



NEVADA MODIFIED SOBEK PROCEDURE

SUMMARY¹

22 March 2019

The Nevada Division of Environmental Protection, Bureau of Mining Regulation and Reclamation (Division) has determined that the 2019 Update Nevada Modified Sobek Procedure (NMSP) is the only acceptable method for determination of acid neutralization/acid generation potential (ANP/AGP) and will not accept data from other methods without prior approval.

As part of the March 2019 update, the Net Acid Generation (NAG) Procedure Summary was removed from the NMSP since the Division has determined a separate NAG Procedure is necessary. Until the NAG Procedure is posted to the Division website, the current Nevada-approved laboratories shall continue to operate as approved and dictated in the Standard Operating Procedure (SOP) of the laboratories. The NAG Procedure is to aid in the determination of minerals known to result in a false acid generation positive from the NMSP i.e., barite, gypsum, alunite, or similar type minerals. Please contact the Division for further guidance and information.

The 2019 Update NMSP was created referencing the Montana State University Modified Sobek Procedure and the Sobek Procedure. The NMSP is more applicable for the geology found in Nevada. An overview of the NMSP is summarized below.

For all analyses, sample is pulverized to 95% minus 150 mesh.

Acid Neutralization Potential (ANP)

1. Pre-treatment with hydrogen peroxide (siderite correction ^{2,3})
2. If not running siderite correction, prior Division approval of mineralogical analysis is required.

Acid Generating Potential (AGP)

Alternative I

1. Total sulfur (%) reported as AGP as tons CaCO₃ per 1000 tons material (T/kT);
2. Paste pH;
3. Calculate Net Neutralization Potential (NNP) as ANP-AGP and determine ANP/AGP ratio. If ANP/AGP ratio is <1.2, sulfur speciation per Alternative II below and recalculation of ANP/AGP ratio is required, otherwise no further work is required.

Alternative II

1. Water-Soluble Sulfates (water soluble acid-forming sulfates, %) via calculation
2. Non-Water Soluble Sulfates (sulfate sulfur, %) via calculation
3. Pyritic Sulfur (%) via calculation
4. Non-Extractable Sulfur (%) via calculation

5. Calculate AGP from the Potential Acid Generating Sulfur. Potential Acid Generating Sulfur⁴ is the sum of Pyritic Sulfur content (AGP-PYR) and Water-Soluble Sulfate (S-SO₄ (H₂O)). Calculate NNP as ANP-AGP and determine ANP/AGP ratio.

Reporting of Analytical Results

The Division will require laboratories and Permittees (as applicable in reports) to use the same terminology as specified in this guidance.

All calculated values that report as non-detect shall be reported to the Division as the reportable limit value preceded by the “<” symbol.

For the purposes of calculations, any non-detect values for ANP and Total Sulfur shall be completed as ½ the reportable limit and any non-detect values for the Sulfur Species (the rinse residues) shall be completed using the value of zero.

Footnotes:

¹This document can be found on the Division website at:

<https://ndep.nv.gov/land/mining/regulation/guidance-policies-references-and-requirements>

² Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L. and Ziemkiewicz, P. (1997), *Neutralization Potential of Overburden Samples Containing Siderite*, Journal of Environmental Quality, v26, n3, p673-681

³Unless mineralogical analysis has been completed and documentation of the results of the mineralogical analysis has been submitted to the Division for review and approval, there is no definitive method for the laboratory to determine if ferrous iron is present. Therefore, unless otherwise approved, the siderite-corrected ANP procedure is required.

⁴ If barite, gypsum, alunite, or similar type minerals that have been known to result in false positive results from the NMSP for acid generation are thought to be present, the operator must provide either X-ray Powder Diffraction (XRD) or Scanning Electron Microscopy (SEM) analysis data and the appropriate NAG test data (single addition or sequential) in conjunction with the NMSP results. Until the NAG Procedure is posted by the Division, a summary of the Nevada-approved NAG Procedure can be found in:

Stewart, W., Miller, S., and Smart, R., *Advances in Acid Rock Drainage (ARD) Characterisation of Mine Wastes*, Paper presented at the 7th International Conference on Acid Rock Drainage (ICARD), March 26-30, 2006, St. Louis MO. R.I. Barnhisel (ed.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502.

