

Static Tests

(Acid – base accounting)

- Developed for the coal industry.
- Hard rock mining industry started using static tests in the late 1970ies.
- There is a widely used version (Sobek) and many variations (see EPA source document on your disk).
- We'll cover the Sobek method.

What they do and don't do

- Determine the sulfur content of a sample.
- Determine how much acid a sample will neutralize.
- No information about if or when acid generation will occur, acid generation and neutralization reaction rates, or effluent water quality.

Assumptions

- All reported sulfur occurs as pyrite (this has been modified).
- Pyrite is completely oxidized to sulfate and ferric hydroxide.
- Hydrogen ions produced are neutralized by CaCO_3 .
- All reactions are instantaneous.

Determining acid generation potential (AP)

- The sample is crushed 60 mesh (0.25 mm), and split into three parts.
- Total sulfur is determined from a split using a Leco sulfur analyzer (sample mass, 0.5 to 2 grams).
- Sulfate sulfur is determined from a second split by HCl extraction. Sulfate sulfur equals total sulfur minus acid extractable sulfur.

Determining AP

- Organic sulfur (nonextractable) is the total sulfur content of the HNO₃-treated split. Organic sulfur is determined from a third split by HNO₃ extraction.
- Acid-extractable, Acid-soluble sulfide sulfur (e.g., pyrite) is the difference between the total sulfur contents of the HCl-treated and HNO₃-treated splits.

Determining AP

- AP is the sulfur content (expressed in weight percent) of a sample multiplied by the conversion factor 31.25.
- The conversion factor is derived from the oxidation and neutralization reactions.
- AP is reported either as kilograms of CaCO_3 equivalent per metric ton of sample, or tons of CaCO_3 per thousand tons of waste.

AP Confounding Factors

- Samples don't represent most mine waste well.
- Sample masses are small.
- Highly acid generating sulfide is removed erroneously by HCl.
- All sulfide sulfur is considered acid forming regardless of the sample mineralogy.
- Sulfur from acid-insoluble sulfates minerals (e.g., barite) reports as sulfide sulfur.
- Sulfate sulfur from acid-insoluble sulfate minerals (e.g., jarosite, alunite, melanterite) is not recognized as an immediate or long-term acid source.

Determining neutralization potential (NP)

- NP is determined by mixing a sample with a known quantity of acid, determining the base equivalent amount of acid consumed by the sample, and converting measured quantities to NP.
- The quantity of acid needed for NP determination is estimated by adding HCL to a small amount of sample and observing the intensity of the "fizz".
- The sample is assigned a fizz rating ("no", "slight", "moderate", or "strong"). The rating determines the quantity and/or normality of acid that is used for NP determination.

Determining NP

- The sample is placed in hot hydrochloric acid.
- The mixture is titrated with sodium hydroxide to a pH of 7 to determine the amount of unconsumed acid.
- The amount of titrated base is converted to a calcium carbonate equivalent (same units as AP).

NP Confounding factors

- Fizz ratings are observational and thus, subjective.
- NP values may differ from a few percent to a few hundred percent based on one or two category changes in fizz rating.
- Neither neutralization reaction rates nor final neutralization pH are predicted.
- The test overestimates NP in samples with abundant calcic feldspar, chlorite, clay, pyroxene and olivine.

More NP Confounding factors

- Small particle size may produce unrealistically high values for NP.
- Hot acid digestion may overestimate NP.
- Hot acid digests iron carbonates and clay minerals that increase NP but provide little real neutralization.
- Back-titrating pH to 7.0 or 8.3 overestimates NP.
- Metal hydroxide precipitation during sodium hydroxide addition overestimates NP.

Making the Call

Net Neutralizing Potential (NNP)

Neutralizing Potential Ratio (NPR)

- Some use NNP, which is $NP - AP$, to determine if a sample is non-acid generating. Samples with $NNP > 20$ are considered "safe".
- Others use NPR, which is NP/AP , to determine if a sample is non-acid generating. NPRs ranging from 1 to 4 are considered safe, depending on whom you reference.

