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Siderite Correction Can Substantially and Erroneously Overestimate Effective Neutralization Potential and Underestimate ARD Risk

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Abstract

A general geochemical concept is that the presence of siderite (ferrous-iron carbonate or FeCO_3) can lead to an overestimation of Neutralization Potential (NP) as part of acid-base accounting (ABA) of a solid-phase sample. This is because siderite theoretically provides no net neutralization, but does so in an NP analysis because the dissolved ferrous iron does not fully oxidize. However, there are major documented exceptions to this general concept, especially inside of full-scale minesite components. Thus, siderite may or may not provide some neutralization depending on several site-specific conditions discussed in this case study.

Nevertheless, a “siderite correction” was devised by Skousen et al. (1997) to “correct” and lower Sobek NP analyses. However, this siderite correction is based on:

- flawed chemical equations, and
- the relatively large addition of hydrogen peroxide to the NP solution that can lead to higher, lower, or similar NP values relative to uncorrected values, for many reasons related to hydrogen peroxide itself and to other redox couples.

This is suggested by some ABA datasets where siderite-corrected NP is substantially higher, not lower, than non-siderite-corrected NP.

Skousen et al. (1997) presented five chemical equations to describe the sequential titrations in the NP procedure with siderite to ~pH 2 and back to ~pH 7. However, these equations do not accurately represent acidification and neutralization because of these following flawed assumptions.

- Irreversible chemical reactions always proceed to completion, like ferrous-iron oxidation, despite the obvious reversibility and equilibrium.
- A titration from acidic to neutral conditions (~pH 7) does not generate any bicarbonate, and CO_2 gas remains the dominant carbon species at neutral pH.
- Aqueous ferrous iron does not substantially oxidize to ferric iron within hours when exposed to the open atmosphere, which is not always correct.

Without any technical justification or detail, Skousen et al. (1997) then selected 5 mL of 30% H_2O_2 to be added to the 100 mL of NP solution that had leached 2 g of solids. Apparently, the unexplained rationale was that ferrous iron had to be fully oxidized and hydrogen peroxide could do this. This 5 mL addition overlooked known complexities and problems with hydrogen peroxide, like:

- Hydrogen peroxide also reduces ferric iron to ferrous iron as part of a catalytic reaction.
- Hydrogen peroxide does not necessarily decompose directly to oxygen in the presence of aqueous iron and some other elements, but instead can decompose to reactive oxygen-radical species.
- Chemical stabilizers like pH-buffering phosphoric acid added to the hydrogen peroxide lead to the erroneous “creation” of additional NP by this siderite correction.
- This approach by Skousen et al. (1997) forced hydrogen peroxide to be a reactant rather than a catalyst, with the 5 mL addition typically leading to orders of magnitude more hydrogen peroxide than can be consumed by a sample containing siderite.

Unfortunately for this method by Skousen et al. (1997), the large excess addition of hydrogen peroxide means that “siderite correction” also unavoidably includes “reduced-manganese and rhodocrosite correction”, “reduced-selenium (arsenic, antimony, etc.) correction”, “reduced-nitrogen correction”, “organic-carbon correction”, etc. As a result, these other unavoidably included corrections built into the siderite correction:

- may not be needed or warranted depending on site-specific conditions;
- can erroneously “create” NP in the procedure; and
- can erroneously “lower” NP in the procedure beyond that suggested by siderite.

Again, these many included “corrections” in the “siderite correction” can raise or lower the final NP value in unexpected ways if the redox couples and their leaching are not understood in detail. This detailed element-specific redox understanding for each sample is rare.

Therefore, the NP value for siderite correction may have little correlation with any level of siderite in some samples. This ambiguity is one major consequence of using hydrogen peroxide which is a general oxidant, reductant, catalyst, and reactant. In light of this, ABA discrepancies are not surprising where siderite-corrected NP values are substantially higher than non-siderite corrected NP values.

Finally, the detailed assessment of this “siderite correction”, and of the resulting reactive and effective NP, by Skousen et al. (1997) were based only on 13 kinetically-tested samples of “overburden” from the U.S. States of Pennsylvania and West Virginia, kinetically tested for only nine weeks using the “soxhlet” method. This testing includes flawed assumptions and information, such as any kinetic sample not acidic after only nine weeks of kinetic testing will never become acidic.

It is amazing that such limited and flawed work, on limited samples, of limited rock units, from a limited area of the world, is currently used worldwide as a reliable generic approach for hydrogen-peroxide-based siderite correction in NP analyses. This siderite correction with hydrogen peroxide is not reliable as a general correction. It is not surprising that this siderite correction can return unreliable NP values much higher than non-corrected NP values.

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1. Introduction

Siderite (FeCO_3) is a ferrous-iron carbonate mineral that can provide significant neutralization of acidity even in trace amounts (e.g., Morin and Cherry, 1986 and 1988; Morin et al., 1988). In apparent contradiction, other references say siderite provides no net neutralization of acidity and thus should not be considered effective Neutralization Potential (e.g., Skousen et al., 1997).

Skousen et al. (1997) created a procedure to adjust measurements of Neutralization Potentials (NP) from the standard Sobek/EPA-600 procedure (Sobek et al., 1978). The intent of this adjustment was to ensure that the presence of siderite in a sample would not significantly raise and overestimate the resulting NP value (the “siderite correction”). Alarming, there are datasets that show the siderite correction based on Skousen et al. indeed raises the NP value far above the uncorrected Sobek values even when siderite is not detectable (e.g., Figure 1-1).

