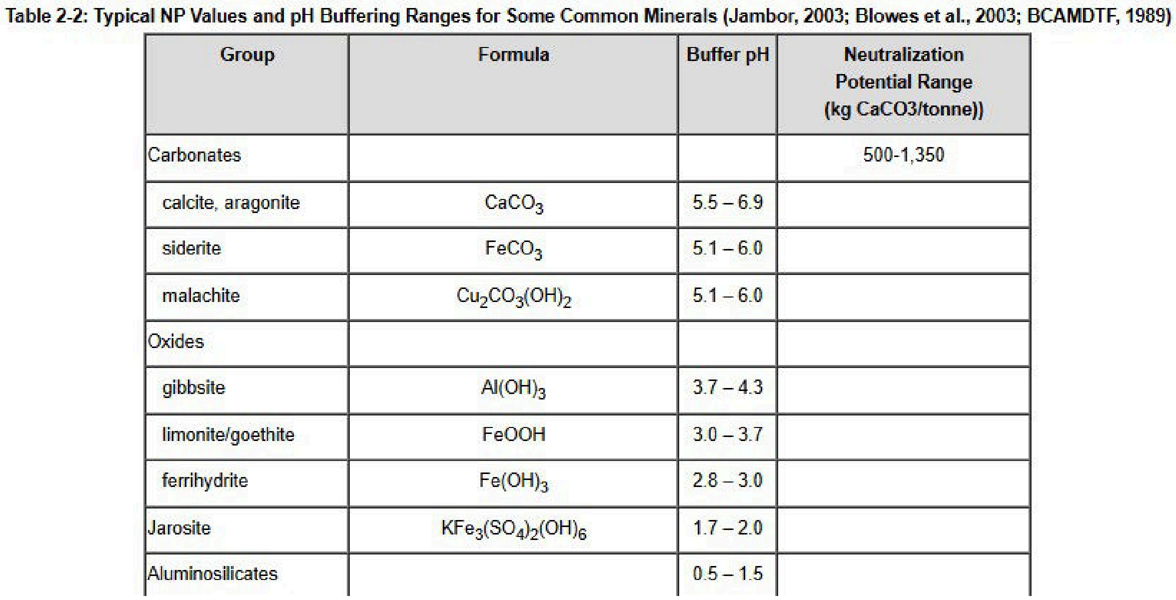

Table 2-2: Typical NP Values and pH Buffering Ranges for Some Common Minerals (Jambor, 2003; Blowes et al., 2003; BCAMDTF, 1989)

Group	Formula	Buffer pH	Neutralization Potential Range (kg CaCO3/tonne))
Carbonates			500-1,350
calcite, aragonite	$CaCO_3$	5.5 – 6.9	
siderite	$FeCO_3$	5.1 – 6.0	
malachite	$Cu_2CO_3(OH)_2$	5.1 – 6.0	
Oxides			
gibbsite	$Al(OH)_3$	3.7 – 4.3	
limonite/goethite	FeOOH	3.0 – 3.7	
ferrihydrite	$Fe(OH)_3$	2.8 – 3.0	
Jarosite	$KFe_3(SO_4)_2(OH)_6$	1.7 – 2.0	
Aluminosilicates		0.5 – 1.5	

Figure 2-2. Screen shot of Table 2-2 from the INAP GARD Guide.

- Table 2-2 (see the screen shot above) says that "Typical NP Values" for Carbonates shockingly range from "500-1,350" kg/t. This means that carbonate minerals "typically" form ~50% to 135% of mine wastes, which is ridiculous.
- Table 2-2 says that the "Buffer pH" of "calcite, aragonite" is 5.5-6.9. Common knowledge of calcite dissolution since at least the 1930's shows that pH values around 8 are typically produced (e.g., abrasion pH in MDAG Table 2-1 below and in Morin, 2024). This is a sign that "Buffer pH" for pH plateaus does not simply reflect the mineral stated, but the precipitation-dissolution of up to several minerals simultaneously (explained further in Section 4 below).
- Of the three references in the title of the table, only one pre-dates Broughton and Robertson (1992) discussed above: "BCAMDTF, 1989":

  > British Columbia Acid Mine Drainage Task Force (BCAMDTF), 1989. Draft Acid Rock Drainage Technical Guide - Volume 1. Prepared by Steffen Robertson and Kirsten (SRK), Vancouver, BC.

