DEVELOPMENTS IN PREDICTING AND MANAGEMENT OF ACID FORMING MINE WASTES IN AUSTRALIA AND SOUTHEAST ASIA[1]

Stuart D. Miller, John J. Jeffery, and Theresa A. Donohue[2]

Abstract: The acid-base account (ABA) is the most commonly used procedure for identifying potentially acid-forming materials at mine sites in Australia and Southeast Asia. The ABA is a very useful screening tool for classifying materials as either potentially acid-forming or non-acid forming. Confirmation of the ABA calculation usually requires a kinetic leaching test, which may run for a long period and require a major commitment of resources. Environmental Geochemistry International Pty Ltd have been developing a simple hydrogen peroxide oxidation procedure for quantifying the acid-generating capacity of a sample. This procedure, known as the net acid generation (NAG) test, provides a direct measure of the net amount of acid produced by a sample. The procedure is simple and low in cost and is currently used to identify potentially acid-forming materials at a number of mine sites in Australia, New Zealand, Papua New Guinea, and Indonesia.

The NAG test provides information on the risk of acid formation by mine waste materials, the relative reactivity of the contained sulfides, a measure of the amount of acid a material can generate. This information can then be used for planning and implementing waste rock and tailings disposal operations.

Research funded through the Australian Mining Industry Research Association (AMIRA) and sponsored by individual mining companies in Australia is currently being carried out to refine the net acid generation (NAG) procedure for predicting the acid-generating potential of mine waste materials. A component of this research is aimed at evaluating the kinetics of the NAG test reaction using pH and temperature profiles of the effect of rapid oxidation on a range of mine rock and process residue samples. This information will be related to the leaching characteristics and acid formation reaction kinetics (or lag period) observed in column tests and in the field.

The study commenced in September 1993 and will run over 18 months. Waste rock and tailings samples from 17 mine sites in Australia, New Guinea, and Indonesia are included in the program. This paper provides some background on developments of the NAG procedure to date and also outlines the research program being undertaken to further refine the method. Examples of pH and temperature profiles during the NAG test are given and related to ABA results.

Additional Key Words: acid mine drainage, prediction, hydrogen peroxide test, net acid generation test, acid-base account, lag period.

Introduction

Acid-forming rock and process wastes are a common occurrence at many base metal, gold, and coal mines in Australia and Southeast Asia. If poorly managed, acid-forming material can be difficult to rehabilitate and can produce drainage of unacceptable quality for discharge to the environment. Treatment of acid drainage is often difficult and costly.

---

[1] Paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994.

[2] Stuart D. Miller, Managing Director, John J. Jeffery, Principal, and Theresa A. Donohue, Environmental Scientist, Environmental Geochemistry International Pty Ltd, Balmain, NSW, Australia.

Proceedings America Society of Mining and Reclamation, 1993 pp 177-184

DOI: 10.21000/JASMR94010177

https://doi.org/10.21000/JASMR94010177

Incorrect identification and inappropriate management of acid-forming mine wastes has significant cost as well as environmental implications for the mining industry. In the Southeast Asia context, acid drainage can directly affect the livelihood of downstream communities which heavily depend on natural streams and rivers for food, transport, and domestic uses.

The process of acid generation from geological materials is well documented. When materials containing sulfide minerals are exposed to air and water, the sulfides become chemically unstable and react to form sulfuric acid and iron salts. The sulfuric acid may subsequently react with other minerals in the rock, reducing the amount of acidity formed. If the amount of acid generated by sulfide oxidation exceeds the inherent acid neutralization capacity of the rock, then acid conditions will be established; water flowing through such materials will have a low pH, high acidity, and high salt content and may contain elevated concentrations of metals.

Acid-forming mine waste materials include waste rock, mine overburden, and process tailings and acid-forming materials often occur in exposed mine faces in opencut pits and underground workings. Appropriate design and implementation of a waste management plan for the correct placement and disposal of the waste types (i.e. acid generating/acid neutralising) can overcome many of the problems associated with acid forming mine rock and waste. However, such planning requires not only an appreciation of the geochemistry of the materials but also an understanding of the location, nature, and extent of the various waste rock types to be mined and placed within the waste storage area. Therefore a means to accurately predict and identify acid-forming materials on a routine basis is essential for an effective management operation.

