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Silicate Neutralization Potential Focussing on Plagioclase, and the MDAG Silicate NP Model

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Table of Contents

Abstract.....	2
1. Introduction.....	4
2. Neutralization Potential Derived from Carbonate Minerals (“Carbon NP”)	8
4. Past Full-Scale Case Studies of Significant Silicate NP.....	12
5. The MDAG Silicate NP Model, Updated	15
6. A Special Focus on Plagioclase Silicate Minerals	16
7. A New Case Study of Important Fast-Neutralizing Silicate NP by Plagioclase Minerals	18
8. Discussion of Neutralization Potentials	29
9. Conclusion	31
10. References.....	33

Abstract

This MDAG Case Study simplifies the very complex issue of aqueous neutralization of ARD by solid-phase Neutralization Potential (NP) along flowpaths in minesite components. These simplifications lead to estimates of the amounts and the neutralization rates of Fast-Neutralizing Silicate NP and of Slow-Neutralizing Silicate NP in multi-mineral rock samples. Fast-Neutralizing Silicate NP can be added to inorganic-carbonate Carbon NP to obtain Total NP that provides full neutralization above ~pH 6, if the Carbon NP is dissolving rather than forming from atmospheric CO₂ as is more typical in many silicate-neutralizing systems.

Past case studies showed that some minesites do not have ARD on the full scale over decades, and yet ARD arises in smaller-scale testwork in less than a year. The series of plagioclase minerals is often implicated in the additional “undetected” silicate-mineral NP, likely because these minerals form the most abundant group in the earth's crust. However, the plagioclase minerals are often overly simplified in ARD studies to an average molar ratio of calcium and sodium, or to the two endpoint minerals. This MDAG Case Study shows that these oversimplifications can lead to substantial underestimation or overestimation of Fast-Neutralizing Silicate NP.

For more accurate estimates of Fast-Neutralizing Silicate NP in multi-mineral rock and tailings, the amounts of the individual plagioclase minerals are needed, particularly the calcium-rich minerals that have orders-of-magnitude faster neutralization rates. A relatively small amount of calcium-rich plagioclase can provide tens to hundreds times more Fast-Neutralizing Silicate NP than a much larger amount of sodium-rich plagioclase. In other words, there are nonlinear and exponential relationships among the plagioclase minerals and among their rates of neutralization that are not easily applied to the basic concept of NP.

It has been long known that integrated, multifaceted studies were needed to understand and predict Silicate NP across various scales at minesites, but the extent and intensities of such studies needed for a single site were unclear. A recent study in Canada illustrates the intensive studies needed which include the following.

- On-site ML-ARD columns include fresh drillcore, as well as two columns containing ~300 kg of existing 13- to 26-year-old waste rock with one quickly releasing ARD and one releasing ~pH 6.0 to 7.0. More than a dozen laboratory-based kinetic tests of various scales are continuing. Subsamples from all kinetic tests were subjected to static testing like expanded U.S. EPA 600 acid-base accounting (ABA).
- Innovative and state-of-the-art analyses were conducted for (1) oxidation-by-oxygen (oxycon) testing and (2) mineralogy using x-ray diffraction (XRD), scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM/EDX), visual petrographics, and microscopic Raman spectroscopy. This included the updated 2021 RockJock x-ray-diffractogram library, the Raman Renishaw's Library backed up by visually assessed spectra developed for the Perseverance Rover on Mars, and mineral-specific Calcium Molar Ratios using SEM/EDX.
- ABAs of dozens of ML-ARD samples were carefully selected based on (1) sulphur geostatistics approximating lognormal distributions using tens of thousands of sulphur analyses for drillcore, (2) dominant rock units, and (3) 3D spatial

distributions along and among drillholes.

- The MDAG Silicate NP Model described below was applied to the results of this testwork.

The updated spreadsheet-based MDAG Silicate NP Model (free at MDAG.com), based on published information particularly by the U.S. Geological Survey, calculates the following.

1. (Total) Silicate NP in kg CaCO₃ equivalent/tonne based on the sum of each silicate mineral's abundance in a multi-mineral sample, the stoichiometry of each silicate mineral, and its total per-mole capacity to neutralize.
2. The (total) Rate of Silicate Neutralization in mg CaCO₃ equivalent/kg/week which is the sum of the individual neutralization rates from each silicate mineral in a sample based on each mineral's abundance, particle size, and particle-scale pH.
3. Identification of the silicate minerals in a multi-mineral sample accounting for most of its Rate of Silicate Neutralization, in order to calculate Fast-Neutralizing Silicate NP in kg CaCO₃ equivalent/tonne.

The “fizz ratings” used by the Sobek NP procedure, as well as by the unstandardized Modified NP procedures altered by some laboratories without informing their clients, assume that most of a multi-mineral sample’s NP is Carbon NP. This is wrong for the minesites discussed here. Perhaps a new “rapid” method could be developed for silicate NP, and existing methods like acid titration might suffice, only if:

- testwork persists for at least 60 to 80 days which is rarely the case for rapid methods and titrations, and
- any stagnant “batch” results are converted to realistic, dynamic flowpath assessments.

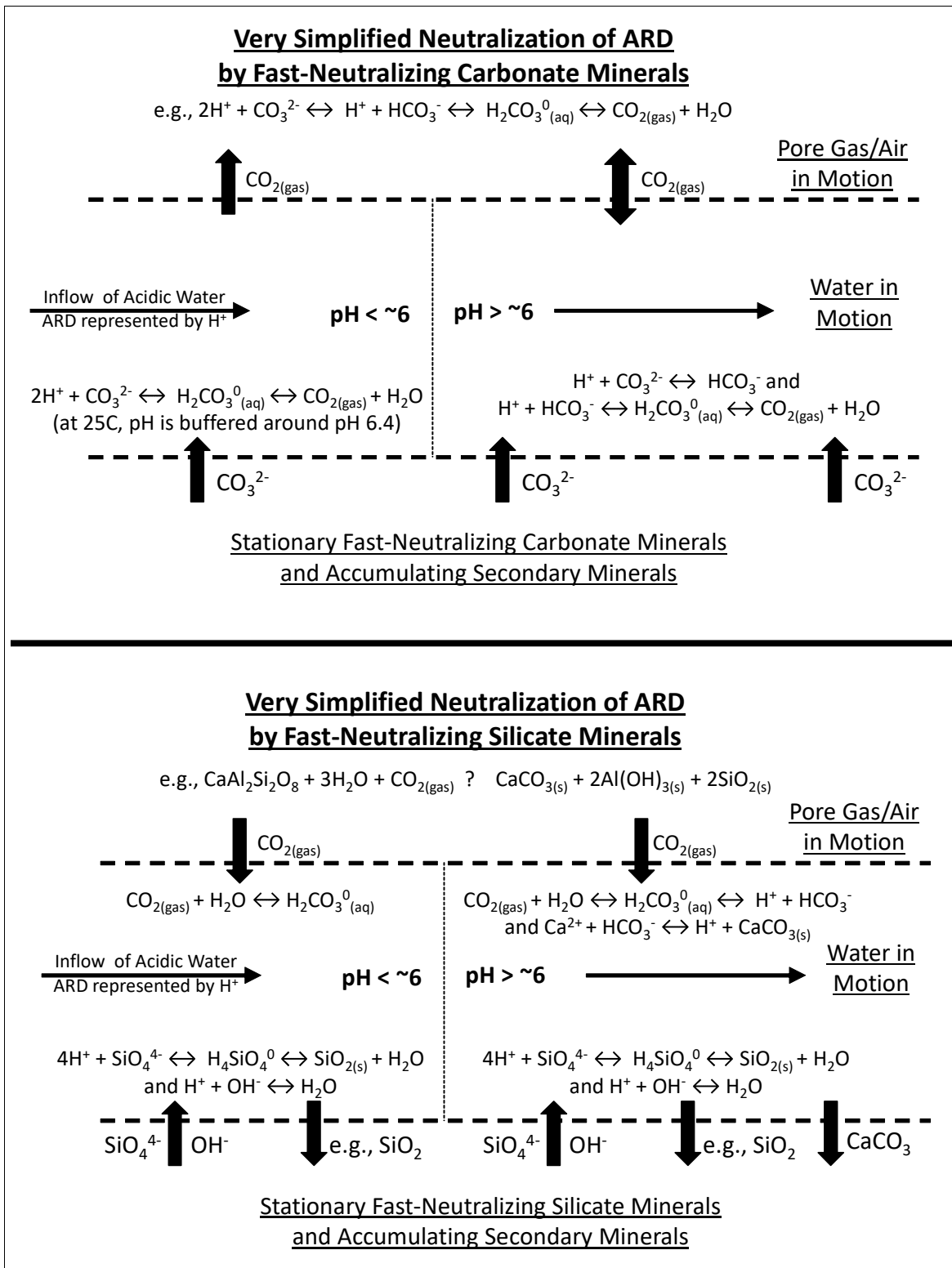
1. Introduction

The concepts of neutralization in water, alkalinity in water, acidity in water, and Neutralization Potential (NP) in solid-phase minerals are phenomenally complex and nonlinear (e.g., Kirby and Cravotta III, 2005a and 2005b; Cravotta III and Kirby, 2004; Morin, 2009; Morin and Hutt, 1997a and 1997b, 2001, 2009). A major reason for this complexity is that they are not “real” like chemical elements. Elements in the Periodic Table are real in that they exist and have a concentration independent of the methods used to analyze them. However, NP, acidity, and alkalinity exist only in terms of the assumptions and procedures used to measure them. These analytical assumptions and procedures are inherently applied to all scales and conditions at a minesite.

Solid-phase NP is typically measured by the standardized U.S. EPA 600 “Sobek” Method or by one of the many unstandardized “Modified” Methods (Price, 2009) that some laboratories have altered without informing clients. In all cases, these are only analytical values of a selected procedure and do not represent robust NP values across all scales and all conditions at a minesite (Price, 2009; Morin and Hutt, 1997a, 1997b, 2001, 2009; Morin, 2009). Additionally, many NP methods start with “fizz ratings” which implicitly assume that NP is mostly fast-reacting carbonate minerals that fizz in acid. Moreover, NP values are reported as some variation of kg CaCO₃ equivalent/tonne where the word “equivalent” involves some gross simplifications and assumptions (Morin and Hutt, 2006). Assessments of NP should be approached with great caution and care.

For decades, instructions for ARD predictions have emphasized the usage of “Effective NP” rather than measured analytical NP (e.g., Price, 2009; Morin and Hutt, 1997a, 2001, and 2008; Sexsmith et al., 2015). Nevertheless, nearly all ARD assessments, including those today, are based solely on measured NP by whatever chosen method. The usage of measured NP values with no adjustments should be a major clue that an ARD assessment was not done reliably. This remains the likely cause for at least 90% of ARD assessments being substantially wrong by underestimating ARD potential.

