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Physical and Chemical Properties of Coarse Coal Refuse from Southwest Virginia

by

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(ABSTRACT)

Coarse coal refuse is difficult to reclaim due to high potential acidity and coarse fragment content, low water holding capacity, low fertility, and other problems. Little is known about coal refuse properties, particularly as they relate to revegetation potential. This study was undertaken to determine the physical and chemical properties of composite samples from 27 coal waste piles of varying age. Selected physical and chemical properties varied widely across this sample set. The mean coarse fragment (>2mm) content of these materials was 60%. The average texture of the fine (<2mm) fraction was a sandy loam with 15% clay. The mean water retention difference, between 0.03 MPa and 1.5 MPa of soil moisture tension, on a whole sample basis was 0.08 g water/g refuse. The pH values varied from 8.3 to 3.0, and the older piles generally had lower pH values than the more recent piles. The saturated paste electrical conductivity (EC) was higher in the younger coal waste materials. Total elemental analysis revealed that Si, Al, Fe, and K were the most abundant elements in these materials. The mineralogy of three selected samples was found to be dominated by quartz in the sand and silt fraction and mica in the clay fraction. The physical factor most limiting to plant growth was found to be low water holding capacity. Low pH was found to be the chemical factor most limiting to plant survival. These findings indicate that some refuse piles may be suitable for direct seeding, but many will require heavy lime and/or organic treatments.

DEDICATORY

To

Mom and Dad

and

The Cows

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INTRODUCTION

Millions of dollars of both public and private funds are spent each year to reclaim active and abandoned coal refuse piles in the eastern United States. Of course, the United States is not the only country blessed with coal refuse. Coal refuse is a problem wherever coal is mined. These materials are difficult to reclaim due to physical problems, high levels of potential acidity, high soluble salt levels, low concentrations of plant nutrients, low water holding capacity, and high summer heat levels. One hundred and thirty-five million tons of coal refuse were produced in the United States in 1983. Of this total, 79% was coarse (> 0.5 mm diam.) refuse (Khan et al., 1986). If the same ratio of clean coal to refuse is assumed, refuse production increased to 153 million tons by 1986. With the passage of the new Clean Air Act, the demand for cleaner coal will increase. Currently much of the coal used in the generation of electricity is not mechanically cleaned. The use of cleaned coal in electricity production is increasing, however, and as the coal industry strives to produce cleaner coal, increasing tonnages of refuse will also be produced.

Coarse refuse is the subject of this study. Coarse refuse is that retained on a 20 mesh (0.5 mm) sieve. Fine refuse (slurry) is another problem that needs to be addressed, but because of the very different nature of that material, it was not included in our study. It is not uncommon for slurry pond dredgings to be incorporated into coarse refuse piles, however. As of 1988, $6.7 million had been spent to reclaim just 255 acres of abandoned coal waste piles in Virginia. This is above and beyond what the private coal companies have spent to reclaim their active refuse disposal areas, as required under the Surface Mining Control and Reclamation Act of 1977.

In short, there is currently a very large sum of money being spent on the reclamation of coal waste. Unfortunately, little comprehensive research has been conducted which would allow those reclaiming refuse areas to base their reclamation strategies on actual waste properties and conditions. To this date most of the "research" conducted on reclamation of coal waste has been unreplicated, site specific studies, on a single pile. However, due to the large amount of variability within and between piles, a reclamation strategy that works well on one pile, or even part of one pile, may completely fail on another pile. There have also been very few studies in which the refuse properties were evaluated, and then used to design replicated trials to evaluate the performance of different treatments.

In the 1970s the coal industry came under increasing pressure to reduce the detrimental effects of mining. This led to the passage of the National Surface Mining Control and Reclamation Act (SMRCA; PL-95-87, 1977). This act set new minimum standards for reclamation of all surface mines in the United States. Since refuse is disposed of on the land surface, it is also regulated under this act. Until this point in time, very little attention had been paid to refuse revegetation. The act (SMRCA) required that the miners post a monetary performance bond prior to disturbance of an area. If the performance of the vegetation is adequate, (generally $\geq$ 90% cover) inspected, and approved after 5 years, then the bond is returned to the miner and his responsibility for the area ends.

