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## MDAG.com Internet Case Study 81

# The Complex Nexus of Sulphide Oxidation, Silicate-Mineral Dissolution, and Passive CO<sub>2</sub> Capture

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### Table of Contents

1. Introduction . . . . .	2
2. Anomalous and Unexpected Full-Scale Geochemical Conditions at the Small Percentage of Minesites Found at the Nexus of the Three Geochemical Processes . . . . .	5
3. References . . . . .	11

## 1. Introduction

This MDAG Case Study briefly discusses three geochemical processes (Figures 1 and 2) relevant to multi-mineral mined rock, tailings, and mine walls, namely:

- 1) sulphide-mineral oxidation and associated generation of acidity;
- 2) dissolution of silicate minerals, particularly plagioclase minerals that comprise about 40% of the earth's crust; and
- 3) passive capture of gaseous carbon dioxide (CO<sub>2</sub>) as carbonate minerals.

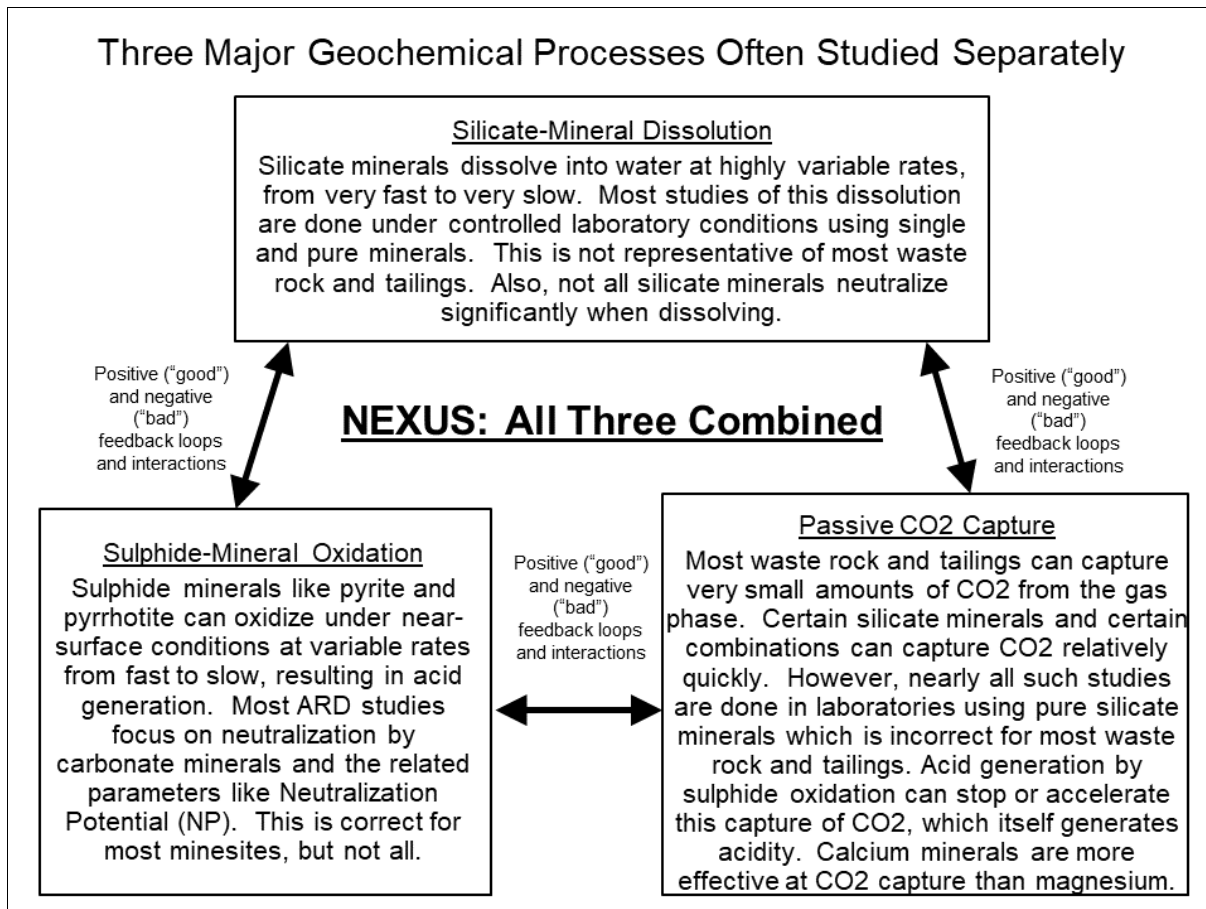
This is not a literature review for any one of these processes because of the abundant literature available on all three. Passive capture of CO<sub>2</sub> has received strong attention only recently due to increased concerns over atmospheric levels of CO<sub>2</sub>, and thus relatively less literature is published on it compared with the other two.