References:

Montana State University, Reclamation Research Unit – Modified Sobek Method, p. A108-A128.

Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L. and Ziemkiewicz, P. (1997), *Neutralization Potential of Overburden Samples containing Siderite*, Journal of Environmental Quality, v26, n3, p673-681.

Sobek, A.A., Schuller, W.A., Freeman, J.R. and Smith, R.M. (1978), *Field and Laboratory Methods Applicable to Overburden and Minesoils*, EPA 600/2-78-054, 203pp.

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SIDERITE-CORRECTED ACID NEUTRALIZATION POTENTIAL

The siderite-corrected acid neutralization potential must be performed unless the Nevada Division of Environmental Protection, Bureau of Mining Regulation and Reclamation (the Division) has determined that siderite is not present in a given mine-specific rock type based on a Division-approved mineralogical analysis.

Principles

The amount of neutralizing bases, including carbonates, present in mined materials is found by treating a sample with a known excess of standardized hydrochloric acid. The sample and acid are heated to ensure that the reaction between the acid and the neutralizers goes to completion.

The calcium carbonate equivalent of the sample is obtained by determining the amount of unconsumed acid by titration with standardized sodium hydroxide.

Comments

A fizz rating of the neutralization potential is made for each sample to ensure the addition of sufficient acid to react all the calcium carbonate present.

During digestion, do not boil samples. If boiling occurs, discard sample and rerun. Before titrating with acid, fill burette with acid and drain completely. Before titrating with base, fill burette with base and drain completely to assure that free titrant is being added to the sample.

Chemicals

1. Carbon dioxide-free water: Heat distilled water just to boiling in a beaker. Allow to cool slightly and pour into a container equipped with ascarite tube. Cool to room temperature before using.
2. Hydrochloric acid (HCl) solution, 0.1 Normality (N), certified grade (Fisher So-A-54 or equivalent).
3. Sodium hydroxide (NaOH), approximately 0.5 N: Dissolve 20.0 grams (g) of NaOH pellets in carbon dioxide (CO₂) free water and dilute to 1.0 liter. Protect from CO₂ in the air with ascarite tube. Standardize solution by placing 50 milliliters (ml) of certified 0.1 N HCl in a beaker and titrating with the prepared 0.5 N NaOH until a pH of 7.00 standard units (SU) is obtained.

Calculate the Normality (N₂) of the NaOH using the following equation:

$$N_2 = (N_1 V_1) / V_2, \text{ where}$$

V₁ = Volume of HCl used, ml;

N₁ = Normality of HCl used;

V₂ = Volume of NaOH used, ml;

N₂ = Calculated Normality of NaOH.

4. NaOH, approximately 0.1 N: Dilute 200 ml of 0.5 N NaOH with CO₂-free water to a volume of 1.0 liter. Protect from CO₂ in air with ascarite tube. Standardize solution by placing 20 ml of certified 0.1 N HCl in a beaker and titrating with the prepared 0.1 N NaOH until a pH of 7.00 SU is obtained. Calculate the N of the NaOH.

- HCl, approximately 0.5 N: Dilute 42 ml of concentrated HCl to a volume of 1.0 liter with distilled water. Standardize solution by placing 20 ml of the known Normality NaOH prepared in a beaker and titrating with prepared HCl until a pH of 7.00 SU is obtained.

Calculate the Normality (N_1) of the HCl using the following equation:

$$N_1 = (N_2 V_2) / V_1, \text{ where}$$

V_2 = Volume of NaOH used, ml;

N_2 = Normality of NaOH used;

V_1 = Volume of HCl used, ml;

N_1 = Calculated Normality of HCl.

- HCl, approximately 0.1 N: Dilute 200 ml of 0.5 N HCl to a volume of 1.0 liter with distilled water. Standardize solution as before, but use 20 ml of the known Normality NaOH.
- HCl, 1 part acid to 3 parts water: Dilute 250 ml of concentrated HCl with 750 ml of distilled water.

