

## MDAG.com Supplement 1 to Internet Case Study 32

### Additional Discussions on the Non-Intrinsic Nature of Neutralization Potential (NP)

by K.A. Morin

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Morin and Hutt (2009) explained that Neutralization Potential (NP) was not an intrinsic property of a solid-phase sample. The following discussions examine this in more detail and from different perspectives. To begin, an intrinsic property can be defined as:

- a property that is wholly independent of any other object, action, or consequence;
- belonging to the essential nature or constitution of a thing;
- innate, inherent, inseparable from the thing itself.

For example, the solid-phase level of sulphur or copper within a sample of rock is an intrinsic property.

If it can be shown that the action of neutralization on an aqueous solution by a solid sample is independent of the characteristics of the solution, then NP of a solid sample may be intrinsic. Otherwise, NP is not wholly independent of another object - the solution. If it can be shown that NP exactly corresponds an intrinsic property, such as the level of calcite (calcium and carbonate occurring in the pure crystallographic form of  $\text{CaCO}_3$ ), then NP may be at least pseudo-intrinsic or intrinsic. However, NP may reflect a value less than calcite or other intrinsic property (e.g., some calcite containing Fe) or more than calcite (e.g., including some dolomite or aluminosilicate minerals) depending on site-specific mineralogy and purity. If this is the case, then NP is not wholly independent of another object (the site) and is in fact separable from mineralogy. This would make NP extrinsic.

NP is an estimate of the amount of neutralization a solid sample will have on an aqueous solution that comes into contact. If the solution is already literally neutral ( $\text{pH} \sim 7$  with  $[\text{H}^+] \sim [\text{OH}^-]$ ), then a sample with a large amount of NP will literally not neutralize. Thus, the neutralization capacity of a solid sample without an aqueous solution, and the solid's corresponding quantitative NP, are not intrinsic to the solid phase. Instead, they are dependent on the characteristics of the aqueous solution.

Characteristics of aqueous solutions are assumed by NP analytical methods, often reflected in their units of  $\text{CaCO}_3$  equivalent (Morin and Hutt, 2006). However, there is no *a priori* evidence that all the solid samples will contact those assumed solutions. If they contact solutions with other characteristics, then the measured quantitative NP is inapplicable without correction factors. Again, this shows NP is not an intrinsic property of a solid sample.

One fallacy that arises in minesite-drainage chemistry begins with the recognition that mineralogy creates minesite-drainage chemistry (obviously ignoring the importance of the associated aqueous solution). The fallacy arises from the corresponding belief that, if one knows the mineralogy, one can predict the drainage chemistry. This fails for several reasons. Minerals outside laboratories are rarely pure in form and contain many impurities, chemically and in crystal structure. These impurities can affect:

- (1) the additional “trace” elements that can be released into the water to create the drainage chemistry,
- (2) the solubility of the mineral and thus the aqueous concentrations of the major elements under equilibrium conditions, and
- (3) the kinetics of mineral precipitation-dissolution that determine the aqueous concentrations of both major and trace elements under time-dependent non-equilibrium conditions.

For example, a calcareous mudstone contains calcite according to its nomenclature. However, the drainage chemistry from it cannot be predicted in advance just knowing it contains calcite. While the calcite may be intrinsic, its effects on aqueous chemistry, including any neutralization, are not, and would vary with the aqueous solution itself.

These same points apply to the argument that knowing the mineralogy of a sample will indicate its NP. Such a “mineralogical NP” has been discussed for decades and does not accurately reflect effective NP in many samples.

Another interesting argument would be along the line of: the capacity for neutralization is intrinsic to a sample, but the methodology to determine that capacity is not intrinsic. This is just another way of saying what has been proposed previously: a sample contains a unique and distinctive “effective NP” depending on solid and aqueous characteristics, but no method can consistently provide that effective value, at least not with foreknowledge and confidence. This leads to two conclusions:

First, if NP methods provide NP values that are not intrinsic, then NP is not intrinsic.

Second, if an intrinsic NP like effective NP does exist, the existing methods cannot measure it consistently and accurately around the world. As a result, all NP methods require adjustments or correction factors (contested by Miller, 2009), in turn showing no NP method can be generally superior to others.

Thus, even if the argument is accepted that NP is intrinsic but NP methods are not intrinsic, then the problem remains that this intrinsic NP cannot be measured. Flipping the reasoning would also lead to the question: Then how do we know this supposedly intrinsic effective NP exists at all? This circular logic was discussed in Morin and Hutt (2009).

Another interesting argument is that no NP methods can consistently detect effective NP, but the less aggressive method (lower NP result) should be preferred because it is closest. The major problem here is that effective NP is not necessarily closest to the least aggressive method at all minesites (Morin and Hutt, 1997 and 2001), so this is not a valid argument.

Furthermore, the true bias arises when a general survey is made of ranking NP methods by aggressiveness. For example, some believe one of the unspecified Modified Methods is less aggressive than the U.S. EPA-600 Sobek method (although each Modified method can yield a

significantly different NP value). In reality, if neutralization is taken literally as  $[H^+] = [OH^-]$  around pH 7, then there is only one major NP method that reports NP based on titration to pH 7 (Sobek method). Others titrate to above pH 8. This is often attributed to the observation that alkalinity titrations, which are nebulous in their own right (Kirby and Cravotta, 2005a and b) and thus poor scientific justifications, are based on titration to that pH. As a result, these other methods inherently overestimate NP from acidic conditions (“more aggressive”), but underestimate NP from alkaline conditions. These others also typically run for 24 hours, unlike the Sobek method. Thus, the Sobek method is less aggressive in these areas. How can one rank NP methods accurately as a general sequence by their assumed aggressiveness, which varies from site to site and by site-specific mineralogy?

Comparisons of Sobek NP values to corresponding values using one or another Modified Method have shown that Sobek NP can actually be higher or lower than the Modified NP roughly 40-60% of the time when properly conducted (Morin and Hutt, 2009). So the belief that choosing the less aggressive NP method (which remarkably is often considered one of the unspecified Modified methods) is no proof that it provides a more accurate NP value.

Finally, an interesting argument is that the NP method with the least correction factors is the best method. This is akin to arguing that an automobile from 1920 is better than one from 2005 because it has fewer parts and is simpler. Why would the least understood and least studied NP method be the best? In contrast, the NP method with the most correction factors can be an advantage, because its strengths and weaknesses are better understood. Morin and Hutt (2009) explained this was the case for the Sobek method, whereas such work on the “Modified Method” (which notably do not differentiate the several Modified methods) is lacking.

## References

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