This should be a major concern that an analytical procedure, designed only to reduce NP values or not affect them, instead substantially raises them. What is wrong? The remaining chapters below show that there are many things wrong with this siderite correction and with its overly simplistic view of the aqueous-solid carbonate system.

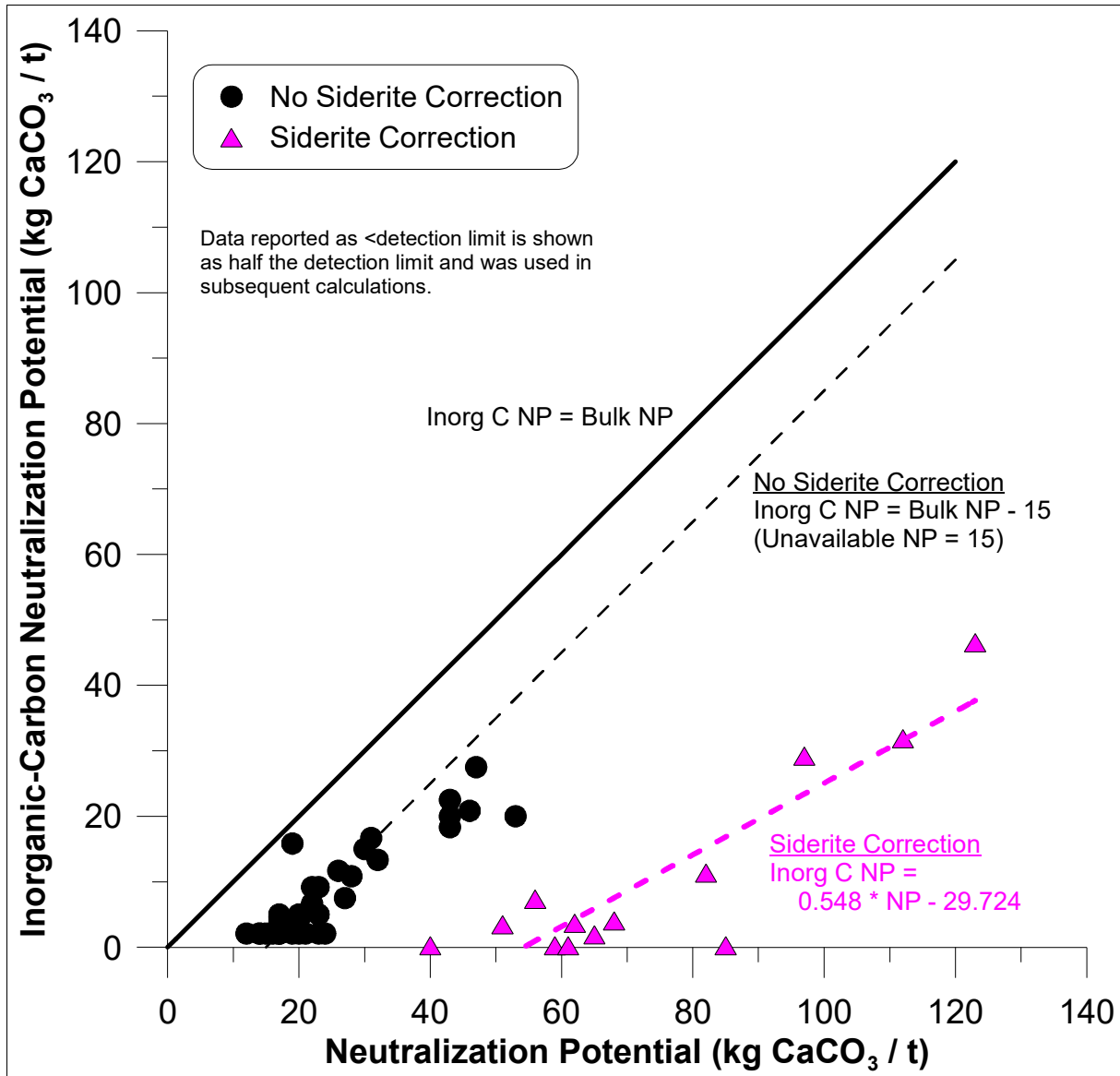


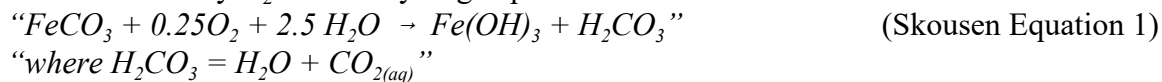
Figure 1-1. A dataset of related rock samples with no detectable siderite (<~1%) comparing inorganic-carbon-based Neutralization Potential (NP) with Neutralization Potential measured with and without siderite correction, showing the siderite correction can erroneously produce much higher NP values rather the equivalent or lower NP values.

2. Overview of Siderite Correction by Skousen et al. (1997) and Initial Problems

Skousen et al. (1997) presented five chemical equations sequentially related to acid addition (HCl) and subsequent titration with base (NaOH) to pH 7 in order to calculate NP in the Sobek procedure. These are the only chemical equations in the manuscript, and oxygen (O₂) is the only oxidant considered. Because the siderite correction is based on the addition of hydrogen peroxide (H₂O₂), which is an oxidant, reductant, catalyst, and reactant (Wikipedia, 2021a; see also Chapters 3 and 4 below), major ambiguities and uncertainties will become apparent in this MDAG case study.

