

COLLECTION AND USE OF GEOCHEMICAL DATA FOR MINE OVERBURDEN MANAGEMENT

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Abstract.--This paper presents a staged investigation strategy for assessing the geochemical nature of overburden and other mining wastes for developing environmentally sound waste management operations. The approach is based on the results of investigations carried out by the author at more than 20 mining operations in Australia, New Zealand and Indonesia. Acidity, salinity, sodium (sodic) and heavy metal aspects are considered and testing programs outlined. Data on acid generation from 10 sites is presented which demonstrates that short term leaching tests can lead to serious errors in the assessment of results.

INTRODUCTION

The fundamental purpose for assessing the geochemical nature of overburden is to identify potentially toxic materials that may contaminate leachate or runoff water or adversely affect reclamation works. Overburden testing is also used to identify alternative topsoil or subsoil material. However, the physical characteristics are generally the major determining factor for 'soil' selection providing the chemical toxicity aspects have been considered. In practice, mine waste handling operations attempt to bury the most toxic strata and make best use of the material left on the surface of spoil after regrading. In most situations this involves covering with topsoil and revegetating according to locally accepted practice.

In Australia, regulations relating to overburden analysis generally state that the material must be chemically characterised and any toxic strata must be disposed of in an environmentally acceptable manner and the site reclaimed to a plan approved by the appropriate regulatory authority. This essentially means that each mining operation is considered independently and site specific factors are taken into account, including climatic and mining considerations.

This paper presents an approach developed for assessing the toxic nature and hazard potential of overburden based on fundamental geochemical processes and site specific conditions. The concept of 'trigger levels' is presented which provides a basis for the practical application of geochemical data under varying environmental and operating conditions.

OVERBURDEN INVESTIGATION STRATEGY

Due to the variable nature of overburden and the variety of potential toxicity problems, a staged investigation strategy is generally applicable.

Stage 1 involves:

- review of available information on geology, mining and general environmental conditions
- overburden sampling from drill core (existing and proposed operations) and highwalls (existing operations)
- chemical and solubility characterisation involving multi-element analysis, total sulfur and acid neutralisation analysis, saturation extract solubility analysis.

Stage 2 investigation program is based on the results of stage 1 and site specific conditions, including the purpose of the investigation and the location and extent of potentially toxic strata identified in stage 1. The emphasis of stage 2 investigations will depend on the nature of the potential toxicity identified in stage 1, ie. whether acid generation, saline or sodic (sodium) issues or heavy metal problems are important. Testing procedures for investigating these problems are outlined in this paper.

Stage 1 Investigations

The sampling phase is the most critical step and the major source of error with any overburden testing program. The number of samples and the

vertical and horizontal coverage will depend on the particular deposit, the mining operation, the stage of development and the purpose of the investigation ie whether the investigation is aimed at preliminary site investigation, overall mine planning or problem solving.

Sampling from drill cores involves selecting sections of core 2 to 5 cm long each 0.5 m down the profile and combining into samples of representative lithology types and /or mining units. The overburden samples collected are crushed to nominal 2mm size and water saturation extracts prepared on all samples. The extracts are analysed for pH, electrical conductivity, total acidity or alkalinity, Ca, Mg, Na, K, SO₄ and Cl. On selected extracts, the concentration of environmentally important heavy metals such as Se, Cu, Pb, Zn, Cd, As, Mn, B, Hg, Co, Mo, Ni, Al and Fe are determined.

Total sulfur and the acid neutralising capacity are determined on all overburden samples. The content of selected heavy metals is determined on the whole rock samples used for the heavy metal solubility analysis in saturation extracts.

The results of these tests are assessed according to the 'trigger levels' shown in table 1 and 2. Table 1 shows trigger levels for assessing the toxicity with respect to acid generation, salinity and sodicity. Table 2 is used for assessing specific ion and heavy metal toxicity. If the trigger level is not exceeded the material

is considered to be non-toxic and no further hazard assessment is necessary. If the trigger level is exceeded, consideration must be given to remedial action and initiation of stage 2 investigations. Remedial action may involve selective placement and covering with suitable material, modification to the mine plan or water management, special surface management and reclamation techniques, chemical treatment eg. lime or gypsum or even selection of an alternative end use for the site.

Table 1
'Trigger Levels' for Coal Overburden Assessment

Parameter	Trigger Level
Net Acid Producing Potential (NAPP)	>0 %CaCO ₃
Total Sulfur	>0.5%
pH of saturation extract	<4.0
EC of saturation extract	> 2.0 mS/cm
Sodium Adsorption Ration (SAR)	>6.0

In table 1 the NAPP is calculated from the total sulfur content and the inherent neutralising capacity and is defined as follows:

$$\text{NAPP (\%CaCO}_3\text{)} = \% \text{ S} \times 3.13 - \text{ANC (\% CaCO}_3\text{)}$$

where ANC = acid neutralising capacity

In the above equation, 3.13 is a constant

Table 2 Trigger Levels for Assessing Heavy Metals and Specific Ion Toxicity

Element	Normal Range			Acceptable Upper Limit	
	Sediments mg/kg	Soils mg/kg	Soil Solution mg/l	Drinking Water mg/l	Aquatic Organisms mg/l
Se	0.42	0.2-2	1-2	0.01	0.01
Cu	33	2-100	0.5-8	1.0	0.005
Pb	19	2-200	3-20	0.05	0.01
Zn	95	10-300	60-400	5.0	0.03
Cd	0.17	0.01-0.7	0.2-9	0.005	0.0002
As	7.7	1-50	0.02-7.5	0.05	0.01
Mn	770	20-3000	1-100	.2	0.02
B	100	1-100	1-5	5	5
Hg	0.19	0.01-0.3	na	0.001	0.0002
Co	14	1-40	0.1-3	ng	ng
Mo	2	0.2-5	0.2-5	na	na
Ni	52	5-500	0.5-2	ng	0.025

na : not available

ng : no water quality guidelines

Source : Bowen (1979); Bresler et al(1982) and Lindsay (1979).

calculated from the pyrite oxidation reaction which shows that 1% sulfur (all as pyrite) yields an amount of sulfuric acid that requires 3.13 tonnes of calcium carbonate to neutralise 100 tonnes of material.