Interestingly, each of these three processes has been mostly studied in isolation from the other two. Each is often limited to one or a few minerals and in many cases limited to relatively short-term laboratory-scale testing and evaluation under stable conditions (summarized in Figures 1 and 2). This is likely a matter of convenience and relative simplicity for human understanding.

On the other hand, multi-mineral full-scale mine wastes of waste rock, tailings, and mine walls, which are left at minesites in perpetuity, typically contain many minerals and are “open systems” to varying environmental factors. The increased scale, variable conditions, and very-long-term exposure and weathering are ideal conditions for the emergence of trends and behaviours not seen under short, constant, small-scale conditions for each process (e.g., Morin, 2019 and references therein; Wikipedia, 2024).

Therefore, this MDAG Case Study 81 is an overview of the nexus of the three geochemical processes. At the nexus, their positive (synergistic) and negative (antagonistic) feedback loops can create emergent conditions “unexpected” and inconsistent with one or more of the otherwise human-isolated three processes. These feedback loops, on the full scale under ambient and open environmental conditions, can “lock together” as well-buffered and potentially self-regulating systems in relatively rare cases.

This MDAG Case Study 81 builds on the preceding one of Case Study 80 and its dozens of references (Morin, 2024). Case Study 80 discussed and illustrated in detail the complex issue of aqueous neutralization of acid rock drainage (ARD) by plagioclase-mineral neutralization that included CO<sub>2</sub> capture by calcite formation. These are the three boxes shown in Figure 1.



**Figure 1. Three major geochemical processes listed in boxes that, in isolation, are relatively simple and obvious, but are not accurate and reliable for the small minority of full-scale minesites where all three processes are active and strong. Only at the nexus of all three do unexpected and apparently nonsensical conditions emerge due to positive and negative feedback loops among all three processes.**