  This is an important document for tracing the original identification of pH plateaus, as explained in the next Section 3 below. However, the reference given by the INAP GARD Guide is wrong. The original document actually includes two additional authors as shown in References below (SRK et al., 1989). However, SRK employed Broughton and Robertson at the time so it makes sense the other authors were deleted for the GARD Guide.

Table 2-1. Abrasion pH for various minerals (from Stevens and Carron, 1948; additional data in Stevens, 1934)

	Composition		*Abrasion pH*											
			Acidic						Neutral	Alkaline				
Mineral	Formula	Type[1]	1	2	3	4	5	6	7	8	9	10	11	12
Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$	b A	■											
Alunogen	$Al_2(SO_4)_3 \cdot 16H_2O$	b A		■										
Pickeringite	$MgAl_2(SO_4)_4 \cdot 22H_2O$	B b A			■									
Potash Alum	$KAl(SO_4)_2 \cdot 12H_2O$	B b A			■									
Aluminite	$Al_2SO_4 \cdot 9H_2O$	b A				■								
Scorodite	$FeAsO_4 \cdot 2H_2O$	b A					■							
Sessolite	H_3BO_3	a					■							
Jarosite	$K_2Fe_6(OH)_{12}(SO_4)_4$	b a					■	■						
Siderite	$FeCO_3$	b a					■	■	■					
Gypsum	$CaSO_4 \cdot 2H_2O$	B a						■						
Pyrophyillite	$Al_2Si_4O_{10}(OH)_2$	b a						■						
Quartz	SiO_2	a						■	■					
Gibbsite	$Al(OH)_3$	b						■	■					
Andalusite	Al_2SiO_5	b a							■					
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	B b a							■	■				
Calcite	$CaCO_3$	B a								■				
Anorthite	$CaAl_2Si_2O_8$	B b a								■				
Microcline	$KAlSi_3O_8$	B b a								■	■			
Talc	$Mg_3Si_4O_{10}(OH)_2$	B a									■			
Albite	$NaAlSi_3O_8$	B b a									■	■		
Dolomite	$CaMg(CO_3)_2$	B B a									■	■		
Borax	$Na_2B_4O_7 \cdot 10H_2O$	B a										■		
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	B B b a										■	■	
Magnesite	$MgCO_3$	B a										■	■	
Brucite	$Mg(OH)_2$	B											■	
Merwinite	$Ca_3Mg(SiO_4)_2$	B B a											■	
Shertite	$Na_2Ca_2(CO_3)_3$	B B a												■

[1] A = strong acid B = strong base a = weak acid b = weak base

3. The Explanation of pH Plateaus in the 1989 British Columbia Acid Mine Drainage Task Force Draft Acid Rock Drainage Technical Guide

The "state-of-the-art" GARD Guide (see Section 2 above) provides a poor explanation of pH plateaus and their original source. Nevertheless, in the title of its Table 2-2, the GARD Guide provides a clue that eventually leads to the origin: "BCAMDTF, 1989" which was attributed incorrectly to only SRK. However, SRK was not aware of pH plateaus before 1989.

The authors of this 1989 Draft Acid Rock Drainage Technical Guide were, in fact, Steffen Robertson and Kirsten (B.C.) Inc., Norecol Environmental Consultants, and Gormely Process Engineering. Kevin Morin (the author of this MDAG Case Study) was employed by Norecol at this time and taught SRK about pH plateaus in 1989.

Starting on Page 2-9, this Draft Acid Rock Drainage Technical Guide explains the pH plateaus.

