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On the Nonsense of Arguing the Superiority of an Analytical Method for Neutralization Potential

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Nonsense - communication that has no meaning or is untrue.
"Nonsense only makes good sense to those who do not know what it means." - Anonymous

Abstract

For minesite-drainage chemistry, the quantitative measurement of a solid-phase sample's capacity to neutralize aqueous acidity is often called Neutralization Potential (NP) or Acid Neutralisation Capacity (ANC). However, unlike a chemical element in the Periodic Table, NP is not an intrinsic property of a sample, that is, it is not wholly independent of any other object, action, or consequence. In fact, NP is dependent on, and defined by, its methodology, as shown by the many NP methods currently available (see Table 1 for the details of some methods).

The concept of effective NP has arisen as a pseudo-intrinsic property that all NP methods strive to measure. However, even effective NP may be method-dependent, but this will not be known in the near future. Until then, correction factors are applied to obtain effective NP from the NP results of any method. These corrections include the effects of unavailable NP, particle size, slow-reacting and silicate NP, and iron- or manganese-bearing carbonates.

Because no NP method apparently measures effective NP on a consistent basis at minesites around the world, all NP methods require correction factors. Therefore, no one NP method is superior or inferior to any other in a general sense. This contrasts with current arguments, like the INAP GARD Guide claiming one of the unspecified Modified Methods "prevent[s] over-estimation of NP or AP relative to Sobek method", and the draft EU standard recommending a unique NP method. This also contrasts with other arguments, like a method providing a lower NP for a particular sample must inherently be better.

Despite the lack of superiority of any NP method, there are advantages and disadvantages. A major advantage, not related to any superiority in the methodology, is the widespread usage for decades, and detailed studies of correction factors, for the U.S. EPA-600-compliant Sobek et al. NP method. Any other NP method with similar usage and documented correction factors would have the same advantage, but we cannot identify another one.

Other advantages, which may be relevant to certain sites but not all, apply to many methods. For example, the proposed EU standard has much greater acid-addition discretization in the lower-NP range, and thus may detect lower-NP values more reliably at some sites. Also, some Modified Methods may not detect NP reliably above 125 kg/t, and thus other methods may be better in some cases. However, such site-specific advantages have not been well characterized and confirmed.

So, when will the nonsensical arguments on the general superiority of an NP method stop? When will people stop creating new NP methods, with no well-documented correction factors, implying their new method is superior?

1. Introduction

In the realm of minesite-drainage chemistry, the quantitative capacity of a sample of rock, tailings, or soil to neutralize acidity and maintain near-neutral pH is typically called “Neutralization Potential” (NP) or “Acid Neutralisation Capacity” (ANC). We cannot recall the number of times we have been frustrated by consultants, professors, students, regulators, and citizens arguing over which NP method is “right”, or “better”, or in some other way superior. Some regulators are even considering specifying one particular NP method as a standard in their jurisdictions (e.g., European Committee for Standardization, 2008).

We do not understand why this nonsense continues. We start below from basic principles, and from the current level of studies and knowledge, to demonstrate that no NP method can be generally superior now or in the near future.

2. Neutralization Potential is Not an Intrinsic Property

The first important observation is that NP is not an intrinsic property of a sample or minesite component; it is not like an element from the Periodic Table. An intrinsic property can be defined as specific to a sample or component, and wholly independent of any other object, action or consequence. In this case, NP is not intrinsic because it is dependent on, and defined by, the particular method used to measure it. It has no independent existence outside its methodology.

The concept of neutralization can be independent, such as the aqueous condition of $[H^+] = [OH^-]$ around pH 7. However, the quantitative measurement of the solid-phase Neutralization Potential is not. NP is a composite of elemental compositions, mineralogical forms, and aqueous conditions that can and do vary from sample to sample, from site to site.