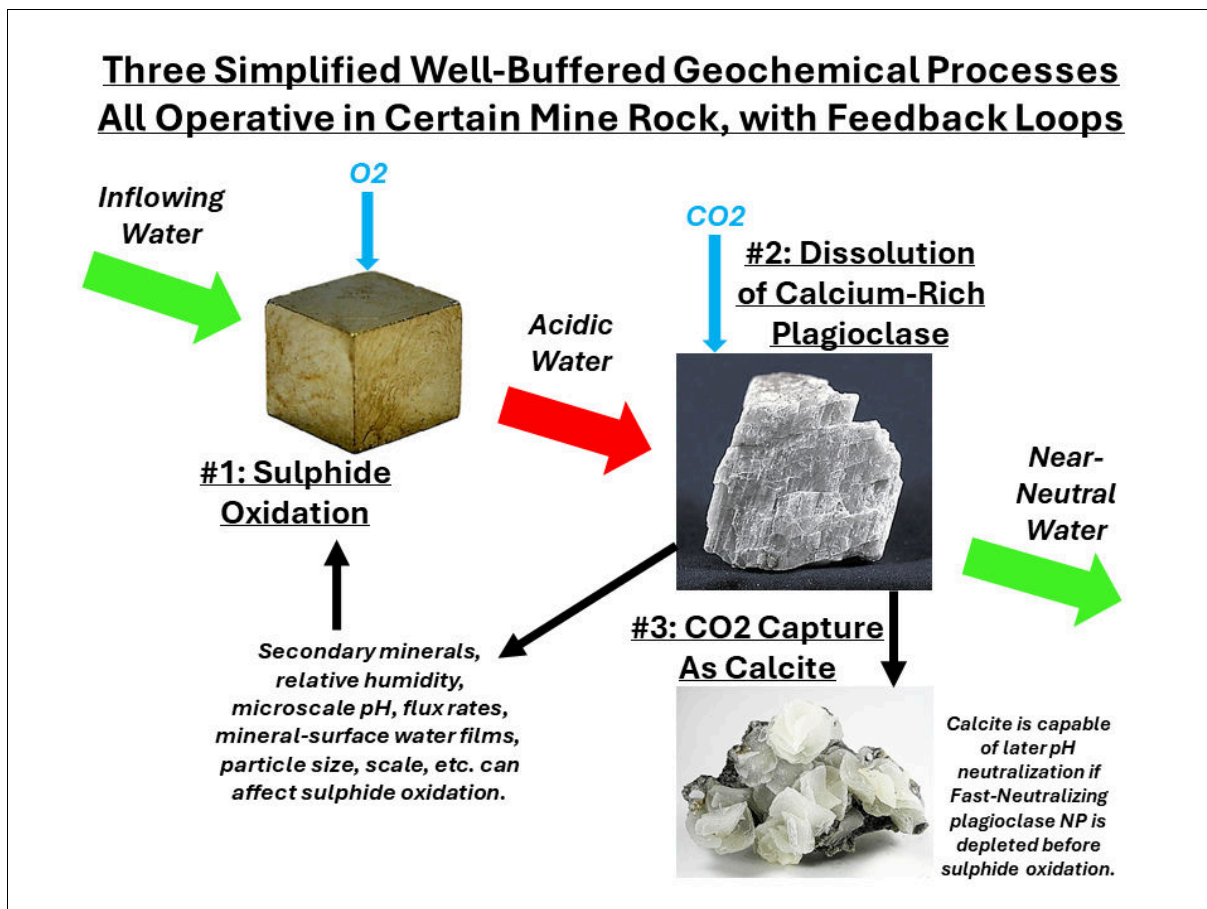


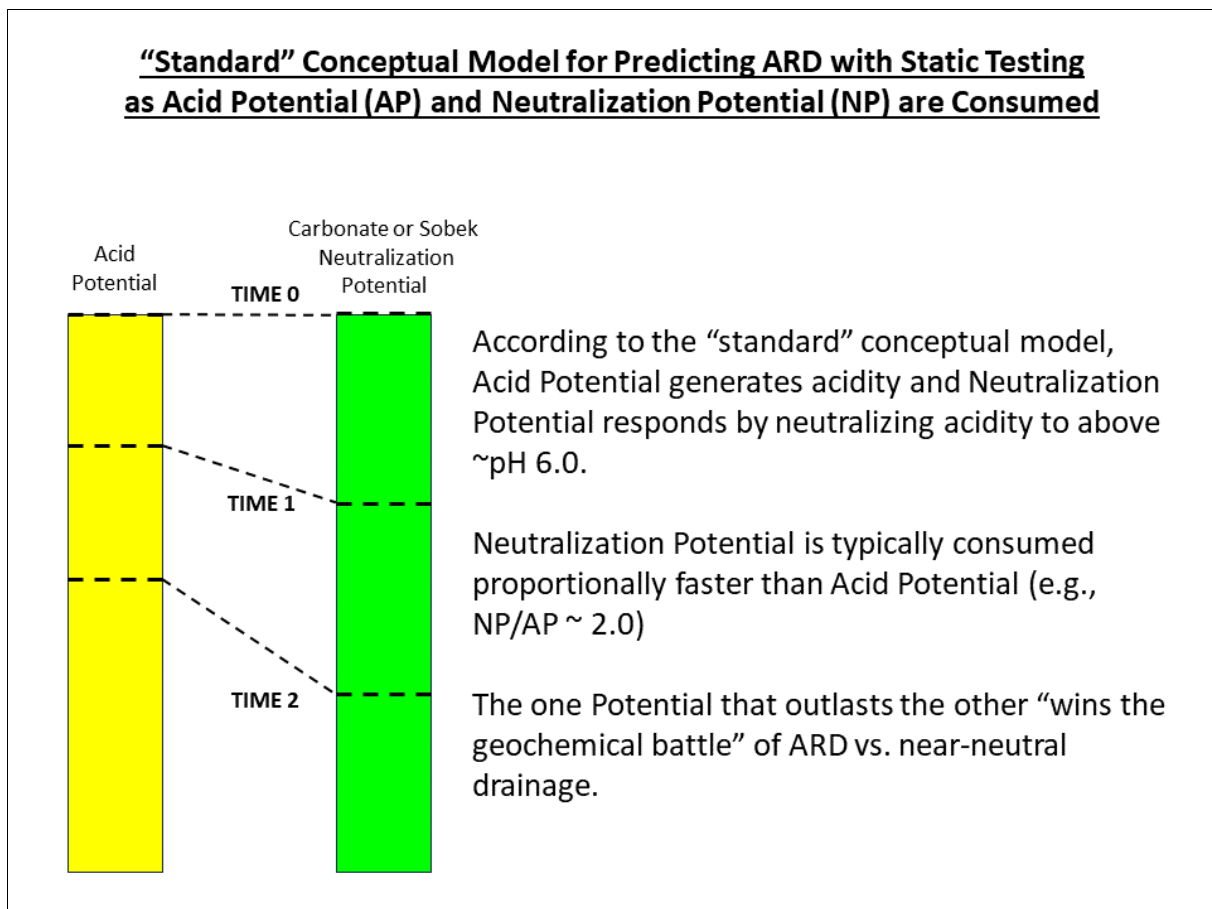
Figure 2. An alternative version of Figure 1 with fewer details but with more realistic “flowpaths” shown among the geochemical processes.