> "The step-like degradation of pH through dissolution of neutralizing minerals has been defined through field studies and computer simulations (Morin et al. 1988a and b; Morin and Cherry, 1988). Based on evaluation of acidic seepage from six tailings impoundments in Canada and the U.S.A. and from one series of laboratory-based column experiments (Morin, 1988) the pH values (plateaus) expected from the dissolution of various neutralizing minerals are:
>
> | Mineral | pH Range |
> |---|---|
> | Calcium-based carbonate | 5.5-6.9 |
> | Siderite (iron-based carbonate) | 5.1-6.0 |
> | Aluminum hydroxide | 4.3-5.0 |
> | Iron hydroxide | 3.0-3.7 |
>
> "For example, if acid generation persists at a sufficient rate to remove all neutralizing minerals except iron hydroxide, the pH of the water will be around 3.0 to 3.7 and will then return to the ambient water pH as the rate becomes negligible. This type of behaviour has been noted in numerous laboratory-based experiments for a proposed gold mine in British Columbia (City Resources, 1988) and for coal mines in Maryland and Pennsylvania (Helz et al, 1987).
>
> "The step-like degradation of pH highlights the care that must be taken in any type of "batch" test where a pre-defined amount of rock is mixed with a pre-defined quantity of acid. The resulting neutralization by the rock will simply reflect the plateau that is reached with that particular ratio of solid:liquid (Morin and Cherry, 1988). A greater proportion of acid may lower the pH to the next plateau or completely remove all neutralizing minerals. For this reason, it is important to define the initiation, variation in rate, and duration of acid generation using kinetic tests ..."

This quotation on the pH plateaus refers to four publications with the senior author of Morin: Morin (1988), Morin and Cherry (1988), and Morin et al., (1988a and 1988b). These are provided in the References at the end of this MDAG Case Study. Not obvious here is that these four publications, in turn, all point to Morin (1983) as the primary source, origin, and delineation of pH plateaus, as explained in detail in the next section below.

4. The Original Source and Delineation of pH Plateaus/Geochemical Sub-regions from 1983

With careful tracing, the documents in the previous sections of this MDAG Case Study eventually lead to the original source and delineation of pH plateaus: Morin (1983). This is the Ph.D. thesis of Dr. Kevin Morin of MDAG. The title page, abstract, and Table of Contents are inserted at the end of this MDAG Case Study as Appendix A.

Some of this work on the delineation of pH plateaus, and their importance to full-scale field studies of ARD, was published a year earlier in the Canadian Geotechnical Journal (Morin et al., 1982). This work was considered so novel and important that this publication was awarded the 1983 Canadian Geotechnical Society Prize.

It is important to understand that "pH plateau" is a satisfactory description for a one-dimensional line (e.g., MDAG Figure 2-1 above). In reality at full-scale minesites, there are three-dimensional zones, experiencing spatial and temporal variations in pH. This is why the pH plateaus were originally called geochemical "sub-regions" rather than "plateaus" by Morin (1983).

The simplest explanation of the pH plateaus and geochemical sub-regions begins with nonlinear buffering (Morin, 2015), whose "nonlinear aspects show that complexity can lead to unexpected trends and that cause and effect are not often proportional" (see Figure 4-1 below). Buffering of pH can reflect (1) aqueous reactions such as bicarbonate/carbonic acid around pH 6.4 and (2) often to a much greater degree various solid-liquid interactions like mineral precipitation-dissolution.

Due to kinetics, the pH value of a pH plateau or sub-region during ARD neutralization typically reflects relatively fast-reacting minerals that reach equilibrium. In this case, the pH value of each sub-region is called its "equilibrium pH", which a complex result of each mineral's abrasion pH (MDAG Table 2-1 above). Nevertheless, this does not rule out the occasional occurrence of stable pH values reflecting a set of slower reactions reaching a non-equilibrium "metastable" pH.

Some nonlinear characteristics of each sub-region or pH plateau include: (1) downgradient pH does not fall immediately to the most acidic, input value, and (2) the downgradient boundary of each sub-region migrates faster than its upgradient boundary, in effect "stretching out" each sub-region with time and distance. This is shown graphically in Figures 4-2 and 4-3 below for (1) increasing distance along a flowpath at one point in time and (2) increasing time at one location on the flowpath. These show that Figures 1-1 and 2-1 above represent increasing time at a single location. The two variables of time and distance can be combined into pseudo three dimensions for a more complex diagram (Figure 4-4).

Of note, Table 4-1 below lists "Dominant Mineral Group Controlling pH". This indicates competing or complementary precipitation-dissolution of more than one mineral group can create and account for the equilibrium pH in addition to the Dominant Mineral. Morin (1983) explained, "the pH and chemistry of each sub-region is dominated by one of the compounds of the conceptual model". Most full-scale sites with ARD will show only a few sub-regions at most, depending on the primary and secondary mineralogy.

