NEVADA DIVISION OF
ENVIRONMENTAL
PROTECTION

STATE OF NEVADA
Department of Conservation & Natural Resources

Bureau of Mining Regulation and Reclamation

NEVADA MODIFIED SOBEK PROCEDURE

6 January 2025

Summary

The Nevada Division of Environmental Protection, Bureau of Mining Regulation and Reclamation (Division) has determined that the 2024 Update Nevada Modified Sobek Procedure (NMSP) is the only acceptable acid base accounting (ABA) method for determination of acid neutralization/acid generation potential (ANP/AGP) in Nevada and will not accept data from other methods without prior approval.

The Nevada 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.

The Division has determined that Sulfur Speciation is the default procedure for ABA analysis. Unless prior approval has been granted, sulfur speciation will be required for acid generating potential, not total sulfur.

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

The Division has determined the pH of the extraction fluid, DI Water, used in this test method should reflect the pH of precipitation in the geographic region in which the mine rock is being evaluated," the Division has made the determination that the pH of rainwater in Nevada ranges between 5.5 and 6.0 SU.

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) Calculation

1. Total sulfur (%) reported as AGP as tons $CaCO_3$ per 1000 tons material (tons per kiloton, T/kT);
2. Paste pH;
3. Water-Soluble Sulfates (water soluble acid-forming sulfates, %) via calculation;
4. Non-Water-Soluble Sulfates (sulfate sulfur, %) via calculation;
5. Pyritic Sulfur (%) via calculation;
6. Non-Extractable Sulfur (%) via calculation;
7. Calculate AGP from the Potential Acid Generating Sulfur. Potential Acid Generating Sulfur[4] is the sum of Pyritic Sulfur content (AGP-PYR) and Water-Soluble Sulfate [$S\text{-}SO_4$ (H_2O)]. 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 proceeded 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:

1. This document can be found on the Division website at Regulation Branch Guidance Documents.
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.
3. Unless 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 NAG test data in conjunction with the NMSP results. The Nevada Modified NAG Test can be found on the Division's website.

Method Revisions:

Revision 00: March 2019, Net Acid Generation (NAG) Procedure Summary was removed

Revision 01: 2 November 2021; updates to clarify calculations

Revision 02: 22 July 2024, moved step 16 of the Acid Neutralizing Potential to Step 10. added clarification on the calculations of sulfur species, addition of centrifuge option; Addition of Reagents section, clarification/method for screening for residual chloride and nitrate following extraction; Paste pH – addition of analysis timeframe.

Revision 03: 6 January 2025, removal of the word 'near' in the paste pH method, and added ability to use other methods to screen for chlorides and nitrates. Added requirements for DI water.

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, p 673-681.

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.

MEND 1.20.1 Prediction Manual for Drainage Chemistry from Sulphidic Geologic Materials, pg. 403

NEVADA MODIFIED SOBEK PROCEDURE
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 (CO_2) free water and dilute to 1.0 liter. Protect from CO_2 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 (N_2) of the NaOH using the following equation:

   $N_2 = (N_1V_1) / V_2$, where

   V_1 = Volume of HCl used, ml;

   N_1 = Normality of HCl used;

   V_2 = Volume of NaOH used, ml;

   N_2 = Calculated Normality of NaOH.

4. NaOH, approximately 0.1 N: Dilute 200 ml of 0.5 N NaOH with CO_2-free water to a volume of 1.0 liter. Protect from CO_2 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.

5. 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:

   $N_1 = (N_2V_2) / V_1$, 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.

6. 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.
7. HCl, 1 part acid to 3 parts water: Dilute 250 ml of concentrated HCl with 750 ml of distilled water.

Materials

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

Procedure

1. Place approximately 0.5 grams of sample (95% minus 150 mesh) on a piece of aluminum foil;
2. 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";
3. Rate the bubbling or "fizz" in step 2 as indicated in Table 2.

Table 1: Volume and Normality of Hydrochloric Acid Used for Each Fizz Rating (from Sobek et al., 1978)

FIZZ RATING	HCl (ml)	HCl (NORMALITY)	REACTION EXPLANATION
0 None	20	0.1	None
1 Slight	40	0.1	Visible bubble that do not break quickly
2 Moderate	40	0.5	Visible bubbles that break quickly and are audible
3 Strong	80	0.5	Explosive/Vigorous reaction on impact

4. Weigh 2.00 grams of sample (95% minus 150 mesh) into a 250 ml Erlenmeyer flask or equivalent;
5. Run a blank for each volume or Normality using steps 6, 8, 9, and 16.
6. Carefully add HCl indicated by Table 1 into the flask containing sample;
7. Heat nearly to boiling, swirling flask every 5 minutes (min.), until reaction is complete. NOTE: the reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask;
8. Add distilled water to make a total volume of 125 ml;
9. 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;
10. 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;
11. 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 1;

Siderite Screening Procedure:

12. Add boiling chips to beaker and cover with watch glass;
13. Boil gently for 5 min. then allow to cool;
14. Vacuum or gravity filter contents using No. 40 Whatman or finer filter paper;
15. Add 5 ml of 30% hydrogen peroxide (H_2O_2) to the filtrate;
16. Boil gently for an additional 5 min. (with boiling chips and watch glass) then cool;
17. Titrate with standard NaOH to achieve and hold an endpoint pH of 7.0 SU;
18. If greater than 3 ml of the NaOH is required to obtain a pH of 7.0 SU, it is likely that there was a significant contribution to the sample acidity from siderite (or other minerals that were not oxidized during the initial digestion), and 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 1.