2.1 Skousen et al. (1997) Chemical Equation 1

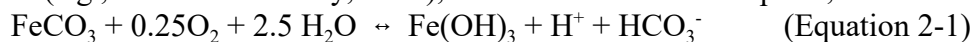
Skousen et al. (1997) described their first chemical equation as siderite dissolution creating “a neutral . . . to slightly acidic solution . . .” without clearly stating this also includes 100% of ferrous-iron oxidation by O₂ and not hydrogen peroxide:



Some important observations about this Skousen Equation 1 are:

- Skousen et al. (1997) uses “→” for Equation 1 and the other four chemical equations (below), which indicates the reactions are irreversible and are complete from reactants (left side) to products (right side). In reality, Equation 1 and the other four are reversible and can reach equilibrium, so “↔” and Le Chatelier’s Principle should be used. This leads to problems with the siderite correction discussed in more detail below.
- Skousen et al. (1997) are wrong that this irreversible equation is dominant under “neutral” conditions above ~pH 6.3, like the endpoint of ~pH 7 for Sobek NP or even higher for other “modified NP” methods. Skousen Equation 1 would be dominant only at “slightly acidic” to more acidic solutions. This error appears again in Skousen Equation 5 (below).

The correct, reversible equation for neutral pH where aqueous bicarbonate would be dominant (e.g., Morin and Cherry, 1986), like the NP titration endpoint, is:



This Equation 2-1 highlights the importance of reversibility and the resulting pH buffering in the aqueous-solid carbonate system. Skousen Equation 1 applies only in the pH range of ~pH 3.5 to ~pH 6.3.

- Skousen et al. only clarify in their irreversible Equation 2 (below) that “ $\text{H}_2\text{CO}_3 = \text{H}_2\text{O} + \text{CO}_{2(\text{aq})}$ ” also leads to $\text{CO}_{2(\text{gas})}$ (at acidic pH), where open system vs. closed system conditions are important for proper interpretations of Skousen Equation 1.

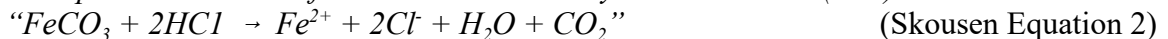
At this point, it is important to keep in mind the following reversible Equation 2-2 that applies to the aqueous carbonate system:



The first two terms are dominant at acidic pH (< ~pH 6.3) and the third term is dominant at neutral pH where NP titrations end. Nevertheless, all three terms are “interactive” and affect each other at acidic, neutral, and alkaline pH.

2.2 Skousen et al. (1997) Chemical Equation 2

“The first step in the reaction of siderite with excess hydrochloric acid (HCl) is:



“Because the solution is [now] acidic, the CO₂ is exsolved as a gas.”

Some important observations about this Skousen Equation 2 which represents the first step of acid addition in the NP procedure are:

- A simple statement is made that “the CO₂ is exsolved as a gas”. This means that a gas-phase reservoir (e.g., the atmosphere) is in contact with the solution, which creates an “open system”.
- As with the other equations, Skousen et al. use “→”. In reality, “↔” is correct, allowing Le Chatelier’s Principle to reverse Skousen Equation 2. As a result, the reverse reaction (stopping siderite dissolution and/or forming new siderite) can eventually occur whenever CO₂ is not “exsolved” (such as in the saturated zone of a full-scale tailing impoundment) or whenever partial pressure of CO₂ in the adjacent gas phase is high (such as orders of magnitude higher in some waste rock dumps, e.g., Morin, 2017).
- Thus, Skousen Equation 2 applies only to a fully open system where CO₂ gas can “exsolve” fully and completely. This may be somewhat correct for a laboratory, but can be wrong for the reality of full-scale minesite components.
- Therefore, the arguments of Skousen et al. on why siderite does not provide net neutralization is limited only to certain conditions, like a laboratory analyzing small-scale samples outside real minesite components. In turn, the arguments for a lack of net neutralization by siderite become more limited. More evidence for this is now presented.

2.3 Skousen et al. (1997) Remaining Chemical Equations 3 to 5

“The ferrous iron (Fe²⁺) produced by reaction 2 is also unstable and will slowly oxidize to ferric iron (Fe³⁺) and consume additional HCl:

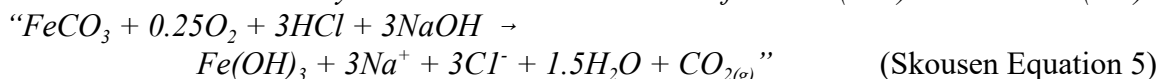


“The ferric iron (Fe³⁺) produced will consume base ions upon titration with sodium hydroxide

(NaOH) and precipitate as ferric hydroxide:



“The overall reaction is essentially reaction 1 with the addition of sodium (Na^+) and chloride (Cl^-):



It is important to note that the “overall reaction” in Skousen Equation 5 contains an error. Skousen et al. (1997) describe a stepwise titration reaction down to ~pH 2 and then back to ~pH 7, all combined into Equation 5. In reality, during the titration back to ~pH 7, little, or some, or most of the “exsolved” CO_2 gas (Skousen Equation 2) will be taken back into solution, depending on open vs. closed system and the partial pressure of CO_2 .