A negative NAPP means that there is excess acid neutralising capacity in the material. A positive result indicates that the material is acid or may become acid in the long term.

The SAR is a measure of the sodic nature (or sodium hazard) of spoil. A high proportion of sodium ions in spoil is of particular concern because of the adverse affect on clay stability and permeability. This can result in surface crusting, increased erosion, subsurface piping and collapse of spoil, and moisture stress on plants.

An estimate is made of the sodic nature of spoil by determining the sodium adsorption ratio (SAR) on saturation extracts. The SAR is defined as :

$$\text{SAR} = (\text{Na} + \text{Mg}) / \{(\text{Ca} + \text{Mg})/2\}^{1/2}$$

where Na, Ca and Mg are in meq / l.

Where the levels of heavy metals and specific ions approach or exceed the upper limits shown on table 2, consideration should be given to possible phytotoxicity and possible contamination of leachates.

Stage 2 Investigations

The most critical geochemical problem with overburden is caused by sulfide generated acidity and associated high salinity and high levels of soluble heavy metals. Acid problems and sodic problems rarely coexist in the same material, however they can occur in the same overburden sequence at different locations. Salinity problems and sodic problems frequently coexist in overburden and under the climatic condition which occur in the major coal mining areas in Australia, upward salt migration and concentration at the spoil surface can occur in saline-sodic spoil (Miller 1981).

Specific ion or heavy metal toxicity rarely occurs in overburden in the absence of acid or saline problems. In Australia, the only exceptions to this are the presence of elevated levels of arsenic and boron which have been observed in some overburdens.

The investigations required for assessing potential toxicity due to acidity, salinity or sodicity and the implications for mining and reclamation are outlined below.

Acid Generating Potential

Examination of the mineralogy of overburden and the crystal structure of pyrite, in addition to the determination of the sulfur forms i.e. pyritic, sulfate and organic, provide essential data for

interpreting subsequent solubility and leachate test results.

Batch shaker tests are carried out on crushed (nominal 2mm size) overburden using deionised water. The volume of water added is equivalent to the saturation moisture content or the amount of water required to enable the sample to flow. Tests are carried out at the natural pH and at pH 3 (if the natural pH is greater than 3). The pH is adjusted using a known amount of H_2SO_4 and all samples are inoculated with a solution containing iron and sulfur oxidizing bacteria. The pH and electrical conductivity are monitored until steady state or equilibrium conditions are achieved and the solution is removed for analysis. It is extremely important that the role of bacterially catalysed sulfide oxidation be considered when determining steady state or equilibrium. The extract is analysed for major cations and anions as well as relevant heavy metals. The results are used to assess the maximum solubility of elements and the potential for long term release. Thermodynamic equilibrium modelling can be used on samples that have achieved an equilibrium condition to provide additional information on overburden geochemistry particularly in relation to solid phase controls on element solubilities and long term conditions.

Sequential batch oxidation tests are also carried out to determine the rate and mechanism of contaminant release. These tests involve aerating moist (wet) samples and sequentially flushing the oxidation products from the sample at set intervals (weekly to monthly). The samples are leached with deionised water. However, in samples where the inherent acid neutralising capacity is limiting acid generation, the samples are leached with dilute H_2SO_4 to establish conditions suitable for bacterially catalysed oxidation. The results are reported as mg of element released per kg of sample and the total release and rate of release of elements can be calculated. This information is used to classify the toxic potential of overburden and can also be used in hydrogeochemical modelling to predict dump leachate quality in high rainfall environments. Figure 1 shows the typical acid generating nature of waste materials, using deionised water, from a number of operating and proposed mining operations in Australia, Indonesia, New Guinea and New Zealand. Similar plots are available for SO_4 , Fe, Mn, Al, Zn and other metals and the results for a particular site can be compared with material with a known field behaviour to support the interpretation of results and classification of the hazard potential. Those materials requiring acid leaching are assessed with respect to sulfate and metal release.

Four acid toxicity categories are identified on figure 1 as low, medium, high and very high. The mechanism of acid generation can vary between material types and the lag phase is clearly evident in some of the plots shown on figure 1 reflecting inherent acid neutralising materials and the time necessary to establish an effective bacterial population for catalysing sulfide oxidation. The

mechanisms of acid generation shown on figure 1 demonstrate that short term leaching tests can lead to serious underestimation of acid toxicity and potential leachate quality. In some overburden and coal reject materials acid conditions can take many years to establish under natural leaching. This is caused by buffering mechanisms within the waste which neutralise any acid produced thus delaying the establishment of bacterially catalysed sulfide oxidation until the buffering system breaks down. It is therefore important to develop a detailed understanding of the geochemistry of a particular waste and not to rely on short term leaching or weathering tests.

The mechanism of acid generation can have a bearing on the mining and waste disposal operation. Materials that rapidly achieve a very high rating must be buried immediately deep within the core of spoil and isolated from leaching water. In the mining operation, benches should not be located in this material. It is apparent that in these materials, bacterially catalysed oxidation is not essential for rapid acid release. Materials which take some time to reach a high acid rating and require bacterial involvement can be controlled by limiting the availability of oxygen by burying approximately 2 metres below the final spoil surface. Medium acid material can be effectively treated by blending with non acid/ neutralising overburden during mining and reshaping. Some follow up liming may also be necessary. Low acid material is usually amenable to lime or limestone treatment at normally acceptable agricultural application rates.