Interpreting results

Table C-1. Summary of Commonly Used Static Test Methods

Static Test Method	Reference	Comments
Sobek	Sobek et al. (1978)	AP uses sulfur speciation and Leco analyzer. NP uses fizz test and heated HCl that dissolves carbonates and most silicate minerals; NaOH titration endpoint of 7.0. This is an aggressive test that provides "best case" values.
Modified Sobek NP	Lawrence and Wang (1997)	NP uses fizz test and HCl at ambient temperature that dissolves carbonates and reactive silicate minerals; NaOH titration endpoint of 8.3. Less aggressive test due to use of ambient temperature acid. Lapakko (1992) suggested that the alkaline titration endpoint may lead to overly optimistic estimates of NP.
Sobek NP Siderite Correction	Skousen et al. (1997)	NP uses fizz test and heated HCl; hydrogen peroxide added prior to titration to oxidize ferrous iron from dissolved siderite. Yields less alkaline NP than standard Sobek method when siderite is abundant.
BCRI Initial	Duncan and Bruynesteyn (1979)	AP uses total sulfur by Leco furnace or wet chemistry. NP uses H ₂ SO ₄ added to pH 3.5 at ambient temperature that dissolves carbonates and possibly limonite and chlorite; gives "most likely case" values.
Lapakko NP	Lapakko (1994)	NP uses H ₂ SO ₄ added to pH 6.0 at ambient temperature for up to 1 week that dissolves carbonates; gives "worst case" value.
Net Acid Generation (NAG)	Miller et al. (1997)	Crushed sample is boiled with hydrogen peroxide then titrated to pH 4.5 with NaOH. NAG value, expressed in units of kg H ₂ SO ₄ /tonne, provides indication of potential for net acidification.
Carbonate Carbon	ASTM (1997)	Samples are either dissolved in acid or combusted and the amount of CO ₂ gas evolved is measured and converted to CaCO ₃ equivalent.
Paste pH	Sobek et al. (1978) Page et al. (1982)	Sample is mixed with water and pH measured by meter. pH value provides indication of potential for net acidification.
Summaries include information from Mills (1998a and 1998b).		

Interpreting results

Table C-2. Suggested Guidelines for Static Test Interpretation

Guidelines from Robertson and Broughton (1992)				
	Potentially Acid Generating	Uncertain Behavior *	Potentially Acid Neutralizing	
NNP	< -20 tonnes/kilotonne	> -20 to < +20 tonnes/kilotonne	> + 20 tonnes/kilotonne	
NPR	< 1	1 to 3	> 3	
* Samples exhibiting uncertain behavior should be tested kinetically.				
Guidelines from Price et al. (1997)				
	Paste pH	NPR	Potential for ARD	Comment
Sulfide-S <0.3%	>5.5	---	None	No further ARD testing required provided there are no other metal leaching concerns. Exceptions: host rock with no basic minerals, sulfide minerals that are weakly acid soluble.
Sulfide-S >0.3%	<5.5	<1	Likely	Likely to be ARD generating.
		1 - 2	Possibly	Possibly ARD generating if NP is insufficiently reactive or is depleted at a rate faster than that of sulfides.
		2 - 4	Low	Not potentially ARD generating unless significant preferential exposure of sulfides occurs along fractures or extremely reactive sulfides are present together with insufficiently reactive NP.
		>4	None	No further ARD testing required unless materials are to be used as a source of alkalinity.

Interpreting results

- The previous table illustrates that, NNP and NPR have “gray” areas.
- Some believe the gray area for NNP is between -20 and +20
- Some believe the grey area for NPR ranges between 1 and 3 or between 1 and 4).
- EPA says that samples falling into the uncertain areas should be tested kinetically.
- EPA also says that representative samples from all geochemical groups should be tested for metals mobility regardless of their acid generation potential.

Discussion

- Do static tests accurately predict acid generation by themselves?
- Do static test work better on some earthen materials?
- Are they cat's meow, conditionally useful, no good at all?
- Why would static tests work better on some earthen materials?

Appropriate/Inappropriate

- Dredge spoils?
- Waste rock?
- Cyanide leached ore?
- Mill tailings?
- Coal overburden?

Conclusions

- Static test are useful when the acid generation behavior of a waste is known or has been characterized by other tests.
- The 3:1 ratio applied to static test data is not definitive for determining acid generation potential of mine waste.