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Increasing Errors in ARD Prediction by Assuming Non-Extractable "Insoluble Sulphur" is a Real Sulphur Species and Excludes Acid-Generating Sulphur

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Abstract

A relatively new source of error by underestimation is becoming increasingly frequent among ML-ARD predictors. It involves the "flip side" of Effective NP overestimation, by underestimating acid-generating sulphide and Acid Potential.

Total sulphur in a rock sample can consist of many sulphur species, such as sulphide, elemental sulphur, relatively soluble sulphate, relatively insoluble sulphate, and organic-bound sulphur. However, the concept of "insoluble sulphur", or synonymously "non-extractable sulphur", is not a real, distinct sulphur species like the previous ones. It is simply what is "left over" after one or more sequential extractions/leaches. Therefore, insoluble sulphur should be considered an undefined mixture of one or more real sulphur species, which based on probability includes some acid potential.

The concept of insoluble sulphur may have originated or expanded with ASTM Method D2492. Some laboratories have applied this ASTM Method to many types of rock to obtain insoluble/non-extractable sulphur. However, (1) the formal title of this ASTM method is, "Standard Test Method for Forms of Sulfur in Coal", (2) according to ASTM this method is designed strictly for coal, and (3) D2492 has been "withdrawn, no replacement" by ASTM in January 2021.

Two examples in Canada, from one mining project and one non-mining construction site, show that virtually 100% of insoluble sulphur was acid-generating pyrrhotite or pyrite. This is known based on additional information under the "Wheel Approach" including mineralogy, visual observations, and documented ARD locally or from kinetic tests. However, all this additional information was ignored in order to erroneously claim that Acid Potentials of samples were low and not a concern.

These two examples are only the "tip of the iceberg". There are many more errors and underestimations of ARD potential where insoluble/non-extractable sulphur is reported. Alarmingly, the frequency of this error appears to be increasing, leading to this MDAG Case Study.

It is very important to understand that:

(1) insoluble/non-extractable sulphur is not a real, distinct sulphur species,
(2) insoluble/non-extractable sulphur can be a mixture of one or more sulphur species which, based on probability, are more likely to be acid generating or acid releasing than not,
(3) assessments and predictions including insoluble/non-extractable sulphur should include other, complementary analyses under the "Wheel Approach" to assess the insoluble sulphur, and
(4) such assessments can show that virtually 100% of insoluble/non-extractable sulphur can be acid-generating sulphide like pyrrhotite or pyrite.

Then and now, most predictions of full-scale ML-ARD are wrong by underestimating ML-ARD. As a minimum, this error caused by misuse of insoluble/non-extractable sulphur should be eliminated as quickly as possible.

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1. Introduction

Nearly all predictions of full-scale metal leaching and acid rock drainage (ML-ARD) have been wrong (estimated at roughly 95% by me). These errors are not by overestimating water contamination, but by consistently underestimating it. This is an interesting bias in the error, because it indicates it is not likely to be statistically random. Most ML-ARD predictions were wrong decades ago and they are still wrong this year.

There are many ways that people predicting ML-ARD ("ML-ARD predictors") repeatedly underestimate full-scale water contamination. For example, most predictors still assume that 100% of measured Neutralization Potential (NP) is reactive and available, despite decades of full-scale case studies showing this is normally wrong (e.g., Price, 2009; Morin and Hutt, 1997, 2001, 2005, 2006, 2008a, 2008b; Hutt and Morin, 1999; Morin et al., 2001; Morin 2018). Decades of information are ignored so that full-scale ML-ARD can be underestimated by predictors.

A relatively new source of error by underestimation is becoming increasingly frequent among ML-ARD predictors. It involves the "flip side" of NP overestimation, by underestimating acid-generating sulphide and Acid Potential.

2. Issues with Sulphur Species for ML-ARD Predictions, including Laboratory Liability

For simplicity, the ability of a sample to generate acidity ("Acid Potential" in kg $CaCO_3$ equivalent/tonne) is often calculated by multiplying some solid-phase sulphur measurement in %S by 31.25. A common, and often conservative, solid-phase measurement is total sulphur in %S. This is appropriate where a significant portion of total sulphur, like more than 50%, consists of acid-generating minerals like pyrite and elemental sulphur or acid-releasing minerals like melanterite.

However, this approach can be too conservative and misleading if total sulphur is comprised mostly, like more than 50%, of non-acid-generating and non-acid-releasing sulphur-bearing minerals. Interestingly, such "passive sulphate minerals" commonly only include gypsum and anhydrite. As a result, total sulphur is often a safe and even appropriate value to use for Acid Potential.