Selective placement in truck and shovel mining

operations and selective pushing during reshaping in dragline operations are effective control options for high, medium and low acid material. Selective mining and burial of high acid material is essential in dragline and truck and shovel operations.

Salinity and Sodic Hazard

Assessment of the salinity status is generally based on the composition of saturation extracts and the toxicity is based on the effect on plant growth using the generally accepted values presented in Richards (1954). In special circumstances additional sequential batch shaker tests can be undertaken to assess salt release rate for modelling salt movement within a dump. In non acid systems salt release is generally controlled by solubility and not kinetic processes. Therefore, sequential batch tests can be conducted over a short time period and the results assessed on a soil water volume and soil mass basis.

To assess the impact of leachates on surface and groundwater resources details of the site and spoil hydrology are required. It is necessary to assess the impact on a site specific basis. In the major coal mining areas in Australia (Hunter Valley in NSW and the Bowen Basin in Queensland) potential evapotranspiration far exceeds precipitation for most months of the year and leachate volumes are small, if they occur at all.

The sodic hazard is also determined from the composition of the saturation extract. The majority of coal mine spoil in Australia is sodic and reclamation techniques generally aim at

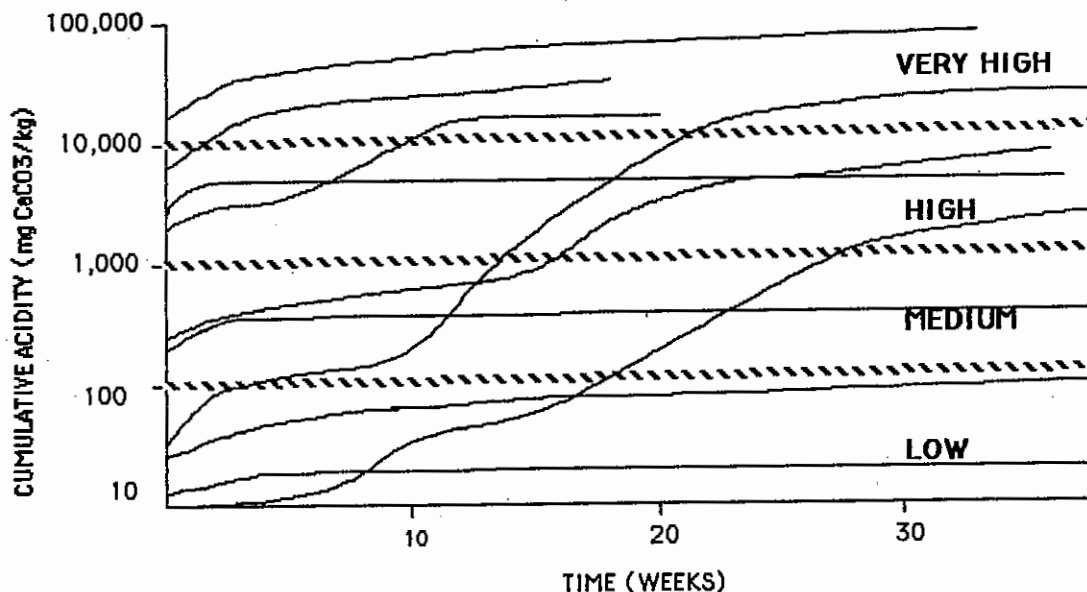


FIGURE 1: Typical Acid Generation Curves for Mining Waste
- Showing Acid Toxicity Categories

— acid generation curve
- - - toxicity division

note: acidity determined by titration to pH 7.

Table 4: Spoil Permeability and Gypsum/Reject Treatment

Sample	Flow (Q) ml/s	Permeability(K) cm/s	Suitability for Plant Growing Medium
Spoil	.0008	3.0E-5	Poor
Spoil + 5 t/h	.006	2.2E-4	Adequate
Spoil + 10 t/h	.014	5.2E-4	Adequate
Spoil/reject mix	.007	2.2E-4	Adequate
Reject over Spoil			
5cm	.003	5.6E-5	Poor
2cm	.002	5.9E-5	Poor
1cm	.002	5.1E-5	Poor
Topsoil over Spoil			
5cm	.013	5.0E-4	Adequate
1cm	.013	5.0E-4	Adequate

t/h: tonnes of gypsum per hectare

overcoming this problem. The benefit of using gypsum and in some cases coal reject for ameliorating sodic spoil has been demonstrated in the laboratory and in the field. However, wide spread acceptance of the use of gypsum has not been achieved. The rate of gypsum application generally is 2 to 10 tonnes per hectare incorporated into the surface 15 to 20 cm. The application rate and the effectiveness of gypsum for a particular spoil can be determined by simple column permeability tests. Some typical results are shown on table 4. The results in table 4 show that gypsum and coarse reject mixed into the spoil are effective at overcoming the problem of low permeability in sodic spoil. Reject placed over spoil was not effective. However, as little as 1 cm of topsoil significantly improved the permeability.

Generally the most sodic material is in the weathered section of the overburden and normal mining practices result in the burial of this material unless it is selectively placed for geotechnical reasons related to the physical stability of spoil dumps. Selective placement for reclamation or environmental considerations is not generally required.