Materials

- Flasks, Erlenmeyer, 250 ml;
- Burette, 100 ml (one required for each acid and one for each base);
- Hot plate, steam bath can be substituted;
- pH meter equipped with combination electrode;
- Balance, can be read to 0.01 gram;
- LECO (or equivalent) filterable and non-filterable crucibles;
- No. 40 Whatman or finer filter paper;
- Glass microanalysis vacuum filter holder(s) or equivalent.

Procedure

- Place approximately 0.5 grams of sample (95% minus 150 mesh) on a piece of aluminum foil;
- Add one or two drops of 1:3 HCl to the sample. The presence of CaCO_3 is indicated by a bubbling or audible "fizz";
- Rate the bubbling or "fizz" in step 2 as indicated in Table 2;

FIZZ RATING	HCl (ml)	HCl (NORMALITY)
0 - None	20	0.1
1 - Slight	40	0.1
2- Moderate	40	0.5
3 - Strong	80	0.5

Table 2: Volume and Normality of Hydrochloric Acid Used for Each Fizz Rating (from Sobek et al., 1978)

- Weigh 2.00 grams of sample (95% minus 150 mesh) into a 250 ml Erlenmeyer flask or equivalent;
- Carefully add HCl indicated by Table 2 into the flask containing sample;

6. Heat nearly to boiling, swirling flask every 5 minutes (min.), until reaction is complete. NOTE: reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask;
7. Add distilled water to make a total volume of 125 ml;
8. Gently boil contents of flask for one minute and cool to slightly above room temperature. Cover tightly and cool to room temperature. CAUTION: Do not place rubber stopper in hot flask as it may implode upon cooling;
9. Titrate using 0.1 N NaOH or 0.5 N NaOH (exact concentration known), to pH 7.0 SU using a calibrated electrometric pH meter and burette. The concentration of NaOH used in the titration should correspond to the concentration of the HCl used in step 5. NOTE: Titrate with NaOH until a constant reading of pH 7.0 SU remains for at least 30 seconds;
10. Add boiling chips to beaker and cover with watch glass;
11. Boil gently for 5 min. then allow to cool;
12. Vacuum or gravity filter contents using No. 40 Whatman or finer filter paper;
13. Add 5 ml of 30% hydrogen peroxide (H₂O₂) to the filtrate;
14. Boil gently for an additional 5 min. (with boiling chips and watch glass) then cool;
15. Titrate with standard NaOH to achieve and hold an endpoint pH of 7.0 SU;
16. If less than 3 ml of the NaOH is required to obtain a pH of 7.0 SU, it is likely that the HCl added was not sufficient to neutralize all base present in the 2.00 grams of sample. A duplicate sample should be run using the next higher volume or concentration of acid as indicated in Table 2;
17. Run a blank for each volume or Normality using steps 5, 7, 8, and 15.

Calculations

1. Constant (C) = (volume (ml) acid in blank) / (volume (ml) base in blank);
2. ml acid consumed = (volume (ml) acid added) - (volume (ml) base added x C);
3. ANP = (Tons CaCO₃ equivalent / thousand tons of material (T/kT)) =
(volume (ml) of acid consumed) x (25.0) x (N of acid).

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PASTE pH

Procedure

1. Mix one part solid to one part de-ionized (DI) water allowing capillary action to wet the sample (i.e. no stirring)
2. After the initial wetting, followed by mixing, add soil or water to near saturated conditions. Water should not be puddled nor dry soil appear at the surface. (At saturation, the soil paste glistens as it reflects light and the mixture slides off the spatula easily.)
3. Measure paste pH. Record pH of slurry in standard units (SU) to one decimal place, i.e. two significant figures.

NEVADA MODIFIED SOBEK PROCEDURE

ACID GENERATION POTENTIAL

Alternative I

Procedure for Total Sulfur

1. Weigh 0.500 ± 0.005 grams¹ (95% minus 150 mesh) of sample into non-filterable crucible;
2. Analyze for sulfur using LECO or equivalent combustion furnace;
3. Report as Total Sulfur, [S (T)].