Net Acid Producing Potential

At the present time, the acid-base account (ABA) procedure is the most commonly used method for assessing the acid-forming potential of mine waste materials (Ferguson and Erickson 1988). This procedure provides a theoretical estimate of the net acid-producing potential (NAPP) of the waste and is based on the difference between the acid-forming and acid-neutralizing capacities of the material (Miller and Murray 1988). The acid-forming capacity is estimated from the total sulfur (or pyritic sulfur) content of the material, and the acid neutralization capacity (ANC) is measured directly in the laboratory. The NAPP is calculated as follows--

$$\text{NAPP} = \text{Total sulphur} \times 30.6 - \text{ANC}$$

While the NAPP indicates the potential for acid formation to occur, it does not provide any indication on the likely time it will take. Furthermore, the NAPP procedure is not suited to field applications, such as in-pit identification of potentially acid-forming waste rock types because the analyses required to calculate the NAPP are relatively time consuming and require specialized laboratory equipment.

The use of total sulfur for estimation of the total acid generation capacity presumes that all sulfur can participate in the acid generation processes. This may result in an overestimate of the acid generation capacity (Miller et al. 1991a). The laboratory procedures used for measurement of ANC can also overestimate the availability of ANC in the field, particularly when carbonate minerals such as dolomite and ferroan dolomite are present. These minerals often have limited solubility at the pH of acid sulfate systems and may not contribute significantly to the true ANC in the field.

Net Acid Generation Test

Preliminary investigations of the net acid generation (NAG) test have been carried out by Environmental Geochemistry International Pty Ltd (EGI) to assess its suitability for identification of acid-forming rock and mining wastes. These preliminary investigations have produced promising results (Miller et al. 1991b) that suggest the NAG test could be used in conjunction with the acid-base account to identify and predict acid rock drainage for new mining ventures. The NAG test also has potential as a "stand alone" method for field identification and operational monitoring of waste types at existing mines. This field capability makes the NAG test a very attractive procedure and worthy of further development.

The NAG procedure is based on a test developed by Finkelman and Giffin (1986) in which hydrogen peroxide was used to quantify the pyrite content and acid mine drainage potential of overburden sediments and spoil materials from coal mining operations. Other researchers have also investigated the use of peroxide for assessing sulfide content and acid potential of mine waste materials (Smith et al. 1974, Sobek et al. 1978, O'Shay and Hossner 1984, Coastech 1989, O'Shay et al. 1990).

The hydrogen peroxide reacts with sulfide minerals, generating heat and acid. The acid in turn reacts with any inherent acid-neutralizing minerals in the material. Therefore, the amount of acid remaining in solution at the completion of the reaction, which is quantified by titration, represents the net acid generated. The final pH of the NAG solution also provides a measure of the activity of hydrogen ions in solution and an indirect measure of the acidity generated. To date, the NAG test has been mainly used to verify the findings of the ABA procedure; for example, to test whether a material classified as potentially acid-forming on the basis of the sulfur and ANC contents does in fact produce acid when the sulfide minerals are oxidized.

NAG Method

The NAG working procedure (which will be further developed in this study) is presented here. The NAG test involves the addition of 250 ml of 15% hydrogen peroxide (unstabilised 30% hydrogen peroxide diluted 1:1 with deionised water) to a 2.5 ± 0.1 g sample of pulverised waste rock or tailings. 500 ml conical glass beakers covered with watchglasses are used for the testwork and samples are kept in a fume hood during the test. The oxidation reaction results in the production of heat in some samples. Samples are considered to have finished reacting when: (1) the sample solution boils and then cools, or (2) after at least 12 hours has elapsed. Any excess hydrogen peroxide left in the sample solution is broken down by heating all NAG solutions on a hotplate at 100 ^{o}C until all effervescence ceases and the solution boils. Samples which react violently resulting in lost sample solution are repeated using a 1 litre beaker.

After the solution has cooled, the pH and acidity of the solution is measured. Measurement of the acidity involves titrating the NAG solution with standardised NaOH (0.100 N NaOH if $pH > 2.5$ and 0.500 N NaOH if $pH < 2.5$) to an endpoint of pH 7.0 using an Orion 960 autochemistry system. Samples with a NAG result of > 25 kg/mt H_2SO_4 are repeated using 1.0 g of sample.

Monitored samples record pH and temperature over the reaction period of the test. pH and temperature probes are placed in the sample solution and the pH, temperature and time are recorded using a MacLab analog digital instrument, which transfers the data onto a MacIntosh computer. Parameters are measured continuously and the average reading each 10 seconds is recorded and plotted.