Specific Ion and Heavy Metal Hazard

Examination of specific ion and heavy metal toxicity generally involves the application of fundamental geochemical principles for the specific elements and examining the mineralogy and solubility aspects. Equilibrium and sequential batch shaker tests at varying pH conditions are carried out. The results are assessed with respect to phytotoxicity and leachate water quality. With respect to leachates, the attenuation factors operating within the spoil and on site are considered to decide whether control or treatment measures are required. These procedures are based

on those presented by Young and Wilson (1982). A similar strategy can be developed using a modified EP toxicity test (EPA, 1980) using variable pH leachates rather than the recommended pH 5 acetic acid. However, this procedure has limitations for assessing phytotoxicity and for incorporating site and spoil attenuation factors.

CONCLUSION

A two staged approach for assessing the chemical toxicity and hazard potential of overburden and other mining wastes has been presented. This procedure has been developed from geochemical investigations carried out on more than 20 current and proposed mining operations in Australia, New Zealand and Indonesia. Stage 1 of the investigation involves determining the acid generating potential of overburden and the composition of saturation extracts. Stage 2 involves detailed geochemical evaluation of the potential toxicities identified in stage 1.

The results from a wide variety of mining wastes show that the major potential chemical problems with overburden are sulfide generated acidity, high salinity and high sodium (sodic) levels. Heavy metal contamination is generally associated with acid generation and only in rare circumstances do high levels of heavy metals occur in the absence of acid or salinity problems.

A procedure for determining the hazard potential of overburden and waste is presented along with broad recommendations for remedial action.

Data presented show that interpretation of results from short term leaching studies can lead to serious underestimation of the long term acid potential of waste. Interpretation of any laboratory tests must be based on a sound

understanding of the short term and long term geochemical processes and interaction with the site specific environmental conditions.

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CARBONACEOUS MATERIALS

PROBLEMS ASSOCIATED WITH RECLAMATION¹

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Abstract.--Highly carbonaceous materials have been attributed with producing acidity upon oxidation. Problems associated with sulfur determination may have led to the indication that organic sulfur contributes to the acid production phenomena.

Small coal lenses, stringers, and carbonaceous shales have been recognized as extraordinary concentrators of trace elements. Most trace elements and sulfide minerals occur in significantly higher concentrations in the finer grained sedimentary rocks associated with coals: roof shales, underclays and partings. Trace elements which are enriched in carbonaceous materials from Wyoming include: As, B, Cd, Hg, Mo, Pb and Se.

INTRODUCTION

The Wyoming Environmental Quality Act of 1973 and Land Quality Division of the Department of Environmental Quality (DEQ) Rules and Regulations promulgated by the Act require the identification and isolation of all toxic and acid-forming materials on lands to be affected by mineral extraction. Currently, the Department requires that all toxic and/or acid-forming materials be identified and covered with a minimum of 4 feet of nontoxic and noncombustible materials within 30 days after it is exposed. If toxic and/or acid-forming materials are disposed of in the pit backfill or spoil pile, these materials shall be selectively handled to prevent leaching of acid-forming or toxic materials into surface or subsurface waters (Chapter IV, Section 3.c.(3) (a)-(d) of the WDEQ/LQD Rules and Regulations and 35-11-406(b) (ix) of the Wyoming Environmental Quality Act).

ACID PRODUCTION

Since 1978, Wyoming has required analysis for the determination of the acid forming potential of geological materials. Prior to 1978 it had been assumed that the potential for acid production in mined land reclamation was negligible since the western region is predominately a semiarid, alkaline system.

Extensive research has shown that acid production predominantly results from the oxidation of sulfides such as pyrite and marcasite. In the eastern United States, oxidation of sulfides is the major source of acidity on mined lands and is caused by carbonaceous rider seams and bone coal (May and Berg, 1966). Because climatic and depositional differences exist between eastern, southern and western coal producing regions, it has been assumed that acid production is not a problem in the west. However, as information is developed from mines in Wyoming, it is being found that acid production can cause problems with surface reclamation (Table 1).

Acid production from carbonaceous materials has been recently documented in the Powder River Basin, Big Horn Basin, Hanna Basin and the Southwestern coal regions of Wyoming (Schnitzer and Fransway, 1982; Boon, 1984a; Boon and Smith, 1985). Extremely acid mine soils, overburden and abandoned coal spoils have recently been identified in New Mexico, Texas and Montana

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(Fisher and Munshower, 1984; Miller, et al., 1976; Arora, et al., 1980; Hagener, 1985).

Table 1.--Chemical analysis from reclaimed spoils, Powder River (A), and Hanna Basins (B), Wyoming.

Site	A	B
pH	2.8	3.8
SO ₄ - S (ug/g)	3024	2600
Exch. Al (ug/g)	530	--
H+ (meg/100g)	0.6	--
Total S %	--	0.72
CaCO ₃ %	0.1	0.1
ABP	-0.3	-21.3

It should be mentioned that a wide range of textural materials other than carbonaceous shales are capable of producing acidity in the western United States (Fisher and Munshower, 1984; Boon, 1984b; Boon and Smith, 1985).

Highly carbonaceous materials (rider coal, partings, leonardite and carbonaceous shales) have been attributed with producing acidity upon oxidation. Pettijohn (1957) has defined carbonaceous shale as containing greater than 3 percent organic carbon. Carbonaceous materials typically contain high concentrations of sulfur (S) and often contain greater quantities of pyritic sulfur than associated coal (Merritt, 1983). Hinkley, et al. (1978) demonstrated that carbonaceous shales have higher pyrite concentrations than non-carbonaceous shales. Sulfide minerals occur in significantly higher concentrations in the finer grained sedimentary rocks associated with coals: roof shales, underclays and partings (Arora et al., 1980; Valkovic, 1983; Boon, 1984b). Although pyrite is the dominant sulfide mineral in coal, significant amounts of other sulfide minerals have been identified: marcasite, sphalerite, galena, chalcopyrite and arsenopyrite (Finkelman, 1981; Valkovic, 1983). Dreher, et al. (1985) recently identified galena, sphalerite, pyrite and chalcopyrite in Wyoming coal and overburden. However, overburden samples had far fewer sulfides than the coal. The chalcophilic elements are those which commonly form sulfides. In addition to sulfur they include: Zn, Cd, Hg, Cu, Pb, As, Sb, Se, and others.