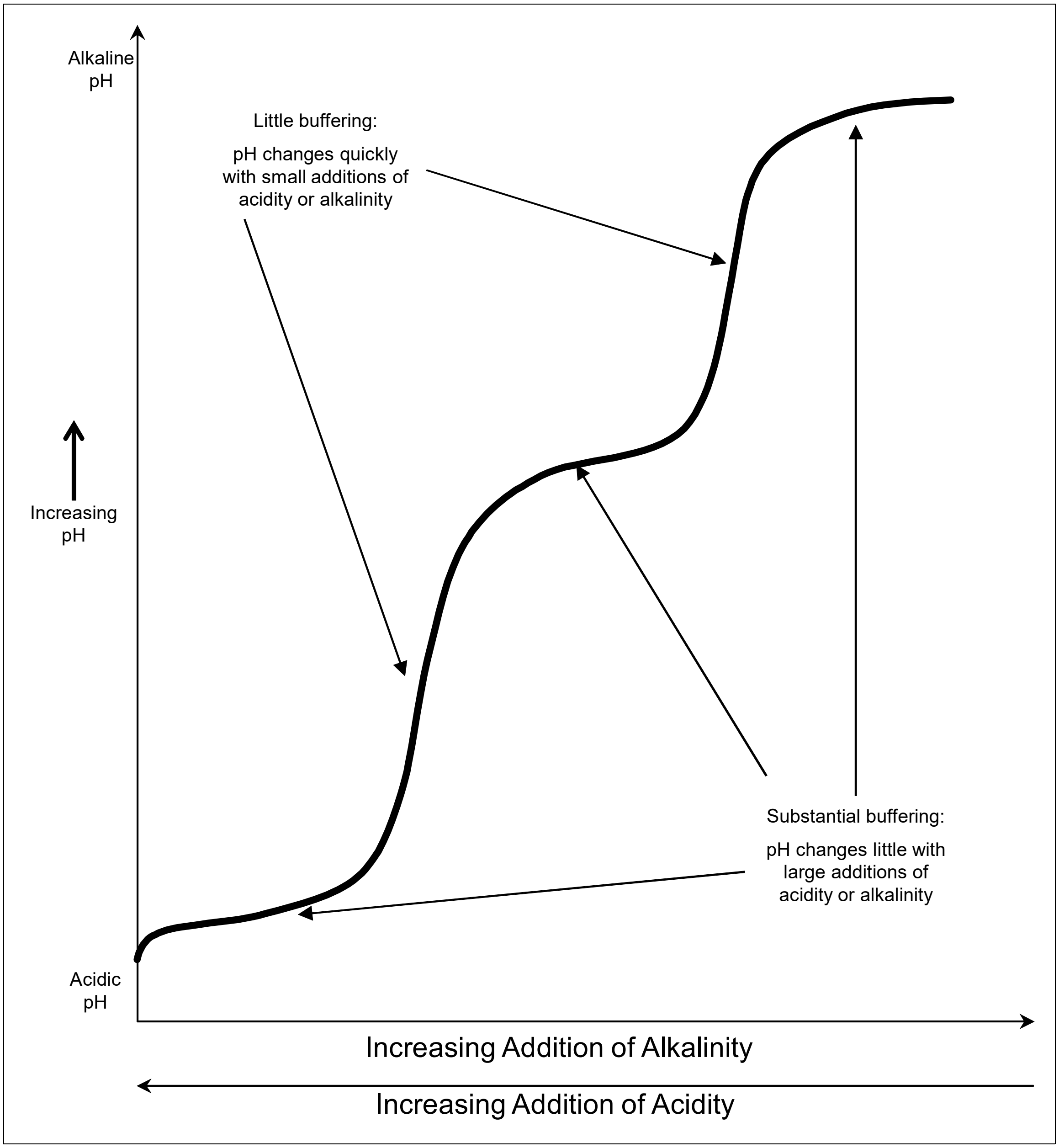

Figure 4-1. A simplified example of pH buffering in "batch" mode, such in laboratory analyses of Neutralization Potential or titrations, without regard for time and distance along flowpaths; pH increases (upwards on the y-axis) nonlinearly as alkalinity is added (rightwards on the x-axis), or with pH decreasing (downwards on the y-axis) nonlinearly as acidity is added (leftwards on the x-axis).