NAG Test Development

Research funded through the Australian Mining Industry Research Association (AMIRA) and sponsored by individual mining companies in Australia is currently being carried out to refine the net acid generation (NAG) procedure for predicting the acid-generating potential of mine waste materials. The main objectives of the current study are -

1. To develop the NAG procedure as a simple low cost test for identifying acid-forming mine rock and waste materials for use in premining and operational phases of mining ventures.

2. To study the kinetics of the NAG reaction on monitored samples and evaluate whether they can be extrapolated to the field situation for prediction of the kinetics of the acid generation and neutralization reactions in the field and the exposure time necessary before acid formation occurs (i.e., the lag period).

3. To assess on-site application of the NAG test, including in-pit monitoring of acid-forming materials.

The study is being sponsored by 8 mining companies and includes 119 waste rock and tailings samples from gold, nickel, base metal, iron ore, and coal mining projects. The study will compare NAG, NAPP, and leach column results for an extensive and wide-ranging group of mine rock and process residue samples. Table 1 shows the types of samples available for the NAG testwork.

Table 1. Samples available for NAG testwork program.

Sample Type	Number of Samples	Number of Mines	Ore Deposit				
			Gold	Iron Ore	Nickel	Base metal	Coal
Tailings	23	11	8	-	11	1	3
Waste Rock	78	15	54	8	6	3	7
Ore	18	8	13	-	3	2	-

Results to date

119 samples have been analysed for ABA and NAG including final pH of NAG solution. Total sulfur results range from 0.1 to 40%S, ANC from 0 to 425 kg/mt H_2SO_4 and NAPP from - 390 to 1230kg/mt H_2SO_4. Figure 1 shows NAPP vs NAG results and the results from 0 to 60 kg/mt H2SO4 are shown in more detail in figure 2. The results indicate that the calculated NAPP is predominantly higher than the acid generated by oxidation. The NAG solution pH for the samples in figure 2 are plotted in figure 3 and show that samples with a slightly positive NAPP can produce neutral or alkaline NAG solutions and samples with an NAPP of >10 all have a pH <4.5. These results will be further evaluated via changes to the NAG procedure, kinetic studies, column leaching and field observation.

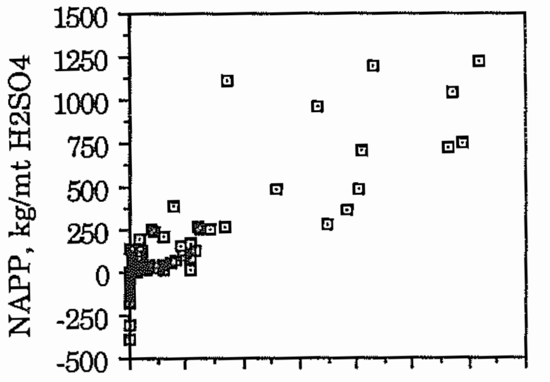

Figure 1. NAPP vs NAG result for all samples.

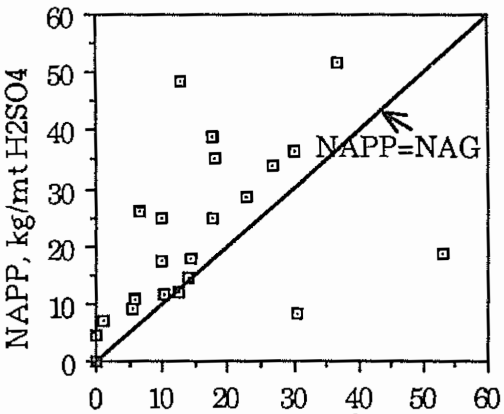

Figure 2. NAPP 0 to 60 kg/mt H2SO4 vs NAG result.

Monitored NAG solutions

Monitored NAG tests provide information regarding the pH and temperature change over time and preliminary investigations suggest that the time to reach the temperature maximum during the NAG test is a function of sulfur content, sulfur reactivity and ANC of the material (Miller et al. 1991b). These properties all affect the length of the lag period that precedes acid formation in the field.

Figures 4 to 8 show NAG test profiles of pH and temperature for five mine waste samples that are classified as potentially acid-forming by the standard ABA procedure. The ABA results for the five samples are given in table 2.

