PROBLEMS IN ACIDITY AND ALKALINITY MEASUREMENTS IN MINE DRAINAGE[1]

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Additional Keywords: theoretical, measured, standard methods, treatment, net alkalinity

Extended Abstract

Introduction and Methods

Not all mine drainage is acidic, and problems in the interpretations of alkalinity and acidity measurements arise especially in mine drainage containing alkalinity. Synthetic and field samples of mine drainage were analyzed using seven titration methods, and the results were compared to theoretical definitions and calculated concentrations of alkalinity and acidity.

Synthetic mine drainage solutions were prepared with known concentrations of Fe(II), Fe(III), ± Al, ± Mn, ± HCO_3^-, ± CO_2, ± N_2 (to drive off O_2). Field samples with with varying concentrations of metals, HCO_3^-, and pH values were collected. Samples were titrated by three alkalinity methods (Standard Methods [APHA, 1992]; H_2O_2 addition; H_2O_2 addition + one week storage) and four acidity methods (Standard Methods [APHA, 1992]; H_2O_2 addition; H_2O_2 addition + one week storage; N_2-purge + H_2O_2 addition). Samples were analyzed for metal concentrations using inductively coupled plasma spectroscopy and colorimetry.

Calculated acidity was determined using

$$\text{Acidity}_{\text{calc}} = 50[(2\text{Fe}^{2+}/56) + (3\text{Fe}^{3+}/56) + (3\text{Al}/27) + 2\text{Mn}/55 + 1000(10^{-\text{pH}})] \quad (1)$$

from Hedin *et al*. (1994), where metal concentrations are in mg L^{-1} and acidity is in mg $CaCO_3$ L^{-1}. Acidity was also calculated from PHREEQC (Parkhurst, 1995) speciation.

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[1] Paper was presented at the 2002 National Meeting of the American Society of Mining and Reclamation, Lexington KY, June 9-13, 2002. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

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Results and Discussion

Figures 1-3 show titration results. Samples with pH < 4.5 gave consistent results for all titration methods, causing no problem in the interpretation of the acidity in such samples. In synthetic samples containing alkalinity, standard methods for alkalinity returned the same values as calculated alkalinity before metal oxidation and hydrolysis are allowed. Following metal oxidation and hydrolysis, calculated alkalinity can be negative, but measured alkalinity is constrained be greater than or equal to zero.

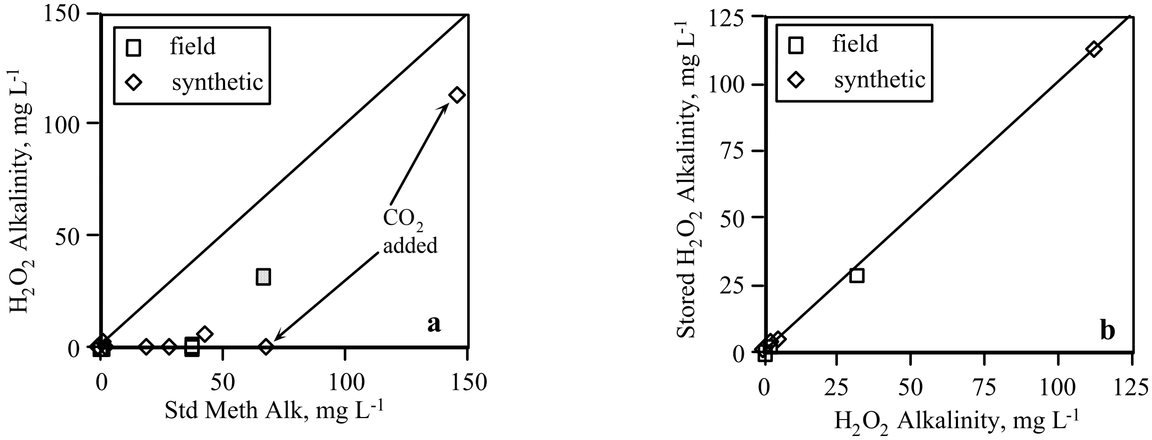

Figure 1. Comparisons of measured alkalinity methods. All alkalinities are reported in mg L^{-1} as $CaCO_3$. The diagonal line shows where values on the x- and y-axes are equal.

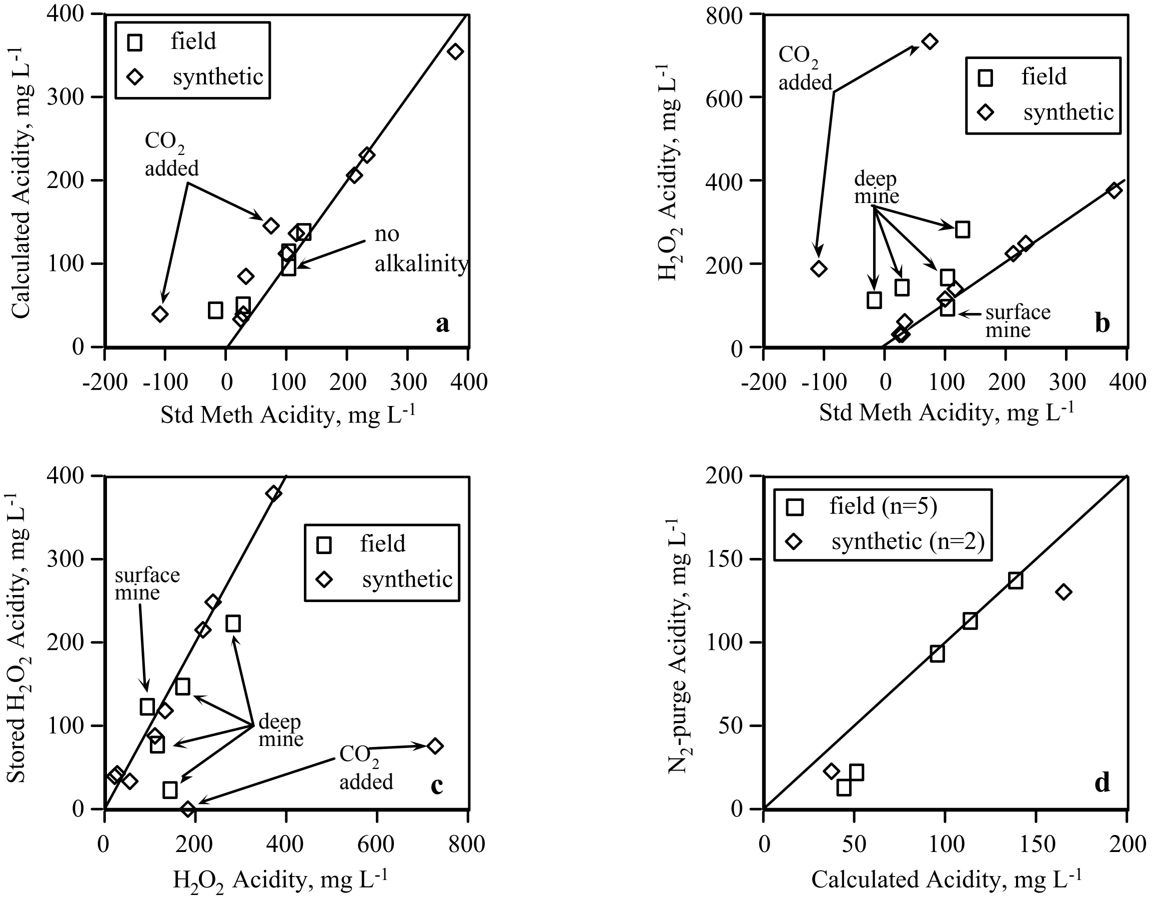

Figure 2. Comparisons of acidity methods. All acidities are reported in mg L^{-1} as $CaCO_3$. The diagonal line shows where values on the x- and y-axes are equal.

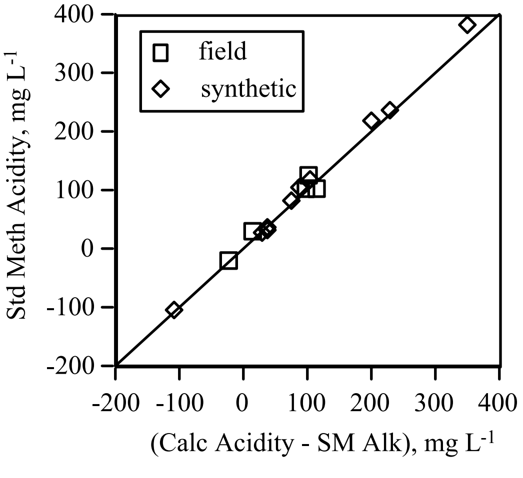

Figure 3. Standard Method acidity *versus* net acidity (calculated acidity [Eqn. 1] minus Standard Method alkalinity). All values are reported in mg L^{-1} as $CaCO_3$. The diagonal line shows where values on the x- and y-axes are equal.