Calculations

1. Convert Total Sulfur to CaCO₃ equivalents.
$$S(T) \times 31.25 = \text{tons CaCO}_3 \text{ equivalent}/1000 \text{ tons material}$$
2. Calculate Net Neutralization Potential (NNP) as ANP-AGP and determine ANP/AGP ratio. If ANP/AGP ratio is less than 1.2, sulfur speciation per Alternative II below and recalculation of ANP/AGP ratio is required. Otherwise, no further work is required.

Alternative II

Procedure for Sulfur Speciation

The following procedures assume laboratory knowledge and experience utilizing LECO or equivalent combustion furnace for analyses of sulfur. A LECO or equivalent combustion furnace analysis is the only acceptable procedure. The Division requires filtration, using either filterable crucibles or 25-millimeter (mm) vacuum filters, for sulfur speciation.

Procedure for Hot Water Extraction for Determination of Water-Soluble Sulfate

1. Weigh 0.500 ± 0.005 grams¹ (95% minus 150 mesh) of sample into a filterable ceramic crucible or vacuum filtering apparatus (glass microanalysis 25 mm vacuum filter holders or equivalent);
2. Add approximately 5 ml of near boiling deionized (DI) water to the sample in the crucible. Repeat until a total volume of 50 ml has been added;
3. If vacuum filtration is used, allow sufficient time between volume additions for the reaction to occur before applying vacuum. Otherwise, allow excess solution to drain freely;
4. Wash well with DI water (minimum 3 volumes) and vacuum filter or allow to drain freely;
5. Dry crucible and contents at 100°-105°C for at least 3 hours or until visibly dry;
6. When dry, analyze for sulfur using LECO or equivalent combustion furnace;
7. Report as Hot Water Rinse Residue, [S (H₂O)].

Procedure for Hydrochloric Acid (HCl) Extraction for Determination of non-Water Soluble Sulfate

1. Weigh 0.500 ± 0.005 grams¹ (95% minus 150 mesh) of sample into a filterable ceramic crucible or appropriate 25 mm vacuum filtering apparatus;
2. Add approximately 5 ml of near boiling 2:3 HCl to the sample in the crucible. Repeat until a total volume of 50 ml has been added;
3. If vacuum filtration is used, allow sufficient time between volume additions for the reaction to occur before applying vacuum. Otherwise, allow excess HCl to drain freely;
4. Wash well with DI water and vacuum filter or allow to drain freely. Repeat a minimum of six times to ensure complete removal of excess HCl or until rinsate tests clean for chlorides;
5. Dry crucible and contents at 100°-105°C for at least 3 hours or until visibly dry;

6. When dry, analyze for sulfur using LECO or equivalent combustion furnace;
7. Report as HCl Rinse Residue, [S (HCl)].

Procedure for Nitric Acid (HNO₃) Extraction for Determination of Pyritic Sulfur

1. Weigh 0.500 ± 0.005 grams¹ (95% minus 150 mesh) of sample into a beaker or suitable container;
2. Add 50 ml of 1:7 HNO₃ to the sample in the beaker;
3. Place sample(s) in a water bath at 80°-85°C for 8 hours;
4. Transfer entire contents of beaker, in appropriate aliquots, to a filterable crucible or appropriate 25 mm vacuum filtering apparatus and vacuum filter or allow excess HNO₃ to drain freely. Decanting of solution will invalidate results and is not an acceptable practice;
5. Wash well with DI water and vacuum filter or allow to drain freely. Repeat a minimum of six times to ensure complete removal of excess HNO₃ or until rinsate tests clean for nitrates;
6. Dry crucible and contents at 100°-105°C for at least 3 hours or until visibly dry;
7. When dry, analyze for sulfur using LECO or equivalent combustion furnace;
8. Report as HNO₃ Rinse Residue [S(HNO₃)].