A sample contains a definite amount of copper or sulphur, and one can argue over the superiority of methods to measure it. Also, one can strive to create more accurate and superior methods to measure the concentration of an element. However, the creation of another NP method just creates another solid-phase measurement of something to do with aqueous neutralization, reflecting the details of the methodology (Table 1). For example all other aspects being equal, an NP method with a lower titration-endpoint pH will result in a lower NP value, such as pH 7.0 (intrinsically neutral, as in $[H^+] = [OH^-]$) for the Sobek method (Table 1). However, "all other aspects being equal" does not apply to any two NP methods. Superiority is not derived from a particular NP methodology.

3. Effective Neutralization Potential is a Pseudo-Intrinsic Property

So what do most people mean when they discuss "Neutralization Potential"? NP is a quantitative solid-phase amount of an aqueous action, not a property like an element. Morin and Hutt (1997a and 2001) defined NP simply as: "the analytical bulk capacity of a sample for neutralizing acidity". It is often expressed in units of kg $CaCO_3$ equivalent/tonne (Table 1), but there are assumptions hidden in these units that do not apply to all minesites and that add ambiguity to the understanding of NP (Morin and Hutt, 2006).

Attempts have been made to give a solid-phase sample or component a pseudo-intrinsic property reflecting neutralization, and this is sometimes called "effective Neutralization Potential". Morin and Hutt (1997a and 2001) defined effective NP as: "the capacity of mined materials to neutralize acidity to pH 6.0 or above under the site-specific in-field (1) environmental conditions, (2) mineralogy, (3) grain sizes, and (4) rates of mineral reactions." Thus, effective NP is not truly intrinsic, because it is not wholly independent of any other object, action or consequence.

4. Reconciling Neutralization Potential and Effective Neutralization Potential

To determine effective NP, analytical measurements of NP require correction factors for aspects like Unavailable NP, Slow-Reacting NP, and some carbonate minerals under aerobic conditions. This gives the illusion that effective NP is an intrinsic property, but is simply an attempt to give some meaning to NP outside of the methodology. For example, one cannot create a chemical element by simply defining some analytical procedure for it. Still, the pseudo-intrinsic concept of effective NP has worked well, because it has lessened the argument on which NP methodology is "right".

Nevertheless, the superiority argument continues on in some circles. For example, the recently created INAP GARD Guide (INAP GARD Guide as of February 2009, at http://www480.pair.com/aturner/gardwiki/index.php/Table_5-1) says the "Modified Sobek Method", which is in fact several methods that can yield significantly different NP values (Table 1), "prevent[s] over-estimation of NP or AP relative to Sobek method".

Table 1. Examples of Methods for Measurement of Neutralization Potential
(other methods like Mineralogical, Carbonate, and BC Research are not listed here)

Reference	Sobek et al. (1978)[1]	Modified NP (1989 version)[2]	Modified NP (1996 version)[3]	Modified NP (1997/2004 version)[4]	Draft European Union Neutralisation Potential[6]	Acid Neutralization Potential (ANPA)[5]
Particle Size	< 60 mesh	80% <200 mesh	80% <200 mesh	"pulverized"	95% <100 mesh	<100 mesh
Weight of Sample	2 g	2 g	2 g	2 g	2 g	1 g
Initial Test to Determine Acid Addition	Sobek fizz	Sobek fizz	non-Sobek fizz	non-Sobek fizz	Carbonate Rating (CR) from CO_2 analysis	none
Initial pH check[7]	None; if already acidic, the resulting negative NP estimates the initial net acidity	None, but test is invalid if final pH after 24 hours is not between 1.5 and 2.0	None, but test is invalid if pH after 24 hours is not between 2.0 and 2.5	None, but test is invalid if pH < 2 after 22 or more hours	After 15 minutes of stirring, do not start test if pH < 2.0	Not until initial acid addition; see below
Initial Volume of water/acid	20-80 mL of variable-strength HCl; based on four-increment Sobek fizz test	20-80 mL of variable-strength HCl; based on four-increment Sobek fizz test	90 mL distilled water, plus a specified amount of 0.1 N HCl based on a modified four-increment fizz test	90 mL distilled water, plus a specified amount of 0.1 N HCl based on a modified four-increment fizz test	90 mL demineralised water; 10 increments of acid addition at Time = 0 and 2 hours based on CR; no pH check at 2 hours to determine if more acid needed	100 mL of 0.01 M H_2SO_4; if pH > 4, add 10 mL of 1.0 M H_2SO_4
Temperature and Stirring	heat to near boiling, swirling every 5 minutes, until reaction complete	near ambient; shake continuously for entire test	near ambient; shake continuously for entire test	near ambient; shake continuously for entire test	stirred "between acid additions" at 20°C	80°C
Duration	variable, but often a few hours; until reaction complete	24 hours	24 hours	at least 24 hours	24 hours	1 hour