Samples containing both alkalinity and acidity present serious problems in the interpretation of laboratory results and comparison to theoretical values. Measured acidity values varied significantly among titration methods. Standard acidity titration methods intentionally cause the hydrolysis of iron, which allows H^+ to react with alkalinity present in the sample. PHREEQC modeling of synthetic samples supports this conclusion. Standard methods also can return negative values for acidity, but some laboratories report negative values as zero. Standard method acidity results (*if negative values are reported*) are consistent with the most rigorously defined theoretical calculated acidity (if CO_2 is excluded).

Using "net alkalinity" (measured alkalinity – measured acidity) to design mine drainage treatment can lead to ineffective systems with insufficient alkalinity to neutralize metal and H^+ acidity. The use of (measured alkalinity – calculated acidity) is recommended in the planning of mine drainage treatment.

Literature Cited

American Public Health Association (APHA). 1992. *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Assoc., Washington, DC.

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Parkhurst, D. L. 1995. *User's Guide to PHREEQC - A Computer Program for Speciation, Reaction Path, Advective-transport, and Inverse Geochemical Calculations*, Water. Resour. Invest. Rep. No.95-4227, US Geol. Survey, Lakewood CO.

PROBLEMS IN ACIDITY AND ALKALINITY MEASUREMENTS IN MINE DRAINAGE

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Presented at

American Society for Mining & Reclamation Conference, Lexington, KY

June 9-13, 2002

ABSTRACT

Not all mine drainage is acidic, and problems in the interpretations of alkalinity and acidity measurements arise especially in mine drainage containing alkalinity. Synthetic and field samples of mine drainage were analyzed using seven titration methods, and the results were compared to theoretical definitions and calculated concentrations of alkalinity and acidity.

Samples with pH < 4.5 gave consistent results for all titration methods, causing no problem in the interpretation of the acidity in such samples. In synthetic samples containing alkalinity, standard methods for alkalinity returned the same values as calculated alkalinity before metal oxidation and hydrolysis are allowed. Following metal oxidation and hydrolysis, calculated alkalinity can be negative, but measured alkalinity is constrained be greater than or equal to zero.

Samples containing both alkalinity and acidity present serious problems in the interpretation of laboratory results and comparison to theoretical values. Measured acidity values varied significantly among titration methods. Standard acidity titration methods intentionally cause the hydrolysis of iron, which allows H^+ to react with alkalinity present in the sample. PHREEQC modeling of synthetic samples supports this conclusion. Standard methods also can return negative values for acidity, but some laboratories report negative values as zero. Standard method acidity results (*if negative values are reported*) are consistent with the most rigorously defined theoretical calculated acidity (if CO_2 is excluded).

Using "net alkalinity" (measured alkalinity – measured acidity) to design mine drainage treatment can lead to ineffective systems with insufficient alkalinity to neutralize metal and H^+ acidity. The use of (measured alkalinity – calculated acidity) is recommended in the planning of mine drainage treatment.

Mine drainage and other waters can have both alkalinity <u>and</u> acidity -
not mutually exclusive

Acidity sources in mine drainage:

- **Metal acidity: $Fe^{3+} + H_2O = FeOH^{2+} + H^+$**
- **H^+ acidity: “free” H^+ in solution**
- **CO_2 acidity: $CO_2 + H_2O = H_2CO_3$**

Alkalinity sources in mine drainage:

- **Carbonates: $CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$**
- **Sulfate reduction: $2CH_2O + SO_4^{2-} = H_2S + 2HCO_3^-$**

What we hope to show:

Acidity is underestimated by standard method titrations because alkalinity present in samples reacts with acidity before or during titration

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+$$
$$H^+ + HCO_3^- = H_2CO_3$$

$$Fe^{3+} + H_2O + HCO_3^- = FeOH^{2+} + H_2CO_3$$

Alk from sample consumed in Acidity titration, but counted in Alk titration

Acidity driven off as CO_2 in Std Method, not counted

Why is this important?

- Design of treatment systems using standard methods for alkalinity and acidity can result in inadequate treatment of AMD
- Example

Fe(II)	Alk_{meas}	$\text{Acidity}_{\text{meas}}$	$\text{Acidity}_{\text{calc}}$	Net Alk Use meas acidity	Net Alk Use calc acidity
20	66	-18 (or 0)	44	84 (or 66)	22

  - pH of this sample drops to 4.5 with aeration
  - Lab result suggests (incorrectly) that no base is needed for treatment

OBJECTIVES

- Examine theory and practice of alkalinity and acidity measurements
- Examine calculation and use of “net alkalinity”

HYPOTHESES

- Standard Method (APHA) and EPA acidity measurements underestimate metal acidity in samples containing alkalinity
- Net Alkalinity = (alk-acidity) based on above is not correctly interpreted
- Should use ($\text{alk}_{\text{measured}}$ - $\text{acidity}_{\text{calculated}}$) = net alkalinity

Table 1. Summary of alkalinity and acidity definitions. Print out or choose “Slide Show” for better viewing.

Derivation of definition	Source	Definition	Negative values?	Comments
		Theoretical Alkalinity		
Charge balance (electroneutrality)	Drever, 1997	Sum (conservative cations) - sum (conservative anions) = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$	yes	Primarily H_2O-CO_2, can be extended to other species
Charge balance	Geotechnical Services, 1982	$[HCO_3^-] - ([H^+] + [HSO_4^-] + 3[Al^{3+}] + 2[AlOH^{2+}] + [Al(OH)_2^+] + 3[Fe^{3+}] + 2[FeOH^{2+}] + [Fe(OH)_2^+] + 2[Fe^{2+}] + [FeOH^+])$	yes	Reference conditions differ from definition immediately below
Proton condition (charge and mass balance)	Parkhurst, 1995	PHREEQC definition; similar to above; but metals are assigned different alkalinities than above based on reference conditions, e.g., $Fe^{2+} = 0$, $Fe^{3+} = -2$	yes	Consistent with Morel and Hering, 1993; Stumm and Morgan, 1996
		Laboratory Alkalinity		
Titration	Stumm and Morgan, 1996	"equivalent sum of the bases that are titratable with strong acid"; does not include H+ or some other negative contributions to alkalinity	no	Does not measure negative alkalinity; endpoints should be adjusted for total carbon
		Theoretical Acidity		
Practical; based on charge balance	Hedin et al., 1994	$50[(2Fe^{2+}/56) + (3Fe^{3+}/56) + (3Al/27) + 2Mn/55 + 1000(10^{-pH})]$; metals in mg L^{-1}	no	Suggested for pH < 4.5
Proton condition	Stumm and Morgan, 1996	Mineral acidity = $[H\text{-}Acy] = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-]$	yes	Primarily H_2O-CO_2; consistent with many texts
Proton condition	Stumm and Morgan, 1996	CO_2-acidity = $[CO_2\text{-}Acy] = [H_2CO_3^*] + [H^+] - [CO_3^{2-}] - [OH^-]$	yes	Primarily H_2O-CO_2; consistent with many texts
Practical; based on charge balance	Langmuir, 1997	Example total acidity for acid mine drainage: $[H^+] + [HSO_4^-] + 2[Fe^{2+}] + 3[Fe^{3+}] + 2[FeOH^{2+}] + 3[Al^{3+}]$	no	Not for mine drainage with significant positive alkalinity
Practical; based on charge balance	Drever, 1997	Example acidity for Al-rich water: $[H^+] - [HCO_3^-] + 3[Al^{3+}] + 2[AlOH^{2+}] + [A(lOH)_2^+] - [Al(OH)_4^+]$	yes	Ignores CO_3^{2-} and OH^-; can be modified for Fe species
		Laboratory Acidity		
Titration	Stumm and Morgan, 1996	"equivalent sum of the acids that are titratable with strong base"; standard titration methods	Yes, *if lab reports negative values*	Excludes acidity due to CO_2; allows HCO_3^- consumption

Note that theoretical alkalinity values can have negative values due to [H+], but lab alkalinities cannot have negative values.

Note that lab acidity values can be negative, but many labs (*e.g.*, PA DEP; Wilson, pers. comm.) do not report negative values.

METHODS

- **Nature of samples**
  - **10 Synthetic AMD samples ± Fe, ± Al, ± Mn**
    - **pH ˜ 3, oxic**
    - **pH ˜ 6.3, anoxic**
    - **pH ˜ 7, anoxic**
    - **pH 5 & 6, anoxic with CO_2**
  - **5 Field AMD samples**
    - **pH ˜ 3, oxic**
    - **pH ˜ 4.5-6, anoxic with CO_2**
    - **pH ˜ 7, anoxic with CO_2**

METHODS, cont.

Alkalinity Titrations

- Alk1: Std. Method
  - titrate with H_2SO_4 to pH 4.5
- Alk2: H_2O_2
  - add H_2O_2 to oxidize metals
  - titrate with H_2SO_4 to pH 4.5
- Alk3: stored H_2O_2
  - add H_2O_2 to oxidize metals
  - store 1 week open to atmosphere
  - titrate with H_2SO_4 to pH 4.5

Acidity Titrations

- Acid1: Std. Method
  - if pH = 4.5, add H_2SO_4 to pH 4
  - add H_2O_2 to oxidize metals
  - boil 2-5 minutes, allow to cool
  - titrate with NaOH to pH 8.3
- Acid2: H_2O_2
  - add H_2O_2 to oxidize metals
  - titrate with NaOH to pH 8.3
- Acid3: stored H_2O_2
  - add H_2O_2 to oxidize metals
  - store 1 week open to atmosphere
  - titrate with NaOH to pH 8.3
- Acid4: N_2-purge, H_2O_2
  - bubble N_2 to displace CO_2
  - add H_2O_2 to oxidize metals
  - titrate with NaOH to pH 8.3

METHODS, cont.