Nevertheless, ML-ARD studies often include speciation of sulphur in acid-base accounting (ABA), to determine if non-acid-generating forms of sulphur do comprise much of the total sulphur. There are many possible sulphur species.

In consistent units of solid-phase %S:
Total sulphur = sulphide + elemental sulphur + thiosalts + thiosulphate + pH-neutral relatively leachable sulphate + acid-releasing soluble-or-insoluble sulphate + relatively insoluble sulphate (like barite) + organic-bound sulphur + . . . (Equation 2-1)

For this MDAG Case Study, it is important to note that Equation 2-1 does not include "non-extractable sulphur" or synonymously "insoluble sulphur" which is simply what is "left over" after one or more leaches/extractions. This Case Study shows that this form of sulphur must be comprised of one or more sulphur species from Equation 2-1. It is not a real, independent, and exclusive sulphur species. As shown in the examples of Section 3 below, ML-ARD predictors assuming otherwise have made serious errors and underpredictions of ARD.

Therefore, it is appropriate to think of "insoluble sulphur" or "non-extractable sulphur" as "currently unidentified one or more sulphur species". To do otherwise leads to the problems illustrated in Section 3 below.

Where does the concept of insoluble sulphur come from? In a general sense, it is the amount of sulphur left over after one or more extractions of some type selected by someone for some reason.

Formally, a major source is Method ASTM D2492-02. Some laboratories have applied this ASTM Method to many types of rock to obtain insoluble sulphur. However, the formal title of this ASTM method is, "Standard Test Method for Forms of Sulfur in Coal". As a result, there are two significant problems.

First, this method for sulphur speciation in coal should not be applied to non-coal rock, because this method attempts to characterize organic-bound sulphur that cannot be easily measured. In fact, ASTM itself clarifies, "This test method is not applicable to coke or other carbonaceous materials", so it is literally applicable only to coal.

Second, ASTM formally states this method is “withdrawn, no replacement” in January 2021.

Therefore, insoluble/non-extractable sulphur is no longer a well justified and supported parameter even for coal. It has apparently never been justified for non-coal samples and it is certainly not a real and distinct “sulphur species”. Wherever it is used in an ML-ARD assessment, further work should be done to characterize its composition, as explained next.

Price (2009) summarized and reviewed analytical techniques for sulphur species. For ASTM D2492 and for other approaches that use sequential extractions, Price stated,
“Potential disadvantages of sequential extraction are:

- errors are compounded throughout the test;
- nitric acid may oxidize sulphide and other reduced sulphur species;
- the weight of sulphur extracted must be measured by analysis of the leachate or precipitation of the extracted sulphate as BaSO4 rather than the Leco procedure; and
- conducting test procedures in series is time consuming.”

Price (2009) further points out that sulphur speciation and ABA should not be the only analyses and should be combined with others like mineralogy and total solid-phase elements. This has been colloquially called the “Wheel Approach” (Morin and Hutt, 1997, 1999, and 2001; Figure 4.1 of Price, 2009; and Figure 2-1 below).

As shown in the examples of Section 3 below, a prudent ML-ARD predictor following Price (2009) and the Wheel Approach would not make such serious errors. The errors would have been obvious and should have been corrected early in those ML-ARD studies.

There is another important issue: legal liability for ML-ARD errors. Laboratories rarely point out the limitations and uncertainties in their sulphur-species analyses. More concerning, some laboratories include formally certified Net Potential Ratio (NPR) and Net Neutralization Potential (NNP) values when they have no other information under the Wheel to ensure the reliability of these predictive values. In some jurisdictions, the laboratory analysts are not registered professional geologists or geoscientists. As a result, the laboratories doing this interpretive work of NPR and NNP are assuming major liability because their analytical certificates are legal documents. I have pointed this out and received arrogant “mind-your-own-business” responses from laboratories. A large lawsuit would smarten up those laboratories.

In turn, many ML-ARD predictors have not learned, or ignore, the limitations of geochemical analyses by laboratories. This is a sure way to predicting ML-ARD incorrectly, which turns out to be the preferred way of predicting ML-ARD. ML-ARD predictors should understand the details and limitations of all analytical methods being used on their samples.

Some examples of this will now be given.