## 2. Anomalous and Unexpected Full-Scale Geochemical Conditions at the Small Percentage of Minesites Found at the Nexus of the Three Geochemical Processes

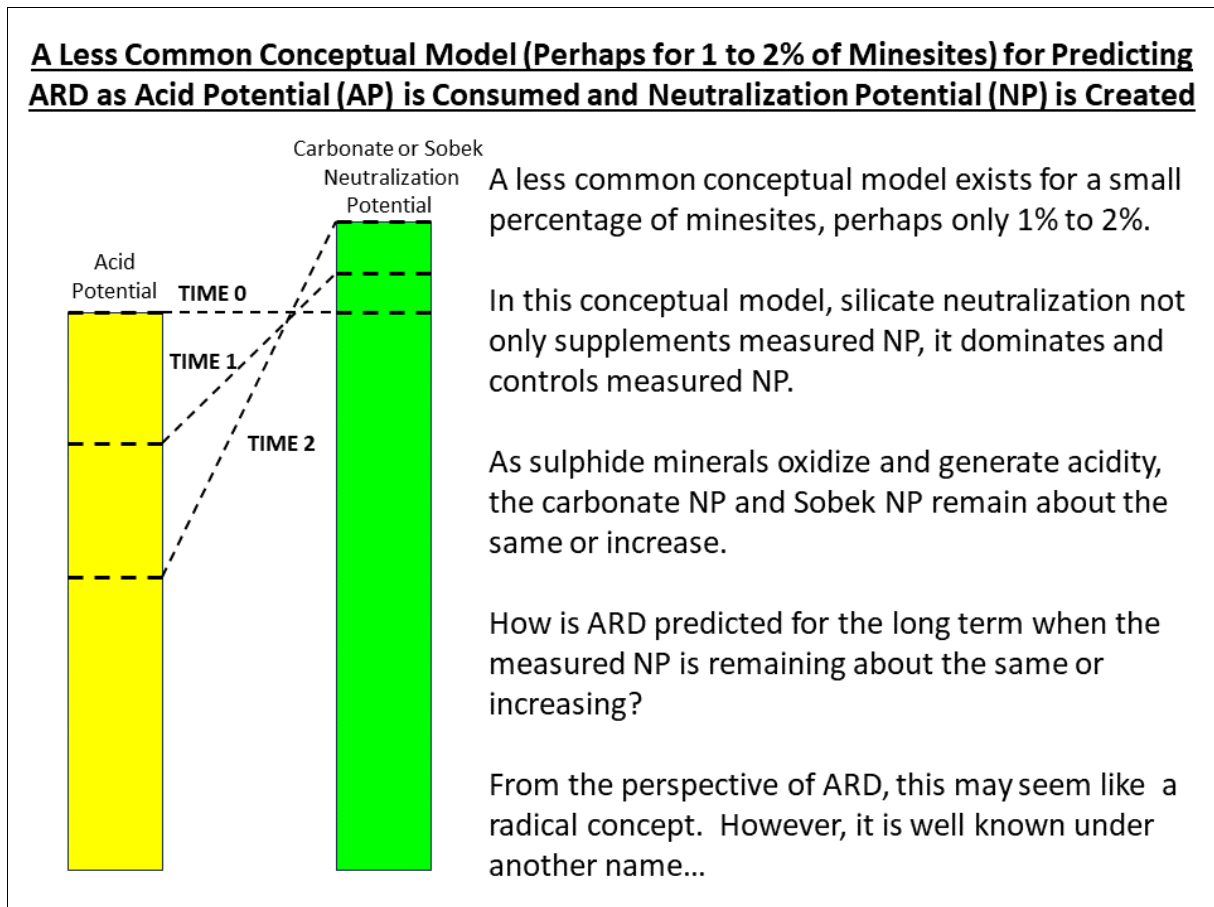
Although not readily apparent in Figures 1 and 2, the nexus of all three geochemical processes, at the small percentage of minesites where all three are significant at the same time, result in unusual, unexpected, and not easily explained full-scale conditions and observations. These include the following.