PHREEQC modeling

- The geochemical computer code PHREEQC (Parkhurst, 1995) was used to model selected synthetic mine waters which were initially anoxic and contained alkalinity. Charge balance was maintained by adjusting SO_4^{2-} concentrations.

- The first step in modeling was to calculate equilibrium concentrations for the anoxic, CO_2-free solution based on measured metal concentrations (all iron and manganese were assumed to be Fe(II) and Mn(II), respectively) and pH.

- For sample SYN7, the P_{CO2} was estimated by running the model iteratively until the measured pH was reproduced.

- In step 2 or 3, the addition of H_2O_2 was modeled by allowing the solution to equilibrate with atmospheric O_2. In steps 3 or 4, the solution was allowed to equilibrate with respect to amorphous $Fe(OH)_3$ or crystalline MnO_2 solids.

- The modeling was designed to simulate reactions that occur due to the addition of H_2O_2 and degassing of CO_2 during titrations; it does not simulate the addition of acid or base during titrations.

Std. Method Acidity (Acid1 method) can be negative:

$$\text{SM acidity} = \frac{(\text{eq base/L}) - (\text{eq acid/L})}{\text{volume of sample}}$$

but labs often report a negative value as zero.

Calculated acidity, mg/L as $CaCO_3$

$= 50\ (\ 3\ \text{Fe(III)}/56 + 2\ \text{Fe(II)}/56 + 3\ \text{Al}/27$

$+ 2\ \text{Mn(II)}/55 + 1000(10^{-pH})\ )$

may be extended to include species such as H_2CO_3, $FeOH^{2+}$ and others

Table 2. Synthetic AMD compositions

		Concentration, mg/L				Calc. acidity,	
#	pH	Fe(II)	Fe(III)	Al	Mn(II)	mg/L as CaCO3	gasses
1	2.8	0	56	0	0	231	oxic
2	3.0	0	0	54	0	353	oxic
3	6.1	117	0	0	0	210	anoxic
4	6.0	91	0	0	0	163	anoxic
5	7.2	40	0	0	20	107	anoxic
6	6.6	0	0	0	19	34	anoxic
7	7.0	0	0	0	0	33	anoxic, add CO_2
8	5.5	85	0	0	0	152	anoxic, add CO_2
9	6.7	85	0	0	0	151	anoxic
10	4.1	0	0	0	18	38	anoxic

Table 3. Field AMD compositions

		Concentration, mg/L				Calc. acidity,	DO, mg/L
Site #	pH	Fe(II)	Fe(III)	Al	Mn(II)	mg/L as CaCO3	
8	3.6	0.4	0.6	17	2	114	9
23	3.4	7.2	3.3	7.6	6.9	96	< 0.3
51	5.4	67	2.7	0.06	6.6	139	< 0.3
20	5.7	23	1.4	0.04	3.5	51	0.9
49	5.9	19	1.2	0.03	3.0	44	< 0.3

Table 4. Field & Synthetic AMD titration results - all in mg/L as $CaCO_3$

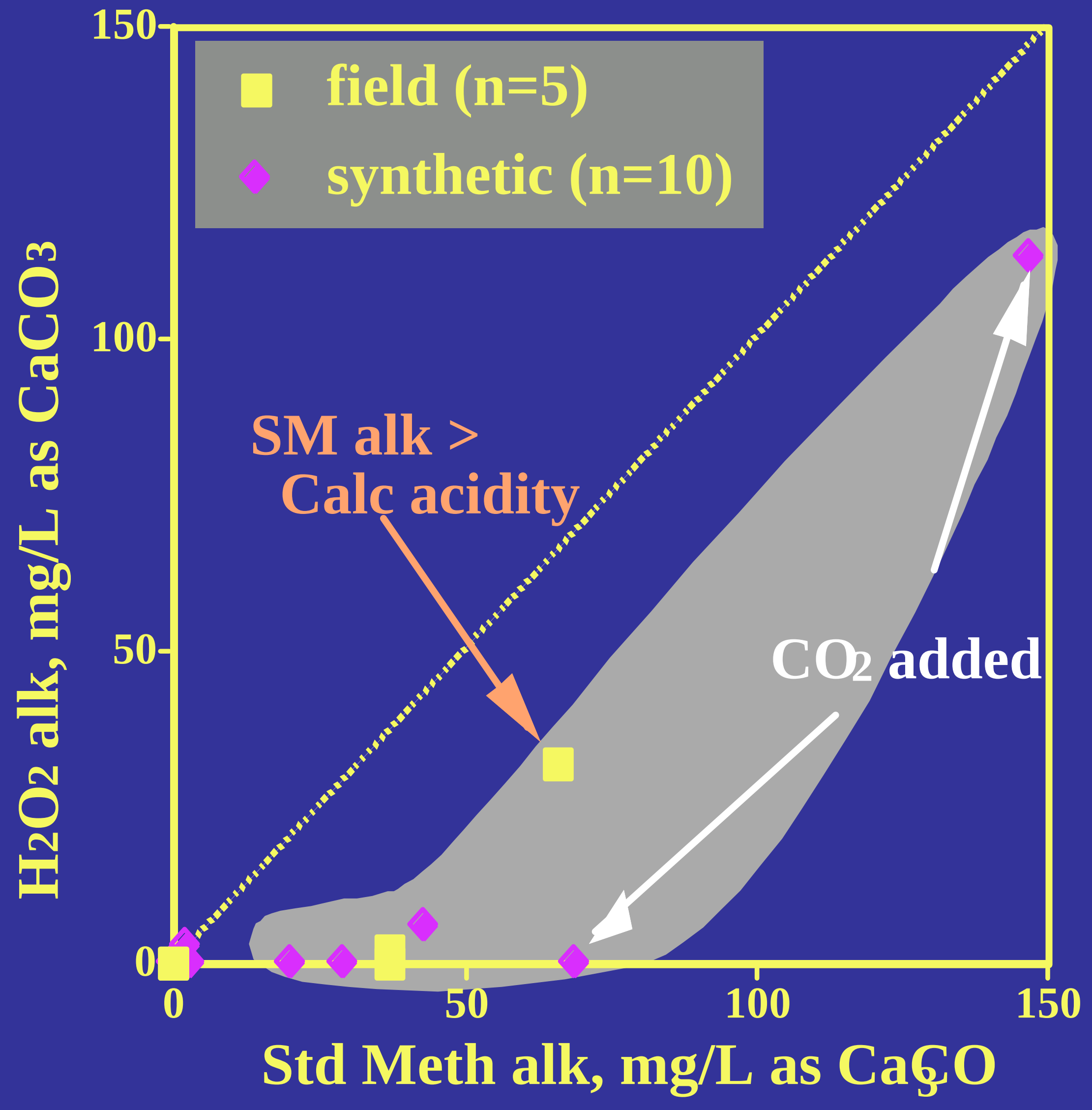
Sample	SM alk	H_2O_2 alk	Stored H_2O_2 alk	SM acidity	H_2O_2 acidity	Stored acidity	N_2-purge acidity
Site 8	0	0	0	105	95	125	113
Site 23	0	0	0	105	172	149	94
Site 51	37	0	0	128	283	223	138
Site 20	37	2	2	30	144	25	23
Site 49	66	32	29	-18	116	78	13
SYN1	0	0	0	235	nd	249	nd
SYN2	0	0	0	382	nd	379	nd
SYN3	3	0	0	217	225	214	nd
SYN4	20	0	0	103	118	87	nd
SYN5	43	6	4	36	61	34	nd
SYN6	2	3	3	27	32	38	nd
SYN7	147	113	112	-104	190	0	22
SYN8	69	0	0	79	737	75	130
SYN9	29	0	0	118	140	119	nd
SYN10	0	0	0	33	34	41	nd

Have Alk

Have Alk

Note negative values for acidity, which would usually not be reported; such negative values only occur in samples containing alkalinity.