Reference	Sobek et al. (1978)[1]	Modified NP (1989 version)[2]	Modified NP (1996 version)[3]	Modified NP (1997/2004 version)[4]	Draft European Union Neutralisation Potential[6]	Acid Neutralization Potential (ANPA)[5]
Intra-Test checks and Adjustments	None	Check pH after ~6 hours, and re-adjust to pH 1.5-2.0 as needed	Add more acid based on four initial increments after two hours, with no pH check at 2 hours to determine if more acid is needed; check pH at 22 hours; if pH > 2.5 at 22 hours, add acid to obtain pH 2.0-2.5; if pH < 2.0 at 22 hours, restart test from the beginning with less acid	Add more acid after two hours, although the 2004 instructions say "for some samples, particularly those with an acidic paste pH, the second addition of acid [after two hours] will not likely be required", while the 1997 reference does not say this; check pH at 22 hours and 24 hours; if pH > 2.5, add acid to obtain pH 2.0-2.5, agitate for another two hours, check pH again, continue process until pH remains 2.0-2.5 after two hours; if pH < 2.0, restart test with less acid	Add more acid based on 10 initial increments of acid addition after two hours, with no pH check at 2 hours to determine if more acid is needed; check pH at 22 hours; if pH>2.5, add acid to obtain pH 2.0-2.5 at 24 hours; terminate test if the volume of late-added acid is more than original acid volume added at 0 and 2 hours; if pH<2.0, terminate and restart with less acid	Cool to ambient; if pH > 4, add 10 mL of 1.0 M H_2SO_4; after filtering supernatant off, add 5 mL of 30% H_2O_2; boil gently for 5 minutes; cool to ambient
Termination	When reaction is complete	Final pH after 24 hours must be in the range of 1.5-2.0	Terminate at 24 hours, ensuring final pH is 2.0-2.5	If pH > 2.5, add acid to obtain pH 2.0-2.5, agitate for another two hours, check pH again, continue process until pH remains 2.0-2.5 after two hours; if pH < 2.0, restart test with less acid	Terminate and check pH at 24 hours; repeat test if pH is not between 2.0 and 2.5.	One hour unless pH>4
Adjustment to Final Volume	Add distilled water to obtain 125 mL; boil for one minute; cool to near ambient;	None specified; titrate final volume (varies with sample) as created during the test	Adjust final volume to at least 125 mL with deionized water	Adjust final volume to at least 125 mL with deionized water	Adjust final volume to 125 mL	None specified

Reference	Sobek et al. (1978)[1]	Modified NP (1989 version)[2]	Modified NP (1996 version)[3]	Modified NP (1997/2004 version)[4]	Draft European Union Neutralisation Potential[6]	Acid Neutralization Potential (ANPA)[5]
Titration Endpoint pH	7.0 for at least 30 seconds; with NaOH	8.3 for at least 30 seconds; with NaOH	8.3 (no time interval given, so ignores drifting); with NaOH	8.3 (no time interval given, so ignores drifting); with NaOH	8.3 (no time interval given, so ignores drifting); with NaOH	8.2 for 30 seconds
Final NP Units	kg $CaCO_3$ equivalent/ tonne	kg $CaCO_3$ equivalent/tonne	kg $CaCO_3$ equivalent/tonne	kg $CaCO_3$ equivalent/tonne	mol H^+/kg and kg $CaCO_3$ equivalent/tonne	% CO_2