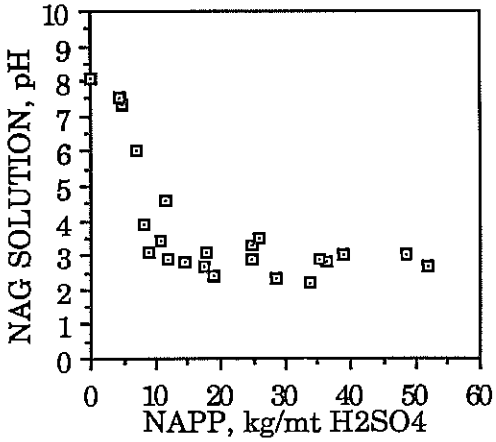

Figure 3. NAG Solution pH vs NAPP 0 to 60 kg/mt H2SO4.

Although all samples are classified as potentially acid-forming by the ABA method, the NAG test results demonstrate significantly different oxidation kinetics and rates of acid formation. For example, sample 1 is a high S-low ANC material that reacts rapidly under NAG test conditions. Figure 4 indicates that the NAG solution effectively boiled within 55 min of commencement of the test from the heat generated by the exothermic oxidation of the sulfides in the sample. Simultaneously, the pH of the solution decreased to around pH 2.5.

Sample 2 contains less S and has a greater ANC than sample 1. In this case the time to react was slower, taking approximately 160 min for the solution to boil (fig. 5).

Sample 3 also has a lower S content than sample 1 as well as a low ANC. This sample did not produce a "boiling peak", but the pH of the solution did steadily decrease to approximately pH 3 in about 500 min.

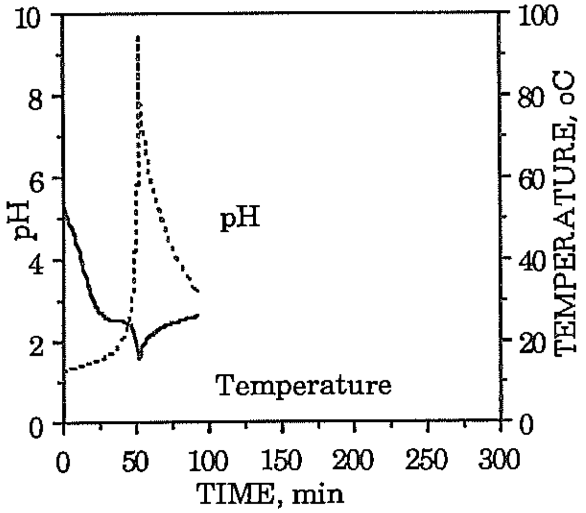

Figure 4. Monitored NAG test on mine waste rock sample 1 (NAPP=125 kg/mt H2SO4).

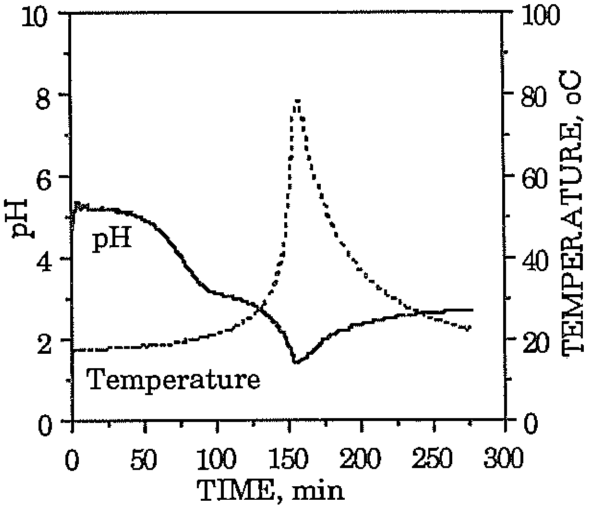

Figure 5. Monitored NAG test on mine waste rock sample 2 (NAPP=55 kg/mt H2SO4).