Figure 1. Comparing Alkalinity Methods

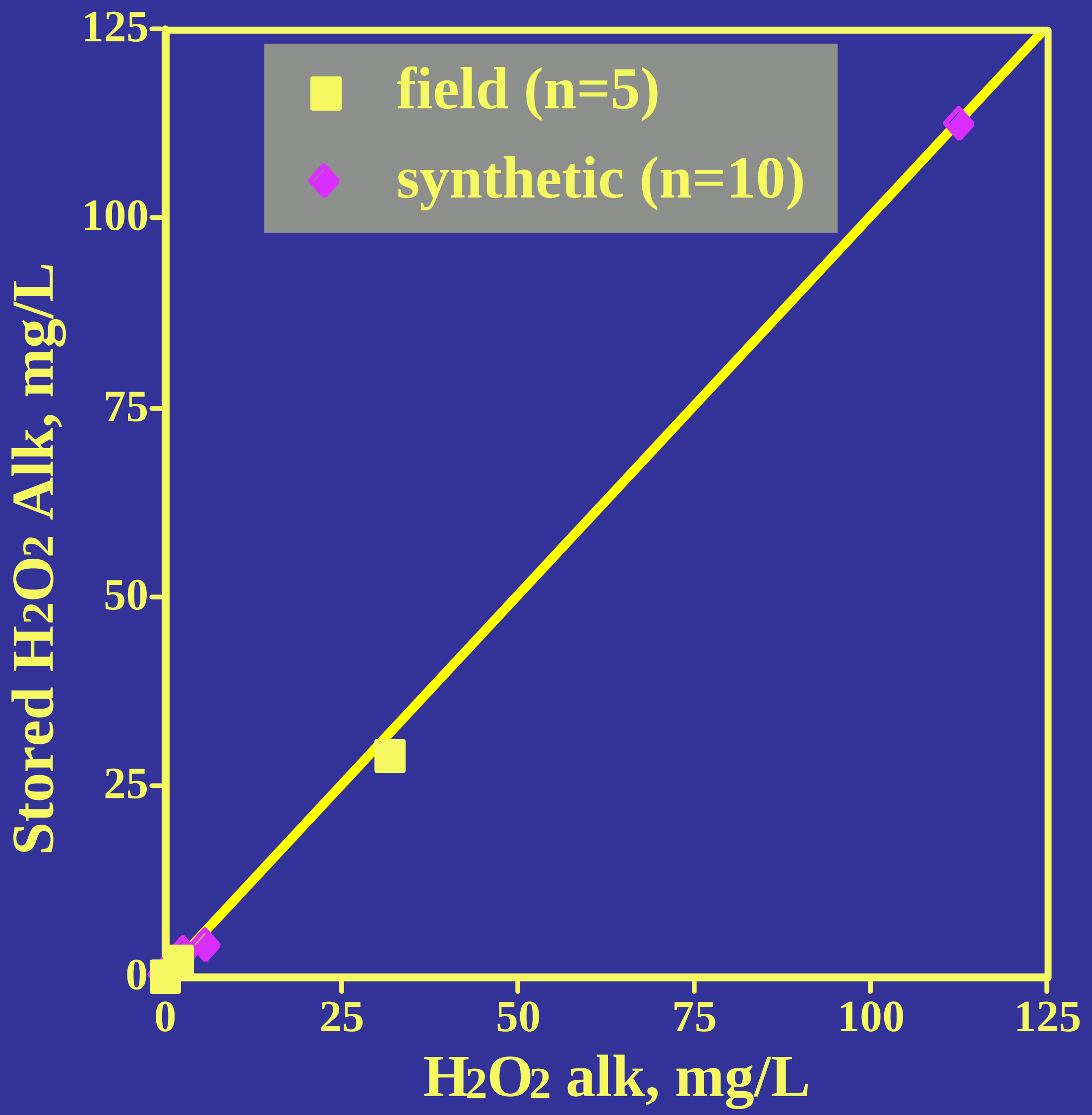


Samples in shaded area all have alkalinity which neutralizes acidity

Addition of H_2O_2 mimics oxidatioin during sample storage; results show that storage can lower measured alkalinity

Diagonal line shows where x-axis value = y-axis value.

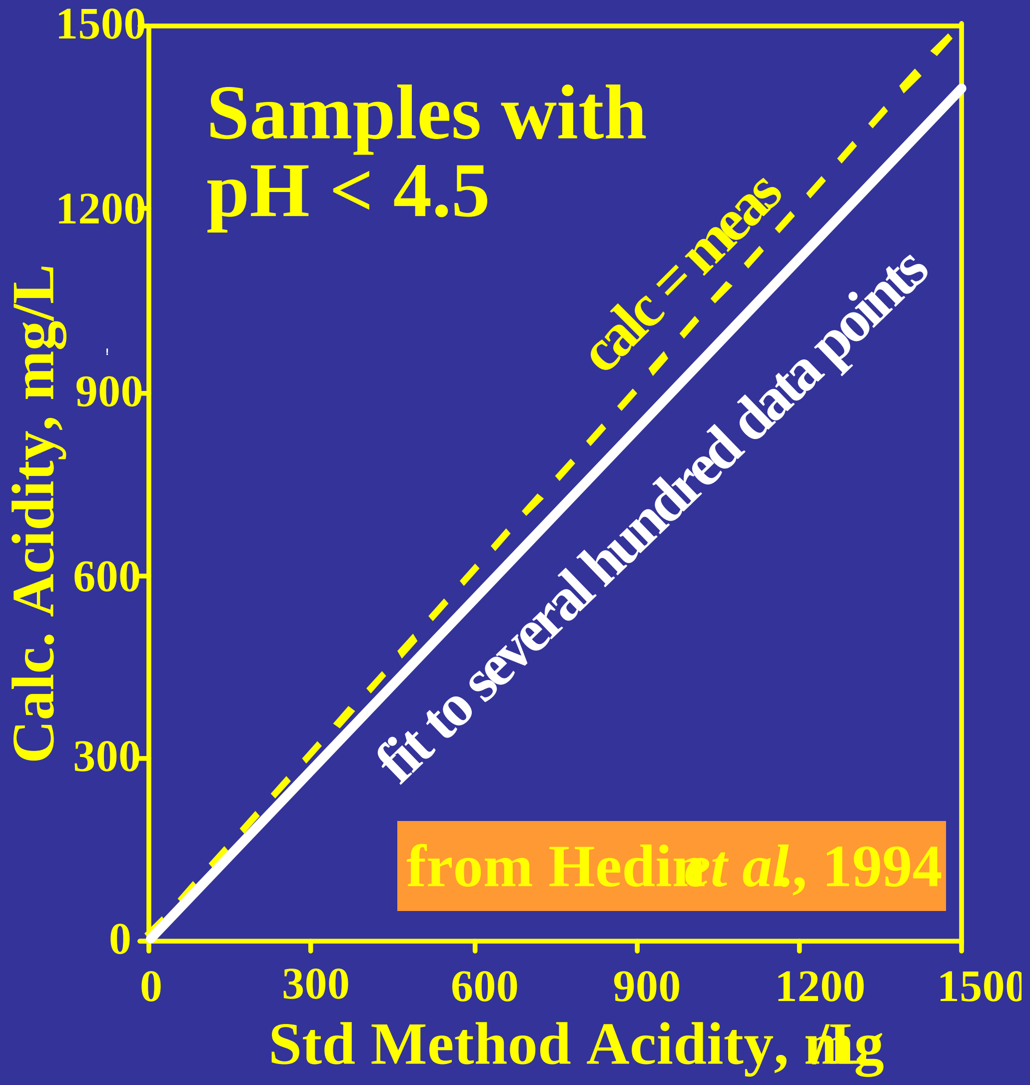
Figure 2. Comparing Alkalinity Methods



Stored H_2O_2 alkalinity returns same value as non-stored H_2O_2 alkalinity; suggests that oxidation of metals is rapid upon H_2O_2 addition

Diagonal line shows where x-axis value = y-axis value.