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 $CaCO_3$ equivalent / thousand tons of material [T/kT]) =

   (volume [ml] of acid consumed) x (25.0) x (N of acid).

NEVADA MODIFIED SOBEK PROCEDURE
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 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. Following sample saturation allow the sample to react for an hour, measure paste pH within 30 minutes after the hour of reaction. Record pH of slurry in standard units (SU) to one decimal place (i.e., two significant figures). Record the temperature of the paste pH as well.

NEVADA MODIFIED SOBEK PROCEDURE
ACID GENERATION POTENTIAL

The Division will require full sulfur speciation unless prior approval is granted for only analyzing for Total Sulfur. Even with Division approval to only analyze for Total Sulfur, if the ANP/AGP Ratio if less than 1.2 then sulfur speciation will be required.

Procedures

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.

Reagents

1. 2 parts HCl : 3 parts water .
2. 1 part HNO_3 : 7 parts water
3. Nessler's solution
4. 10% Silver Nitrate (purchased from vendor or made following 4.a)
   - 4.a. To make 0.1 N Silver Nitrate-Nitric Acid reagent ($AgNO_3 - HNO_3$): Using a 1 liter Class A volumetric flask, dissolve 17 grams $AgNO_3$ and 1 milliliter (mL) concentrated HNO_3 in ~900 mL deionized water. Bring to 1 liter with deionized water and mix thoroughly.

Procedure for Total Sulfur

1. Weigh 0.500 ± 0.005 grams[1] (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)].
4. If Total Sulfur [S (T)] is below the reporting limit, then sulfur speciation is not required.

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

1. Weigh 0.500 ± 0.005 grams[1] (95% minus 150 mesh) of sample into a filterable ceramic crucible or vacuum filtering apparatus (glass microanalysis 25 mm vacuum filter holders or equivalent) as appropriate to instrument manufacturer specifications;
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. Separate Solids from Liquid:
   a. Vacuum Filtration
      i. 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;
      ii. Wash well with DI water (minimum 3 volumes) and vacuum filter or allow to drain freely.

   b. Centrifuge method

      i. If centrifuge method is used, add 50 mL of water and bring to near boiling with a hot water bath. Allow the reaction to occur before removal from hot water bath. Shake the sample by hand and allow them to cool to room temperature, then centrifuge the tubes for 5 minutes at 3000 rpms and carefully decant the liquid.

4. Dry crucible and contents at 100º-105ºC for at least 3 hours or until visibly dry;
5. When dry, analyze for sulfur using LECO or equivalent combustion furnace;
6. Report as Hot Water Rinse Residue, [S (H_2O)].

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

1. Weigh 0.500 ± 0.005 grams[1] (95% minus 150 mesh) of sample into a filterable ceramic crucible or appropriate 25 mm vacuum filtering apparatus as appropriate to instrument manufacturer specifications.
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. Separate Solids from Liquid
   a. Vacuum filtration:
      i. 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;
      ii. 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;
      iii. Test leachate for chlorides by an appropriate method. For example: by adding 3 drops of 0.1 N AgNO3. The presence of chlorides will be detected by a white precipitate.
      iv. If a white precipitate appears, discard leachate and repeat Step 3.a.ii with 40mL of DI water until no precipitate forms
   b. Centrifuge method:
      i. If centrifuge method is used, add 50 mL of 2:3 HCl and bring to near boiling with a hot water bath. Allow the reaction to occur before removal from hot water bath. Shake the samples by hand and allow them to cool to room temperature, then centrifuge the tubes for 5 minutes at 3000 rpms and carefully decant the liquid.
      ii. Fill each tube to 40mL with DI water. Shake each tube to mix and then centrifuge at 3000 rpm for 5 minutes. Carefully decant the liquid.
      iii. Test leachate for chlorides by an appropriate method. For example: by adding 3 drops of 0.1 N AgNO3. The presence of chlorides will be detected by a white precipitate
      iv. If a white precipitate appears, discard leachate and add 40mL of DI water until no precipitate forms.
      v. Repeat 3.b.iii to remove the supernatant from the sample.

4. Dry crucible and contents at 100º to 105ºC for at least 3 hours or until visibly dry;
5. When dry, analyze for sulfur using LECO or equivalent combustion furnace;
6. Report as HCl Rinse Residue, [S (HCl)].