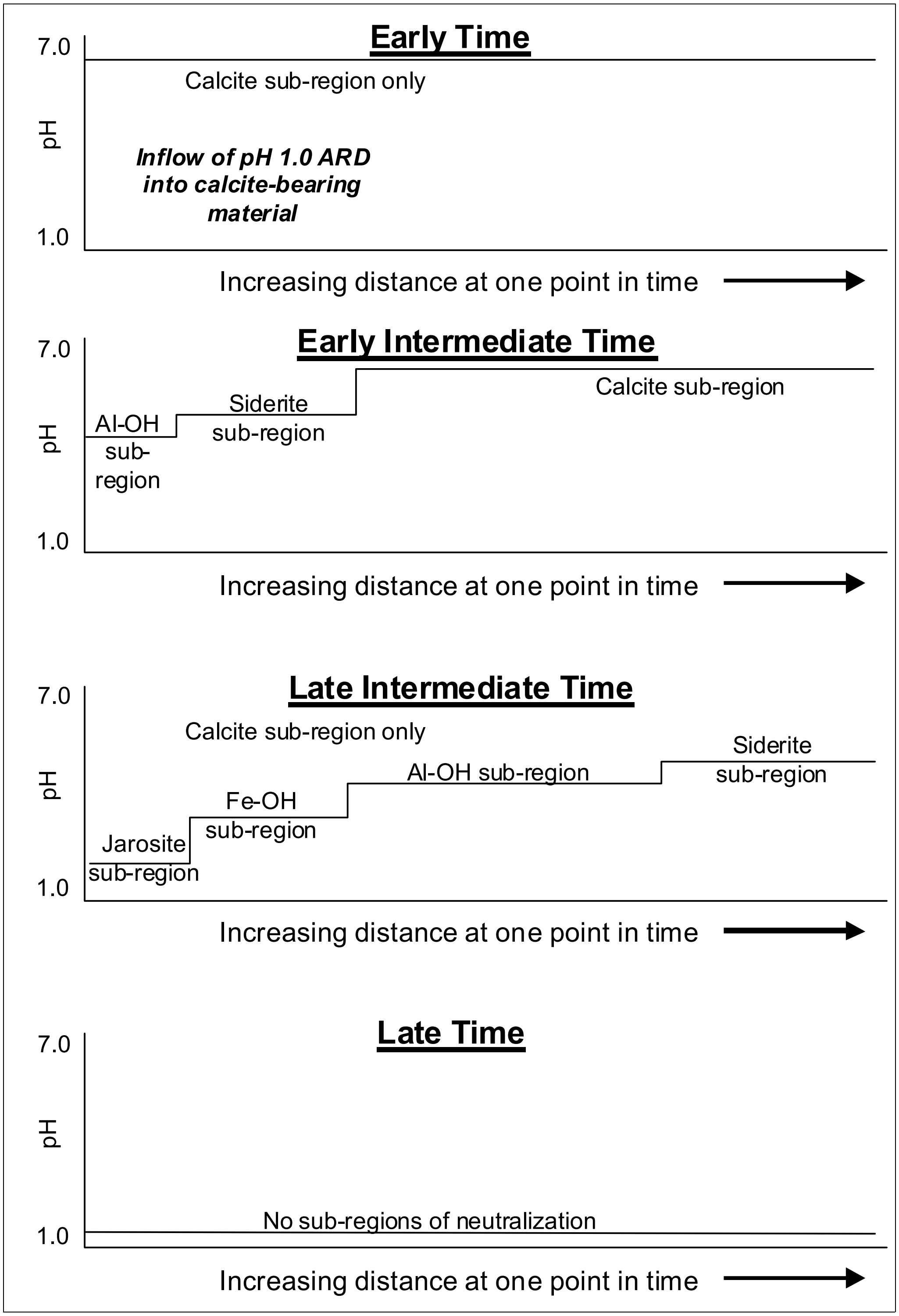

Figure 4-2. Schematic spatial movement and increasing size of geochemical sub-regions during input of pH 1.0 ARD into calcite-bearing material (based on Morin et al., 1982, and Morin, 1983).