This creates additional acidity (thereby reducing the final calculated NP value) by the forward direction of Equation 2-2 above, as HCO_3^- becomes dominant above ~pH 6.3. Skousen Equation 5 misses this additional acidity, and lower final NP value, by listing CO_2 gas as the only final carbonate species at ~pH 7.

Skousen et al. (1997) added:

“... Because the standard NP procedure as outlined by Sobek et al. (1978) does not allow sufficient time for ferrous iron oxidation and subsequent precipitation of ferric hydroxide, the procedure accounts for only the initial reaction, resulting in 3 mol of alkalinity (Eq. [2]-[3]). [MDAG NOTE: Skousen Equation 3 does in fact represent 100% full oxidation of iron and therefore 3 mol of alkalinity implicitly includes iron oxidation, but at this step there is no back titration to ~pH 7.] Therefore, erroneously high NP values can be generated with samples containing high amounts of siderite. [MDAG NOTE: Here is an error, where Equation 3 is believed to be the last one affecting the acid-base balance because Equation 5 was not written correctly.] Such an analytical oversight can lead to incorrect post-mining water quality predictions, result in premature mine closure, and produce costly, long-term reclamation liabilities for mining companies . . . ”

The preceding text shows that Skousen et al. (1997) were wrong to generally declare that siderite had no net effect of neutralization (positive or negative). It is more complicated than that, such as the effect of CO_2 partial pressure in the open system.

Nevertheless, it is clear that the condition-specific amount of neutralization from siderite, as well as from others like redox-active MnCO_3 (see Chapter 4 below), is not a simple acceptance of a simple neutralization equation. However, the five equations of Skousen et al. (1997) do not reliably describe this site-specific and condition-specific neutralization.

2.4 Jumping to Unjustified Conclusions: Add Hydrogen Peroxide!

In any case, Skousen et al. (1997) then jumped to a major conclusion. They recognized that ferrous iron may not oxidize fully within the hours that a heated Sobek NP analysis might take. It is important to note, that if the ferrous iron does indeed oxidize, then no correction is needed because

Skousen Equation 5 (although incorrect) is automatically realized. If some ferrous iron oxidized, there would be less need for a correction. Because Skousen et al. used irreversible reactions, it is “all or nothing” for iron oxidation and the siderite correction.

Thus, Skousen et al. (1997) assumed ferrous iron does not oxidize at all. As a result, a “siderite correction” was defined as the addition of 5 mL of 30% hydrogen peroxide (H_2O_2) to the 100 mL of acidic solution from the diluted HCl addition to 2 g of solid sample.

Remarkably, this siderite correction is not explained or justified at all, such as by rewriting the Skousen Equations using H_2O_2 instead of O_2 (leading to the major concerns as explained below in Chapters 3 and 4). Where is the technical connection between the assumed 100% lack of ferrous-iron oxidation and the need for a strong addition of hydrogen peroxide? The implicit assumptions are telling.

As a minimum, H_2O_2 is implicitly considered by Skousen et al. to be a catalyst for iron oxidation and more likely a reactant (discussed further in Chapter 3 below). There is no technical justification for this particular siderite correction using H_2O_2 , so let’s take a closer look at it numerically.

H_2O_2 and its reactions are phenomenally complex, as summarized in Chapter 3 below. For example, H_2O_2 can both oxidize ferrous iron, which is the assumption of Skousen’s siderite correction, and reduce ferric iron, which is ignored by Skousen’s siderite correction but would “create” NP as an artifact of the method as depicted in Figure 1-1.

As another example, H_2O_2 solutions are unstable and thus include pH-buffering compounds like phosphoric acid to stabilize the H_2O_2 typically somewhere around pH 4 to 5. Thus, the addition of even 5 mL of a pH-buffered solution around 4.5 could neutralize a significant amount of acidity in the 100 mL of solution nominally around pH 2. This would effectively “create” non-existent NP in the solid sample as an artifact. Chapters 3 and 4 discuss more details that show the addition of hydrogen peroxide can lead to ambiguous and complex conditions that may cause a calculated solid-phase NP to be higher or lower than realistic by the siderite correction of Skousen et al. (1997).

2.5 Adding Orders of Magnitude More Hydrogen Peroxide Than Needed

Based on the volume of 30% H_2O_2 in 5 mL, there would be 1.5 mL of H_2O_2 in the siderite correction of Skousen et al. (1997). At a pure density of 1.45 g/cm^3 (Wikipedia, 2021a), there would be approximately 2 g or 0.06 moles of H_2O_2 added to the 100 mL of solution that leached 2 g of solid-phase sample. Based roughly on Equation 3-2 using H_2O_2 instead of O_2 (discussed further in Chapter 3 as similar to Skousen Equation 3), these 0.06 moles of H_2O_2 would oxidize about 0.12 moles of siderite or roughly 14 grams of siderite.

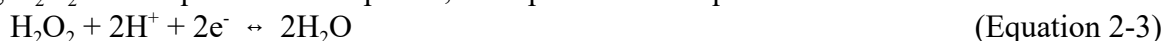
However, the Sobek NP technique leaches only 2 g of solids in total and almost always only a small part of that would be siderite! Therefore, this technically unsupported siderite correction by Skousen et al. (1997) typically adds sufficient H_2O_2 to oxidize orders of magnitude more siderite than the entire solid-phase sample can contain. This leads to a gross excess of H_2O_2 in the 100 mL NP

solution and that leads to further problems and ambiguities.