Procedure for Nitric Acid (HNO_3) Extraction for Determination of Pyritic Sulfur

1. Weigh 0.500 ± 0.005 grams[1] (95% minus 150 mesh) of sample into a beaker or suitable container;
2. Add 50 ml of 1:7 HNO_3 to the sample in the beaker;
3. Place sample(s) in a water bath at 80º-85ºC for 8 hours;
4. Separate Solids from Liquid
    a. Vacuum filtration:
        i. 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 HNO_3 to drain freely. Decanting of solution will invalidate results and is not an acceptable practice;
        ii. 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 HNO_3;
        iii. Test leachate for the presence of nitrates by an appropriate method. For example: by adding 3 drops of Nessler's solution. If nitrates are present the leachate will have yellow flakes within 30 seconds as seen against a white background;
        iv. If the leachate has yellow flakes, discard leachate and repeat rinsing with 40mL of DI water until no nitrates are detected
        v. Repeat 4.a.ii to remove HNO3 from the sample
    b. Centrifuge method
        i. If centrifuge method is used, shake the samples by hand and allow them to cool to room temperature, then centrifuge the tubes for 5 minutes at 3000 rpms and carefully decant the liquid;
        ii. Fill each tube to 40mL with Type II H2O. Shake each tube to mix and then centrifuge at 3000 rpm for 5 minutes. Carefully decant the liquid;
        iii. Test leachate for the presence of nitrates by an appropriate method. For example: by adding 3 drops of Nessler's solution. If nitrates are present the leachate will have yellow flakes within 30 seconds as seen against a white background;
        iv. If the leachate has yellow flakes, discard leachate and repeat rinsing with 40mL of DI water until no nitrates are detected
        v. Repeat 4.b.iii to remove HNO3 from the sample;
5. Dry crucible and contents at 100º-105ºC for at least 3 hours or until visibly dry;
6. When dry, analyze for sulfur using LECO or equivalent combustion furnace;
7. Report as HNO3 Rinse Residue [S(HNO3)].

Calculations

1. H_2O Soluble Sulfur [S-SO_4 (H_2O)] = Total Sulfur [S(T)] minus Hot Water Rinse Residue [S (H_2O)];
2. Non-H_2O Sulfate Sulfur [S-SO_4 (HCl)] = Hot Water Rinse Residue [S (H_2O)] minus HCl Rinse Residue [S(HCl)];
3. Pyritic Sulfur [S-PYR] = HCl Rinse Residue [S(HCl)] minus HNO_3 Rinse Residue [S(HNO_3)], Due to sample character this may result in a negative value;
4. Non-Extractable Sulfur [S-HNO_3] = HNO_3 Rinse Residue [S(HNO_3)];
5. Calculate the Potential Acid-Generating Sulfur [PAG(S)] by adding H_2O Soluble Sulfur [S-SO_4 (H_2O)] and Pyritic Sulfur [S-PYR];
    a. If due to sampling/rounding errors the PAG(S) is larger than S(T) then use S(T) for the calculations.
    b. If S(T) is below the reporting limit (RL) then sulfur speciation is not required and use half the reportable limit from total sulfur [S (T)] for the Potential Acid Generating Sulfur [PAG (S)].
6. Calculate Acid Generating Potential [AGP(T)] = Potential Acid Generating Sulfur [PAG(S)] times 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)]

Tables summarizing the calculations are provided below in addition to a flow chart of the method on the last page.

<u>Footnotes:</u>

1. Use 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
CALCULATION TABLES

Table 2A: Nevada Modified Sobek Procedure Calculation Table with Non-Detect Values

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_2O)**	%	Zero	
HCl Rinse Residue	**S (HCl)**	%	Zero	
HNO3 Rinse Residue	**S (HNO_3)**	%	Zero	

Note: Sulfur species are not needed when Total Sulfur is below the detection limit.

Table 2B: Nevada Modified Sobek Procedure Calculation Table with Formulas

Parameter	I.D.	Units	Formula	Reference/Notes
Total Sulfur	S (T)	%		
H_2O-Soluble Sulfate	S-SO_4 (H_2O)	%	= **S (T)** – **S (H_2O)**	
Non-H_2O Sulfate Sulfur	S-SO_4 (HCl)	%	= **S (H_2O)** – **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_2O) + S-PYR	If PAG (S) is larger than S (T) use S (T)
Calculated AGP	AGP (T)	T/kT	= PAG (S) x 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.
- If Total Sulfur is below the reporting limit (RL), then sulfur speciation is not required; use half the reportable limit from total sulfur [S (T)] for the Potential Acid-Generating Sulfur [PAG (S)].
- For sulfur species that return a value below the reporting limit, the 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 the WPCP.

NEVADA MODIFIED SOBEK PROCEDURE
FLOW CHART