Figure 3. Calculated *vs* Std Method Acidity for low-pH samples

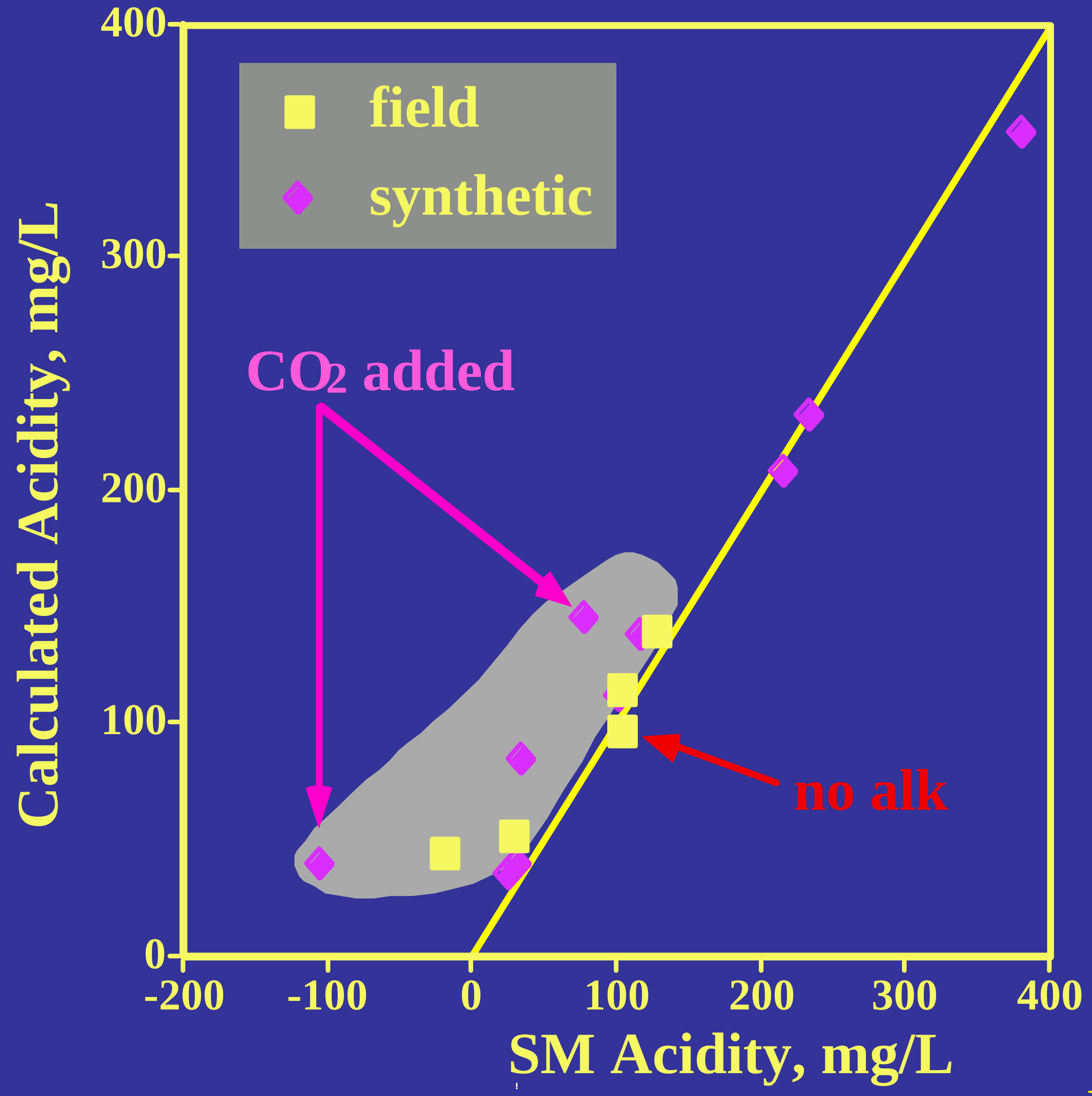


from Hedin *et al*, 1994

Only small discrepancies between Std Method Acidity and calculated acidity for low-pH samples

Diagonal yellow line shows where x-axis value = y-axis value.

Figure 4. Calculated *vs* Std Method Acidity



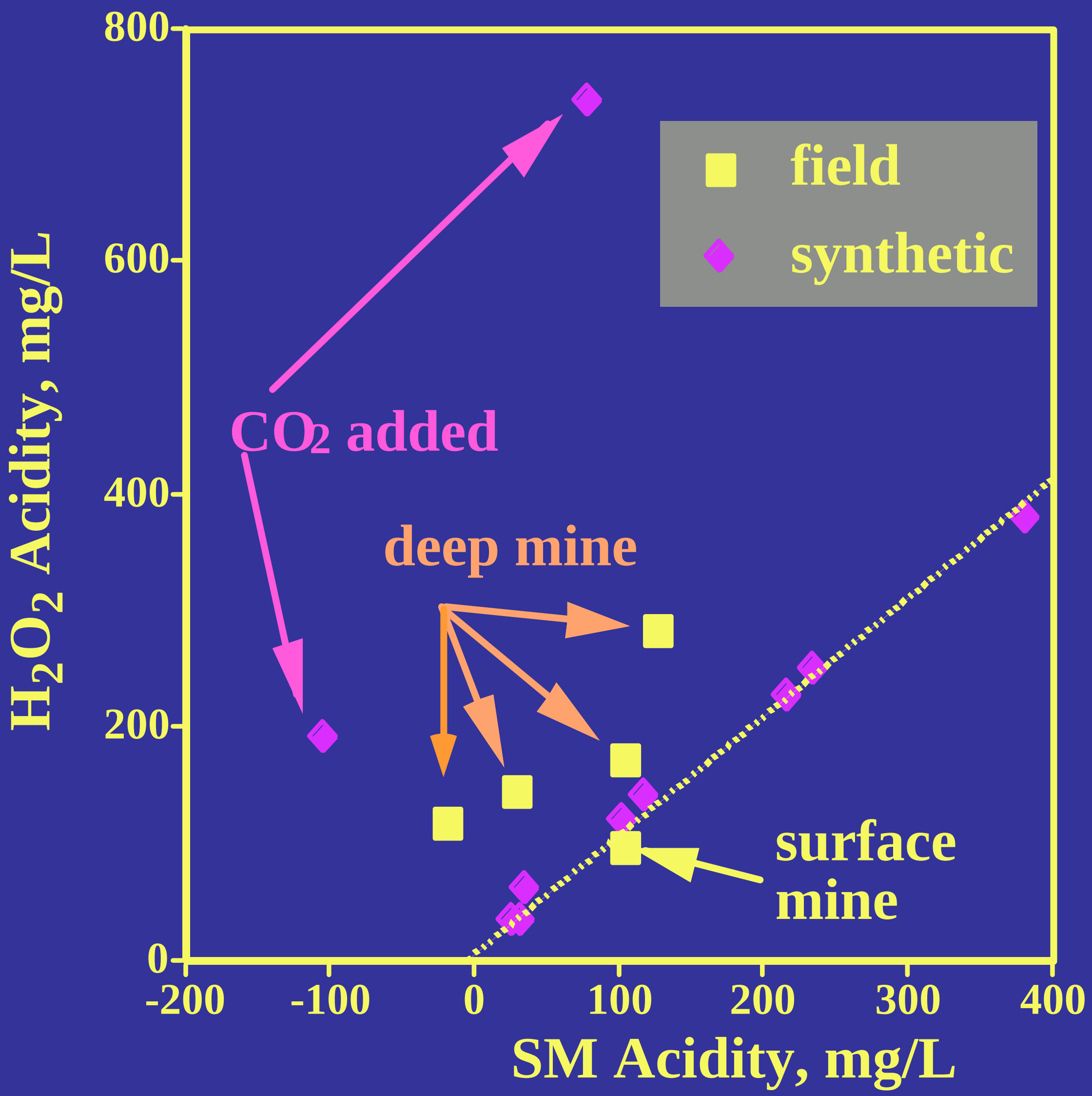
Shaded samples have Calc > SM acidity due to alkalinity that neutralizes acidity during titration

Standard Method can underestimate acidity in samples containing acidity

Degassing of CO_2 can explain discrepancies for some, but not all samples

Diagonal line shows where x-axis value = y-axis value.