2.6 An Overview of What Happens to Most of the Hydrogen Peroxide

As a precursor of what follows in Chapters 3 and 4, we can now ask the question, “What happens to excess H₂O₂ in the siderite correction if there is no ferrous iron, either because there is little to no siderite to start, or because the ferrous iron already mostly oxidized to ferric iron?”

Taking H₂O₂ as an aqueous redox species, a simple half-cell equation would be:



This is startling. In this case, some aqueous acidity may be neutralized, or created, depending on the fate of the two electrons with other redox species (Chapter 4). In this case, there could be an erroneously higher NP calculated for the solid-phase sample (such as seen in Figure 1-1 above and discussed in Chapter 4 below).

Therefore, it is important to return to basics and to examine the details more thoroughly. These show that the siderite correction of Skousen et al. (1997) yields ambiguous or erroneous results for NP analyses. In the words of Skousen et al. themselves, now applied to their own work on siderite correction:

“Such an analytical oversight can lead to incorrect post-mining water quality predictions, result in premature mine closure, and produce costly, long-term reclamation liabilities for mining companies . . . ”

However, their words are more alarming here because their siderite correction can erroneously lead to underestimating ARD risk, which is indeed a major concern.

The details are discussed in Chapter 4 below.

2.7 Other Studies on Siderite Correction and Hydrogen-Peroxide Addition

Detailed published studies of siderite correction with hydrogen peroxide since Skousen et al. (1997) are limited.

Caldwell and Irwin (2018) looked at only one rock from one site (“diluted” to various percentages with Ottawa sand) and thus provided no general information on siderite correction. Furthermore, this 2018 study by Caldwell and Irwin:

- failed to follow the optimum procedure recommended by Skousen et al., like filtration of the suspended pyrite-bearing solids from the solution before adding H₂O₂,
- did not confirm Effective NP with any kinetic testing so all results are only analytical numbers with no confirmation of validity and effectiveness, and
- used unspecified modifications of both the Sobek (1978) and the Modified 1991 NP procedure without explaining and justifying the internal modifications applied by the SGS laboratory.

The Modified 1991 NP procedure (albeit further modified without clarification) by Caldwell and Irwin (2018) is not recognized by the Canadian ML-ARD Prediction Manual (Price, 2009). Thus, Caldwell and Irwin (2018) do not help clarify the siderite correction, but instead added to the confusion and ambiguity.

Interestingly, several of these problems with hydrogen peroxide also apply to the “NAG” test for rapid determination of net capacity to generate ARD. However, this is another story.

3. Some of the Intricate and Misunderstood Details of Hydrogen Peroxide

As explained in Chapter 2 above, Skousen et al. (1997) designed a “siderite correction” for Sobek NP analyses. The stated need for this correction was based on limiting and sometimes wrong assumptions like:

- irreversible reactions go to completion, like ferrous-iron oxidation, despite the obvious reversibility and equilibrium;
- a titration from acidic to neutral conditions (~pH 7) does not generate any bicarbonate, and CO₂ gas remains the dominant carbon species at neutral pH; and
- aqueous ferrous iron does not substantially oxidize to ferric iron within hours when exposed to the open atmosphere, which is not always correct.

A simple correction would be to bubble air (oxygen) rapidly through the NP solutions. However, Skousen et al. did not propose this, presumably because they saw a need to greatly accelerate the rate of ferrous-iron oxidation beyond what they thought oxygen could do. Without any technical justification or detail, they selected hydrogen peroxide (H₂O₂) as the additive that would accelerate and oxidize ferrous iron. This unjustified decision leads to problems with their siderite correction.

Without any technical justification or detail, Skousen et al. (1997) selected 5 mL of 30% H₂O₂ to be added to the 100 mL of NP solution that had leached 2 g of solids. As shown in Chapter 2:

- this addition typically exceeds by orders of magnitude the amount of H₂O₂ needed to oxidize siderite in 2 g of solid sample, resulting in a large excess of H₂O₂; and
- the 5 mL of pH-stabilized 30% H₂O₂ solution could partially neutralize some of the acidity in the 100 mL leading to the erroneous “creation” of additional NP by this correction.

It is now worthwhile to review some properties and characteristics of hydrogen peroxide, which will show that hydrogen peroxide is not the optimum or even appropriate oxidant for ferrous iron. Much of the following is taken from the compiled information in Wikipedia (2021a) and supplemented with other references.

Hydrogen peroxide slowly decomposes to oxygen and water in the presence of light:



This gives the impression that hydrogen peroxide is simply a source of free oxygen, but the story is much more complex than that.

The rate of decomposition (Equation 3-1) increases with increasing pH, concentration, and temperature. The decomposition is catalyzed by transition metals and their compounds, like Ag, Au, Cd, Co, Cr, Fe, Hg, Mn, Mo, Ni, Pt, Zn, and Zr.

Wikipedia (2021a) further explains,

“Certain metal ions, such as Fe²⁺ or Ti³⁺, can cause the decomposition to take a different path, with free radicals such as the hydroxyl radical (HO·) and hydroperoxyl (HOO·) being formed.”