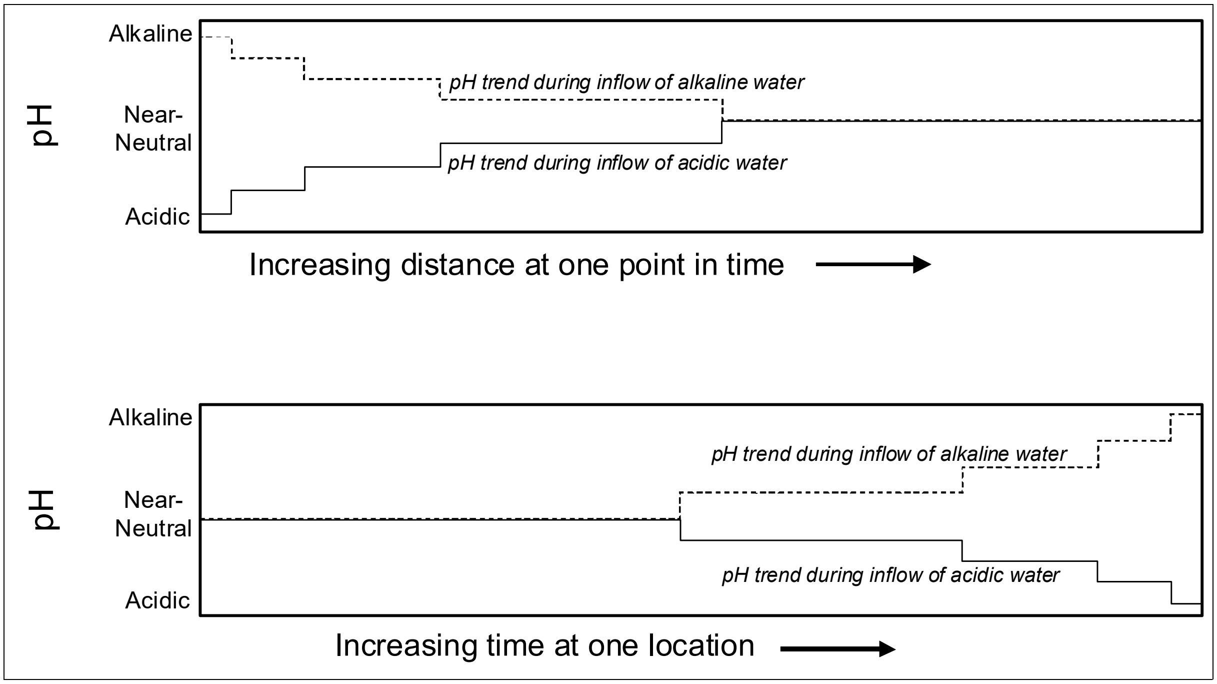

Figure 4-3. More generalized diagrams of the geochemical sub-region concept of neutralization along flowpaths at both increasing distances (top) and increasing times (bottom), for inputs of acidic or alkaline water.