[1] from Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoils. Report EPA-600/2-78-054, U.S. National Technical Information Report PB-280 495. 403 p. A0748

[2] from (a) Lawrence, R.W., and P.B. Marchant. 1989. Acid Rock Drainage Prediction Manual. Canadian MEND Report, Project 1.16.1b. And (b) Lawrence, R.W., P.B. Marchant, and G.W. Poling. 1989. Investigation of Prediction Techniques for Acid Mine Drainage. Canadian MEND Report, Project 1.16.1a.

[3] from Lawrence, R.W., and Y. Wang. 1996. Determination of Neutralization Potential for Acid Rock Drainage Prediction. Canadian MEND Report, Project, 1.16.3, for Hudson Bay Mining and Smelting and for Environment Canada.

[4] from Vizon SciTec Inc. 2004. Standard Operating Procedure for the Modified Acid Base Accounting Procedure for Neutralization Potential (Lawrence 1997). This procedure is attributed to Lawrence and Wang (2007), but there are significant differences.

[5] from Newmont Metallurgical Services Analytical Department. 2001. Method Name: ANPA - Acid Neutralization Potential Acidity.

[6] from European Committee for Standardization. 2008. Characterization of waste - Static test for determination of acid potential of acidic waste. Draft European Standard prEN 15875.

[7] an interesting issue is here is that, with no initial pH check and a zero fizz rate, samples that are initially slightly to strongly acidic will have acid added to them, making them more acidic; for the Sobek method, the final titration will provide an estimate of initial net acidity, but the Modified methods create a repetitive loop in which the samples have to be retested with less acid until/if final pH remains in the specified range.

This common misconception of the superiority of one or more Modified methods is often based on the following assumptions.

- *Effective NP is less than measured NP.* This is often true for the Sobek method (e.g., Morin and Hutt, 2008b), where it has been well documented. This should also be true of one or more Modified Methods and other NP methods, but we cannot find any detailed robust studies comparing results of several NP methods to effective NP. Confirmation of this assumption for one method, accompanied by a lack of confirmation for other methods, does not make the Sobek method inferior or any less correct than others. In contrast, it means the weaknesses of the Sobek method are understood better, but says nothing about superiority or inferiority.

- *Any NP method that measures a lower NP value than the Sobek method must be correct and thus requires no correction factors.* Our understanding from the general lack of studies comparing Modified NP values to effective NP values is that Modified NP values do require correction factors. Thus, if all NP methods require correction factors, which seems to be the current consensus without detailed confirmation, then no method can be superior in a general sense.

- *The numerous Modified methods frequently produce lower NP values for suites of samples.* In fact, comparative studies have been conducted by students and researchers often having little experience in one or both analytical techniques, and without specifying which Modified Method was used, raising questions on analytical reliability. In any case, for several comparative studies, many Modified NP values were similar to or greater than Sobek values, with other methods even low than the Modified values (e.g., Morin and Hutt, 1997b; Lawrence and Wang, 1997). Therefore, Sobek NP cannot be said to be inferior because it produces higher values, when in fact it can just as well produce lower values than one or more Modified methods. Other methods produce even lower values than one or more Modified methods. Does this make them “better”?

Again, the consensus appears to be that no NP method yields the exact value of effective NP, at least not with knowledge of this in advance. Thus, all NP values and methods require correction factors. If all methods require correction factors, then having two different NP values from two different methods cannot prove that one is “right” or “better”, as implied by the GARD Guide. On a site-specific basis, after detailed studies including additional static and kinetic tests, the NP values from one method may be closer to effective NP than from another. However, this is not known in advance, and NP values will still likely require some correction.