Figure 5. H_2O_2 *vs* Std Method Acidity

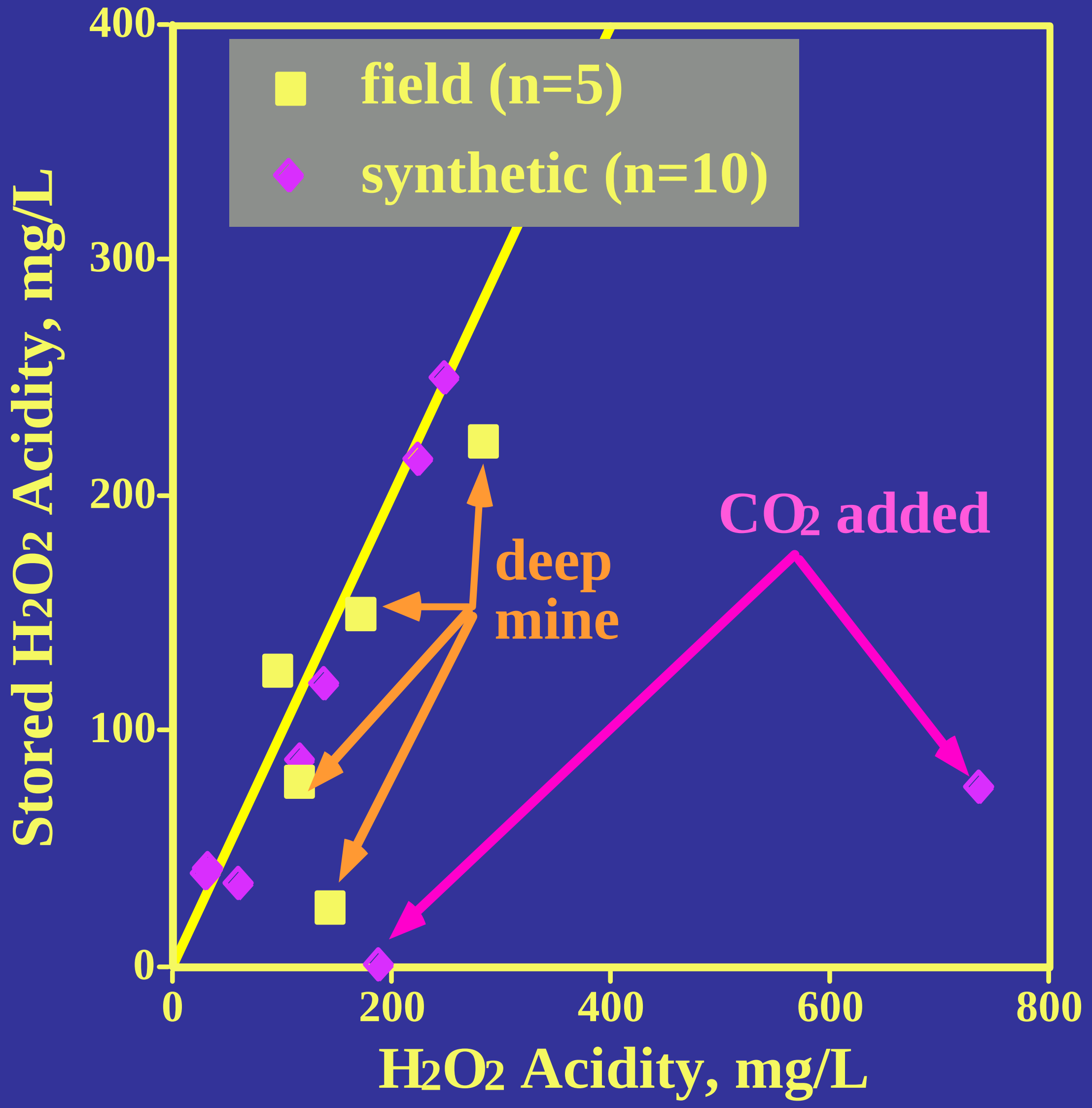


Non-stored H_2O_2 method "counts" acidity due to CO2

Std Meth intentionally does not measure acidity due to CO_2

Diagonal line shows where x-axis value = y-axis value.

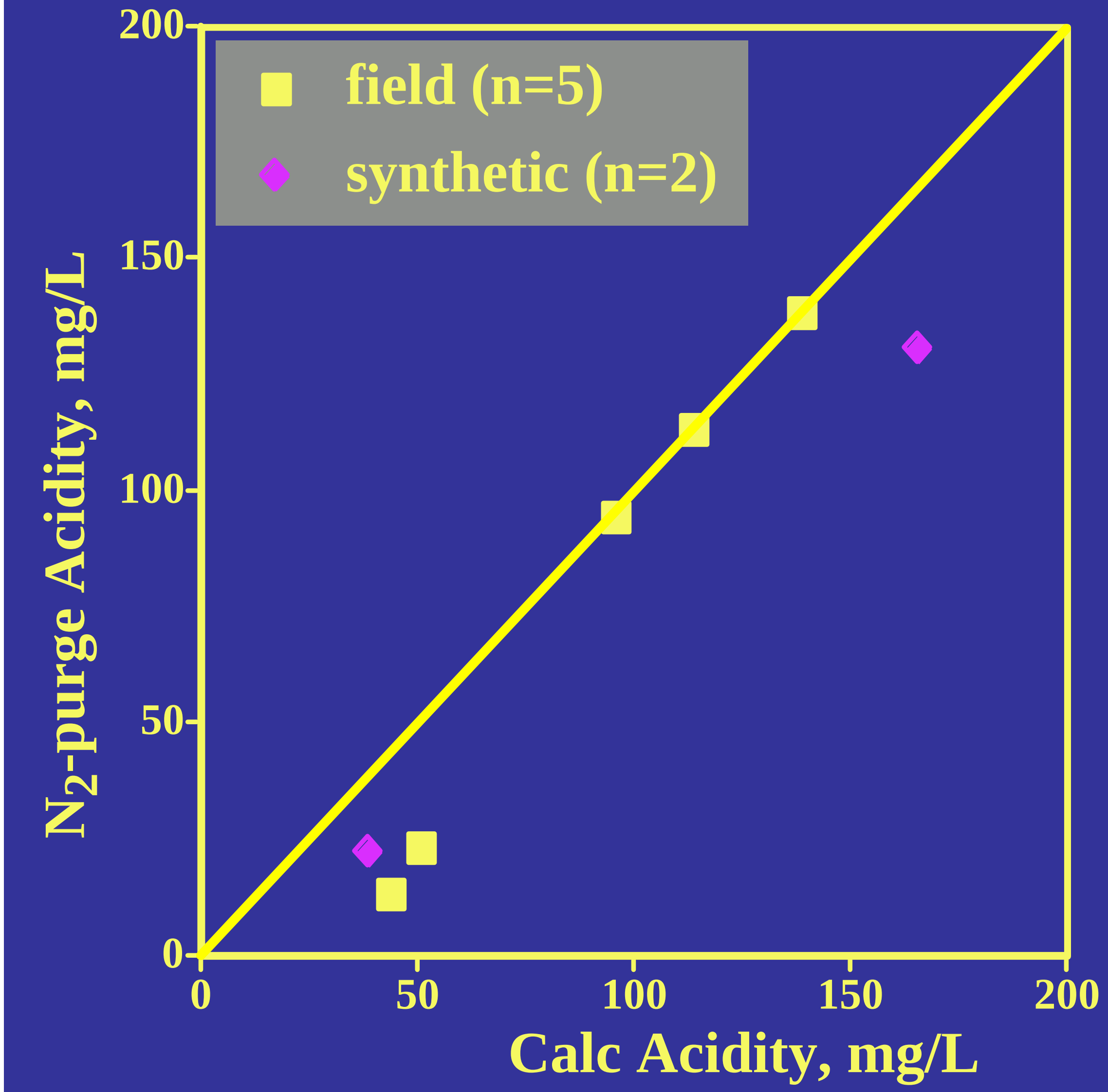
Figure 6. Stored H_2O_2 Acidity vs H_2O_2 Acidity



Storage allows CO_2 to degas, reducing acidity

Diagonal line shows where x-axis value = y-axis value.

Figure 7. N_2-purge *vs* Calculated Acidity



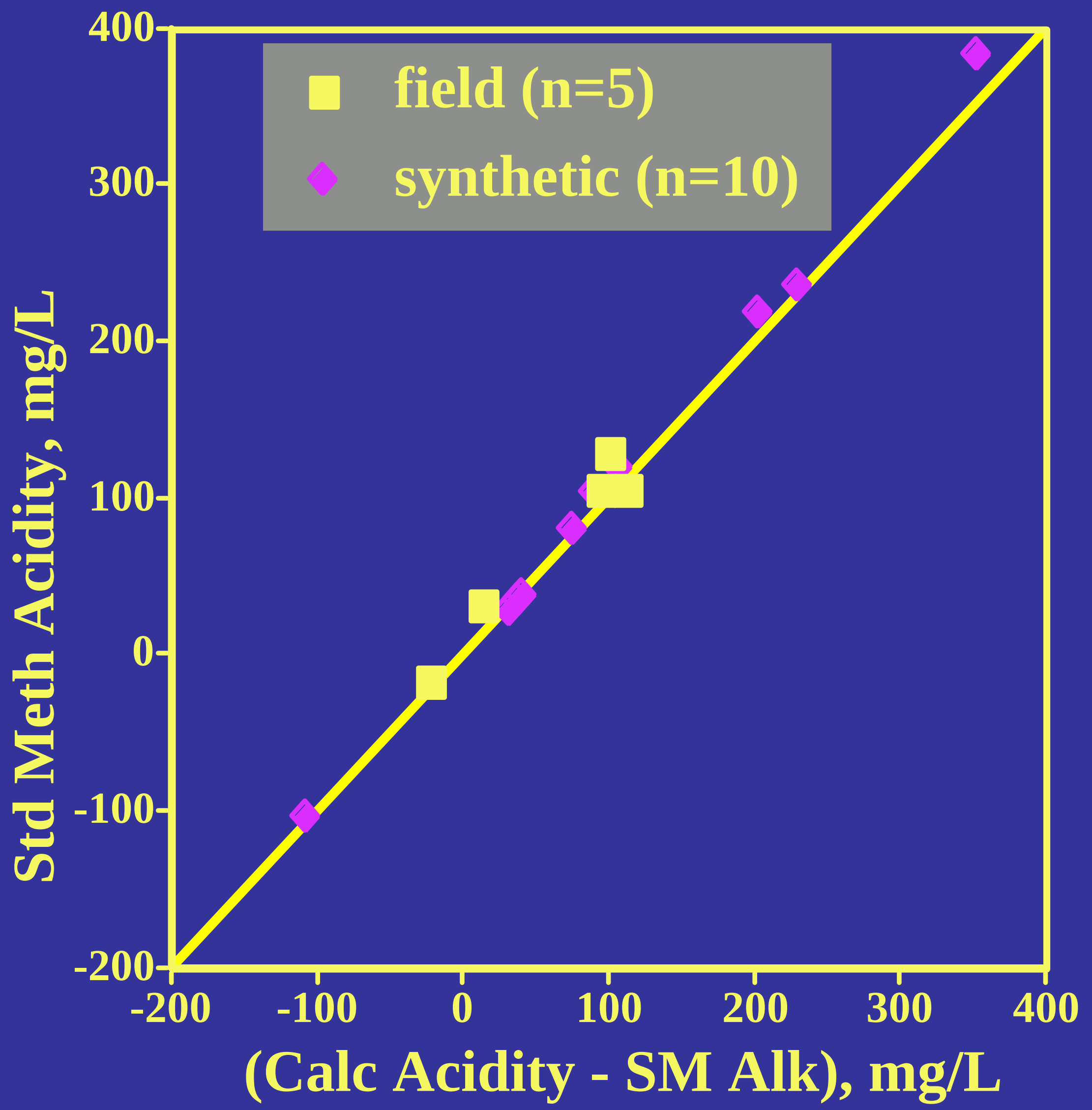
N_2-purge

1) causes pH increase

2) removes CO_2

3) underestimates acidity in samples containing alkalinity

Figure 8. Std Method Acidity *vs* Net Acidity



Std Method Acidity is actually a measure of "net acidity", which can have a negative value