Traditionally, neutralization of acid rock drainage (ARD) is primarily attributed to two mineral groups: carbonates and silicates (Figure 1). “Neutralization” here means “full neutralization” in water from an acidic pH to a pH around 6.0 and above. “Partial neutralization” to a pH less than about 6.0 can also arise from these two mineral groups, as well as from others like oxyhydroxides. For example, the dissolution of some oxyhydroxides partially neutralizes to local equilibrium levels (Figures 2 and 3), creating stable pH levels such as pH ~3.0-3.7 for common Fe-OH minerals and pH ~4.3-5.0 for common Al-OH minerals (Morin et al., 1982; Morin, 1983, Morin and Cherry, 1988; Morin, 2015).



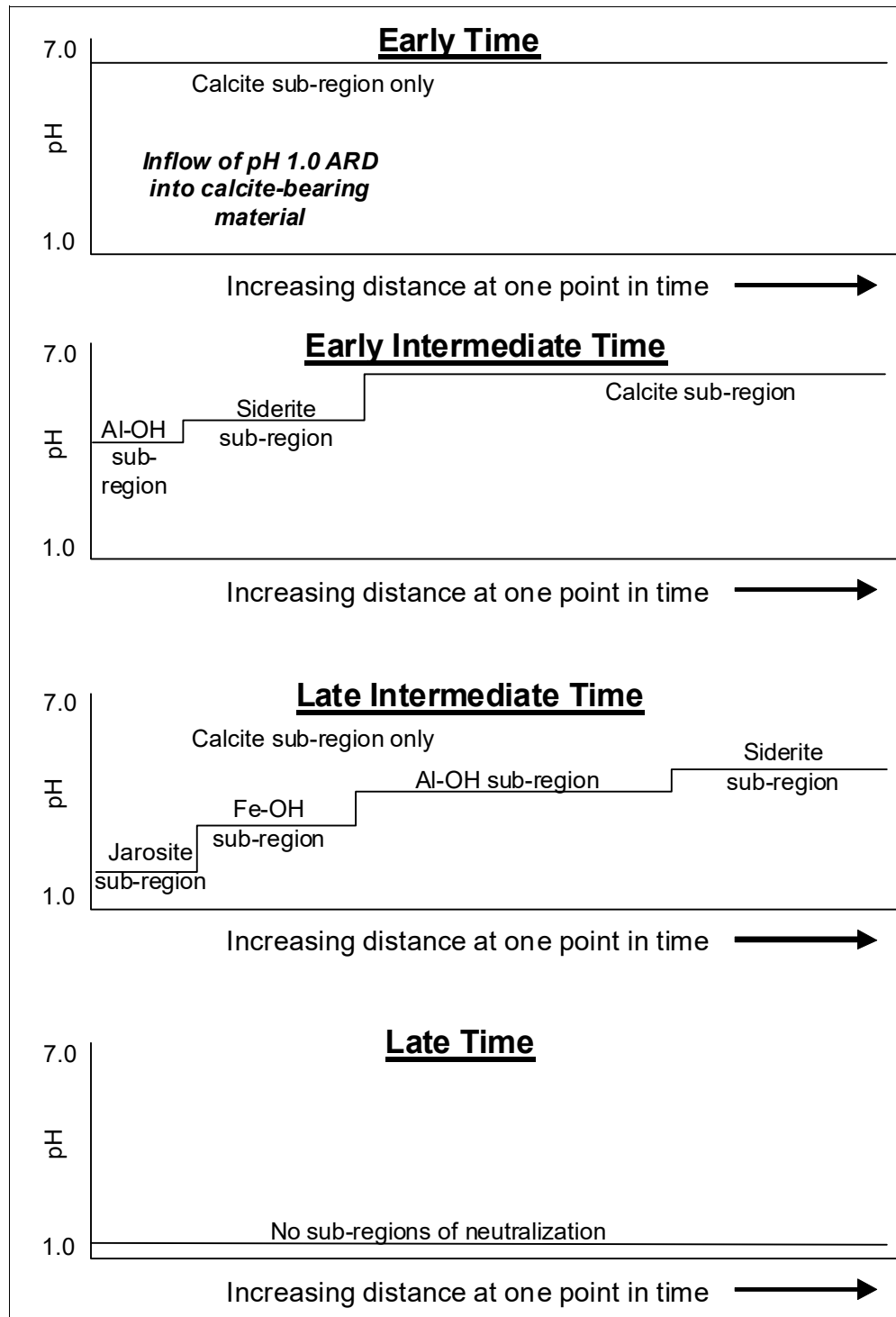


Figure 2. Schematic spatial movement and increasing size of geochemical sub-regions during input of pH 1.0 ARD into calcite-bearing material (based on Morin et al., 1982, and Morin, 1983 and 2015).

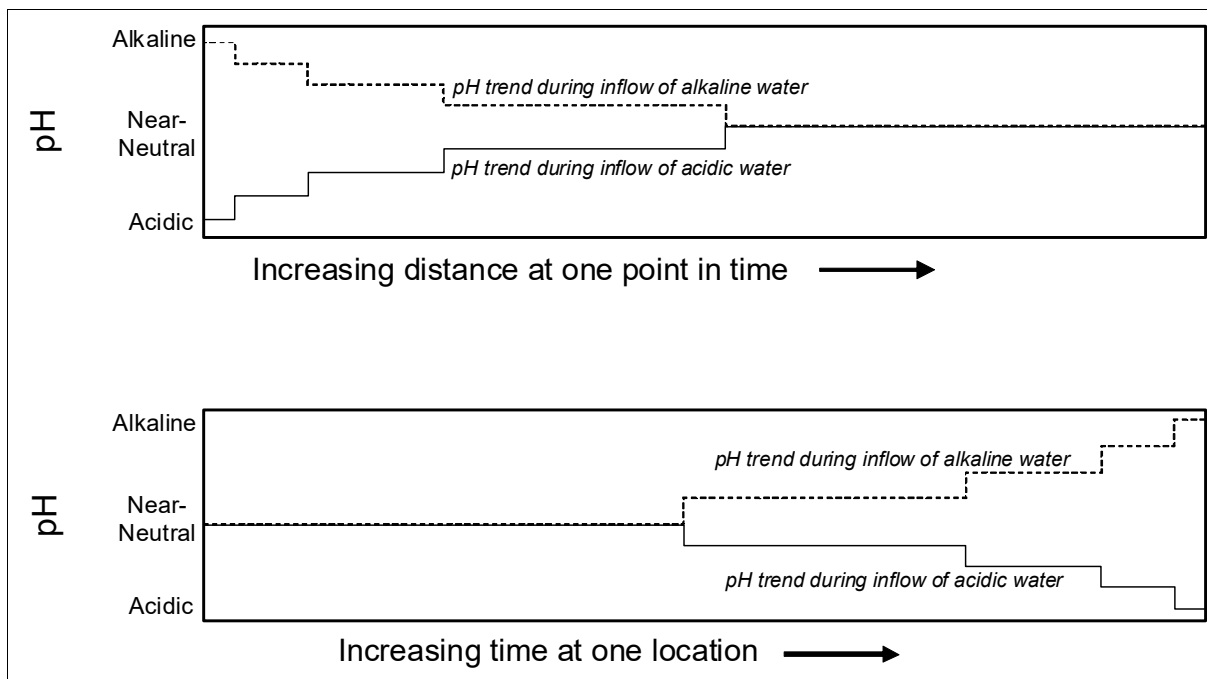


Figure 3. Schematic diagrams of the geochemical sub-region concept at both increasing distances and increasing times, for inputs of acidic or alkaline water (based on Morin et al., 1982, and Morin, 1983 and 2015).

2. Neutralization Potential Derived from Carbonate Minerals (“Carbon NP”)

For the carbonate mineral group, calcium carbonate (e.g., CaCO_3 , calcite, vaterite, amorphous) and certain mixed-element carbonates (e.g., dolomite, some local varieties of ankerite) are typically viewed as fully neutralizing, dissolving virtually instantaneously relative to the residence time of water along flowpaths inside many minesite components. This is called “Carbon NP” here.

However, carbonate minerals like siderite (FeCO_3) may only partially neutralize to a pH less than 6.0 (Morin and Cherry, 1986; Morin, 2015). For redox-active carbonate minerals like FeCO_3 and MnCO_3 , their abilities to partially or fully neutralize depend on many site conditions (Morin, 2021) and thus are not easily generalized. The amount of NP attributable to fast-reacting carbonate minerals has been reported for many decades using techniques such as Chittick, Leco, gravimetric CO_2 release, acid consumption, x-ray diffraction, spectroscopy, and many others (e.g., Fu et al., 2020).

Interpretations and predictions of neutralization by carbonate minerals are often made in “batch mode” where a certain volume of acidic water remains in contact with Carbon NP. In reality, water flowing through and over minesite components follows distinct flowpaths, which lead to more complex and realistic interpretations and predictions (see the top of Figure 1). A relatively simple example is that the precipitation of secondary Al-OH and Fe-OH minerals, as inflowing acidic water repeatedly contacts Carbon NP, leads to a faster consumption of the Carbon NP while at the same time creating capacities for partial neutralization in the secondary minerals for later use. This leads to migrating, step-like, chromatographic-like pH plateaus along flowpaths (e.g., Figures 2 and 3).

3. Neutralization Potential Derived from Silicate Minerals (“Silicate NP”)

For NP derived from silicate minerals, the situation is much more complex than for carbonate minerals (see the bottom of Figure 1). As a general indicator of the complexity, Google Scholar lists about 34,000 documents containing “silicate mineral”.

For silicate minerals, many hundreds of silicate minerals are known, with dozens being common enough to form common rocks (Wikipedia, 2024a). According to their crystal structures, the seven main groups include inosilicates (including pyroxenes and amphiboles) and tectosilicates (including quartz and feldspars). Additionally, silicate minerals reportedly comprise about 90% of the Earth’s crust, with plagioclase minerals forming nearly 40% of the crust and thus being the most abundant mineral group. All this means that there are many silicates that can dissolve at significantly different rates within one multi-mineral sample, with some dissolving very slowly over long geologic times.

As a result, from the perspective of acid neutralization associated with ARD, the importance of silicate NP can range from negligible to important. An early example of this is “abrasion pH” from Stevens (1934) and Stevens and Carron (1948) as shown in Table 1, based on references back to the 1870's.

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

Mineral	Composition		Abrasion pH														
	Formula	Type ¹	Acidic						Neutral	Alkaline							
			1	2	3	4	5	6	7	8	9	10	11	12			
Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	b A	■														
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	b A		■													
Pickeringite	$\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$	B b A			■												
Potash Alum	$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	B b A			■												
Aluminite	$\text{Al}_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$	b A				■											
Scorodite	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	b A					■										
Sessolite	H_3BO_3	a															
Jarosite	$\text{K}_2\text{Fe}_6(\text{OH})_{12}(\text{SO}_4)_4$	b a						■									
Siderite	FeCO_3	b a							■								
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	B a								■							
Pyrophyllite	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	b a									■						
Quartz	SiO_2	a										■					
Gibbsite	$\text{Al}(\text{OH})_3$	b											■				
Andalusite	Al_2SiO_5	b a												■			
Muscovite	$\text{KA}l_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	B b a													■		
Calcite	CaCO_3	B a														■	
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	B b a															■
Microcline	$\text{KA}l\text{Si}_3\text{O}_8$	B b a															■
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	B a															■
Albite	$\text{NaAlSi}_3\text{O}_8$	B b a															■
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	B B a															■
Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	B a															■
Phlogopite	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	B B b a															■
Magnesite	MgCO_3	B a															■
Brucite	$\text{Mg}(\text{OH})_2$	B															■
Merwinite	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$	B B a															■
Shertite	$\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$	B B a															■

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

Based on the current understanding of highly variable neutralization of ARD by silicate minerals, important yet simplistic terminology is depicted in Figure 4. **Silicate NP** consists of:

- (1) **Slow-Neutralizing Silicate NP** which contributes relatively little, partial neutralization, and
- (2) **Fast-Neutralizing Silicate NP** which can fully neutralize pH above ~ 6 (see also the bottom of Figure 1).