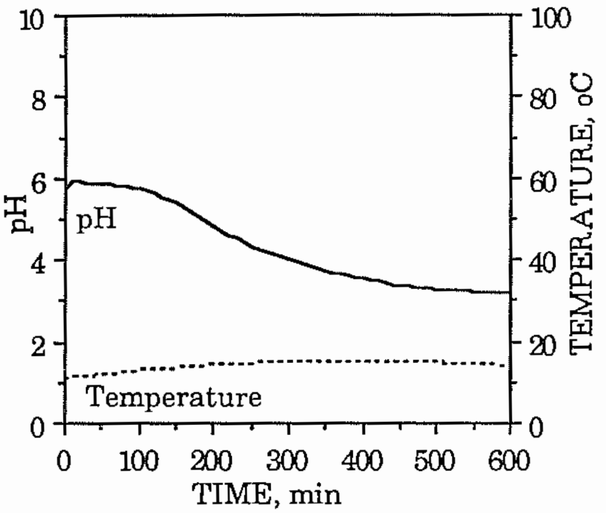

Figure 6. Monitored NAG test for mine waste rock sample 3 (NAPP=33 kg/mt H2SO4)

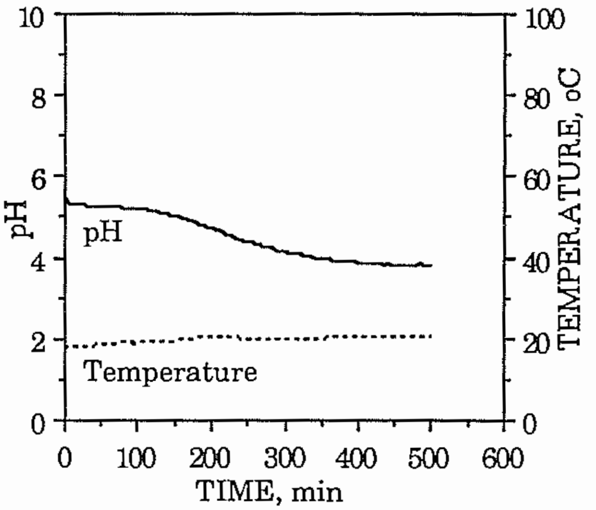

Figure 7. Monitored NAG test for mine waste rock sample 4 (NAPP=11 kg/mt H2SO4).

Samples 4 and 5 contained only slightly less S than sample 3, but the ANC's were significantly greater. Although samples 4 and 5 were classified as potentially acid-forming by the ABA, neither sample generated significant heat and the final pH's of the NAG tests were only weakly acidic at around pH 4 and 5.5, respectively.

The results for these five samples provide an indication of the range of reaction kinetics that occur under NAG test conditions. On the basis of both the ABA and NAG test results, samples 1 and 2 would be described as potentially acid-forming and high risk because of their high NAPP's and the strongly acidic NAG tests.

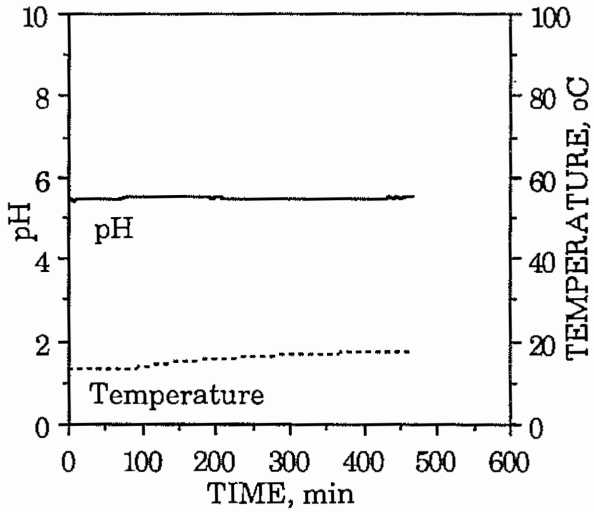

Figure 8. Monitored NAG test for mine waste rock sample 5 (NAPP=6.5 kg/mt H2SO4).

Table 2. ABA results for mine waste rock samples referred to in figures 1 to 5.

Sample	Total S, %S	ANC, kg/mt H_2SO_4	NAPP*, kg/mt H_2SO_4	NNP* kg/mt $CaCO_3$	MPA/ANC* ratio
1	4.1	0.1	125	-125	1255
2	2.4	18	55	-55	4.1
3	1.2	3.9	33	-33	9.4
4	0.89	16	11	-11	1.7
5	0.80	18	6.5	-6.5	1.4

* NAPP= total S x 30.6 - ANC = -NNP, MPA = total S x 30.6

Samples 3 and 4, on the other hand, would be classified as potentially acid-forming but low risk because of their much slower reaction times and/or the generation of only weakly acidic NAG liquors. Sample 5 would be described as non-acid-forming because acid generation in the NAG test was insignificant and the NAPP was close to zero.