The initial requirement for reclamation of these materials is to cover them with a minimum of 1.2 m of topsoil or a suitable topsoil substitute. The pile is then fertilized and seeded. No augmentation with fertilizer is allowed for 5 years, unless an agricultural post mining land use has been designated. In Southwest Virginia, topsoil is at a premium due to steep slopes and erosion. Even using the miners' definition of topsoil as "anything that can be pushed with a bulldozer", it is very difficult and costly to generate enough topsoil to cover a pile with a 1.2 m lift. This has led to an interest in the direct seeding of these materials. This characterization study was initiated to determine which refuse materials are suitable for direct seeding.

Reclamation of refuse piles through the establishment of a permanent vegetative cover is very important for a variety of reasons. Through the establishment of vegetative cover, many of the hazardous properties of coal waste can be minimized or eliminated. First of all, erosion will be reduced. Reduction of erosion by vegetation is necessary because most coal refuse areas are located in the heads of steep watersheds. Vegetation will also stabilize the piles and incidents such as the outslopes of refuse piles sliding into peoples yards could be avoided. Also, vegetation will decrease runoff and thereby improve the water status of a material which has a low water holding capacity. Vegetation will also decrease the total deep leachate production by intercepting and trapping water. Furthermore, once a stable plant cover is established, cycling of plant nutrients can begin, which will vastly improve the nutrient status of these materials. Finally, vegetation, once established, will reduce the high heat loads that develop on bare refuse.

This study characterizes the physical and chemical properties of coal refuse and then relates these properties to reclamation potential. There have been a few studies which examined at coal refuse properties (Bland et al, 1977; Buttermore et al, 1978), but they did so from a total elemental, reprocessing standpoint. Those studies provide useful data on the range of refuse properties, but they make no mention of reclamation potential. This study will aid in the development of a system by which important refuse properties can be analyzed, and then from these parameters a best-choice reclamation strategy can be chosen. This choice will be based on actual properties, and not on what appears to work well in short term field trials.

In order to effectively establish vegetative covers, however, we need to characterize the properties of refuse and modify them as needed. As mentioned earlier, these materials are extremely variable, and this variability coupled with the lack of information about the fundamental relationships among waste properties, weathering processes with time, local site conditions, and long term reclamation success, has in many cases led to the use of inappropriate and expensive ineffective reclamation strategies. This study has given us better insight into coal refuse characteristics and will allow a better chance of reclamation success.

The objectives of this study were:

1. To provide a full chemical, and physical analysis of a broad range of coal waste piles from southwest Virginia. These piles represent most of the major coal seams, and vary in age from the 1920s to the present. The results of the analyses have been be used to estimate the variability of coal waste properties.

2. To determine the effects of weathering/aging on coal refuse with respect to reclamation potential.

In the long term the refuse properties evaluated in this study will be used to develop a classification scheme for coal refuse. This scheme will be used to evaluate refuse with respect to the establishment of a permanent vegetative cover. This study will provide baseline data for the development of this scheme, which will be completed by 1991.

LITERATURE REVIEW

Geologic Setting

The vast majority, if not all, of the coal produced in Virginia comes from the southwest Virginia coal field in Buchanan, Dickenson, Lee, Russell, Scott, Tazewell, and Wise counties. The coal is Pennsylvanian in age and ranges from high- to low-volatile bituminous. The coal beds occur in a sequence of sandstone, siltstone, shale, and occasional calcareous beds of fluvio/marine origin. The Pocahontas formation is the oldest Pennsylvanian coal-bearing formation in Virginia. This formation outcrops at the surface in Tazewell county. The Lee formation overlies the Pocahontas in the central and southwest part of the coal field. Immediately above the Lee formation is the Norton formation. The youngest coal-bearing formation in southwest Virginia is the Wise formation, which overlies the Norton formation. The Harlan formation , which overlies the Wise formation, also outcrops at the highest elevations, but no coal is currently mined from this formation in Virginia (Keystone Coal Industry Manual, 1988). There is a slight dip to the northwest in these strata. The coal seams that outcrop on the valley floors in Wise county occur on the ridgetops in Buchanan county. Most of the coal produced in Virginia is mined from the Norton and Wise formations (Keystone Coal Industry Manual, 1988)