Interestingly, the proportions and absolute amounts of the Slow-Neutralizing Silicate NP and the Fast-Neutralizing Silicate NP are dynamic and mineralogy-specific. The vertical dashed line in Figure 4 can shift left and right depending on variable conditions and properties such as rates of sulphide oxidation and acid generation, particle size, local pH and aqueous chemistry, percentages of minerals, scale, etc. (e.g., Sherlock et al., 1995; van Noort et al., 2018), with important positive and negative feedback loops that are not always obvious (e.g., Sverdrup et al., 2019; Yuan et al., 2019). For plagioclase minerals in multi-mineral rock, Gudbrandsson et al. (2014) succinctly explained,

“The significant scatter and large number of factors influencing plagioclase dissolution kinetics suggests that laboratory measured rates in these and other laboratory studies might only provide a first approximation to the reactivity of plagioclase in natural water-rock systems.”

Based on Figure 4, **Total NP** for full neutralization is the combination of Carbon NP (see Section 3 above) and Fast-Neutralizing Silicate NP. Total NP is a critical parameter for estimating full neutralization. Based on case studies discussed below, fast-neutralizing silicate NP substantially exceeds Carbon NP only at a few minesites and can depend on many factors such as the rate of acid generation, scale including lengths of flowpath, and specific silicate minerals.

Interestingly, Carbon NP and Fast-Neutralizing NP can be locked in site-specific positive and negative interactions. The creation of carbonate minerals by silicate neutralization explains why some authors commonly detect small but potentially important amounts of carbonate minerals in silicate-mineral samples and rock (e.g., Jambor et al., 2002 and 2006; Gudbrandsson et al., 2014; Lehmann et al., 2023), under some conditions caused by “the progressive sorption of atmospheric CO_2 ” (Jambor et al., 2005). Where sulphide minerals are actively generating acidity followed by neutralization with carbonate minerals releasing CO_2 , the opposing uptake of CO_2 by silicate minerals can be close to balanced or can lead to a small net accumulation of carbonate minerals (e.g., Liu et al., 2023).

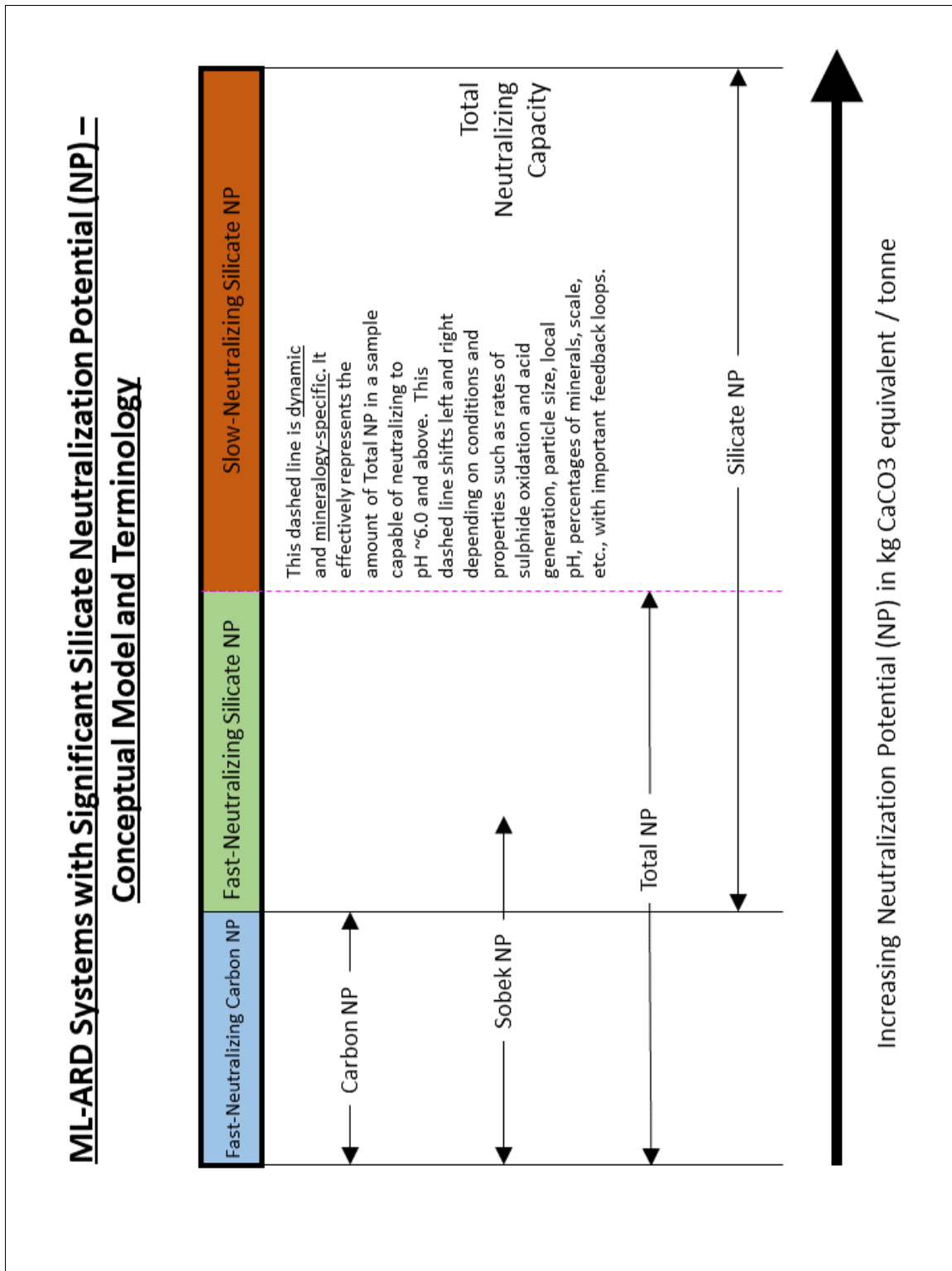


Figure 4. Conceptual model and terminology for various Neutralization Potentials in mine rock and tailings.

4. Past Full-Scale Case Studies of Significant Silicate NP

Detailed studies such as reaction rates of individual silicate minerals go back more than a half century (references in Palandri and Kharaka, 2004). One common observation known for decades is that silicate-mineral reaction rates under small-scale laboratory conditions can be up to orders of magnitude higher than those under full-scale field conditions (e.g., Strömberg and Banwart, 1994; White and Brantley, 2003; Ganor et al., 2005; Sverdrup et al., 2019). However, some of these studies incorrectly combine many minerals like plagioclase when the individual minerals have markedly different, nonlinear rates (discussed in Sections 6 and 7 below).

Because of silicate minerals comprising large portions of rocks, the interest in Silicate NP for ARD is decades old. This section discusses some full-scale case studies going back about 30 years.

Morin et al. (2001) illustrated the violation of common ARD prediction rules for six molybdenum-related minesites where static and kinetic tests predicted ARD but no full-scale ARD had been detected for many decades. This included the Boss Mountain minesite where there appeared to be significant additional NP not measured by the NP procedure, likely calcium-rich plagioclase minerals and hornblende. In fact, the low Sobek-measured NP levels did not decrease as tailings weathered for decades at the surface, implying NP and solid-phase carbonate were being created as sulphide minerals oxidized and generated acidity. This makes sense, as explained above in Section 3 and at the bottom of Figure 1, where silicate neutralization under some conditions can lead to the ongoing creation of solid-phase carbonate and Carbon NP.

Additionally, based on full-scale aqueous sulphate concentrations at Boss Mountain, the rates of sulphide oxidation and acid generation were notably low. Morin et al. (2001) explained,

“... the rates of acid generation at these sites happen to be sufficiently low so that the slowly-dissolving, unmeasured silicate-based NP is able to maintain near-neutral pH on a large scale, but not always on smaller scales. The reason for the depressed oxidation rate is not clear from available information, but could be related to the significant amounts of non-iron-based sulphide minerals. Such a scenario is probably not unique to molybdenum-related minesites, and may be found at other types. Integrated, multifaceted geochemical studies are needed to identify and understand such exceptions and to better predict future aqueous concentrations.”

At that time, it was not clear which “integrated, multifaceted geochemical studies” would be needed for plagioclase-dependent Silicate NP, but it is clearer based on a recent study (see Section 7 below).

Morin and Hutt (2007) discussed the Davidson molybdenum deposit where, in 1968, approximately 2 km of underground tunnels were mined and 60,000 tonnes of waste rock were piled nearby on the surface. Over a half century, no full-scale ARD was detected at Davidson. Despite the many decades of full-scale near-neutral drainage, two of five recent laboratory-based humidity cells became acidic in about a half year, another became acidic after nearly three years, and a fourth was becoming acidic after three years (Figure 5). Although a few silicate minerals were suspected of supplying Fast-Neutralizing Silicate NP, plagioclase minerals of undefined compositions were the only ones implicated in all three acidic cells.