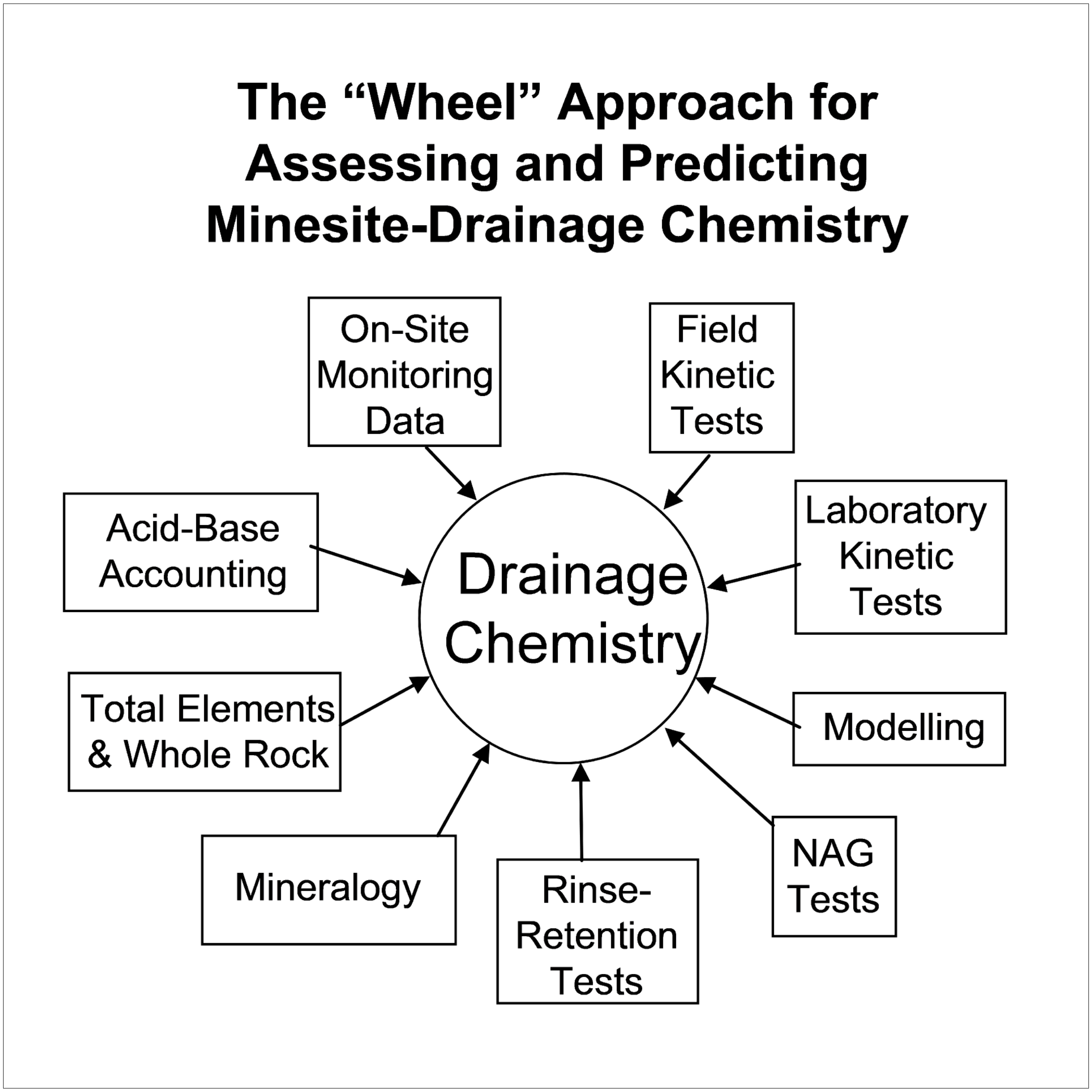


Figure 2-1. The "Wheel Approach" for more reliable ML-ARD predictions using many and partially redundant types of analyses to minimize errors such as those caused by insoluble/non-extractable sulphur and to improve QA/QC.

3. Real Examples of Major ARD Prediction Errors Due To Non-Extractable/Insoluble Sulphur

To illustrate the errors in ARD predictions caused by assuming insoluble/non-extractable sulphur has zero ability to generate or release acidity, two examples are presented here: a mining project in eastern Canada (EC) and a non-mining construction project in western Canada (WC). Unfortunately, more examples are appearing regularly.

3.1 Example EC

Several years ago, the ML-ARD predictor on this mining project declared that there would be no ARD. Government regulators were told this too. Then the company had to backtrack and contradict that prediction based on all the other ML-ARD information available then and now. The naive ML-ARD predictor continues to tell people that he advanced the project by showing there would be no ARD, which is categorically false.