Coal Refuse Research

Little work in coal refuse was performed in the United States before 1972. In that year, a refuse pile slid down the side of a mountain and buried the town of Buffalo Creek, WV. Several people lost their lives in this disaster. This disaster sparked interest in the stabilization of these materials. The passage of SMCRA in 1977 also prompted research into coal refuse. Reclamationists realized that reclamation of coal refuse areas would be difficult, and that they needed to find strategies which would work in the hostile conditions presented by coal refuse. It is interesting to note that the abandonment date of several piles in this study coincides with the passage of SMCRA. In general, coal refuse is not a well studied topic. Many inferences have been drawn between coal properties and refuse properties, but little work has been done to verify that these inferences hold true.

Coal Waste Weathering Studies

Coal waste weathering is also a subject which has not been well studied. The classification of soils developed from coal waste using the criteria of Sencindiver (1974) was studied by Delp (1975). In this study, 26 mine soils developed from coal waste were classified to the family level. Two families of Carbolithic Udispolents and two families of Pyrolithic Udispolents were needed to classify the mine soils examined. Carbolithic Udispolents differ from Pyrolithic

Udispolents in that the Pyrolithic Udispolents are coal waste soils which have been burned. Delp (1975) opted not to classify to the series level because the properties of the younger refuse piles were still rapidly changing.

There are several other important features of coal refuse soils documented in the study by Delp (1975). The majority of the surface horizons were topped with a pavement of coarse fragments. Beneath this pavement was a zone, usually 10 - 15 cm thick, which contained more fines than the underlying horizons. Local pockets of differing material were common in most profiles. The soil structure in surface horizons was weak granular or weak platy. The soil structure in subsurface horizons was massive, or coarse fragment controlled. Rooting depth was dependent on soil reaction (pH). He also observed that high carbon coal refuse had a particle density of 1.61 g/cm^3 which is much lower than the 2.65 g/cm^3 commonly used for soils. This is the only study that I was able to locate which examined the effects of weathering on coal waste with respect to soil development.

Coal Refuse Properties

Particle Size

Coal wastes are often coarse in texture. In modern prep plants this is due to separate coarse and fine coal cleaning circuits. The fine (<0.5mm) fraction is usually excluded from the coarse fraction and deposited as a slurry behind a dam of coarse refuse. In older piles the material was hand picked and very few fines were incorporated into the pile. The result of their coarse texture is a low water holding capacity which can be limiting to plant growth. Moulton et al (1974) studied particle size in some West Virginia refuse piles, and they observed that fresh refuse contained 68-95% coarse fragments while refuse that was 18 months to 30 years old contained 47-80% coarse fragments. They found that weathering of the refuse was decreasing the coarse fragment content and increasing the silt and clay content. Davidson (1974) sampled 79 inactive bituminous refuse piles in Pennsylvania and found their coarse fragment content to be 56-69%. The mean coarse fragment content of the piles sampled by Delp (1975) was 60%.

pH

Low pH is likely to be the chemical factor most limiting to the establishment and growth of plants on coal refuse. Although many refuse piles have a neutral or near neutral pH when they are originally deposited, the pH of refuse usually drops rapidly as the weathering of pyritic materials produces acidity. The detrimental effects of low pH have been extolled upon by many authors. For a discussion of these effects see Brady (1984), Foth (1984), or Thomas and Hargrove (1974).

In general, the reported values for pH of weathered coal refuse are in the strongly acid to extremely acid range. Two refuse piles in Illinois were sampled by Medvick and Grandt

(1976) and their pHs were found to be 2.33 and 2.53. Narwot et al., (1986) reports pH values ranging from 2.3 to 3.0 in a study of refuse associated with 4 coal seams from Illinois. The pH of coal refuse in West Virginia ranged from neutral to extremely acid in a study of 26 minesoils developed in coal refuse by Delp (1976). Five refuse piles in Illinois were sampled by Haynes and Klimstra (1975) and their pH values ranged from 2.4-3.0 with a mean of 2.8. Refuse with pH values below 3.5 seem to be indicative of refuse from high (> 2.0%) sulfur coal.