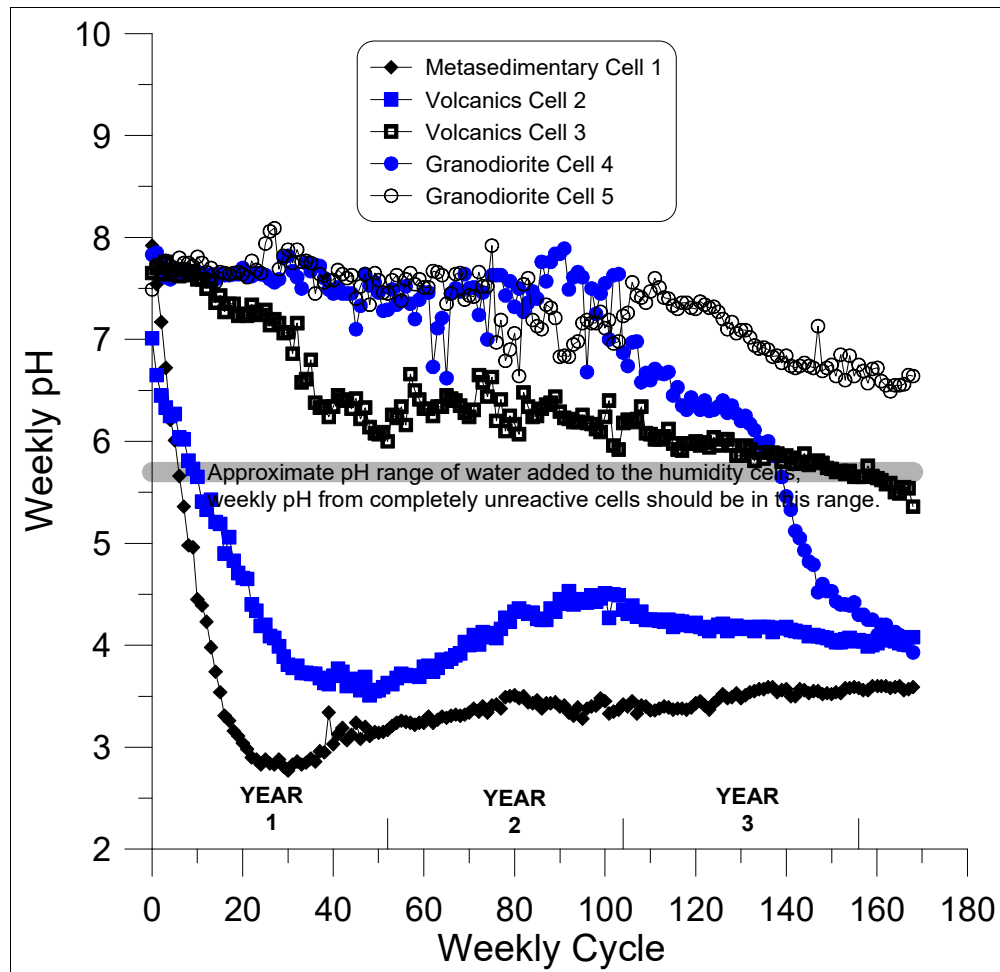


Figure 5. The temporal trends of pH from five humidity cells containing rock from a site producing no full-scale ARD for more than a half century.

Morin and Hutt (2007) noted,

“... [as an anomaly, literature-based] rates of neutralization by aluminosilicate minerals in the near-neutral humidity cells were similar to, or substantially less than, the measured neutralization rates. The substantially larger measured rates apparently reflect (1) the additional contribution of calcite and/or (2) the possibility of micro-scale acidic conditions ($\text{pH} < 6$) around the aluminosilicate mineral grains that would cause them to react faster. However, such a small-scale pH cannot be estimated from available information.”

Also,

“Subsequent conversions to neutralization potentials and alkalinities showed that silicate neutralization played a major role in the partial (below pH 6) to full neutralization (above pH 6) in these humidity cells. This work also showed that calcite was not needed to explain the water chemistry, with atmospheric CO_2 potentially supplying the carbon for alkalinity. However, slightly better agreement was obtained when calcite was included.”

Based on the current understanding of Silicate NP, the suspected importance of micro-scale and particle-scale pH in a flowpath setting (e.g., Figures 1 to 3) is valid for understanding the pH-dependent rates of silicate neutralization. Also correct is the statement that calcite was relatively unimportant, with the bottom of Figure 1 showing how calcite can form during silicate neutralization. These are discussed in more detail in sections below.

The amounts and rates of partial neutralization (Slow-Neutralizing Silicate NP, Figure 4) and full neutralization (Fast-Neutralizing Silicate NP, Figure 4) depend in part on particle-scale pH, which in turn is affected by the rate of sulphide oxidation and acid generation, which in turn can affect the particle-scale pH and degree of neutralization which can affect the rate of sulphide oxidation. This and other factors lead to complex site-specific interplays and feedback loops that are not easily defined (e.g., Figures 2 and 3). On this matter, one simplification made for designing full-scale options to control ARD is to lower the rate of acid generation to match the rate of partial silicate neutralization (Miller et al., 2010; Li et al., 2015; Smart et al., 2015). In reality, lowering the rate of acid generation can raise the particle-scale pH which in turn can lower the rate of silicate neutralization so that ARD still occurs. The sections below in this MDAG Case Study avoid this simplification.

Silicate minerals reportedly comprise about 90% of the Earth's crust, with plagioclase minerals forming nearly 40% of the crust and thus the dominant mineral group. While this MDAG Case Study and previous studies above focus on neutralization by plagioclase minerals, there are studies focussing on other silicate minerals. For example, Khaidar Ali et al. (2020) identified the local silicate neutralizing minerals as muscovite, illite, smectite, kaolinite, dickite and gypsum at the Barani Pit in Indonesia. At the Aitik minesite in Sweden, Strömberg and Banwart (1994) identified the primary neutralizing minerals as biotite in combination with plagioclase minerals simplified to the end members of albite and anorthite. Sections 6 and 7 below show this simplification to end members is unreliable due to nonlinearity. Puura and Neretnieks (2000) identified illite as the primary source of partial silicate neutralization in very acidic alum-shale waste rock in Estonia.

5. The MDAG Silicate NP Model, Updated

Morin and Hutt (2007) created the spreadsheet-based MDAG Silicate NP Model with three primary objectives in its calculations (see also Figure 4):

1. (Total) **Silicate NP** in kg CaCO₃ equivalent/tonne based on the sum of each silicate mineral's physical abundance in a multi-mineral sample, the stoichiometry of each silicate mineral, and its total per-mole capacity to neutralize.
2. The total **Rate of Silicate Neutralization** in mg CaCO₃ equivalent/kg/week which is the sum of the individual neutralization rates from each silicate mineral in a sample based on each mineral's abundance, particle size, and particle-scale pH.
3. Identification of the silicate minerals in a multi-mineral sample accounting for most of its Rate of Silicate Neutralization to calculate **Fast-Neutralizing Silicate NP** in kg CaCO₃ equivalent/tonne.

The initial MDAG Silicate NP Model of Morin and Hutt (2007) has been updated here to the current Version 2024.01, freely available at MDAG.com. This upgrade involved a more flexible approach for calculating the effect of particle-scale pH on reaction rates. It is important to understand that the MDAG Silicate NP Model is based on excellent studies conducted by others.

The key reference in the MDAG Silicate NP Model is Palandri and Kharaka (2004), with some supporting information from Eary and Williamson (2006) and Bowser and Jones (2002). Palandri and Kharaka with the U.S. Geological Survey provided a landmark review and compilation of mineral reaction rates including many silicate minerals, based on more than 400 references. Most rates were nominally at 25°C.

In their Section 2.3, Palandri and Kharaka (2004) were clear about the unavoidable limitations and uncertainties in such a wide-ranging compilation. These limitations and uncertainties are not repeated here but are very important and relevant to any assessment of Silicate NP.

6. A Special Focus on Plagioclase Silicate Minerals

With silicate minerals reportedly comprising about 90% of the Earth's crust, the dominant subset of plagioclase silicate minerals forms nearly 40% of the crust. Also, plagioclase minerals have been implicated in past full-scale studies of Silicate NP (see Section 4 above). Thus, it is important to look more closely at this mineral group.

Wikipedia (2024b and 2024c) state,

“Feldspar (sometimes spelled felspar) is a group of rock-forming aluminium tectosilicate minerals, also containing other cations such as sodium, calcium, potassium, or barium. The most common members of the feldspar group are the plagioclase (sodium-calcium) feldspars and the alkali (potassium-sodium) feldspars. Feldspars make up about 60% of the Earth's crust, and 41% of the Earth's continental crust by weight.”

“Plagioclase is the most common and abundant mineral group in the Earth's crust. Part of the feldspar family of minerals, it is abundant in igneous and metamorphic rock, and it is also common as a detrital mineral in sedimentary rock. It is not a single mineral, but is a solid solution of two end members, albite or sodium feldspar ($\text{NaAlSi}_3\text{O}_8$) and anorthite or calcium feldspar ($\text{CaAl}_2\text{Si}_2\text{O}_8$). These can be present in plagioclase in any proportion from pure anorthite to pure albite. The composition of plagioclase can thus be written as $\text{Na}_{1-x}\text{Ca}_x\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_8$ where x ranges from 0 for pure albite to 1 for pure anorthite [see Table 2 below]. This solid solution series is known as the plagioclase series. The composition of a particular sample of plagioclase is customarily expressed as the mol% of anorthite in the sample. For example, plagioclase that is 40 mol% anorthite would be described as An40 plagioclase.”

Name	mole-% $\text{CaAl}_2\text{Si}_2\text{O}_8$ (%An) ^{1,2}	mole-% $\text{NaAlSi}_3\text{O}_8$ (%Ab) ^{1,2}
Anorthite	90 - 100	10 - 0
Bytownite	70 - 90	30 - 10
Labradorite	50 - 70	50 - 30
Andesine	30 - 50	70 - 50
Oligoclase	10 - 30	90 - 70
Albite	0 - 10	100 - 90

¹ The ratio of the two end members can also be expressed as the Calcium Molar Ratio of $[\text{Ca}/(\text{Ca} + \text{Na})]$, such as 0.7 to 0.9 (or 70%-90%) for bytownite.

² There are certain ranges of the Calcium Molar Ratio where plagioclase minerals form alternating intergrowths with different Ratios rather than one mineral with a single Ratio, affecting bulk rates. These intergrowth ranges are between Calcium Molar Ratios of 0.02 to 0.16, 0.43 to 0.58, and 0.67 to 0.90 (Gudbrandsson et al., 2014 and references therein), although other studies say these intergrowths are common over larger ranges of the Ratio.

A major weakness in past silicate-neutralization studies has been the usage of the average Calcium Molar Ratio for all plagioclase in a sample or the usage of the two endpoints of albite and anorthite (see Section 4 above and Section 7 below). Both these approaches cannot reliably provide the Fast-Neutralizing Silicate NP attributable to plagioclase due to nonlinear relationships, as shown in the next section.

Flow-through reactor studies of pure-plagioclase-mineral dissolution using powdered samples (75-150 um particle size) showed that steady state was reached only after 60 to 80 days at pH 3 and 25°C (Stillings and Brantley, 1995). This represents a minimum time for site-specific kinetic testing of plagioclase-bearing rock. At the same time, plagioclase-grain surface areas increased due to weathering and particle breakdown, by 1.5 times for albite and calcium-poor plagioclase minerals, and by 7 times for labradorite and bytownite. This increasing particle-surface area can lead to significant increases in Silicate Neutralization Rate through time.

Stillings and Brantley (1995) reported that the plagioclase dissolution rate increased linearly with the increasing Calcium Molar Ratio of the plagioclase from zero to 0.76 (authors' Figure 3). However, this contradicts earlier and later work showing that the dissolution rate increases exponentially and nonlinearly with increasing Calcium Molar Ratio (e.g., Casey et al., 1991; Palandri and Kharaka, 2004; Gudbrandsson et al., 2014), as shown in the next Section and in Figures 9 and 10 below.

7. A Recent Study of Important Fast-Neutralizing Silicate NP by Plagioclase Minerals

Although plagioclase minerals have been implicated in past full-scale case studies of Silicate NP, their calculated (total) Rates of Silicate Neutralization were sometimes significantly less than measured rates of neutralization (see Section 4 above). As a result, neutralization could not be reliably explained. This can be traced to two primary issues:

- (1) usage of the average Calcium Molar Ratio for plagioclase minerals, and
- (2) the particle-scale pH to which plagioclase minerals are exposed.