Here are some well documented facts related to ARD at this site:

- Total sulphur reaches almost 18%S in the rock and tailings (Figure 3-1) and is almost always above 1% pyrrhotite+pyrite in drillcore (Figure 3-2).
- Most samples contain little to no available Neutralization Potential (<10 kg/t).
- Mineralogy by thin section and x-ray diffraction (XRD) shows the only detectible sulphur minerals are pyrrhotite and lesser pyrite.
- Project geologists regularly logging core at this site have reported that the only observed sulphur minerals are pyrrhotite and lesser pyrite, although rare gypsum was observed a few times; when asked, the geologists refused to believe that anyone with knowledge of the site would say there are negligible levels of sulphide and high levels of some unspecified non-sulphide mineral as the ML-ARD predictor said.
- Several of about two dozen laboratory-based and on-site kinetic tests show initial or delayed acidic drainage (Figure 3-3).

What went wrong? It took two steps:

1) Ignore all other information contradicting the assumed sulphur species under the Wheel Approach (Figures 2-1, 3-2, and 3-3) and listed in the bullets above.
2) Assume zero percent of insoluble sulphur could generate or release acidity, again by ignoring all other information under the Wheel Approach.

Figure 3-4 shows one sample as a detailed example. This sample contains a relatively high measured total sulphur of 12.28%S. Most of that (11.28%S) is insoluble sulphur (top of Figure 3-4) and little is sulphide (0.81%S). But what is the insoluble sulphur composed of? Based on Section 2 above, there is no reason to assume it is non-acid-generating sulphur, and no further characterization of it was done. On the other hand, XRD mineralogy, visual observations, known geology, and kinetic tests offer strong proof that most or all of the insoluble sulphur is acid generating.