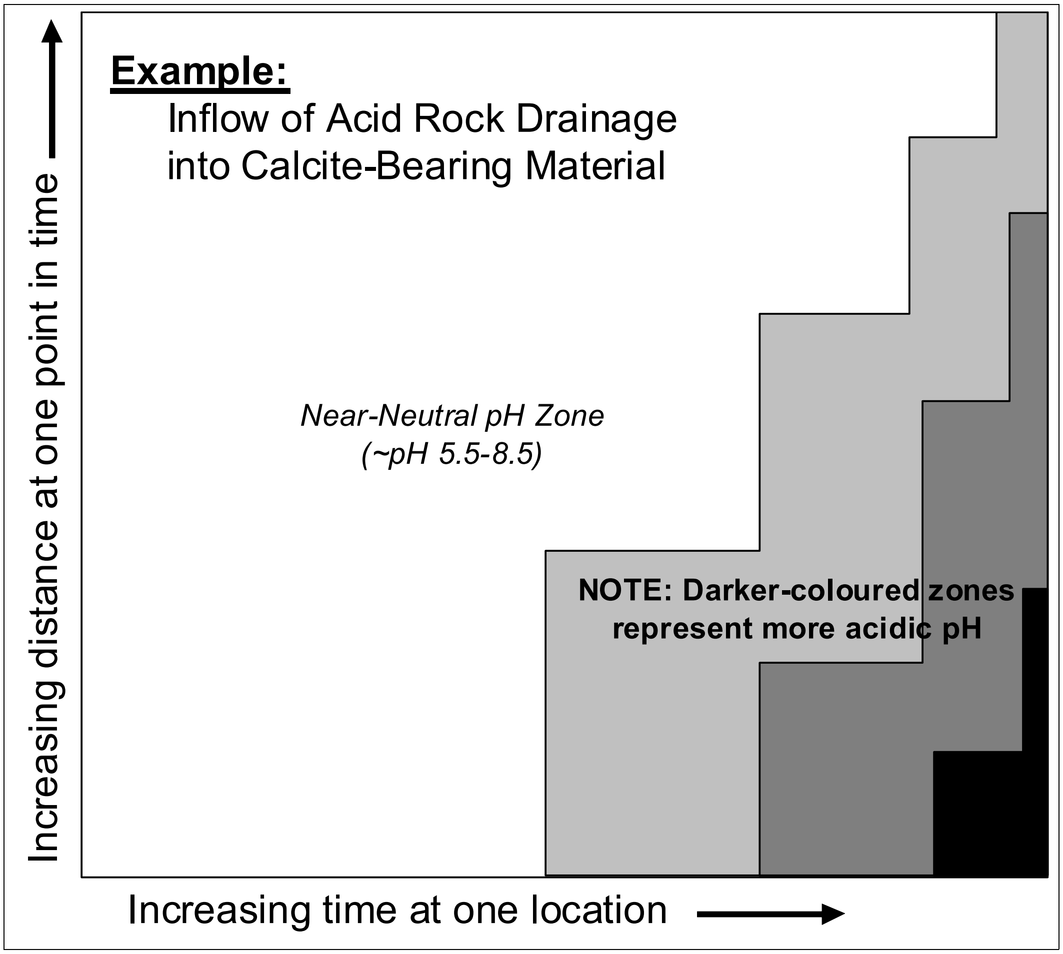

Figure 4-4. Pseudo-three-dimensional schematic diagram of the geochemical sub-region concept for an input of acidic water.

Table 4-1. Examples of equilibrium pH within geochemical sub-regions (compiled from data and references in Morin et al., 1982; Morin, 1983; Section 4.5 of Morin and Hutt, 1997 and 2001; Morin and Cherry, 1988; and Jurjovec et al., 1995)

Dominant Mineral Group Controlling pH	General pH Range
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

The equilibrium pH value of 1.3 for "aluminosilicates" in Table 4-1 is from Jurjovic et al. (1995), but is not representative of all aluminosilicate minerals. Table 2-1 above shows that various aluminosilicate minerals, individually on their own, can create pH from acidic to alkaline values.

Morin (1983) created the computer program, ADNEUT (Acid Drainage Neutralization) and related codes, to simulate sub-regions and many different aqueous concentrations. ADNEUT simulated full-scale minesites and well as smaller tests like laboratory columns. Thus, it is not clear why the INAP GARD Guide shows only that geochemical sub-regions apply to "pH in Micro Environment Around Minerals" (see Section 2 of this MDAG Case Study).

ADNEUT simulations relied on pH, pe (Eh), and 41 aqueous complexes and ion pairs, such as Fe^{3+}, $FeSO4^{+}$, $FeOH^{2+}$, $Fe(OH)_2^{+}$ for ferric iron. Five minerals and mineral groups were implicitly simulated with user-adjustable solubilities: calcite, siderite, gypsum, Al-OH group, and Fe-OH group. Chemical activities were typically calculated with the extended Davies Equation.

For ARD being neutralized along a flowpath, Morin (1983) found that each upgradient sub-region (with a lower pH, see Figure 4-2 above) generally involved fewer minerals precipitating and dissolving simultaneously. The Fe-OH sub-region in full-scale simulations typically reflected the precipitation-dissolution of only Fe-OH minerals and sometimes gypsum, and thus was the simplest and easiest sub-region to understand.

As an example of nonlinear results, Morin (1983) reported that, in a simulation of one full-scale site, lowering the solubility of Fe-OH minerals by one order of magnitude: (1) lowered the equilibrium pH of the Fe-OH sub-region by only 0.3 pH units, (2) decreased aqueous iron concentrations by about 4%, and (3) roughly doubled the forward movement of the downgradient edge of the Fe-OH sub-region.

As another example of nonlinear results, one full-scale simulation of a full-scale groundwater flowpath produced the following aqueous dissolved iron (ferric plus ferrous) concentrations. At the upgradient, input edge of the simulation, there was 3260 mg/L in the acidic input ARD, then:

- 3570 mg/L immediately downgradient in the Fe-OH sub-region,
- 3220 mg/L in the Al-OH sub-region,
- 5548 mg/L in the siderite sub-region, and finally
- 27 mg/L in the full neutralized, farthest-downgradient calcite sub-region.