In turn, these two issues can be traced to:

- (1) the nonlinear relationship of Calcium Molar Ratio to Rate of Silicate Neutralization, meaning the proportionally smaller amounts of calcium-rich plagioclase are the most important and require separate identification, and
- (2) a near-neutral effluent pH (from the right side of Figure 1) is not indicative of the internal particle-scale pH to which the plagioclase is exposed (the left side of Figure 1), leading to Figures 2 and 3.

A recent study here illustrates these points.

At a currently inactive minesite in Canada, approximately 30 years of repeated geochemical static including acidic rinse pH and repeated kinetic testing have predicted ARD, but decades of full-scale monitoring fail to detect any full-scale ARD. On the other hand, recent kinetic tests using humidity cells containing approximately 1 kg, and on-site columns containing up to about 300 kg, with relatively high solid-phase sulphide levels ($> 1\%$ S) have released ARD around pH 3.4. In these same kinetic tests, lower-sulphur rock has relatively low rates of acid generation with effluent pH around 6.0 to 7.0. Some major rock units, such as diorite (sometimes appearing as gabbro) and mafic volcanic rock, contain substantial plagioclase comprising up to 50% and more of some samples. These conditions are similar to past studies discussed in Section 4 above.

Important recent ARD studies for this site include the following.

- On-site ML-ARD columns include fresh drillcore, as well as two columns containing ~300 kg of existing 13- to 26-year-old waste rock with one quickly releasing ARD and one releasing ~pH 6.0 to 7.0. More than a dozen laboratory-based kinetic tests of various scales are continuing. Subsamples from all kinetic tests were subjected to static testing like expanded U.S. EPA 600 acid-base accounting (ABA).
- The National Research Council of Canada (NRC) conducted innovative and state-of-the-art analyses of (1) sulphide-oxidation-by-oxygen (oxycon) testing and (2) mineralogy using x-ray diffraction (XRD), scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM/EDX), visual petrographics, and microscopic Raman spectroscopy. This included the updated 2021 RockJock x-ray-diffractogram library, the Raman Renishaw's Library backed up by visually assessed spectra developed for the Perseverance Rover on Mars (Shkolyyar et al., 2022), and the mineral-specific Calcium Molar Ratios using SEM/EDX.
- ABAs of many dozens of ML-ARD samples were carefully selected based on (1) sulphur geostatistics approximating lognormal distributions using tens of thousands of sulphur

analyses for drillcore (e.g., Figure 6), (2) dominant rock units, and (3) 3D spatial distributions along and among drillholes (e.g., Figure 7).

- The MDAG Silicate NP Model described in Section 5 above was applied to the results of this testwork.

An important part of the multi-faceted, integrated mineralogic work for this inactive site, using many methods by the National Research Council of Canada as explained above, included identification of the individual plagioclase minerals of Table 2. This produced the rock-specific mineralogy in Table 3. The plagioclase minerals were reactive because some plagioclase grains “were observed to be relatively altered (plagioclase pitting, forming clay, flakes and fines)”.

Based on mineral stoichiometry and total potential per-mole neutralization, the rock of Table 3 contained a Silicate NP (see the definition in Figure 4) of approximately 160 kg CaCO₃ equivalent/t. This was mostly due to the presence of relatively abundant oligoclase and andesine (Figure 8).

As explained above and as illustrated at the bottom of Figure 1, the Rate of Silicate Neutralization and the individual rate for each silicate mineral depend partly on particle-scale pH prior to full neutralization (as well as particle size and other conditions). Figure 9 shows that across the pH range, neutralization by bytownite at 4.32 wt-% represents most of the Rate of Silicate Neutralization for this rock, with labradorite second at about a half to a full order of magnitude lower rate. Figure 9 also shows that the neutralization rate by anorthite (calcium-rich plagioclase, Table 2) would exceed all others if it were present at even 1 wt-%. As Casey et al. (1991) explained:

“it is apparent that [plagioclase] dissolution rates vary nonlinearly with composition and that the rates for the Ca-rich minerals vary more with composition than Na-rich minerals.”

The neutralization rates of oligoclase and andesine in Figure 9 are relatively small and could not neutralize much of the acidity produced by this rock’s sulphide oxidation. Instead, the Fast-Neutralizing Silicate NP in this rock came primarily from bytownite and labradorite that could fully neutralize the measured oxycon rates of acid generation as explained below.

Interestingly, the rate for andesine in Figure 9 represents the weighted average of this rock’s Calcium Molar Ratio of 0.29 for plagioclase, but andesine’s rate underestimates the Fast-Neutralizing Silicate NP. This explains the underestimation of neutralization in some past studies (Section 4 above). Also, the sum of the rates from the two endpoints of anorthite and albite in Figure 9 would overestimate Fast-Neutralizing Silicate NP. Therefore, to estimate reliably Fast-Neutralizing Silicate NP and thus Total NP, the amount of each plagioclase mineral (Table 2) in a sample is needed, as done in Table 3.

It is important to note that Figure 9 is based on simplified conditions, as mentioned above in Section 5 and explained in detail in Palandri and Kharaka (2004). This includes unreliable rates at alkaline pH. Also, albite shows a different, increasing trend at alkaline pH in Figure 9, because it has been studied in more detail in the alkaline range than the other plagioclase minerals (e.g., Palandri and Kharaka, 2004, and Zhu et al., 2016). Furthermore, Gudbrandsson et al. (2014) studied pure plagioclase samples of 45-125 um particle size with Calcium Molar Ratios of 0.02 to 0.89 based on SEM/wavelength dispersive techniques. Gudbrandsson et al. reported that all plagioclase minerals have about the same dissolution rate in flow-through reactors at pH above 6.0 with these rates increasing as pH increases above 8, unlike Figure 9.

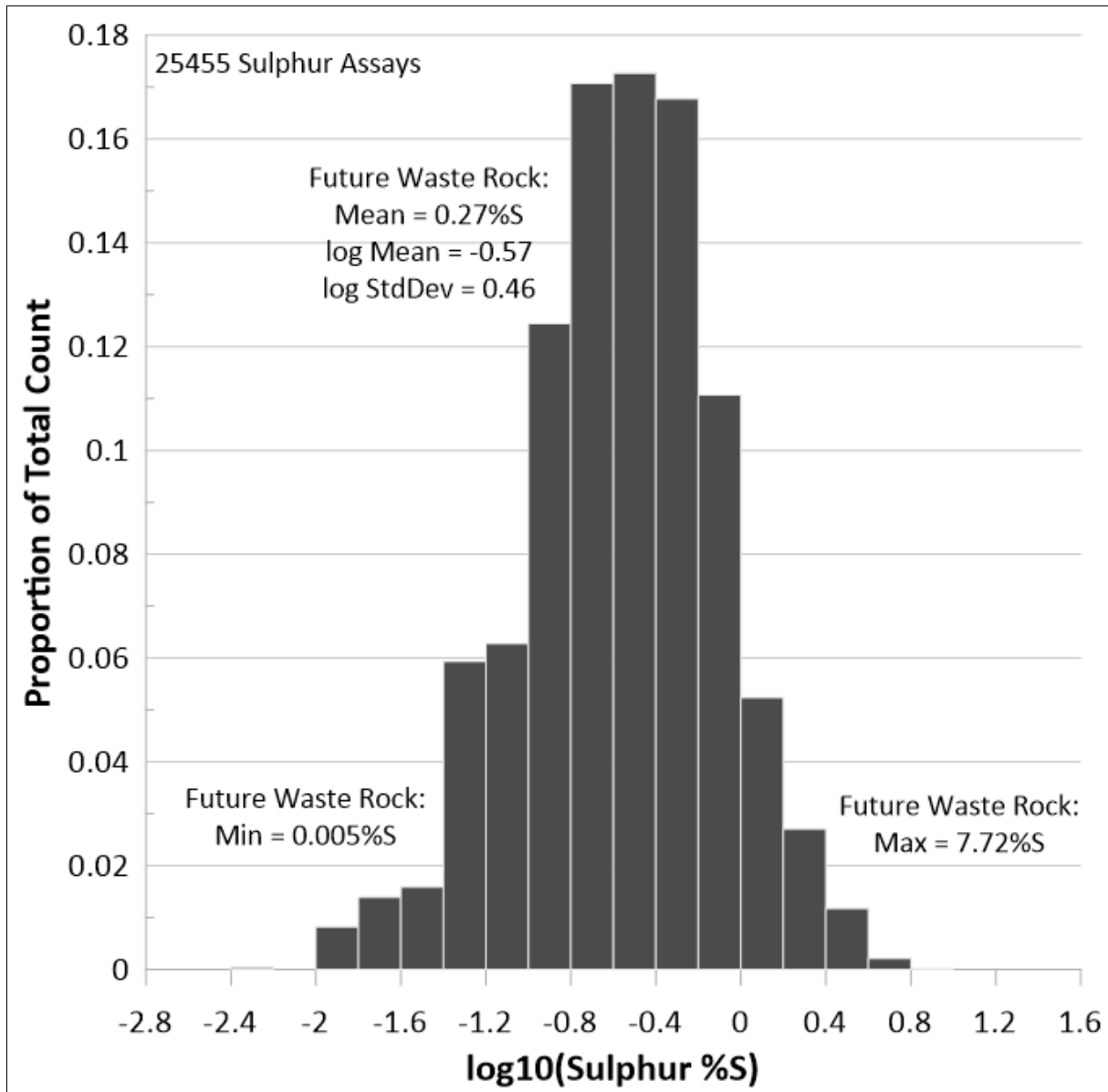


Figure 6. The generally lognormal distribution of 25,455 total-sulphur drillcore analyses in an ore zone.

