

NEVADA MODIFIED SOBEK PROCEDURE

SUMMARY

2015 Update

The Nevada Division of Environmental Protection, Bureau of Mining Regulation and Reclamation (Division) has determined that the 2015 Update Nevada Modified Sobek Procedure (NMSP) is the only acceptable method for determination of acid neutralization/generation potential (ANP/AGP) and will not accept data from other methods without prior approval.

The 2015 Update NMSP is identical to the Montana State University Modified Sobek Procedure with the modifications summarized below.

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

Alternative I

1. Total sulfur (%) reported as AGP as tons CaCO_3 per 1000 tons material (T/kT)
2. Pre-treatment with hydrogen peroxide (siderite correction)^{1,2}
3. Paste pH
4. Calculate Net Neutralization Potential (NNP) as ANP-AGP and determine ANP/AGP ratio. If ANP/AGP ratio < 1.2:1, sulfur speciation per Alternative II below and recalculation of ANP/AGP ratio is required.

Alternative II

1. Sulfates (water soluble acid-forming sulfates, %) via hot water extraction
2. Sulfates (sulfate sulfur, %) via calculation
3. Pyritic sulfur (%) via calculation, reported as AGP (T/kT)
4. Non-extractable sulfur (%) via nitric acid extraction
5. Calculate AGP from pyritic sulfur content (AGP-PYR).³ Calculate NNP as ANP-AGP and determine ANP/AGP ratio.

Footnotes

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

3. If barite, 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 XRD or SEM analysis data and the appropriate NAG test data (single addition or sequential) in conjunction with the NMSP results. The preferred Nevada method can be found in:

Warwick A. Stewart, Stuart D. Miller, and Roger Smart, *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.

NEVADA MODIFIED SOBEK PROCEDURE
SIDERITE CORRECTED ACID NEUTRALIZATION POTENTIAL

2015 Update

The Division requires that, unless it has previously been determined that siderite is not present in a given mine-specific rock type (provide documentation), the siderite-corrected acid neutralization potential must be performed.

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 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 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 s.u. 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 s.u. 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 s.u. is obtained.

Calculate the Normality (N₁) of the HCl using the following equation:

$$N_1 = (N_2V_2) / V_1, \text{ where}$$

V₂ = Volume of NaOH used, ml;

N₂ = Normality of NaOH used;

V₁ = Volume of HCl used, ml;

N₁ = 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 CaCO₃ is indicated by a bubbling or audible "fizz";
3. Rate the bubbling or "fizz" in step 2 as indicated in Table 2;

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

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

4. Weigh 2.00 grams of sample (95% minus 150 mesh) into a 250 ml Erlenmeyer flask or equivalent;
5. 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 s.u. 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 s.u. 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 s.u.;
16. If less than 3 ml of the NaOH is required to obtain a pH of 7.0 s.u., 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. $ANP = (\text{Tons CaCO}_3 \text{ equivalent} / \text{thousand tons of material (T/kT)}) =$
 $(\text{volume (ml) of acid consumed}) \times (25.0) \times (\text{N of acid})$

Paste pH

Procedure (1:1 Solid:Solution Ratio)

Mix 1:1 ratio of 95% minus 150 mesh sample to de-ionized (DI) water, allow to sit for about 1 hour and record pH of slurry to one decimal place, i.e. two significant figures.

NEVADA MODIFIED SOBEK PROCEDURE

ACID GENERATION POTENTIAL

2015 Update

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 mm vacuum filters, for sulfur speciation.

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)].

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 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 H₂O Soluble Sulfate, [S-SO₄ (H₂O)].

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 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 H₂O Soluble Sulfate, [S-SO₄ (H₂O)].

Procedure for Hydrochloric Acid Extraction for Determination of Sulfate Sulfur

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 Sulfate Sulfur, [S-SO₄ (HCl)].

Procedure for Nitric Acid 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 HNO₃ or until rinsate tests clean for nitrates;
6. Repeat Step 4 a minimum of six times to ensure complete removal of excess HNO₃;
7. Dry crucible and contents at 100°-105°C for at least 3 hours or until visibly dry ;
8. When dry, analyze for sulfur using LECO or equivalent combustion furnace;
9. Report as Non-Extractable Sulfur, [S-HNO₃].

Footnotes

1. Use 0.500 ± 0.005 grams or the instrument manufacturer's maximum recommended weight to ± 0.005 gram accuracy. 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.

Calculations

Parameter	I.D.	Unit	Formula	Reference/Notes
Total Sulfur	S (T)	%		
H ₂ O Soluble Sulfate	S-SO ₄ (H ₂ O)	%	= S (T) – S (H ₂ O)	eq. 3.2.6.6.1
Sulfate Sulfur	S-SO ₄ (HCl)	%	= S (H ₂ O) – S (HCl)	eq. 3.2.6.6.2
Pyritic Sulfur	S-PYR	%	= S (HCl) – S (HNO ₃)	eq. 3.2.6.6.3
Non-Extractable Sulfur	S-HNO ₃	%	= S-NXS	eq. 3.2.6.6.4 (Residual sulfur)
AGP from Total S	AGP (S)	T/kT	= S (T) * 31.25	
AGP from H ₂ O Soluble	AGP (H ₂ O)	T/kT	= S-SO ₄ (H ₂ O) * 31.25	
AGP from Pyritic S	AGP (PYR)	T/kT	= S-PYR * 31.25	
Total AGP	AGP (T)	T/kT	= AGP (S-SO ₄ (H ₂ O)) + AGP (PYR)	
ANP		T/kT		Eq. 3.2.3.6 & siderite correction 95% minus 150 mesh; Endpoint pH 7.0
NNP		T/kT	= ANP – AGP (T)	Based on Guidance Document step 4
ANP/AGP			= ANP / AGP (T)	Based on Guidance Document step 4

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.