- Acid-base accounting (ABA) results indicate acid rock drainage (ARD) should be widespread, but no full-scale ARD is detected at sites after decades.
- Small-scale kinetic tests produce ARD within a year or two, although no full-scale ARD is detected on site after decades.
- Calcite and carbonate minerals represent a minor portion of Total Neutralization Potentials (NP), with ongoing weathering of rock apparently producing or maintaining small amounts of carbonate detected in ABA.
- Laboratory-measured NP such as by the U.S. EPA 600 (Sobek) method is relatively the same among variously aged samples and does not change significantly after years or decades of weathering.
- Aqueous alkalinity can be accounted for by ingassing of atmospheric carbon dioxide (atmospheric CO<sub>2</sub> capture).
- Minerals like biotite, magnetite, and epidote theoretically contribute substantially to Total NP, but apparently are usually not reacting sufficiently fast to provide much neutralization.
- Plagioclase minerals apparently provide much of the silicate neutralization. Hundreds of silicate minerals reportedly comprise about 90% of the Earth's crust. The subset of plagioclase minerals forms nearly 40% of the crust and thus is the most abundant mineral group. Calcium released from plagioclase is more effective at CO<sub>2</sub> capture and carbonate-mineral formation than non-plagioclase magnesium minerals.
- Acid-generating sulphide minerals are primarily pyrite and pyrrhotite with some chalcopyrite and molybdenite, and their levels range from "trace" amounts (<~0.1%S) up to ~5%S.
- Rates of sulphide oxidation and acid generation at these sites are relatively low based on (1) the aqueous sulphate concentrations and (2) comparisons to approximately 700 humidity cells at 90 sites in the International Kinetic Database.

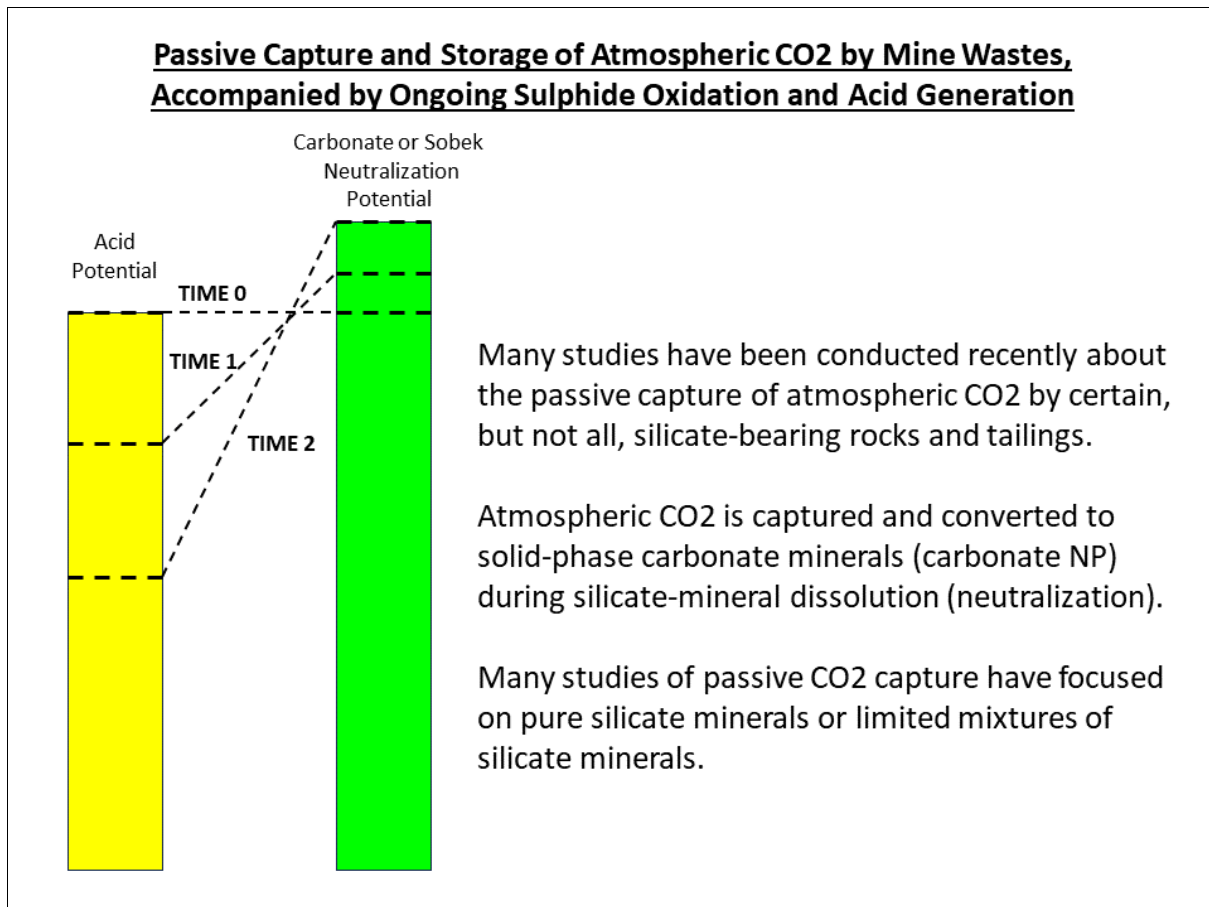
More simply, the "standard" model for predicting ARD (Figure 3) is overturned in rare cases and replaced by a model that is seemingly nonsensical or impossible (Figures 4 to 6). For example, sulphide oxidation and acid generation can assist or hinder the formation of calcite (Figure 6). This is nonsensical for most minesites not at the nexus of all three processes (Figure 1).