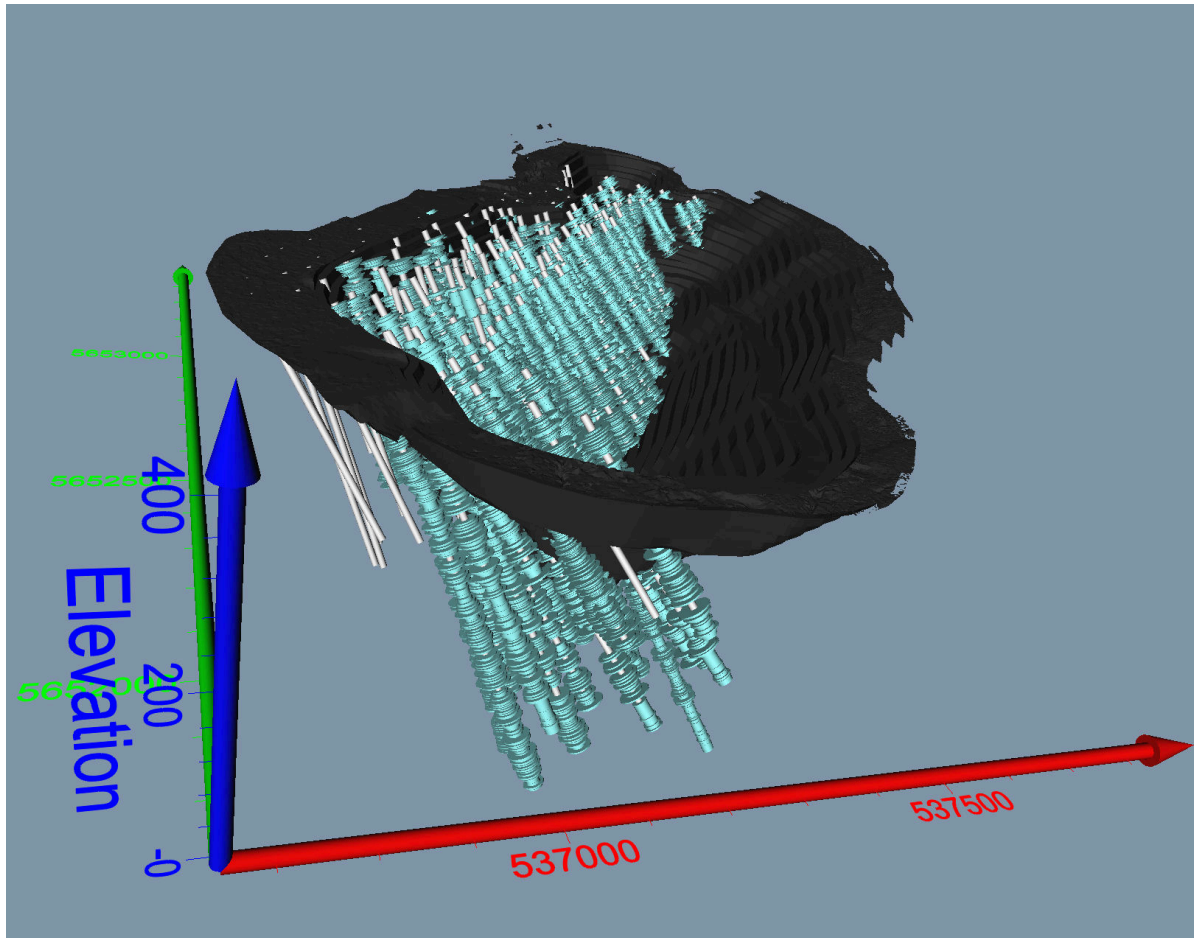


Figure 7. Three-dimensional distribution of total sulphur in an ore zone based on 32,600 drillcore intervals, with the radius of each blue disc indicating the sulphur level of that interval.

Table 3. Average mineralogy of site rock tested by National Research Council of Canada			
<u>Mineral Group</u>	<u>Weight-%</u>	<u>Mineral</u>	<u>Weight-%</u>
Plagioclase ¹	54.35	Bytownite (~80 mole-% calcium, ~20 mole-% sodium)	4.32
		Labradorite (~60 mole-% calcium, ~40 mole-% sodium)	3.35
		Andesine (~40 mole-% calcium, ~60 mole-% sodium)	11.69
		Oligoclase (~20 mole-% calcium, ~80 mole-% sodium)	25.50
		Albite (~5 mole-% calcium, ~95 mole-% sodium)	9.51
Quartz	26.56		
Mica	10.71	Muscovite	1.07
		Phlogopite (magesium-rich biotite)	1.39
		Biotite	8.26
Amphiboles	7.05	Tremolite	5.29
		Actinolite-tremolite	1.76
Pyrite	0.60 ²		
Titanite	0.28		
Calcite ³	0.48 ²		
Unidentified (sillimanite?)	0.44		
¹ The weighted average Calcium Molar Ratio for the plagioclase in this sample is approximately 29 mole-% calcium.			
² Based on the average total sulphur content of 0.49%S, this represents a Total Acid Potential of 15.3 kg CaCO ₃ equivalent/t			
³ The only significant source of carbon in this rock is carbonate occurring in the mineral calcite. Thus, the average 0.058% C was mathematically converted to 0.48% CaCO ₃ and a Carbon NP of 4.8 kg CaCO ₃ /t (or 2.4 kg/t if neutralization is only partial. However, this carbonate may be forming rather than dissolving as shown in the bottom of Figure 1 above.			

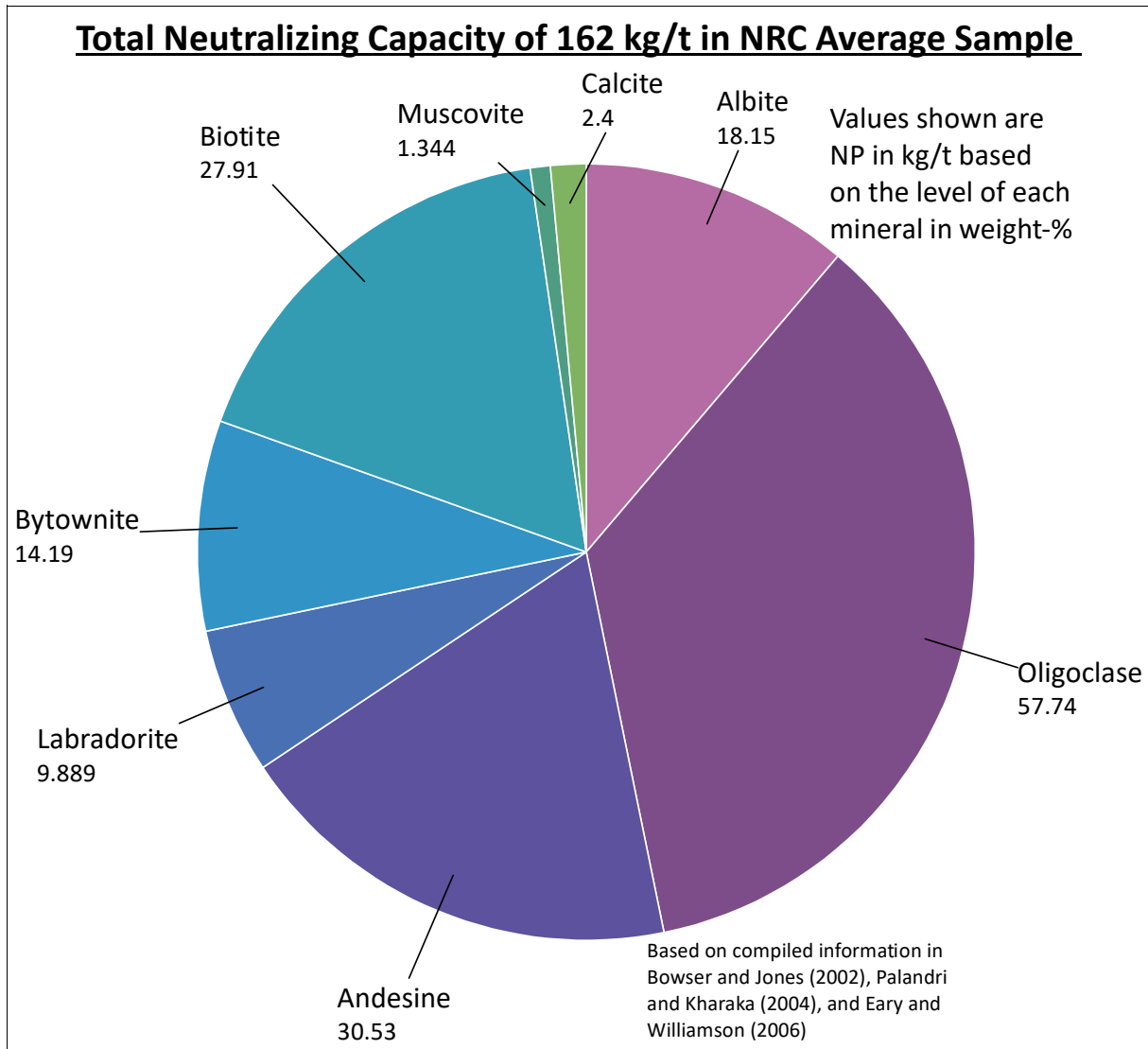


Figure 8. Calculated Total Neutralizing Capacity of 162 kg/t in the average rock sample tested by National Research Council of Canada, with oligoclase and andesine combined accounting for more than 88 kg/t.

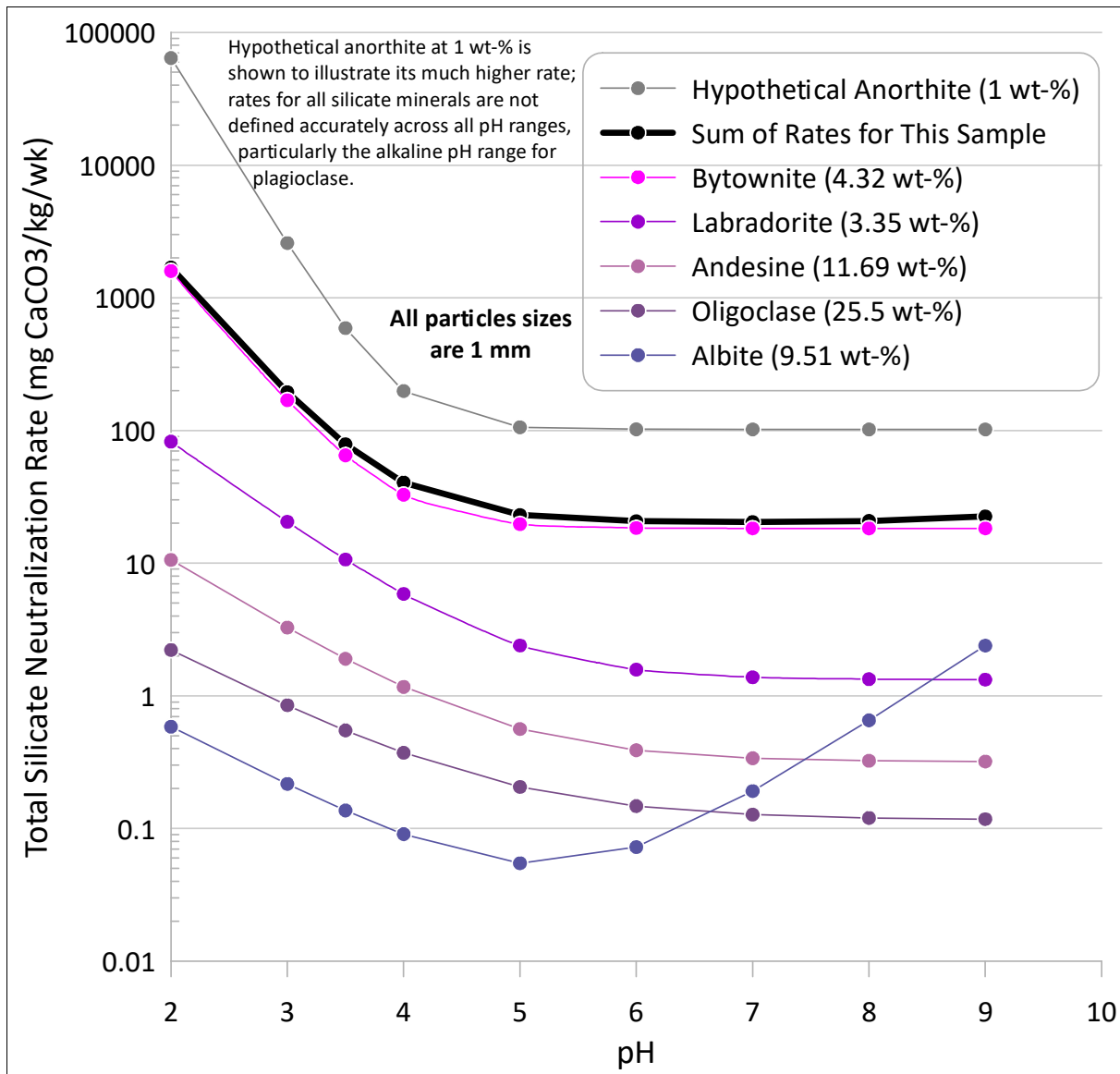


Figure 9. The pH-dependent neutralization rates for the plagioclase minerals in Table 3 at their specified weight percentages and particle size, and their sum as the Rate of Silicate Neutralization (the black heavy line) using the MDAG Silicate NP Model; anorthite was hypothetically added here only to show its much higher neutralization rate at 1 wt-%.