As the results for the five waste rock samples indicate, most potentially acid-forming rocks and mine wastes contain some inherent acid neutralizing capacity which delays or inhibits acid generation for a period of time following exposure. This delay, which is measured in minutes in the NAG test, may relate to a real time of months or years in the field. Also, the reactivity of sulfide varies, which in turn affects the time to acid formation. Because of these factors, acid generation may not be observed until the material has been exposed for months or even years. This lag period is an important consideration for waste management operations because it will determine if materials need to be treated or buried immediately or can be left exposed for a period of time before covering.

Conclusions

At present, there is no rapid routine laboratory procedure for assessing the kinetics of acid formation by sulfidic waste materials. Batch and leaching column tests are sometimes used, but these may need to be maintained for 12 months or longer to provide meaningful results. Consequently there is often a reluctance to use column tests, particularly in the premining phase when time constraints do not allow for long-term waste rock testing. Also, there is often concern in regard to extrapolating column test results to field conditions.

Preliminary testwork has indicated that a relationship may exist between the kinetics of the NAG test and the lag period observed in the field. The current research is aimed at evaluating this relationship; if it is established, it may be possible to provide a time factor for use in waste management design.

An added advantage of the NAG test is that it requires minimal laboratory equipment to carry out and can be completed within hours. This means the NAG test is suited to on-site use and is currently used at mines in Australia and Southeast Asia.

Acknowledgments

The authors wish to thank AMIRA and its members for their sponsorship of this research program. The companies supporting this research are Billiton Australia, BHP Coal Limited, Carpentaria Gold Pty Limited, Hammersley Iron Pty Limited, Peak Gold Pty Limited, Placer Pacific Limited, P.T. Kelian Gold, and Western Mining Corporation Limited - Kambalda Nickel Operations.

Literature Cited

Coastech Research Inc. 1989. Investigation of prediction techniques for acid mine drainage. Report prepared for Canada Centre for Mineral and Energy Technology, Energy Mines and Resources Canada, DSS File No. 30SQ.23440-7-9178.

Ferguson, K.D., and P.M. Erickson. 1988. Pre-mine prediction of acid mine drainage. p. 24-43. In W. Salomons and U. Forstner (eds.), Environmental management of solid waste - dredged material and mine tailings. Springer-Verlag, Berlin.

Finkelman, R.B., and D.E. Giffin. 1986. Hydrogen peroxide oxidation: an improved method for rapidly assessing acid-generating potential of sediments and sedimentary rocks. Reclamation & Reveg. Res. 5:521-534.

Miller, S.D., J.J. Jeffery, and J.W.C. Wong. 1991a. Use and misuse of acid-base account. p. 489-506. In Proceedings of the Second International Conference on the Abatement of Acidic Drainage. (Montreal, PQ, September 16-18, 1991).

Miller, S.D., J.J. Jeffery, J.W.C. Wong, and A.J. Goldstone. 1991b. In-pit identification and management of acid-forming waste rock at the Golden Cross Gold Mine, New Zealand. p. 137-152. In Proceedings of the Second International Conference on the Abatement of Acidic Drainage. (Montreal, PQ, September 16-18, 1991).

Miller, S.D., and G.S.C. Murray. 1988. Application of acid-base analysis to wastes from base metal and precious metal mines. p. 29-33. In Proceedings of Mine Drainage and Surface Mine Reclamation Conference, v.1. (Pittsburgh, PA, April 17-22, 1988). BuMines IC 9183
http://dx.doi.org/10.21000/JASMR88010029

O'Shay, T.A., and L.R. Hossner. 1984. The determination of potential acidity of overburden sediments. p. 13-14. In Proceedings of Surface Mine Reclamation Workshop. TX Agric. Ext. Service and TX A. & M. Univ. (San Antonio, TX, October 9-10, 1984).

O'Shay, T.A., L.R. Hossner, and J.B. Dixon. 1990. A modified hydrogen peroxide oxidation method for determination of potential acidity in pyritic overburden. J. Environ Qual. 19:778-782.
http://dx.doi.org/10.2134/jeq1990.00472425001900040024x

Smith, R.M., W.E. Grube, Jr., T. Arkle, Jr., and A. Sobele. 1974. Mine spoil potential for soil and water quality. U.S. Department of Commerce, EPA-670/2-74-070. 101 p.

Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and laboratory methods applicable to overburdens and mine soils. U.S. Environmental Protection Agency, Cincinnati, OH, EPA 600/2-78-054.