- **CO_2 ignored**
- **Alkalinity in sample allowed to consume some acidity**

Comparison of alkalinity methods to PHREEQC simulations - print out for better viewing

Table 5 shows results of PHREEQC simulations carried out for three synthetic samples and compares the simulation results to measured alkalinity and pH. These examples serve to illustrate the expected changes in solution composition prior to titration, *i.e.*, upon CO_2 degassing, oxidation (saturation with O_2), metal hydrolysis, and precipitation of iron or manganese (solution is allowed to reach saturation with amorphous $Fe(OH)_3$ or pyrolusite, MnO_2). These calculations do not include simulated addition of NaOH to the solutions. SYN 3 contained iron as the only metal, and it had low alkalinity. SYN 5 contained iron and manganese and had significant alkalinity. SYN7 contained iron, had significant alkalinity, and also had CO_2 introduced in stage 2. The measured pH values for stages 1 or 2 were recorded before titrations began. The measured pH values for stages 3 or 4 were recorded after addition of H_2O_2 and metal oxidation/precipitation, but before any addition of NaOH.

In a physical experiment, oxidation will unavoidably be accompanied by precipitation. The simulation results in Table 5 show that the pH decreases upon oxidation alone. This decrease results from the combined effects of oxidation

$$Fe^{2+} + 0.25\ O_2 + H^+ = Fe^{3+} + 0.5\ H_2O, \qquad \text{(A)}$$

which raises pH, and hydrolysis in reactions such as

$$Fe^{3+} + 2\ H_2O = Fe(OH)_2^+ + 2\ H^+, \qquad \text{(B)}$$

which lowers pH. Prior to oxidation in the simulations, the predominant aqueous iron species was Fe^{2+}. Following oxidation, $Fe(OH)_2^+$ and $FeOH^{2+}$ were the predominant aqueous iron species. Bicarbonate alkalinity also decreases.

Following oxidation, iron is allowed to precipitate in the simulation, which further lowers pH as in the following reaction

$$Fe(OH)_2^+ + H_2O = Fe(OH)_{3,\ s} + H^+. \qquad \text{(C)}$$

Two calculated alkalinities are given in Table 5 as follows. The first alkalinity value, calculated by PHREEQC, assigns negative values to H^+, HSO_4^-, and some metal species; these assignments are based on reference conditions for pH 4.5 (Parkhurst, 1995). For example, Fe^{3+} is assigned an alkalinity of -1 eq kg^{-1}, whereas Fe^{2+} is assigned an alkalinity of zero. The second value is calculated based on the PHREEQC speciation, but does not assign alkalinities to metal species. In contrast to the measured values, negative values for alkalinity can and do result from the simulations because both calculations include negative terms. For example, when H^+ exceeds HCO_3^- and other positive terms, the calculated alkalinity is negative.

Both of the calculated acidities are based upon the PHREEQC speciation, and both include negative contributions for species such as OH^-, HCO_3^-, and their complexes. The first calculated acidity includes a positive contribution of CO_2 (1 eq kg^{-1}) to acidity; the second calculated acidity ignores acidity due to CO_2.

continued next page

Table 5. PHREEQC results for SYN3, SYN5, and SYN7 compared to measured values. Calculated values are from PHREEQC simulations. Print out or choose “Slide Show” for better viewing.

	Stage of			Alkalinity, mg L^{-1} as $CaCO_3$			Acidity, mg L^{-1} as $CaCO_3$				Calculated	
sample	titration	meas. pH	calc. pH	meas	calc.[1] w/ metals	calc.[2], no metals	Std Meth	H_2O_2	calc.[3], w/ CO_2	calc.[4] , no CO_2	Fe(II), mg L^{-1}	Fe(III), mg L^{-1}
	1) anoxic	6.13	6.13	3	3	3			209	204	116	0
SYN3	2) oxidize	nd	3.72	nd	-101	-14			211	204	0	116
	3) Fe precip.	3.07	3.19	0	-141	-45	217	225	211	204	0	70
	1) anoxic	7.15	7.15	41	43	41			47	41	27	0
SYN5	2) oxidize	nd	6.02	nd	19	16			73	41	0	27
	3) Fe precip.	5.24	4.18	6	-4	-4			89	41	0	1
	4) Mn precip.	5.24	3.23	6	-40	-39	36	61	83	34	0	1
	1) anoxic, no CO_2	6.80	6.80	nd	145	142			82	36	22	0
SYN7	2) anoxic, $P_{CO2} = 0.092$	6.10	6.10	147	145	142			132	-103	22	0
	3) oxidize, $P_{CO2} = 0.092$	nd	6.00	nd	126	124			150	-106	0	22
	4) Fe precip. , $P_{CO2} = 0.092$	5.93	5.91	113	106	106	-104	190	167	-106	0	0

[1] Includes contribution by metal species
[2] No contribution by metal species
[3] Includes CO_2 contribution
[4] No CO_2 contribution

Note the significant discrepancies between measured and calculated alkalinities and between measured and calculated acidities. The consumption of HCO_3^- by acidity occurs before titrants are added.

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Comparison of alkalinity methods to PHREEQC simulations - print out for better viewing

The measured and calculated pH values for SYN3 and SYN 7 correspond well. The measured pH values for SYN5 were higher than calculated values; the simulation overestimates the pH decrease due to metal precipitation for this sample. The main point of this exercise is to model the decrease in acidity upon oxidation and metal hydrolysis/precipitation in samples that contain alkalinity, even before the addition of base in a titration begins. Both measured (H_2O_2) and calculated alkalinities decrease during these processes in an acidity titration, but the standard methods for measuring alkalinity do not allow metal oxidation/hydrolysis. Therefore, standard method alkalinity titrations reflect the total amount of positive alkalinity in a sample, but standard method acidity titrations underestimate the positive acidity due to metals in samples which contain alkalinity. Alternatively, one could argue that the Standard Method acidity titration returns a value consistent with theoretical definitions of acidity that include both positive and negative contributions to acidity and allow for negative acidity values.

The effect of CO_2 ingassing/degassing can be seen in the SYN5 and SYN7 results in Table 5. SYN7 is initially pH 6.8 before CO_2 addition, and the pH drops to 6.1 following CO_2 addition. Alkalinity is unaffected. The calculated acidity including CO_2 increases primarily due to the increasing H_2CO_3* and H^+ concentration as pH drops. In contrast, the calculated acidity excluding CO_2 decreases to negative values. The Standard Method acidity titration for SYN7 drives off CO_2, so this acidity is negative, whereas the H_2O_2 titration, which retains CO_2, remains positive and increases. The H_2O_2 acidity titration retains CO_2, so this acidity is positive. A similar pattern is observed in the SYN5 results.

Summary:

PHREEQC simulations confirm that

1) Acidity decreases upon oxidation & metal hydrolysis/precipitation in samples containing alkalinity

2) CO_2 degassing reduces acidity, but not alkalinity

3) Std Method alkalinity titrations reflect the total amount of positive alkalinity, but do not measure negative alkalinity

4) Std Method acidity titrations underestimate the positive acidity due to metals in samples which contain alkalinity

5) Std Method acidity titration returns a value consistent with theoretical definitions of acidity that include both positive and negative contributions to acidity and allow for negative acidity values