For some simulations, the solubility of secondary minerals, like Al-OH minerals, at full-scale sites had to vary by up to orders of magnitude from sub-region to sub-region to match measured full-scale chemistry. This occurs, for example, where Al-OH minerals are precipitating along with other minerals in one sub-region and dissolving in another sub-region with or without other minerals.

In general, these sub-regions and pH plateaus exist despite downgradient dispersion and mixing during transport. This is because dispersion into a more-neutral downgradient sub-region will often attenuate the higher, acidic concentration. In this way, the boundaries of sub-regions and their pH plateaus can "sharpen" their edges during movement. As a result, any measured non-abrupt, gradual increase in pH along a flowpath can have a real physical meaning for that flowpath.

Morin (1983) encountered occasional instability in simulations along the discretized flowpaths. This occurred where one cell along the flowpath would provide obviously erratic results at a single time as it transitioned from one sub-region to another. This single-time instability in grid cells were called "PITA" (Pain In The Ass) cells. This inability to reliably simulate transitions to another sub-region using a discretized grid is simply the result of the inability to simulate two equilibrium-based conditions within one grid cell. The resolution would require infinitely small grid cells, which is reminiscent of infinitely small changes demanded by thermodynamics from which chemical equilibrium is derived (Morin, 2021c). As this was not practical, a stable numerical procedure was created to ensure PITA cells would not "crash" a simulation (Morin, 1985 and 1987).

Computationally, PITA cells show that the transition from one sub-region and pH plateau to another is disruptive and chaotic. In reality, this pH transition in laboratory humidity cells and under full-scale site conditions is remarkably not chaotic (Morin, 2019). Consistent with geochemical sub-regions, this "point[s] to mineral-group-specific processes that vary with pH, rather than pH-independent processes".

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APPENDIX A. The Original Source of pH Plateaus and Geochemical Sub-regions: Morin (1983)

(Title page, abstract, and Table of Contents; full download available at:

https://www.mdag.com/MDAG%20Paper%20Database/T0002%20(Morin,%201983).pdf)

Prediction Of Subsurface Contaminant Transport In Acidic Seepage From Uranium Tailings Impoundments

by

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ABSTRACT

A conceptual model for the prediction of aqueous contaminant transport in acidic subsurface seepage from uranium-tailings impoundments is developed based on evaluation of field data obtained during detailed monitoring of a sand aquifer at an inactive tailings area near Elliot Lake, Ontario, and based on published data from other sites. Tailings seepage problems typically occur in unconfined, horizontal, sand aquifers with impermeable bases. The conceptual model divides the aquifers into three sections: the "inner core" adjacent to the tailings, the "neutralization zone", and the "outer zone". The inner core contains tailings water with low pH and high concentrations of iron, aluminum, and sulfate, which has passed unaltered into the aquifer. The outer zone, which is downgradient of the inner core, contains neutral-pH, relatively low-iron, low-aluminum, and low-sulfate water. The neutralization zone is the transition region between the inner core and the outer zone.

As inner-core water flows downgradient, it enters the neutralization zone where calcite is present, and pH and acidity are neutralized. Upon neutralization, aluminum precipitates generally as $Al(OH)_3$ and iron precipitates as $FeCO_3$ (siderite) and/or $Fe(OH)_3$. As a result of calcite dissolution into the high-sulfate solution, gypsum precipitates. Thus, concentrations of major ions decrease and the migration of the inner core is retarded with respect to groundwater velocity. The aqueous behavior of radionuclides and the controls on radionuclide concentrations are evaluated by available information and by the chemical-equilibrium computer program, WATRAD, which was developed as part of this thesis.

In order to simulate the conceptual model, a computer program, ADNEUT, is developed and is applied to case studies in order to simulate the development of present conditions and to predict future migration of the inner core and the neutralization zone with the resulting water chemistry. Emphasis during model development was placed on minimizing execution costs.

ADNEUT also shows that the neutralization zone is composed of several sub-regions; the pH and chemistry of each sub-region is dominated by one of the compounds of the conceptual model. Each sub-region has a unique retardation factor.

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