5. What Proof is Needed That One NP Method is Superior to Another?

Note that those arguing one NP method is superior to another are not using intensive sample-by-sample or site-by-site testing to establish a frequency of the superior performance relative to effective NP. They often compare the results of one NP method to another method on a suite of samples, or to other piecemeal information like mineralogy or carbonate level. Until many dozens of minesites show that one NP method is frequently superior to others and does not require correction factors to obtain effective NP, then arguments over superiority are mostly speculation with limited support and thus nonsense. If such proof ever appears, it would likely be many decades from now.

Furthermore, we have found no detailed studies showing that all NP methods lead to the same exact value for effective NP in a sample, although this can be forced by applying different correction factors for each method. Such forcing does not prove all methods yield the same effective NP, it just means humans have decided to make it so using correction factors. In fact, notice the circular logic in the previous two sentences: how can we know whether effective NP is independent of methodology, when it is not measured directly but calculated from "corrected" results of NP methods. It may be that the effective NP, like the measured NP, is dependent on methodology, and there are many effective NPs for each sample. This will not be known for a long time.

6. What are the Advantages Among the NP Methods Not Related to Superiority?

In our work, we consistently use the standard U.S. EPA-600-compliant Sobek method (Table 1). This is simply because this method has had the longest and widest usage around the world. As a result, correction factors for aspects like unavailable NP, particle size, slow-reacting and silicate NP, and iron- or manganese-bearing carbonates are documented for it (e.g., Morin and Hutt, 2008a and b; Jambor and Dutrizac, 2002; Jambor et al., 2002a and b; Jambor et al., 2006; Morin and Hutt, 2008c; Skousen et al., 1997). This is not the case for the other NP methods.

This widespread usage and correction do not mean the Sobek method is a superior or inferior method. It is simply the most used and corrected, probably as a coincidence of when and where it was first published and circulated.

Among the NP methods, there are differences that suggest one method can be better than another for a particular sample or site. For example, the addition of acid at the start and after two hours in some Modified methods will only detect NP up to approximately 125 kg $CaCO_3$ equivalent/tonne. For higher NP samples, after 22 hours and after many near-neutral reactions are completed like any encapsulation of neutralizing minerals by iron hydroxides, Modified methods detect the fact that additional NP above ~125 kg/t is present and more acid should be added. Perhaps it is too late for this. If not, then a reaction time of only two more hours may be insufficient to dissolve the remaining NP. No one has reported whether the Modified methods are inferior to the Sobek method for samples with more than 125 kg/t. Thus, any arguments over superiority and inferiority on this issue are speculation and nonsense at this time.

On the other hand, some Modified methods have a finer discretization of acid addition for NP below 125 kg/t. One may assume this would provide a more accurate NP measurement in the lower range. However, the amount of acid addition, even when much greater than appropriate, does not always lead to a higher NP, but does in some cases. Since this issue of discretization has not been investigated in detail, its usage to determine superiority and inferiority of NP methods remains speculation and nonsense at this time. If finer discretization is in fact an advantage, then the proposed Modified NP method for the European Union (European Committee for Standardization, 2008) in Table 1, with 10 increments of acid addition, would be even better than the other Modified methods.

7. Conclusion

A quantitative pseudo-intrinsic property is needed for drainage-chemistry predictions, which can be called effective NP. At this time, effective NP can be considered independent of methodology, although we really do not know.

In any case, humans have decided to apply correction factors that should result in the same effective NP from all NP methods. As a result, no one method can currently be shown to consistently provide the exact value of effective NP. Speculation abounds, but no NP method is superior or inferior, and this is unlikely to change in the near future if at all. Thus, arguments about the superiority of NP methods are nonsense.

The only advantage we can see is not based on methodology at all, but on the usage and experience spanning many decades and around the world for the U.S. EPA-600-compliant Sobek method. Correction factors for this method are the widest studied and documented. Again, this does not make the Sobek method superior to any other. Any other NP method with similar extents of studies and corrections would have the same advantage, but we see no others at this time.

So, when will the nonsensical arguments on the general superiority of an NP method stop? When will people stop creating new NP methods, with no well-documented correction factors, implying their new method is superior?

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