Thus, hydrogen-peroxide decomposition in the presence of ferrous iron may not follow the simple

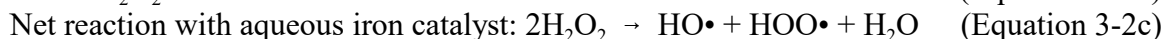
Equation 3-1, but follows more complex pathways that may not always lead to O₂ (see also Chapter 4 below).

To improve its stability, hydrogen peroxide is often stored with a stabilizer and pH buffer such as phosphoric acid, nitrate, tin citric acid, various organic compounds, and many others (e.g., Wikipedia, 2021a; Using-Hydrogen-Peroxide, 2021; USP Technologies, 2021; Pedziwiatr et al., 2018). The failure to consider the additional pH buffering is one criticism of the siderite correction of Skousen et al. (1997), as discussed above in Chapter 2.

Of major importance here, Wikipedia (2021a) explains,

*“Hydrogen peroxide is both an oxidizing agent and reducing agent . . . **The net reaction of a ferric ion with hydrogen peroxide is a ferrous ion and oxygen [MDAG emphasis]. This proceeds via single electron oxidation and hydroxyl radicals. This is used in some organic chemistry oxidations, e.g. in the Fenton’s reagent. Only catalytic quantities of iron ion is needed since peroxide also oxidizes ferrous to ferric ion [MDAG emphasis].”***

This indicates that aqueous ferrous and ferric iron represent a cyclical catalyst for hydrogen-peroxide decomposition (Equation 3-1) that may instead lead to aqueous hydroxyl radicals (Equation 3-2). The equations are listed in Wikipedia (2021b) as:



These radicals can lead to other redox related reactions as discussed in Chapter 4 below.

On the other hand, hydrogen peroxide can also be a reactant at acidic pH to oxidize ferrous iron, its own catalyst. This hints at the complexity of a catalyst and a reactant affecting each other or playing dual roles.

For H₂O₂ as a reactant at acidic pH, Wikipedia (2021a) provides the equation:



Equation 3-3 is comparable to Skousen Equation 3 in Chapter 2 above, but with H₂O₂ as the oxidant instead of O₂, with different stoichiometry, and without the “Cl”.

Do Skousen et al. (1997) consider hydrogen peroxide a source of oxygen, decomposed by the cycling catalytic conversion between aqueous ferrous and ferric iron (Equation 3-2)? The answer must be no, because Skousen Equation 3 (listed in Chapter 2 above) uses “→” to indicate an irreversible reaction. Thus, they consider that there is no significant catalysis by aqueous iron.

As a result, Skousen et al. (1997) must consider hydrogen peroxide an irreversible reactant as in Equation 3-3. However, they do not provide any chemical equations with hydrogen peroxide for clarification.

As explained in Chapter 2 above, the consideration of H_2O_2 as a reactant means that orders of magnitude of excess H_2O_2 is added to the NP analysis under the siderite correction. This raises the question of the fate and the effect of this excess reacting H_2O_2 . This is basically the same question for solid samples with no siderite to start with. This is discussed next in Chapter 4.

4. What Happens to the Large, Unused Excess of Hydrogen Peroxide in the Siderite Correction?

As explained in previous chapters, Skousen et al. (1997) designed a “siderite correction” for Sobek NP analyses. The stated need for this correction was based on limiting and sometimes wrong assumptions like:

- Irreversible chemical reactions always proceed to completion, like ferrous-iron oxidation, despite the obvious reversibility and equilibrium.
- A titration from acidic to neutral conditions (~pH 7) does not generate any bicarbonate, and CO₂ gas remains the dominant carbon species at neutral pH.
- Aqueous ferrous iron does not substantially oxidize to ferric iron within hours when exposed to the open atmosphere, which is not always correct.

Without any technical justification or detail, Skousen et al. (1997) then selected 5 mL of 30% H₂O₂ to be added to the 100 mL of NP solution that had leached 2 g of solids. This 5 mL addition overlooked known complexities and problems with hydrogen peroxide, like:

- Hydrogen peroxide also reduces ferric iron to ferrous iron as part of a catalytic reaction.
- Hydrogen peroxide does not necessarily decompose directly to oxygen in the presence of aqueous iron and some other elements, but instead can decompose to reactive oxygen-radical species.
- Chemical stabilizers like pH-buffering phosphoric acid in the 5 mL lead to the erroneous “creation” of additional NP by this siderite correction.
- This approach by Skousen et al. (1997) forced hydrogen peroxide to be a reactant rather than a catalyst, with the 5 mL addition typically leading to orders of magnitude more hydrogen peroxide than can be consumed by a sample containing siderite.

So what effect can the substantial excess of hydrogen peroxide create?

First, siderite is not the only natural mineral/compound containing ferrous iron. Others include Fe(OH)₂, magnetite, and green rust.

Second, it is important to recognize that aqueous iron is often not the only redox couple in natural waters. Others can include manganese, arsenic, selenium, antimony, nitrogen, and organic carbon.