Buffer capacity

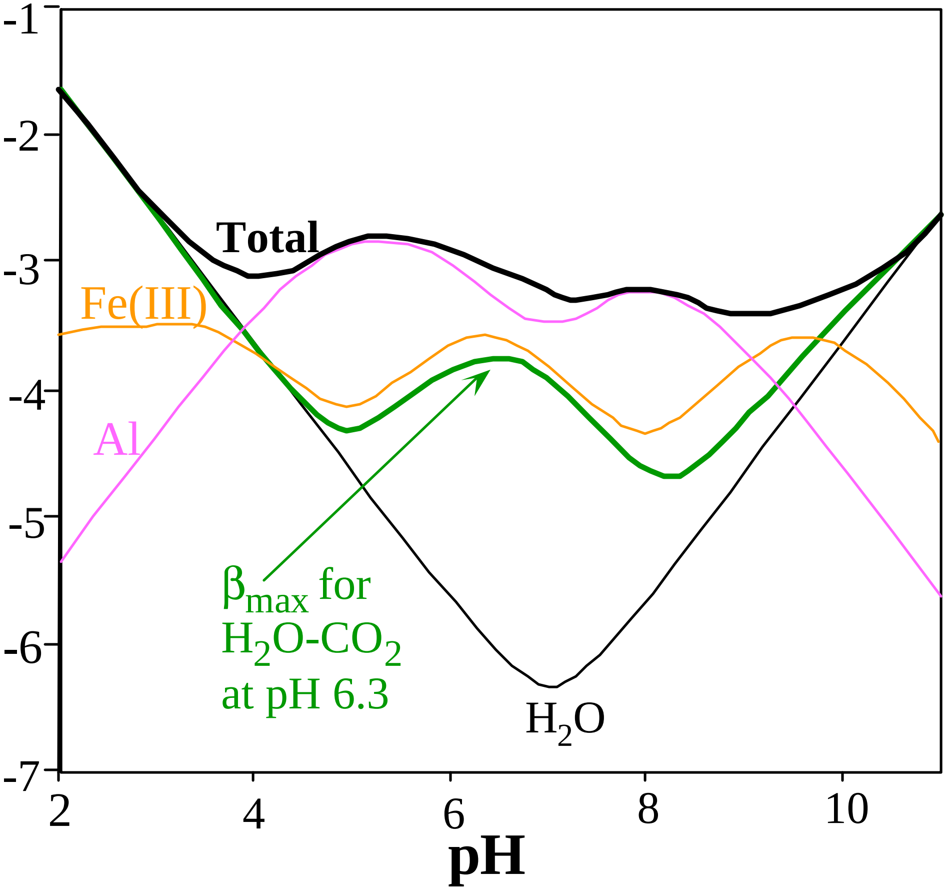
The buffer capacity is a measure of the resistance of a water or a water-rock system to changes in pH. To illustrate the impact of various aqueous species, buffer capacities (β) for H_2O, and CO_2 were calculated exactly as in Langmuir (1997), and $\beta_{Fe(III)}$ and $\beta_{Al(III)}$ were calculated after Langmuir using the equation

$$b_{Me} = 2.3\left\{\frac{K_1C_{Me}\left[H^+\right]}{\left(K_1+\left[H^+\right]\right)^2}+\frac{K_2C_{Me}\left[H^+\right]}{\left(K_2+\left[H^+\right]\right)^2}+\frac{K_3C_{Me}\left[H^+\right]}{\left(K_3+\left[H^+\right]\right)^2}\right\}$$

where K's are the first three stepwise association constants and [Me] is the total dissolved Fe(III) or Al(III) concentration. Because the association constants for $AlOH^{2+}$ and $Al(OH)_2^+$ are similar in value, this approximation introduces some error into the calculation. However, the calculated buffer capacities serve to illustrate the general ability of a water to resist changes in pH due to acid or base addition. Changing CO_2 or metal concentrations would also change the buffer capacities.

Figure 9 shows the individual and total buffer capacities due to water alone, water containing 10^{-3} mol L^{-1} CO_2 , and water with 25 mg L^{-1} Fe and Al. Below pH 4, most of the total buffer capacity is due to water alone. Above pH to 4 to the pH 8.3 titration endpoint, the total buffer capacity is due to a combination of CO_2 and metals. Two of the main goals for mine drainage treatment are to remove metals and leave some alkalinity in the effluent water. The buffer capacity of such an effluent that has reached equilibrium with the atmosphere would be governed by the shaded H_2O-CO_2 curve in Figure 9. Ideally the solution would have a pH = 6.3 because the CO_2 maximum occurs at $pK_1 = 6.3$, giving the solution considerable resistance to a decrease in pH due to further acid addition.

Buffering capacity due to H_2O-CO_2-metals



Metals alter the buffer capacity of a water.

A successfully treated water should have circumneutral pH and be buffered to pH near 6.3 by atmospheric CO_2 (green curve)

Figure 9. A plot of buffer capacity, b, for individual components and the total solution *versus* pH for the CO_2-H_2O system ($T_{CO2} = 10^{-3}$ mol L^{-1}) plus 25 mg L^{-1} Fe(III) and 25 mg L^{-1} Al. The arrow points to the maximum buffer capacity for a solution in which metals have been removed corresponding to pH = pK_1 for carbonic acid.

Recommendations

Standard Method acidity is consistent with theoretical acidities at pH values < 4.5 (Hedin et al. 1994). Such low pH samples will always have $\text{alkalinity}_{\text{measured}}$ equal to zero, and net alkalinities will thus be equal to the negative of the Standard Method acidity. These samples cause no problems in the interpretation of how much alkaline addition is required for treatment.

Using the standard method acidity titration, HCO_3^- is allowed to react with H^+ from metal hydrolysis in higher pH samples which contain alkalinity, but the standard method alkalinity titration does not allow these reactions. A falsely positive value for net alkalinity calculated as $\text{alkalinity}_{\text{measured}}$ - $\text{acidity}_{\text{measured}}$ will result in the incorrect conclusion that a water is net alkaline and can "treat itself" with no alkaline addition, given aeration and adequate retention time in a pond or wetland. For example, the Site 20 sample in this study (Tables 2 and 4) has a Standard Method alkalinity of 37 mg L^{-1} as $CaCO_3$ and a Standard Method acidity of 30 mg L^{-1}, giving a net alkalinity of +7 mg L^{-1}. However, following oxidation, precipitation of metals, and CO_2 degassing during storage, this water has a pH of 5.0, and iron oxidation at this pH would be very slow (Kirby et al., 1999). Calculation of net alkalinity as ($\text{alkalinity}_{\text{measured}}$ - $\text{acidity}_{\text{calculated,}}$ Hedin *et al*. 1994) gives a net alkalinity of -14 mg L^{-1}, suggesting that this water indeed requires alkaline addition for successful treatment.

The goals for mine water treatment include the removal of metals and the establishment of circumneutral pH and sufficient alkalinity to buffer pH against significant decreases. Citizens' watershed groups and regulatory agency personnel often face steep learning curves in their efforts to achieve inexpensive passive treatment for abandoned mine drainage. Although the hydrogen ion conservation approach (Morel and Hering, 1993, Stumm and Morgan, 1996; Johnson and Sigg, 1983) described above is the most rigorous approach, the calculation of net alkalinity as ($\text{alkalinity}_{\text{measured}}$ - $\text{acidity}_{\text{calculated,}}$) is much more easily applied and requires less geochemical background knowledge. In addition, this paper has demonstrated that this simpler approach is a significant improvement over the use of $\text{alkalinity}_{\text{measured}}$ - $\text{acidity}_{\text{measured}}$. Although many monitoring schemes only collect data for total or dissolved iron, this approach does require the speciation of iron into Fe(II) and Fe(III) species. Care must be taken to ensure that water samples for Fe(II) are either analyzed very quickly or preserved (0.02 µm filters, HCl) such that Fe(II) does not oxidize before analysis. For samples with pH values greater than approximately 5, it is possible to use dissolved iron as a reasonable proxy for dissolved Fe(II) concentrations in the absence of data for Fe(II).

An alternative approach to the calculation of net alkalinity is suggested by the fact that net acidity (the x-axis value in Fig. 8) is equal to the Standard Method acidity. *As long as negative values are reported by laboratories*, the negative of the Standard Method acidity can be used as a net alkalinity in treatment design. If this latter approach is used, no alkalinity need be measured, and the holding times for acidity samples may not be critical. ASTM Method D1067(92) (ASTM, 1998) states that time between sampling and analysis be "as short as practically possible" and that "essentially immediate analysis is desirable for those waters containing hydrolyzable salts that contain cations in several oxidation states." The oxidation, hydrolysis, and gas exchange reactions that the short holding times are designed to preclude will occur during a storage period and during a standard method acidity titration. It is likely that standard method acidity values on samples immediately analyzed and samples stored for weeks will be equal. Note that this study did not perform experiments to test this hypothesis.

What we hope to have shown:

Alkalinity present in samples reacts with acidity during

standard methods of titration

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+$$

$$H^+ + HCO_3^- = H_2CO_3$$

$$Fe^{3+} + H_2O + HCO_3^- = FeOH^{2+} + H_2CO_3$$

Alk from sample consumed in Acidity titration, but counted in Alk titration

Acidity driven off as CO_2 in Std Method, not counted

CONCLUSIONS

- Standard Method titrations give consistent results
- Standard Method (APHA & EPA) acidity measurements
  - underestimate CO_2 acidity (not necessarily a problem)
  - underestimate metal acidity (a problem)
- "Net Alkalinity" = (alk-acidity) based on Std Methods is not correctly interpreted & underestimates acidity - may result in inadequate treatment
- CO_2 driven off by Std Meth acidity, not by H_2O_2 method
- PHREEQC modeling supports these interpretations

RECOMMENDATIONS

- Avoid (SM alk - SM acidity) for treatment design
- Use (SM alk - calc acidity) for treatment design
  - requires Fe(II)/Fe(III) speciation from analysis, field pH, and other metal concentrations
- Or, use SM Acidity as a measure of Net Acidity, <u>provided that lab will report negative values</u>
- With the above, use pH of stored-H_2O_2 titration to give reasonable indication of pH of passively treated water

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