**Figure 3. The standard model for predicting ARD within the sulphide-mineral oxidation “box” in Figure 1.**

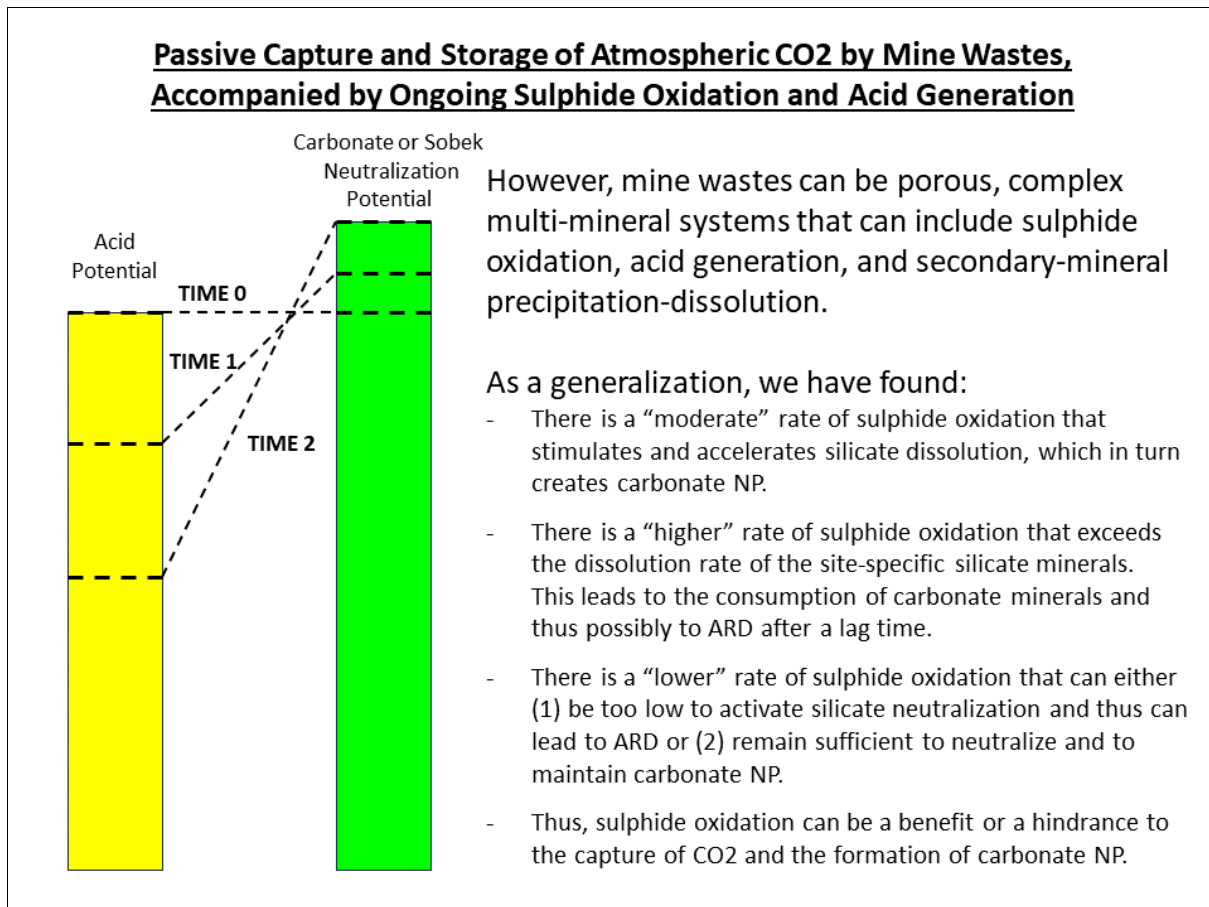


**Figure 4. Part 1: The building of the less common prediction model at the nexus of sulphide-oxidation, silicate-mineral dissolution, and passive CO2 capture shown in Figure 1.**



**Figure 5. Part 2: The building of the less common prediction model at the nexus of sulphide-oxidation, silicate-mineral dissolution, and passive CO<sub>2</sub> capture shown in Figure 1.**





**Figure 6 Part 3: The building of the less common prediction model at the nexus of sulphide-oxidation, silicate-mineral dissolution, and passive CO<sub>2</sub> capture shown in Figure 1.**

Some interesting scenarios arise at the nexus of sulphide oxidation, silicate-mineral dissolution, and passive CO<sub>2</sub> capture. Here are some examples.

- If the rate of sulphide oxidation and acid generation is initially higher than silicate neutralization and then decreases significantly, ARD can be released initially and then “disappear” when silicate neutralization eventually matches the decreasing rate of acid generation.
- There are large, pH-dependent, nonlinear, order-of-magnitude differences in neutralizing rates among individual plagioclase minerals (Morin, 2024, and references therein). Thus, if the rate of acid generation causes particle-scale pH to decrease, the rate of silicate neutralization from individual minerals will increase. As a result, some Slow-Neutralizing plagioclase minerals can become important Fast-Neutralizing plagioclase minerals as particle-scale pH decreases.
- At slower rates of acid generation such as from coarser particles, additional silicate minerals may contribute significant neutralization. This depends on the respective particle sizes.
- The passive capture of CO<sub>2</sub> plus the aqueous calcium dissolved from calcium-bearing plagioclase minerals lead to the formation of calcite. Calcite is less soluble per mole of carbon than dolomite and magnesite that require and form from magnesium-bearing silicate minerals. As a result, neutralizing calcium-bearing plagioclase leads to relatively more CO<sub>2</sub> capture and forms relatively more carbonate mineral than magnesium-bearing silicate minerals.
- The formation of calcite (or some other carbonate minerals) in near-neutral waters is acid generating due to the release of H<sup>+</sup> as CO<sub>3</sub><sup>2-</sup> is being removed to the solid phase. Thus, at the nexus of the three processes, acidity is generated by:
  - 1) sulphide oxidation,
  - 2) CO<sub>2</sub> capture as pH is neutralized above pH ~6.0 by silicate-mineral dissolution, and
  - 3) carbonate-mineral formation.On the other hand, acidity is consumed by:
  - 1) silicate-mineral neutralization and
  - 2) as needed, carbonate-mineral neutralization.
- These interacting reactions and processes at the nexus of the three geochemical processes have been found to be geochemically stable, well buffered, difficult to destabilize, and apparently self-regulating. The well-buffered pH is typically in the range of pH ~6.5-7.0 at the nexus for all three processes, in contrast to pH ~7.5-8.3 for calcite neutralization and pH ~9-11 for strong silicate-mineral neutralization.

### 3. References

Morin, K.A. 2024. Silicate Neutralization Potential Focussing on Plagioclase, and the MDAG Silicate NP Model. MDAG Internet Case Study #80, [www.mdag.com/case\\_studies.html](http://www.mdag.com/case_studies.html)

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