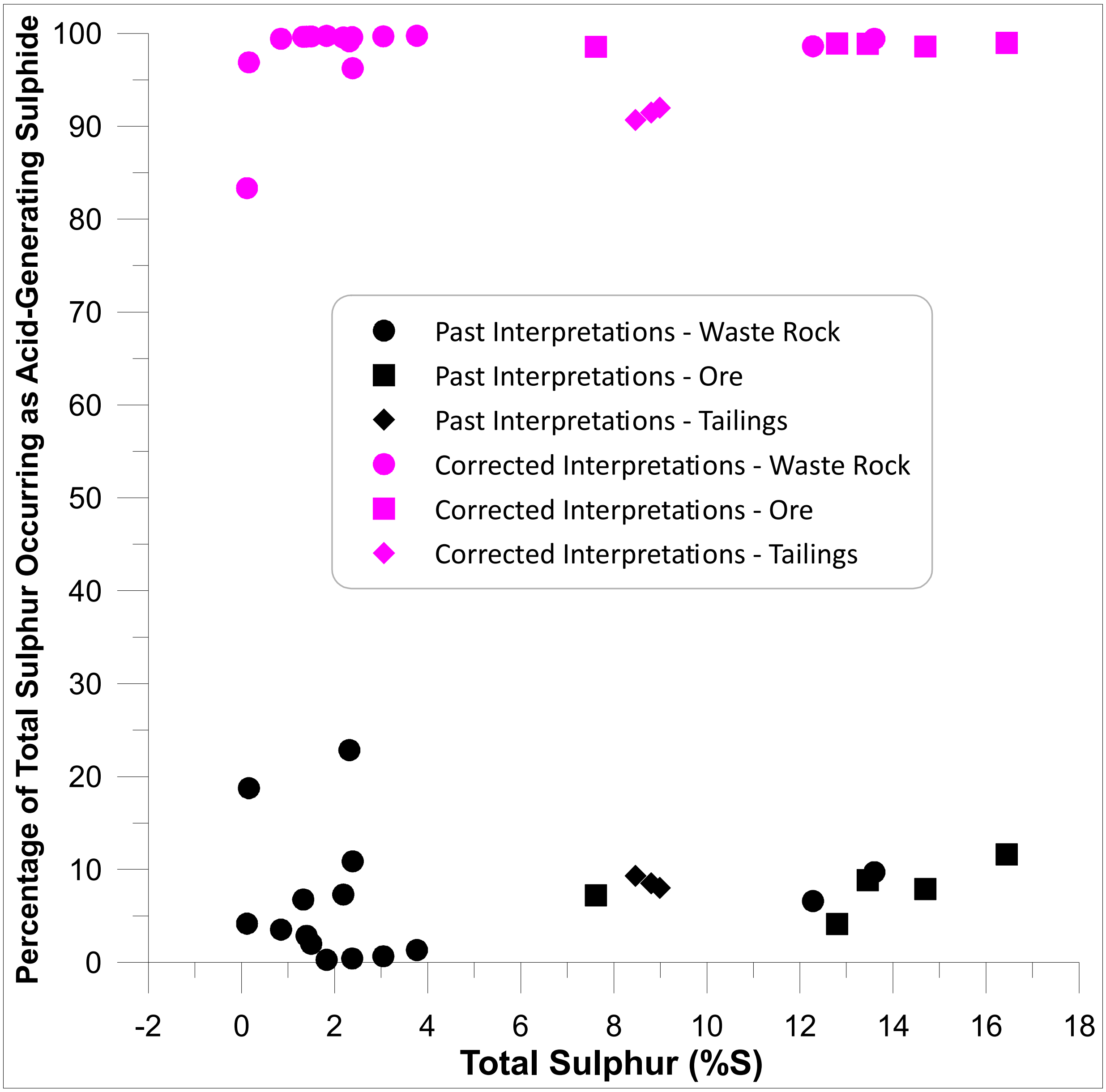


Figure 3-1. Previous and current interpretations of sulphur species for Example EC, showing the percentage of total sulphur composed of acid-generating sulphur; see text for justifications.

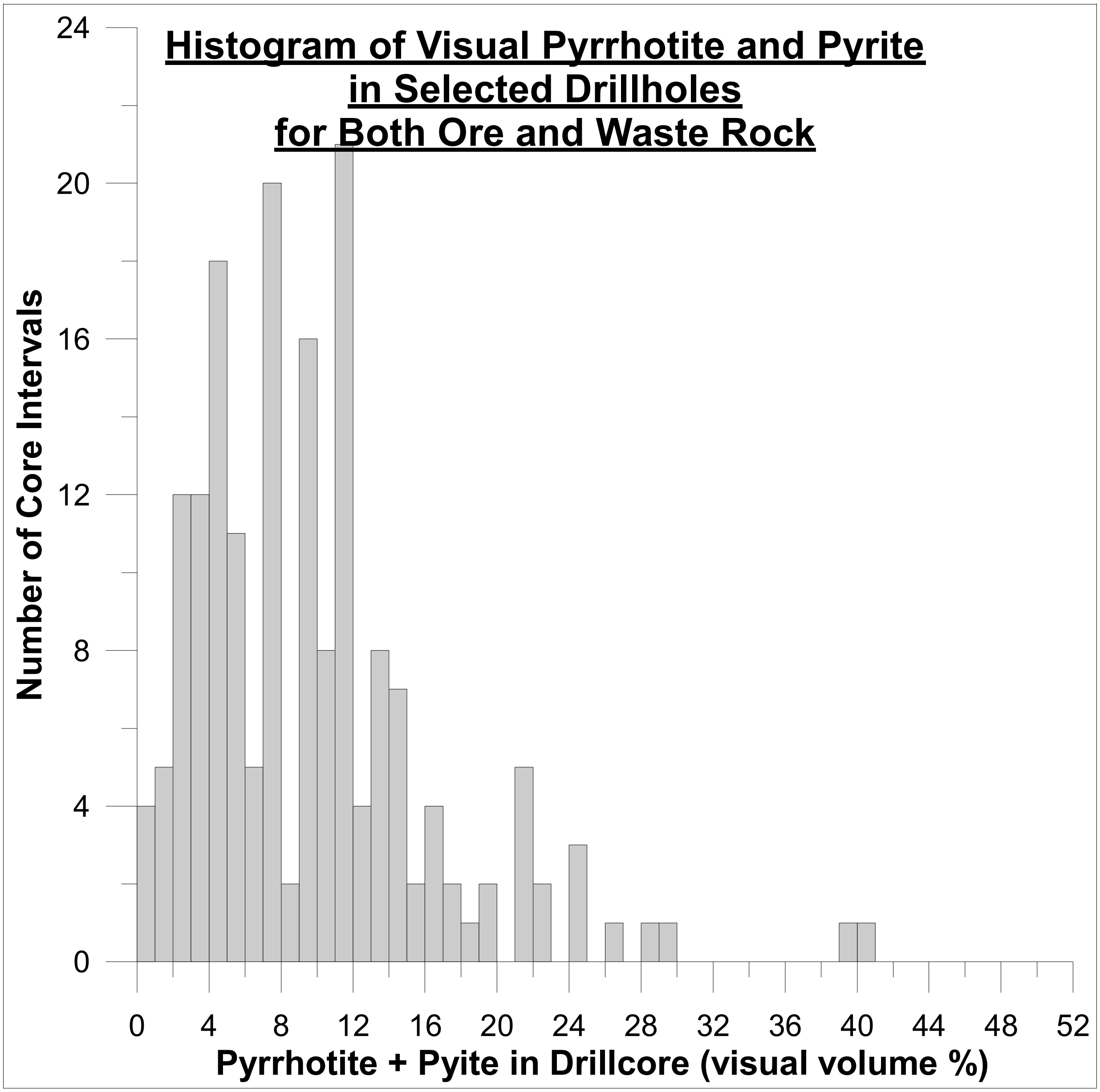


Figure 3-2. Visual observations of pyrrhotite+pyrite in drillcore at Example EC, showing pyrrhotite+pyrite occur at levels mostly above 1%; no other sulphur minerals were observed, leading to the corrections noted in Figure 3-1 above.