Carbonaceous materials deposited in marine environments can contain appreciably more pyrite than fresh water deposits. The mechanisms for sedimentary pyrite formation has recently been reviewed (Berner, 1984). Although total sulfur concentrations in the Powder River Basin seldom exceed 2%, highly pyrite overburden is occasionally identified (Table 2).

Table 2.--Sulfur fractionation, selected overburden sample, Powder River Basin, Wyoming

Depth (ft.)	Total S %	Sulfate S %	Pyritic S %	Organic S %
62.8 - 63	10.9	3.24	5.07	2.59
125.4 - 128.1	5.68	0.01	4.61	1.06

Pyrite appears to be the primary culprit involved in acid production in the west. However, a number of cases seem to indicate that organic sulfurs may be playing a role in the acid production phenomena (Frederick, et al., 1957; Schnitzer and Fransway, 1982; Dollhopf and Russell, 1984; Fisher and Munshower, 1984).

The determination of an elements association with the inorganic or organic fraction relies largely on indirect or circumstantial evidence. Traditionally sink-float separation of coal and carbonaceous material have been the most frequently used approach to elucidate the mode of occurrence of the chemical elements. It is presumed that those elements concentrated in the lighter specific gravity fractions are organically bound. Finkelman (1981) identified micron-size sphalerite, chalcopyrite, pyrite, marcasite, and over a dozen other minerals included in the organic fraction. These minerals were rafted up to the lighter specific gravity fractions by the organic material in which they were encased. Thus, the appearance of an "organic" association for the element was created.

The organic S fraction of Iowa coals was shown to be mostly micron size pyrite and small framboids rather than true organically bound S (Greer, 1976). Pyrite, Al and Si are the primary materials occurring in the lumina of remnant cells in coaly materials (Dutcher, et al., 1983). Pyrite has been detected in the nitric acid insoluble residue from bituminous coals. These small grains of pyrite (1-3 um) are embedded in the organic matrix (Given and Miller, 1978). The authors suggest that the problem can be overcome by performing the nitric acid extraction on - 300 mesh materials instead of the usual - 72 mesh. Finkelman (1981) indicated concurrence with this suggestion through the demonstration that zinc, copper, cadmium and lead occur as fine grained sulfide minerals which are increasingly released from their organic matrices upon grinding to very fine particle sizes. Increased grinding prior to pyrite determinations will yield more quantitative values for pyrite concentrations in overburden materials. Only then can the contribution of organic sulfur to acidification be determined.

Another potential problem in attempting to predict the acid forming capabilities of geologic materials is the reaction time of pyrites. Storage of drill hole cores and chips for differential time periods and varying moisture and oxygen contents introduces unconfined variability in geologic baseline data. Rapid sulfur oxidation may take place once the core is removed from the drill hole. This can be inferred from baseline data when the appropriate parameters such as the pyrite degradation products; aluminum, iron, magnesium, and calcium sulfate salts, are included in the analysis. Simply air drying wet samples after collection can oxidize significant quantities of pyritic materials (Brinkman and Pons, 1972; Dacey and Colbourn, 1979). Unfortunately, the amount of pyrites oxidized during sample collection and preparation has not been quantified.

Sulfur Determination

The traditional method utilized for predicting the maximum acid production or potential in geologic materials is defined by Smith, et al. (1974). Smith outlined two alternate procedures for determining the acid potential, a wet chemistry (peroxide oxidation) and a high temperature induction furnace method. Although it is assumed that both lab procedures measure the total oxidizable sulfur content, these two methods involve different analytical approaches. Hydrogen peroxide is such a strong oxidizing agent that variable amount of organic matter, primary minerals or constituents such as nitrogen are being oxidized concurrently. Analytical results on sample seem to support this contention as sample splits have been found to differ by an order of magnitude. Reproducibility problems with the peroxide oxidation procedure have resulted in the recommendation by WDEQ to use the furnace method for the determination of total sulfur. Recently, O'Shay (1982) modified the peroxide oxidation procedure which resulted in increased reproducibility.

The furnace method measures the total sulfur content after an acid wash to remove the sulfates. By rinsing the sulfates with acid before total sulfur analysis, some acid producing potential is lost. Although a sulfate rinse is justified to remove gypsum within the overburden, acid can dissolve the iron sulfates which will hydrolyze water and produce acid (Caruccio, et al., 1981). As jarosite $KFe_3(SO_4)_2(OH)_6$, weathers it can undergo hydrolysis to ferric oxides, oxyhydroxides or hydroxides producing 3 moles of acidity for every mole of jarosite (Carson, et al., 1982). Iron sulfate minerals found in weathered Illinois coals include: szomolukite, rozenite, melanterite, coquimbite, rosemerit and jarosite. Most ferrous sulfates would be effectively removed by a hydrochloric rinse. Table 3 compares hot water extractable sulfate with HCl extractable sulfates. The HCl extract

removes a significant amount of sulfates not removed by the hot water extract. Sulfate removal with dilute acid is not an acceptable practice due to the removal of acid producing sulfates.