The National Research Council of Canada measured the rate of sulphide oxidation and acid generation in the rock of Table 3 using an oxygen-consumption (oxycon) technique in a sealed chamber, for particles nominally at 1 mm and 5 mm diameter. These two oxycon rates are plotted as horizontal dashed lines in Figure 10. They intersect their Silicate Neutralization Rates (with the 1 mm Rate already shown in Figure 9) both at around pH 3.4. This means the particle-scale pH around the plagioclase is likely around pH 3.4 (on the left side of Figure 1 where the acidity is being generated and added).

Not coincidentally, a 261-kg on-site column has been releasing ARD at around pH 3.4. Based on the comparison of aqueous sulphate to acidity, this column's effluents show that about half the initial acidity was already partially neutralized (acidity in mg/L = ~ 0.5 * sulphate in mg/L). Although no doubt well buffered around pH 3.4 (Morin, 2015), a non-buffering assumption would estimate the particle-scale pH at around 3.1 ($= 3.4 + \log_{10}(0.5)$). Thus, the particle-scale pH prior to any substantial neutralization is around 3.1 to 3.4, and likely around 3.4 due to buffering.

Therefore, simplified to pH 3.5, the combined neutralization rates of bytownite and labradorite account for about 96% of the Silicate Neutralization Rate (Figure 11). However, bytownite and labradorite combined represent only ~ 24 kg/t of the Silicate NP (Figure 8). Therefore, according to Figure 4, the Fast-Neutralizing Silicate NP in this rock was ~ 24 kg/t, and the Slow-Neutralizing Silicate NP was ~ 136 kg/t. With a Carbon NP of 4.8 kg/t, the Total NP was 29 kg/t.

Because the Total Acid Potential (TAP) is approximately 15 kg/t (Table 3), the Net Potential Ratios (NPR = NP/TAP) for this rock are above the silicate-neutralization criterion of 1.0. Based on Total NP, the NPR is 1.93 (29/15). Based only on Fast-Neutralizing Silicate NP if the Carbon NP is currently forming rather than dissolving (see the bottom of Figure 1), the short-term NPR is 1.60 (24/15), but would revert to 1.93 or higher if the Fast-Neutralizing Silicate NP were exhausted early and the accumulating Carbon NP began dissolving and neutralizing.

These observations lead to several complex observations and predictions based on various positive and negative feedback loops for silicate-mineral neutralization. For example:

- If the initial oxycon rate of sulphide oxidation and acid generation did not decrease by at least 95% of the current initial rates within weeks to months, as it did in long-term kinetic testing, then ARD could appear from this sample as bytownite was consumed.
- However, if this later ARD resulted in a pH below the current particle-scale of \sim pH 3.4, then the Silicate Neutralization Rate would increase (Figures 9 and 10). For example, if pH fell to 3.0 but at a lower rate of acid generation after all bytownite was consumed, then the rate of neutralization from labradorite alone would accelerate sufficiently to neutralize overall pH above pH 6.
- At slower rates of acid generation such as from coarser particles, additional silicate minerals can contribute significant neutralization, like andesine, which also means that there would then be additional Fast-Reacting Silicate NP in this rock above the 24 kg/t from bytownite and labradorite.

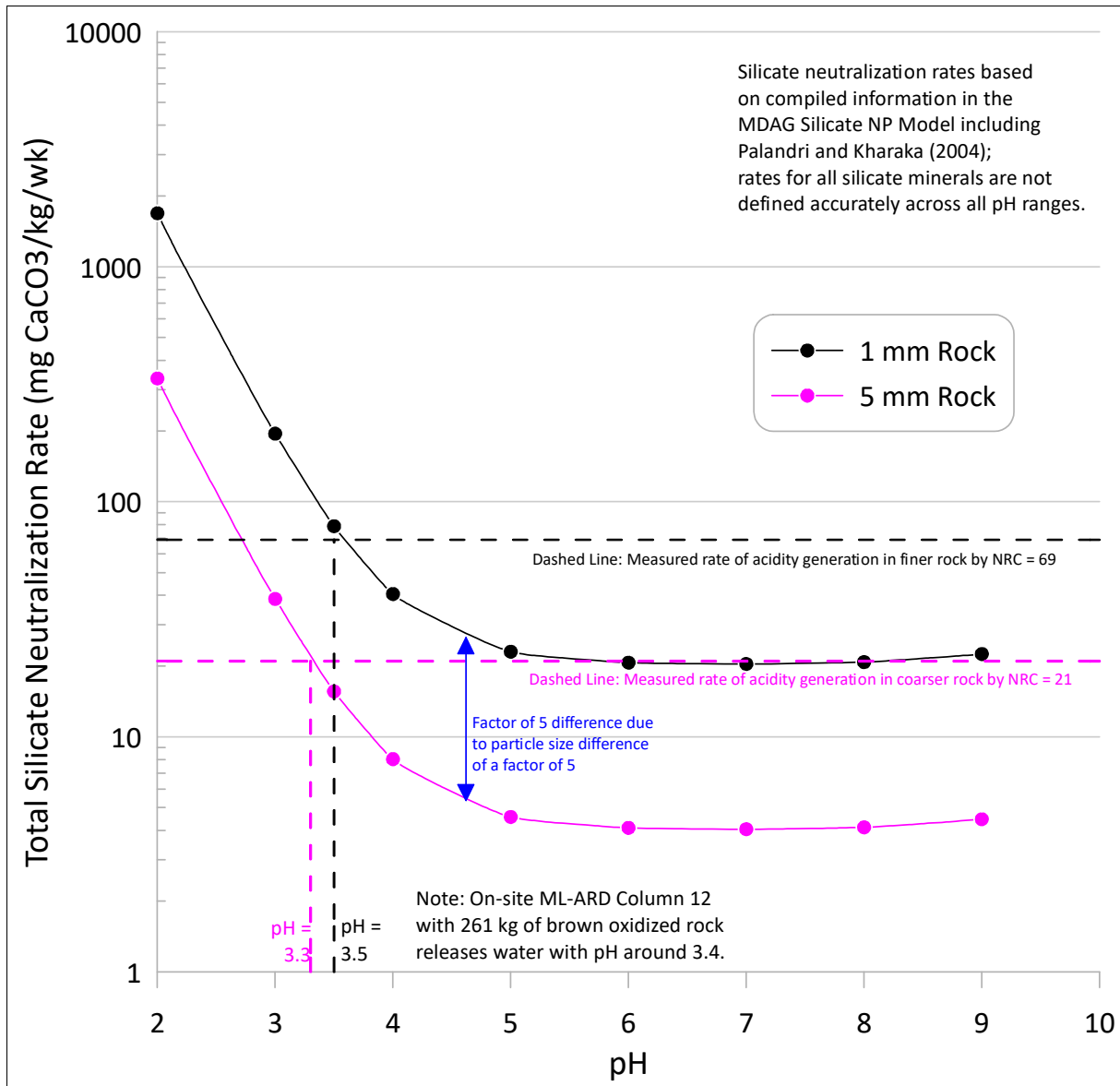


Figure 10. The pH-dependent (total) Silicate Neutralization Rates for two particle sizes (solid curved lines) and measured particle-size-dependent rates of acidity generation by the National Research Council of Canada (dashed horizontal lines), showing that ARD is produced internally around pH 3.4, consistent with on-site ML-ARD containing 261 kg of ARD-releasing rock.

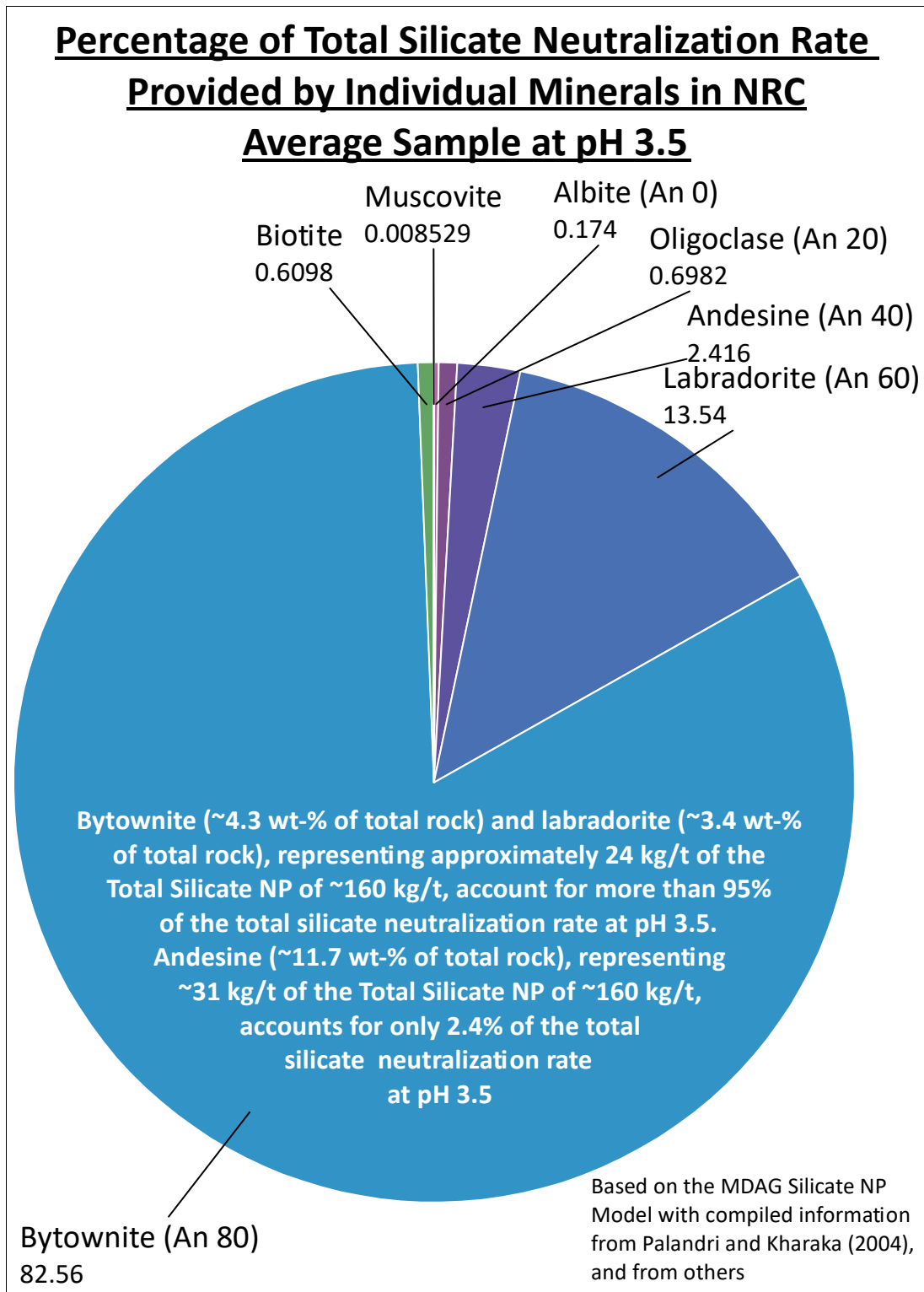


Figure 11. The percentage of the total Silicate Neutralization Rate at pH 3.5 accounted for by each relevant mineral in the rock sample examined by the National Research Council of Canada.