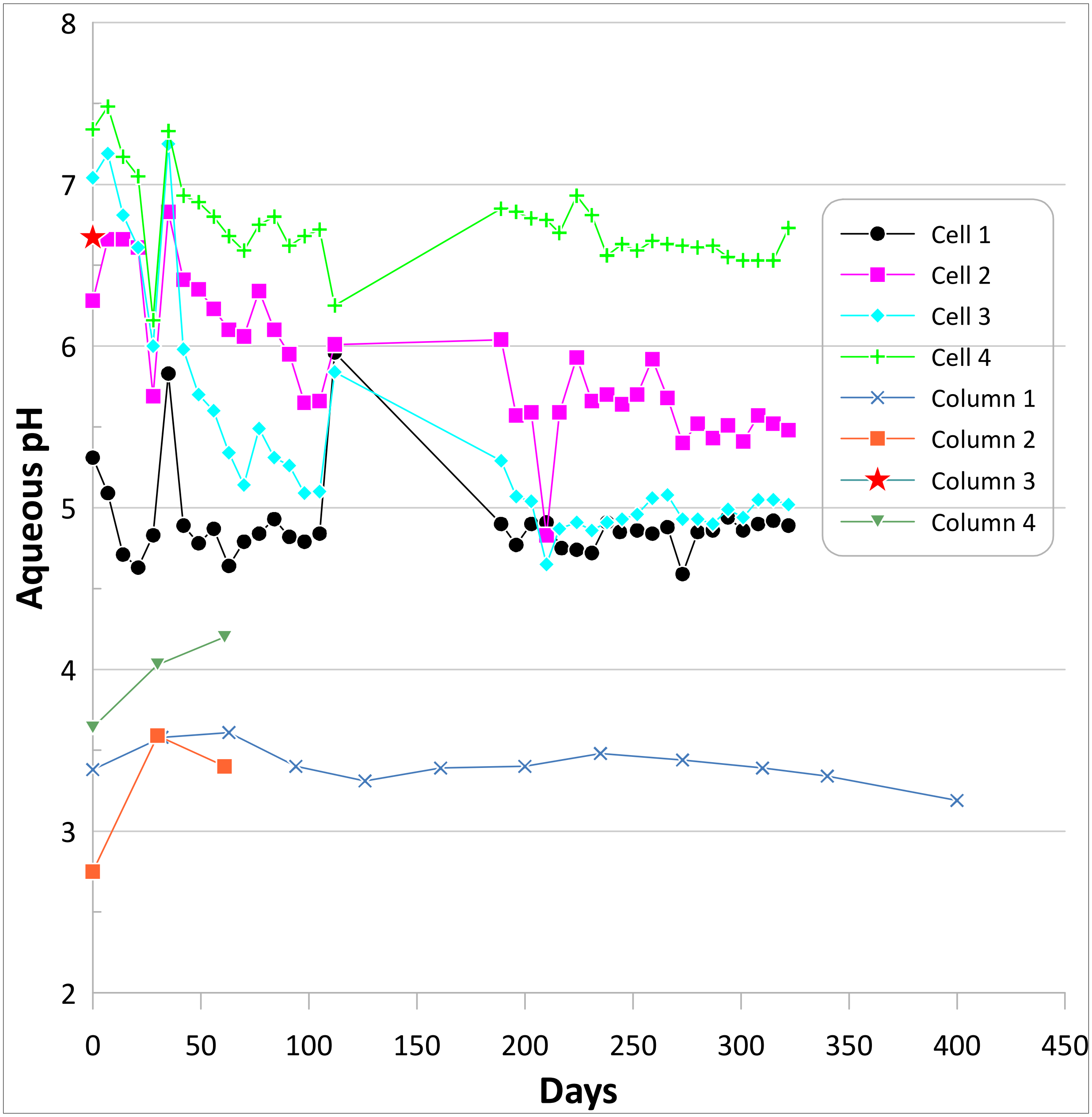
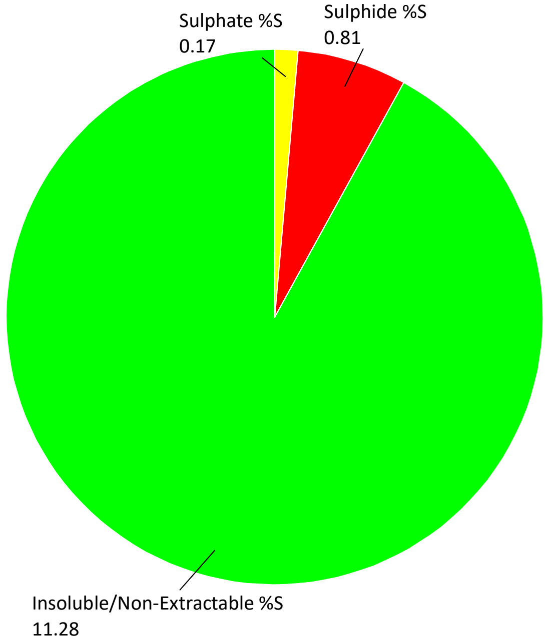