Table 3.--Sulfate extraction, hot water versus HCL

Total S%	HCL Sulfate S%	Hot Water Sulfate %	Difference %
1.51	0.95	0.36	0.59
0.97	0.70	0.28	0.42
0.86	0.58	0.30	0.28
0.45	0.44	0.04	0.44
0.18	0.13	0.06	0.07

An excellent assessment of the methodologies for iron pyrite determination in coal mine spoils has been published (Dacey and Colbourn, 1979). Many analytical techniques for measuring pyritic sulfur are based on the principle that pyrite is soluble in nitric acid. Samples are predigested in hydrochloric acid then digested in nitric acid. Pyritic sulfur is based on the iron released during the nitric acid digest. As pointed out earlier, the hydrochloric digestion procedure removes iron sulfates. Finely disseminated pyrite can be resistant to nitric acid if contained within coal macerals or clay aggregates (Stanton and Renton, 1981; Levinson and Jacobs, 1977; Given and Miller, 1978).

Neutralizing Bases

Carbonates are of particular interest in overburden materials because of their potential role in neutralizing acidity. The buffering capacity or neutralizing potential produced by overburden weathering is usually determined by measuring the amount of titratable alkaline earth carbonates that are present. The most widely used method involves acid neutralization (Richards, 1954). This procedure often results in higher values since soil constituents other than carbonate may react with the acid. Thus the buffering capacity of the ABP calculation is probably overestimated using a hot hydrochloric acid digestion to dissolve all the carbonates.

A more accurate determination of carbonates can be achieved utilizing the Allison (1960) procedure. The procedure has recently been outlined (Nelson, 1982). Inorganic carbonates are decomposed by treating the soil sample with 2N H_2SO_4 containing $FeSO_4$ as an antioxidant to prevent release of CO_2 from organic material. The evolved CO_2 is then measured gravimetrically or with other appropriate methods.

Since the weathering of Fe (siderite) and Mn carbonates may involve oxidation and consumption of hydroxyl during precipitation as Fe or Mn oxides and oxyhydroxides they will not aid in neutralizing acidity (Dixon, et al., 1982). If Fe or Mn carbonates are present in the overburden, an overestimation of the neutralization potential is realized.

Lime requirements are difficult to make for spoils that contain carbonates. The problem is due to the uncertainty of the particle size distribution of the natural carbonates. Native carbonates usually occur as large particles which are inefficient in neutralizing acid generated by the oxidation of sulfides (Barnhisel, et al., 1982). Sample preparation for the neutralization potential requires finely ground material, thus the data collected no longer represented field conditions and the in situ neutralization potential is overestimated.

If carbonates are coated with iron oxides, this will effectively eliminate this material from neutralizing any acid which is produced in the replaced spoil (Caruccio and Geidel, 1981). In lignite overburden from Texas, carbonates are often occluded within a shell of goethite in the oxidized zone thus eliminating any additional neutralization potential (Dixon, et al., 1982). Carbonates coated with iron oxides have been reported for sandstone spoils in Kentucky (Barnhisel, et al., 1982). This iron oxide coating is broken down during sample preparation thus exposing the carbonate to neutralization reactions. The result is an overestimation of the actual neutralization potential. Iron oxide coating of carbonates have been identified in Wyoming coal and uranium overburden and spoils.

Geidel (1979) has shown that infiltrating soil water quickly becomes saturated with respect to CaCO_3 whereas the soil water system is continually undersaturated with respect to pyrite as long as oxygen is present. In a replaced spoil situation it is quite possible to effectively leach all the CaCO_3 from the surface materials and leave behind significant amounts of pyrite in an oxidizing environment. In the long term, this process could produce significant pH drops in the surface spoil materials and create an unsuitable reclaimed surface. This process would be significantly reduced in the arid west but may be a major factor in higher precipitation areas such as Texas.

Mitigation of Acid Spoils

Mitigation practices include neutralization reactions (liming) and burial of acid materials below a cover of suitable materials.

Liming practices are based on agricultural principles of a plow layer depth of about 18 cm. The purpose of liming is to raise the soil pH to an acceptable level. Field reaction rates vary inversely with pH, lime particle size, and

solubility of the liming agent. The laboratory lime requirement value is customarily multiplied by a conversion factor (often two or more) to more realistically estimate the amount of lime needed to achieve a given field pH. Lime requirement based on buffered solutions or potential acidity test may have to be doubled to ensure adequate pH levels over an extended time period (Akin, 1966; Ebelhar, 1977). For mined lands, greater quantities are needed in order to react with upward movement of acid water from below the zone of lime incorporation (Barnhisel, et al., 1982).

Barth (1984) demonstrated that acidification of topsoil placed over acid-mine spoils can occur in Wyoming. Five years after plot construction, acidification extended from 5 to 10 cm into the overlying soil, and pH values of soil in the acidification zone decreased from 1.0 to 1.8 units. A soil depth of approximately 100 cm was required over acid spoils to achieve grass production comparable with rangelands in good condition.

Adequate mixing of lime is a serious limitation in reclaiming acid-mine spoils. Under the most optimum conditions depths of incorporation of only 15 to 20 cm may be obtained (Barnhisel, et al., 1982). Mitigation of acid spoils with lime may only be a temporary solution since most plants require rooting depths of more than 15 to 20 cm and upward acidification may occur.

TRACE ELEMENTS

The mechanisms for trace elements accumulation in coals and carbonaceous materials have been summarized (Finkelman, 1981; Valkovic, 1983). Trace elements which are enriched in coal and carbonaceous materials include Hg, F, Cr, Mo, Pb, As, Se, Cd, B, Sb and Cl. Table 4 identifies the trace element composition for the Anderson (Roland-Smith) coal seam, Campbell County, Wyoming. The National Research Council (1980) lists the trace elements of greatest concern in coal and coal resource development as: As, B, Cd, Hg, Mo, Pb and Se.