Third, as summarized in Chapter 3 above, the redox behaviour of hydrogen peroxide in an aqueous solution can be as simple as O₂ production and as complex as reactive hydroxide radicals from the catalytic oxidation and reduction of aqueous iron. This can be simplified, and hopefully not oversimplified, by considering hydrogen peroxide in an aqueous solution as a redox couple with the half-cell reaction of (repeating Equation 2-3 here for convenience):



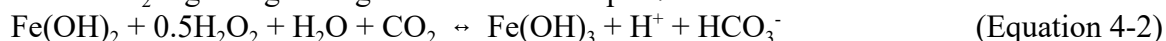
Equation 4-1 is a generic version of hydrogen-peroxide decomposition in Equation 3-1 and is consistent with hydrogen peroxide as a reactant according to the interpretations of Skousen et al. (1997). Nevertheless, other half-cell reactions for hydrogen peroxide besides Equation 4-1 are

possible. Thus, Equation 4-1 is used as an example to show how complex the redox reactions can be with hydrogen peroxide as a reactant.

4.1 “Siderite Correction” is also “Ferrous-Mineral Correction”

As explained in previous chapters, Skousen et al. (1997) chose the addition of hydrogen peroxide without technical justification to oxidize aqueous ferrous iron after siderite dissolution. As a result, they failed to realize this “siderite correction” also affects the final NP value when other ferrous-iron minerals are present, like $\text{Fe}(\text{OH})_2$, magnetite, and green rust (this subsection), and when other redox-active couples are present (Subsections 4.2 to 4.5 below).

For example, in low-carbonate systems, ferrous iron may form $\text{Fe}(\text{OH})_2$ rather than siderite. As a result, the addition of hydrogen peroxide in the NP titration can lead to this equation, including some allowance for CO_2 ingassing during titration back to $\sim\text{pH } 7$:



This is similar to Equation 2-1 for siderite. Therefore, “siderite correction” is also “ferrous-mineral correction”, but other ferrous-bearing minerals like magnetite would have different effects on the final NP value.

4.2 “Siderite Correction” is also “Reduced-Manganese and Rhodocrosite Correction”

Samples containing carbonate minerals like siderite and calcite often also contain some manganese, such as rhodocrosite or minor MnCO_3 in other carbonate minerals. This manganese is in the 2+ state, similar to ferrous iron, and is released into solution, similar to ferrous iron.

Thus, the excess hydrogen peroxide in the siderite correction can also oxidize aqueous manganese as Mn^{2+} through Mn^{3+} to insoluble Mn^{4+} that would then form oxidized minerals like MnO_2 :



comparable to oxidation of aqueous iron:



As a result, the excess hydrogen peroxide in the siderite correction is also a “reduced-manganese correction” no matter if it is wanted, warranted, or relevant.

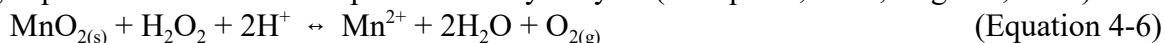
If the aqueous Mn^{2+} originates from MnCO_3 and implicitly allowing for some ingassing of CO_2 during titration to $\sim\text{pH } 7$:



This is comparable to the corresponding iron equation (Equation 2-1). Therefore, the final NP value following the procedure of Skousen et al. (1997) is a correction for both siderite and manganese-bearing carbonate including the purer form of rhodocrosite.

Skousen et al. do not mention this, but the NP titration for any sample with significant reduced manganese (Mn^{2+}) and little to no siderite can behave as if siderite is present.

However, as with iron, the final result on NP is not so simple. MnO_2 can also be reduced by hydrogen peroxide to Mn^{2+} ion as part of a catalytic cycle (Wikipedia, 2021; Pilgaard, 2021):



Wikipedia (2021a) further explains,

“The net reaction of hydrogen peroxide and permanganate or manganese dioxide [MnO_2] is manganous ion [Mn^{2+}]; however, until the peroxide is spent some manganese ions are reoxidized to make the reaction catalytic. This forms the basis for common monopropellant rockets.”

Therefore, the interaction of hydrogen peroxide with aqueous manganese, as with aqueous iron, can generate acidity, neutralize acidity, or have no effect depending on many site-specific conditions. In turn, hydrogen peroxide can cause siderite-corrected NP values to be higher or lower, or have no net effect, when interacting with iron or manganese.

4.3 “Siderite Correction” is also “Reduced-Selenium (Arsenic, Antimony, Etc.) Correction”

Another redox example showing unexpected effects on NP by the “siderite correction” is selenium.

Based on the NP titration starting at neutral pH, decreasing down to ~pH 2, adding hydrogen peroxide, and then increasing back to ~pH 7, the net oxidation reaction with aqueous Se^{4+} and Se^{6+} is:



As a result, the siderite-corrected NP will be higher than appropriate (H^+ is consumed and thus appears as solid-phase NP) when relatively significant aqueous levels of selenium are obtained during the NP titration.

However, if the sample is already acidic at the start, then aqueous selenium would make little contribution to the siderite-corrected NP:



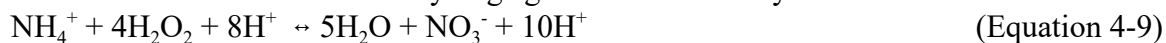
Similar or different contributions to the siderite-corrected NP can also be made by redox couples like As^{3+}/As^{5+} and Sb^{3+}/Sb^{5+} , depending on initial pH of the sample.

Therefore, “siderite correction” also “corrects” (whether warranted or not) for other reduced elements like selenium, arsenic, and antimony.