Figure 3-3. Aqueous pH trends for a few of the many laboratory-based and on-site kinetic tests for Example EC, showing acidic drainage does occur despite initial predictions of no ARD.



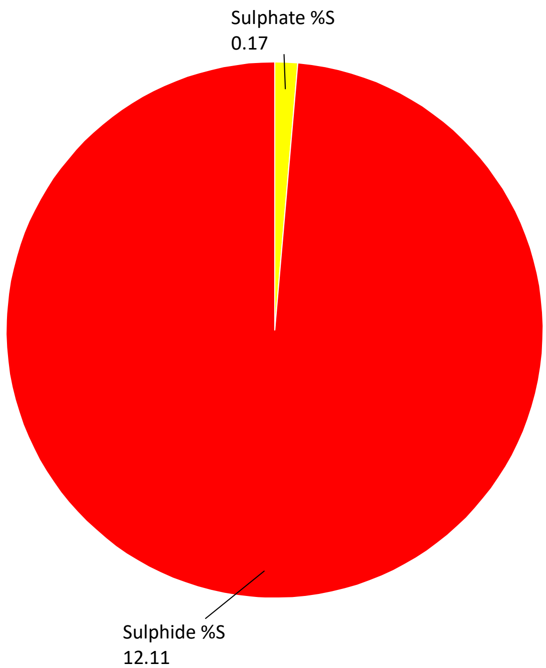


Figure 3-4. A comparison of sulphur-species interpretations for a sample in Example EC with the red portion representing Acid Potential: (top) results from the analytical laboratory assuming non-extractable sulphur contained no acid-generating/releasing sulphur, (bottom) corrected interpretation based on XRD mineralogy, visual observations, known geology, and kinetic tests; it is wrong to assume that insoluble/non-extractable sulphur contains no acid-generating/releasing sulphur.

3.2 Example WC

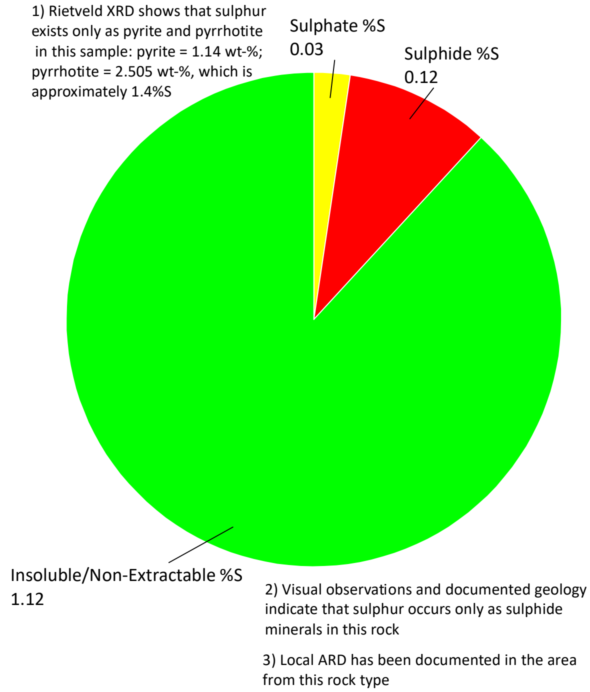
For this example from a non-mining construction site in western Canada, the analytical laboratory used "Modified ASTM D2492-02 Method", which includes the serious issues discussed above in Section 2. Additionally, the laboratory provided values for NPR and NNP based on:

1) non-extractable sulphur containing absolutely no acid-generating/releasing sulphur,
2) Acid Potential calculated only from the minor residual sulphide,
3) 100% of measured NP being available and reactive, and
4) values of measured NP below the ranges applicable to the reported fizz ratings, so too much acid had been added and NP likely overestimated.