Calculations

1. H₂O Soluble Sulfur [S-SO₄ (H₂O)] = Total Sulfur [S(T)] minus Hot Water Rinse Residue [S (H₂O)]
2. Non-H₂O Sulfate Sulfur [S-SO₄ (HCl)] = Hot Water Rinse Residue [S (H₂O)] minus HCl Rinse Residue [S(HCl)]
3. Pyritic Sulfur [S-PYR] = HCl Rinse Residue [S(HCl)] minus HNO₃ Rinse Residue [S(HNO₃)]
4. Non-Extractable Sulfur [S-HNO₃] = HNO₃ Rinse Residue [S(HNO₃)]
5. Calculate the Potential Acid Generating Sulfur [PAG(S)] by adding H₂O Soluble Sulfur [S-SO₄ (H₂O)] and Pyritic Sulfur [S-PYR]
6. Calculate Acid Generating Potential [AGP(T)] = Potential Acid Generating Sulfur [PAG(S)] x 31.25
7. Net Neutralizing Potential [NNP] = Acid Neutralizing Potential [ANP] minus Acid Generating Potential [AGP(T)]
8. ABA Ratio [ANP/AGP] = Acid Neutralizing Potential [ANP] divided by Acid Generating Potential [AGP(T)]

A table summarizing the calculations for both Alternative I and Alternative II is provided on the next page (page 9) in addition to a flow chart of the method on page 10.

Footnotes:

¹Use 0.500 ± 0.005 grams or the instrument manufacturer's maximum recommended weight to ± 0.005 gram precision. Laboratory must document the weight deviation through manufacturer specifications. Additionally, a reduced sample weight does not justify a reduced digestion volume – the 50 ml volume represents an excess acid volume and is required to ensure that reactions are complete. The leaching of sample volumes greater than 0.5 grams is not approved or allowed and the sub-sampling of a larger leached sample volume is not an acceptable practice.

**NEVADA MODIFIED SOBEK PROCEDURE
 CALCULATIONS TABLE**

Alternative I				
Results				
Parameter	I.D.	Units	Non-Detect Calculation Value	Reference/Notes
Paste pH		S.U.		
ANP		T/kT	½ Reportable Limit	Use siderite correction as applicable
Total Sulfur	S (T)	%	½ Reportable Limit	
Calculations				
Parameter	I.D.	Units	Formula	Reference/Notes
AGP from Total S	AGP (S)	T/kT	= S (T) * 31.25	
NNP		T/kT	= ANP – AGP (T)	
ANP/AGP			= ANP / AGP (T)	If this value is < 1.2:1, continue sulfur speciation per Alternative II below

Alternative II				
Results				
Parameter	I.D.	Units	Non-Detect Calculation Value	Reference/Notes
Paste pH		S.U.		
ANP		T/kT	½ Reportable Limit	Use siderite correction as applicable
Total Sulfur	S (T)	%	½ Reportable Limit	
Hot Water Rinse Residue	S (H ₂ O)	%	Zero	
HCl Rinse Residue	S (HCl)	%	Zero	
HNO ₃ Rinse Residue	S (HNO ₃)	%	Zero	
Calculations				
Parameter	I.D.	Units	Formula	Reference/Notes
Total Sulfur	S (T)	%		
H ₂ O-Soluble Sulfate	S-SO ₄ (H ₂ O)	%	= S (T) – S (H ₂ O)	
Non-H ₂ O Sulfate Sulfur	S-SO ₄ (HCl)	%	= S (H ₂ O) – S (HCl)	
Pyritic Sulfur	S-PYR	%	= S (HCl) – S (HNO ₃)	
Non-Extractable Sulfur	S-HNO ₃	%	= S (HNO ₃)	
Potential Acid Generating Sulfur	PAG (S)	%	= S-SO ₄ (H ₂ O) + S-PYR	
Calculated AGP	AGP (T)	T/kT	= PAG (S) * 31.25	
NNP		T/kT	= ANP – AGP (T)	
ANP/AGP			= ANP / AGP (T)	

Reminders/Requirements

- Mineralogical analysis must be included in the characterization documentation for all rock types which ANP/AGP <1.2.
- Acid Neutralizing Potential must be completed with the siderite-correction, unless otherwise approved by the Division.
- For Sulfur Species that return a value below the reporting limit (RL) shall be reported quantitatively by listing the RL value preceded by the “<” symbol and the value to be used in the calculations shall be zero.
- All associated laboratory analytical reports, including test results, test methods, chain-of-custody forms, and quality assurance/quality control documentation shall be included in an electronic format minimum with the report. Part II.E.5 of WPCP.

NEVADA MODIFIED SOBEK PROCEDURE FLOW CHART