Small coal lenses, stringers, and carbonaceous shales have been recognized as extraordinary concentrators of trace elements. Most elements occur in significantly higher concentrations in the finer-grained sedimentary rocks associated with the coals; roof shales, underclays and partings (Valkovic, 1983). Thinner bedded coals and carbonaceous materials typically have higher trace element concentrations than thicker seams. Although elements may be concentrated within any bench of a coal, higher concentrations are more commonly observed at the top and/or bottom of the seam.

During the mining process, carbonaceous materials which formed in an acid reducing environment are exposed to an oxidizing

environment. Increases in water solubility and mobility of many trace elements can occur following oxidation. Carbonaceous materials placed within the top four feet of regraded spoil (potential rooting zone) may release phytotoxic levels of boron. In addition, molybdenum and selenium may become available to reclaimed vegetation in quantities large enough to produce toxicities to grazing livestock. Increased trace element solubility may result in backfill water quality degradation if these materials are buried in a water saturated zone.

Table 4.--Summary of trace element composition for the Anderson (Roland) Coal Seam, Campbell County, Wyoming

Element	Average	Maximum	Minimum	Sample Size
	------(ug/g)-----			
Arsenic (As)	1.2	19	0.1	67
Boron (B)	32	202	4	67
Bromine (Br)	17	79	0.2	11
Cadmium (Cd)	1.4	13.1	0.3	67
Chromium (Cr)	18	690	2	67
Copper (Cu)	21	138	3	26
Fluoride (F)	80	294	0.01	64
Mercury (Hg)	0.3	7	0.01	67
Molybdenum (Mo)	4	25	0.2	11
Nickel (Ni)	7	29	0.8	67
Lead (Pb)	12	47	0.4	67
Selenium (Se)	5.8	44	0.2	11
Uranium (U)	5.7	32	1	10
Zinc (Zn)	26	260	3	26

Ebens and McNeal (1977) suggest that any reclamation efforts in the Northern Great Plains should treat shale materials as chemically suspect due to trace element concentrations. Pettijohn (1957) found unusually high trace element concentrations in carbonaceous shale. Hinkley, et al. (1978) demonstrated that carbonaceous shales have higher trace element concentrations than non-carbonaceous shales and sandstones.

Table 5 demonstrates increased Pb and Cu concentrations in carbonaceous shale, carbonaceous mudstone and lignite associated with a uranium roll front deposit.

Boron

Boron (B) toxicity of plants is of particular concern in arid regions where naturally high levels of boron exist. Materials that contain appreciable biologically inert organic carbon, such as carbonaceous shales, sonardite, or coal slack, may contain toxic levels of boron (Power, et al., 1978). Average

boron concentrations for shale of the Fort Union formation in the Northern Great Plains Coal Province are reported to be 98 ug/g with an expected 95 percent confidence range of 51-190 ug/g (Ebens and McNeal, 1977). Analysis of sandstones of the same formation gave an average boron concentration of 51 ppm. Observed ranges of boron measured 0.5 - 26.0 ug/g hot water soluble (HWS-B) in spoils at twelve western coal strip mines (Severson and Gough, 1981, 1983). Extremely high B levels in soil, overburden, spoil and plants at a Wyoming mine (110-610 ug/g) are indicative of phytotoxic conditions and only the most B tolerant species should be expected to survive (Gough and Severson, 1983).

Table 5.--Selected overburden data, Sweetwater Uranium District, Wyoming

Drill Hole	Depth (ft)	pH	Cu	Pb	Lithology*
			--ug/g--		
1136C	132-140	8.6	0.8	3.1	ss
	140-145	8.7	5.8	44.0	carb-sh
	145-149	7.3	14.0	51.0	lig
	149-156	8.8	1.7	22.0	sis
1407	156-165	8.4	1.0	6.0	ss
	0-5	9.5	1.3	3.2	ms
	15-25	8.6	2.2	6.4	sis
	25-40	7.5	5.8	34.0	carb-ms
	40-55	7.7	2.3	7.5	ss

* ss sandstone
sh shale
sis siltstone
lig lignite
carb carbonaceous
ms mudstone

Selenium

Selenium is the most strongly enriched element found in coal (Valkovic, 1983). Selenium can replace sulfur in organic complexes. Because of this substitution of Se in organic complexes and in sulfides, the Se content of organic shales and coals may be many times its crustal abundance (Dreher, et al., 1985). These same authors have identified lead selenide in Wyoming coal. Selenium concentration in sedimentary rocks of the western United States range from 0.1 - 890 ug/g (Lakin, 1961). The average selenium concentration for coal in the Powder River Basin is 5.8 ug/g (Table 4).

Overburden data for the Hanna Basin (Table 6) demonstrates Se enrichment of coaly and carbonaceous materials.

Table 6.--Selected overburden data, Hanna Basin, Wyoming

Depth (ft)	Lithology*	Se (ug/g)
46-52	ss	0.05
52-62	sh-carb sh	0.30
62-83	sis	0.03
83-85	sh	0.02
91-94	sis-c	0.12
94-97	sh-carb sh	0.35
97-102	sis	0.08
101-105	sh	0.06

* ss	sandstone
sh	shale
carb	carbonaceous
c	coal
sis	siltstone

Ingestion of Se contaminated plants has resulted in substantial livestock losses in Wyoming (Beath, 1982). Plants containing greater than 5 ug/g Se are considered toxic to livestock (National Research Council, 1976). The Wyoming Department of Environmental Quality - Land Quality Division (1984) recently lowered the "suspect" level for Se in overburden to 0.1 ug/g. This value is based on the work of Olsen, et al., (1942) and Soltanpour and Workman (1980). Both studies suggested that hot water extractable Se in excess of 0.1 ug/g (100 ppb) be considered suspect in producing toxic feed.