- At some faster rates of acid generation, neutralization by bytownite and others would no longer be able to “keep up” and ARD would appear, unless pH around mineral grains falls below 3.4 to cause a higher rate of Silicate Neutralization Rate from the remaining silicate minerals (Figures 9 and 10).

Although not explained here in detail in this MDAG Case Study, the amount of Fast-Neutralizing Silicate NP related to the calcium-rich plagioclase minerals in this rock can be estimated from only four-acid-digestion ICP-MS analyses. This requires (1) the measured ICP-MS solid-phase concentrations of total calcium and (2) the sample’s solid-phase ICP-MS Calcium Molar Ratio based on measured $[\text{calcium} / (\text{calcium} + \text{sodium})]$.

8. Discussion of Neutralization Potentials

As explained in Section 1 of this MDAG Case Study, solid-phase NP is typically measured by the standardized U.S. EPA 600 “Sobek” Method or by one of the many unstandardized “Modified” Methods (Price, 2009) that some laboratories have altered without informing clients. In all cases, these are only analytical values of a selected procedure and do not represent robust NP values across all scales and all conditions at a minesite (Morin and Hutt, 1997a, 1997b, 2001, 2008, and 2009; Morin, 2009).

Notably, many authors incorrectly state the standardized Sobek NP overestimates the NP of samples (e.g., Lawrence and Wang, 1996; Puura and Neretnieks, 2000) and that the many unstandardized Modified Methods produce lower NP values that are more realistic. These misconceptions were debunked decades ago (e.g., Lapakko, 1993 and 1994; Lapakko et al., 1995). Reliable NP analyses show that Modified NP values can just as easily be higher than Sobek NP values, depending on the mineralogy.

In any case, Sobek NP, just like the many modified Modified NPs, can overestimate or underestimate Effective NP (e.g., Morin and Hutt, 2008, on Unavailable NP) depending on sample mineralogy. This natural variability and uncertainty is ignored in most ARD studies which simply use measured NP (by whatever method) as applicable. In the recent study of Section 7 above, Sobek NP substantially underestimates Effective Total NP in most samples (Figure 12), contradicting common statements, while still showing some samples containing typical Unavailable NP. Under the false belief that the many modified Modified NP values are always less than Sobek NP, then their lower values would render them even worse than Sobek NP in Figure 12.

In Figure 12, the vertical alignment of many datapoints represents a maximum “detection limit”. This is due to the fizz rating, also used by Modified NP methods and thus subject to the same anomaly, detecting primarily the relatively minor Carbon NP. As a result, these existing analytical NP methods are insufficient to capture the additional Fast-Neutralizing Silicate NP when it is significant.

Perhaps a “rapid” method could be developed for estimating Fast-Neutralizing Silicate NP. For example, titrations of samples with acid may detect more of the Fast-Neutralizing Silicate NP in a rock sample, but only if:

- the titration steps last for at least 60 to 80 days each (e.g., Stillings and Brantley, 1995) which is rarely the case, and
- the stagnant “batch” results are converted to dynamic flowpath assessments like Figures 2 and 3.

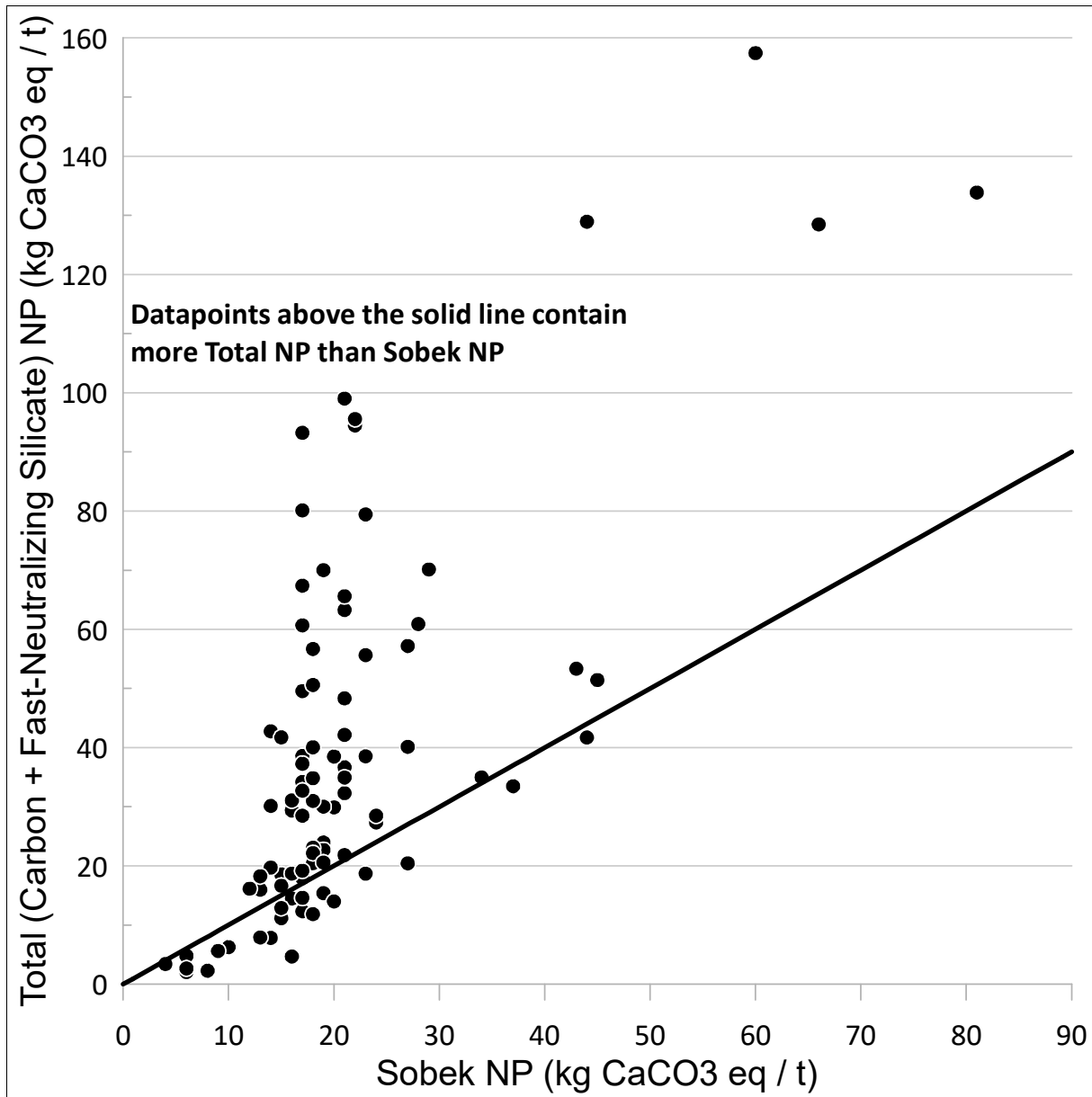


Figure 12. Comparison of Sobek NP and Total NP, showing that Sobek NP does not underestimate Effective Total NP, as often incorrectly rumoured.

9. Conclusion

This MDAG Case Study discussed silicate-mineral neutralization within the framework of water and ARD migrating along flowpaths in multi-mineral minesite components (Figures 1, 2, and 3). Silicate neutralization and its related concept of solid-phase Silicate Neutralization Potential (NP) are impressively complex and linked with various positive and negative feedback loops when suites of minerals are present.

By simplifying silicate neutralization of ARD into Fast-Neutralizing Silicate NP and Slow-Neutralizing Silicate NP (Figure 4), progress is made here on estimating Total NP which can fully neutralize above ~pH 6. Total NP is the combination of Fast-Neutralizing Silicate NP and inorganic-carbonate Carbon NP. Carbon NP can typically form rather than dissolve as silicate neutralization proceeds, meaning that Total NP of a sample can change with time. Furthermore, Fast-Neutralizing Silicate NP, and thus Total NP, of a multi-mineral sample can also change dynamically and nonlinearly with conditions such as rates of sulphide oxidation and acid generation, particle size, local pH and aqueous chemistry, percentages of minerals, scale, etc.

Past studies showed that some minesites do not have ARD on the full scale over decades, and yet ARD arises in smaller-scale testwork in less than a year. The series of plagioclase minerals is often implicated in the additional “undetected” silicate-mineral NP, likely because these minerals form the most abundant group in the earth's crust. However, the plagioclase minerals are often overly simplified in ARD studies to an average molar ratio of calcium and sodium, or to the two endpoint minerals. This MDAG Case Study shows that these oversimplifications can lead to substantial underestimation or overestimation of Fast-Neutralizing Silicate NP.

For more accurate estimates of Fast-Neutralizing Silicate NP in multi-mineral rock and tailings, the amounts of the individual plagioclase minerals are needed, particularly the calcium-rich minerals that have orders-of-magnitude faster neutralization rates. A relatively small amount of calcium-rich plagioclase can provide tens to hundreds times more Fast-Neutralizing Silicate NP than a much larger amount of sodium-rich plagioclase.

The spreadsheet-based MDAG Silicate NP Model (Section 5), based on published information particularly by the U.S. Geological Survey, was updated and calculates the following.

1. (Total) Silicate NP in kg CaCO₃ equivalent/tonne based on the sum of each silicate mineral's abundance in a multi-mineral sample, the stoichiometry of each silicate mineral, and its total per-mole capacity to neutralize.
2. The (total) Rate of Silicate Neutralization in mg CaCO₃ equivalent/kg/week which is the sum of the individual neutralization rates from each silicate mineral in a sample based on each mineral's abundance, particle size, and particle-scale pH.
3. Identification of the silicate minerals in a multi-mineral sample accounting for most of its Rate of Silicate Neutralization to calculate Fast-Neutralizing Silicate NP in kg CaCO₃ equivalent/tonne.

A new study in Section 7 illustrates the integrated and multi-faceted studies needed to identify and quantify Silicate NP and Fast-Neutralizing Silicate NP, especially when several plagioclase minerals are involved. Section 8 explains why existing NP methods are not suitable for characterization of Fast-Neutralizing Silicate NP, and why there may be no “rapid” technique to estimate it.

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