On the other hand, relevant information under the Wheel (Figure 2-1) included:

1) Rietveld XRD showing that sulphur exists only as pyrite and pyrrhotite in this rock,
2) visual observations and documented geology indicating sulphur occurs only as sulphide minerals in this rock, and
3) local ARD and acidic paste pH documented in the area from this rock type.

As a result, ARD potential in Example WC had been grossly underestimated in all samples (Figure 3-5 and Table 3-1), as it was in Example EC above (Section 3.1).



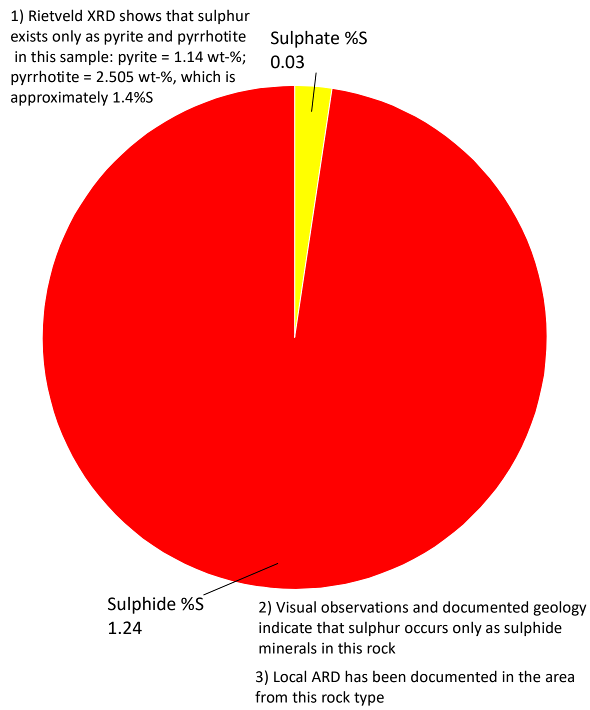


Figure 3-5. A comparison of sulphur-species interpretations for a sample in Example WC with the red portion representing Acid Potential: (top) results from the analytical laboratory that assumed non-extractable sulphur contained no sulphide, (bottom) corrected interpretation based on XRD mineralogy, visual observations, known geology, and locally documented ARD; it is wrong to assume that insoluble/non-extractable sulphur contains no acid-generating sulphur.

Table 3-1. Percentage of Total Sulphur Composed of Acid-Generating Sulphide for Example WC [1]

Sample Number	% of Total Sulphur Excluding Insoluble/Non-Extractable S [2]	% of Total Sulphur Including Insoluble/Non-Extractable S
1	2.5	92.5
2	9.6	96.8
3	15.1	97.8
4	9.4	97.6
5	29.6	98.4
6	10.5	96.5
7	33.3	96.7
8	5.1	97.4
9	11.1	94.4
10	1.9	98.1
11	1.6	96.8
12	29.9	99.4
13	9.7	98.4
14	13.3	97.8
15	1.3	98.7

[1] 1) Rietveld XRD shows that sulphur exists only as pyrite and pyrrhotite in this sample; 2) Visual observations and documented geology indicate that sulphur occurs only as sulphide minerals in this rock; 3) Local ARD has been documented in the area from this rock type.

[2] The analytical laboratory used these results to calculate NPR and NNP, which were clearly erroneously high based on all known ARD information about this rock.

4. Conclusion

The two examples in Section 3 are only the "tip of the iceberg". There are many more errors and underestimations of ARD potential where insoluble/non-extractable sulphur is reported. Alarmingly, the frequency of this error appears to be increasing, leading to this MDAG Case Study.

It is very important to understand that:

(1) insoluble/non-extractable sulphur is not a real, distinct sulphur species,

(2) insoluble/non-extractable sulphur can be a mixture of one or more sulphur species which, based on probability, are more likely to be acid generating or acid releasing than not,

(3) assessments and predictions including insoluble/non-extractable sulphur should include other, complementary analyses under the "Wheel Approach", and

(4) such assessments can show that virtually 100% of insoluble/non-extractable sulphur can be acid-generating sulphide like pyrrhotite or pyrite.

Then and now, most predictions of full-scale ML-ARD are wrong by underestimating ML-ARD. As a minimum, this error caused by misuse of insoluble/non-extractable sulphur should be eliminated as quickly as possible.

5. References

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