The value of 0.1 ug/g has been proposed for both topsoil and overburden. Olsen, et al. (1942) observed that subsoil feeding of soil Se by plants was necessary to account for the plant Se concentrations. Kubota and Cary (1982) suggest that subsoil feeding may contribute to the lack of correlations between soil Se and plant concentration. Soltanpour, et al. (1982a) found that the concentration of selenium in wheat grain was predictable using the NH_4HCO_3 - DTPA (AB-DTPA) soil test if soil samples were obtained to a depth of 90 cms. Shallow samples were not effective.

Historically, hot water soluble (HWS) selenium has been recommended for evaluating plant available Se. Since the advent of inductivity coupled plasma-atomic emission spectrometry (ICP) soil testing labs have developed multi-element extraction techniques for simultaneous multi-element analysis. The ammonium bicarbonate - DTPA soil test (AB-DTPA) was developed for multi-element extraction of macro- and micro-nutrients (Soltanpour and Schwab, 1977) and more recently has been used to assess availability and toxicity of selenium to plants (Soltanpour and Workman, 1980). High linear correlations were found between AB-DTPA and hot water soluble Se in coal mine soil and overburden materials from coal mines in western

Colorado (Soltanpour and Workman, 1980). More selenium was extracted by AB-DTPA than HWS. It appears that AB-DTPA can be used to assess selenium availability as well as hot water in soils and overburden.

Many soils contain less than 50 ug/l of water extractable Se. Low levels of Se in aqueous solutions have been successfully measured using hydride generation (Pierce, et al., 1976; Thompson, et al., 1978). Only Se (IV) is readily reduced to selenium hydride (SeH_2) by NaBH_4 (Thompson, et al., 1978). However, most of the water soluble selenium in soils of arid regions is in the selenate (+6) form (Olsen, et al., 1942). Organic constituents in the extracts interfere with selenium hydride generation (Workman and Soltanpour, 1980). Therefore, it is imperative that a procedure for destroying organics and reducing Se (VI) to Se (IV) be utilized prior to selenium hydride generation. A procedure for pretreatment of soil extracts to be analyzed for selenium has been published (Workman and Soltanpour, 1980; Soltanpour, et al., 1982b). This procedure is currently recommended for Se analysis of soil and overburden in Wyoming (Wyoming Department of Environmental Quality - Land Quality Division, 1984).

The importance of selenium solubilization and mobility is not confined to plant uptake from the surface four feet of reclaimed spoil. Increased solubility and mobility of Se following oxidation of carbonaceous materials can occur if backfilled into a saturated zone. Overburden column leach analysis (Table 7) exemplify the potential for Se solubilization. The source of Se in the leachate from column B was determined to be a 5-15 foot thick coaly shale.

Table 7.--Selected overburden column leach analysis, Powder River (A) and Hanna Basins (B), Wyoming

	A	B	C**
Pore volume	1,2,3*	1	
pH	--	8.1	6.5-8.5
EC (umhos/cm)	--	3490	
TDS (mg/l)	2330	2590	5000
$\text{SO}_4\text{-S}$ (mg/l)	--	1500	3000
Selenium (mg/l)	0.21	0.545	0.05

* Composite pore volumes

** Wyoming LEQ-DEQ standards for livestock use

The correlation of Se concentrations in overburden and the initial effluent in numerous column leach studies from Wyoming demonstrated the solubility and mobility of Se in coal

overburden. The greatest Se concentrations in the effluent typically results from carbonaceous shales and top-of-coal cleanings. Top-of-coal cleanings and carbonaceous shales have been implicated in producing elevated Se concentrations in spoil wells at one mine in Wyoming. However, selenium concentrations have continued to decline over the past several years (Table 8) apparently due to increasingly reduced conditions.

Table 8. Selenium contaminated spoil well, Powder River Basin, Wyoming

	DATES					
	11/8	1/20	6/6	9/7	12/1	3/28
	82	83	83	83	83	84
pH	7.0	6.4	6.3	6.8	6.4	6.6
EC umhos/cm	6500	6200	6500	6400	5700	5520
Sulfate (mg/l)	3040	2950	3130	3080	3350	2900
Selenium (mg/l)	0.945	0.840	0.650	0.630	0.560	0.440

CONCLUSIONS

Reclamation efforts in the Northern Great Plains should treat shale material as chemically suspect due to trace element enrichment (Ebens and McNeal, 1977). Hinkley, et al. (1978) recommend that carbonaceous shales should be segregated for reburial away from the soil surface and groundwater zones. Merritt (1983) recommends that carbonaceous materials should always be selectively handled and placed four feet below the reclaimed surface and above the post-mining water table.

Highly carbonaceous materials (small coal lenses, stringers, partings, roof and floor shales) have been shown to produce acidity upon oxidation. The potential for acid production is a result of greater sulfide concentrations in these materials. Identified sulfides include: pyrite, micasite, sphalerite, galena, chalcopyrite and arsenopyrite. These same highly carbonaceous materials are recognized as containing extraordinary concentrations of trace elements. Trace elements which are enriched in carbonaceous materials from Wyoming include: As, B, Cd, Hg, Mo, Pb and Se. The oxidation and random placement of carbonaceous materials either within the surface four feet or within a saturated environment may reduce reclamation success through surface acidification, phytotoxicities, production of toxic vegetation or degradation of backfill water quality.

Several areas need further investigation.

- 1) Determine the contribution of organic sulfur to the acidification process.

- 2) Determine the grinding intensity (particle size) necessary to quantitate pyrite analysis.
- 3) Determine the occurrence, mobility and geochemistry of selenium in overburden and spoil materials.
- 4) Evaluate top-of-coal cleanings to determine their elemental composition and acid potential.
- 5) Monitor the weathering of mine backfill for acid production and increased trace element solubility over time.

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