4.4 “Siderite Correction” is also “Reduced-Nitrogen Correction”

As an example of hydrogen peroxide with redox-active nitrogen, a sample could contain some ammonium either naturally or as a large amount from blasting with common ammonium-nitrate

explosives. This can result in a relatively large generation of acidity:



Thus, even a little ammonium could result in a much lower NP value from “siderite correction”.

Therefore, “siderite correction” also “corrects” (whether warranted or not) for reduced nitrogen species.

4.5 “Siderite Correction” is So Much More Than That

As shown in the preceding subsections, the siderite correction by Skousen et al. (1997) also “corrects” for many other redox species, whether warranted and justified or not. Also, Skousen et al. apparently tested “overburden” from coal minesites, where the organic carbon also reacts with hydrogen peroxide to distort the calculated amount of NP. These many additional “corrections” can raise or lower the final NP value in unexpected ways if the redox couples and their leaching are not understood in detail. This detailed element-specific redox understanding for a sample is rare.

Therefore, the NP value for siderite correction may have little correlation with any level of siderite in a sample. This ambiguity is one major consequence of using hydrogen peroxide which is a general oxidant, reductant, catalyst, and reactant (Chapter 3). In light of this, discrepancies like Figure 1-1 are not surprising.

5. Limited Number of Samples and Methods Used to Test the Siderite Correction

Skousen et al. (1997) is apparently the only primary reference justifying a siderite correction for NP analyses, although limited and erroneous secondary references are available (Caldwell and Irwin, 2018; see also Section 2.7). Therefore, one may have the impression that many samples were tested from around the world to justify the widespread acceptance and usage of siderite correction by hydrogen peroxide. That impression is wrong.

First, Skousen et al. (1997) explained that only 31 samples were collected only in the U.S. States of Pennsylvania and West Virginia.

Second, they referred to these samples as “overburden”. Although overburden can refer to soils, Skousen et al. apparently used “overburden” to mean rock from coal-mining locations. Presumably, many to all samples were sedimentary rock, but this is not explained.

Third, they analyzed these 31 samples with various modifications to the standard Sobek NP method, summarized in their Table 1. The NP results for each of the 31 samples were compiled in their Table 6. However, these reported NP values have no intrinsic validity, because NP is not an intrinsic value to start with (Morin and Hutt, 1997, 2001, and 2009; Price, 2009). Instead, long-term kinetic testing is needed to show which NP value is applicable and “effective”.

Fourth, Skousen et al. (1997) conducted short-term “soxhlet” kinetic testing only on 13 of the original 31 samples. This kinetic testing was conducted for less than 9 weeks instead of the common minimum of 40 weeks.

Nevertheless, even after less than 9 weeks, 5 of the 13 samples were acidic. Despite this, they assumed that any sample that had not become acidic after the short 9 weeks would never become acidic at any future time, which is simply wrong.

Therefore, the detailed assessment of the “siderite correction”, and of the resulting reactive and effective NP, by Skousen et al. (1997) is based only on 13 kinetic-tested samples of “overburden” from the U.S. States of Pennsylvania and West Virginia. Even then it includes flawed assumptions and information, like all those discussed in previous chapters, as well as that any kinetic samples not acidic after only 9 weeks of kinetic testing will never become acidic.

It is amazing that such limited and flawed work, on limited samples, of limited rock units, from a limited area of the world, is currently used worldwide as a reliable generic approach for hydrogen-peroxide-based siderite correction in NP analyses. This siderite correction with hydrogen peroxide is not reliable and it is not surprising that this siderite correction can return unreliable NP values much higher than non-corrected NP values (e.g., Figure 1-1 above).

6. Conclusion

A general geochemical concept is that the presence of siderite (ferrous-iron carbonate or FeCO_3) can lead to an overestimation of Neutralization Potential (NP) as part of acid-base accounting (ABA) of a solid-phase sample. This is because siderite theoretically provides no net neutralization, but does so in an NP analysis because the dissolved ferrous iron does not fully oxidize. However, there are major documented exceptions to this general concept, especially inside of full-scale minesite components. Thus, siderite may or may not provide some neutralization depending on several site-specific conditions discussed in this case study.

Nevertheless, a “siderite correction” was devised by Skousen et al. (1997) to “correct” and lower Sobek NP analyses. However, this siderite correction is based on:

- flawed chemical equations, and
- the relatively large addition of hydrogen peroxide to the NP solution that can lead to higher, lower, or similar NP values relative to uncorrected values, for many reasons related to hydrogen peroxide itself and to other redox couples.

This is suggested by ABA datasets where siderite-corrected NP is substantially higher, not lower, than non-siderite-corrected NP (Figure 1-1).

The detailed assessment of this “siderite correction”, and of the resulting reactive and effective NP, by Skousen et al. (1997) were based only on 13 kinetically-tested samples of “overburden” from the U.S. States of Pennsylvania and West Virginia, kinetically tested for only nine weeks using the “soxhlet” method. This testing included flawed assumptions and information, such as any kinetic sample not acidic after only nine weeks of kinetic testing will never become acidic.

It is amazing that such limited and flawed work, on limited samples, of limited rock units, from a limited area of the world, is currently used worldwide as a reliable generic approach for hydrogen-peroxide-based siderite correction in NP analyses. This siderite correction with hydrogen peroxide is not reliable as a general correction. It is not surprising that this siderite correction can return unreliable NP values much higher than non-corrected NP values.

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