The mechanism responsible for the low pH of coal refuse is pyrite oxidation. This is the primary reason why so much coal refuse/minespoil/acid-mine-drainage research dwells on the pyritic sulfur content of these materials. The factors affecting the rate of pyrite oxidation are outlined by Caruccio et al.,(1988), and include surface area per unit volume, temperature, pH, oxygen concentration, and the presence of iron oxidizing bacteria such as *T. ferrooxidans*. The oxidation of pyrite takes place in a series of reactions which feed back upon each other once the process is started. The following equations for the oxidation of pyrite are taken from Caruccio (1988).

$$FeS_2(s) + 7/2\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad [1]$$

$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \qquad [2]$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3\ H^+ \qquad [3]$$

$$FeS_2(s) + 14\ Fe^{3+} + 8H_2O = 15Fe^{2+}\ 2\ SO_4^{2-} + 16\ H^+ \qquad [4]$$

In the first step (reaction 1) pyrite is oxidized to form sulfate, and ferrous iron and acidity are released into solution. It is interesting to note that only S is oxidized in the first step of this series. In reaction 2, ferrous iron is oxidized to form ferric iron. Singer and Stumm (1970) have characterized this reaction as the rate limiting step in this reaction series. Hydrolysis of the ferric iron produced in reaction 2 produces ferric hydroxide and acidity (reaction 3). At low pHs (<4) ferric iron may oxidize iron directly (reaction 4). Once sufficient quantities of ferric iron have been produced, sulfide is oxidized through reaction 4 and oxygen is only involved in the oxidation of reaction 2 (Caruccio et al., 1988).

At low pHs, bacteria such as *T. ferrooxidans* can greatly increase the oxidation rate of ferrous iron. The rate of oxidation of ferrous iron in the presence of *T. ferrooxidans* has been shown to be increased by more than 10^6 over the rate of ferrous iron oxidation by oxygen alone (Caruccio et al., 1988). Controlling acidity by controlling the rate determining step is the basis for the anti-bacterial, heavy P, and lime treatments used in the mitigation of acid mine drainage problems.

There are several results of pyrite oxidation that have a direct impact on the properties of coal refuse. The first of these is a reduction in pH due to the acid loads produced. This acidity can attack minerals causing alteration and release of cations into the system. Salts can form which increase the soluble salt content of soil solution to levels which can be toxic in some plants. Heavy metals such as Zn, Ni, and Cd which are impurities in the pyrite structure are also released during pyrite oxidation.

Electrical Conductivity

Measurement of the electrical conductivity (EC) of a solution in equilibrium will give an indication of the amount of soluble salts present in that soil. There is a correction factor to convert EC to ppm soluble salts (Rhoades, 1982), however most tables for plant salt toxicity use EC values. Differences in methodology make assessment of EC values difficult. The standard method uses the extract from a saturated soil paste. Other methods such as 1:1 and 1:5 soil to water extracts are also used. Care must be taken in making interpretations based on EC values whose methodology is not documented. The salts produced during pyrite oxidation and subsequent acid attack of minerals will produce elevated EC values. EC values ranging from 0.03 to 0.30 S m^{-1} were reported by Haynes and Klimstra (1975) for a study of five Illinois refuse piles. Medvick and Grandt (1976) observed EC values ranging from 0.2 to .62 S m^{-1} in experimental plots established on two refuse piles in Illinois. EC values of 0.4 S m^{-1} are considered to be growth inhibiting to the growth of plants which are salt sensitive (Bower and Wilcox, 1965).

Heavy surface applications of lime were found to reduce the EC of surface samples (0.22 S m^{-1}) as compared to deep samples (0.66 S m^{-1}) (Narwot et al., 1986).

Extractable Cations

Little information is available about the extractable cation status of refuse. Most studies measure a pH and a percent sulfur, but few go beyond this. Exchangeable cations were measured by Haynes and Klimstra (1975) in five refuse samples from Illinois. The mean extractable cation contents were; K 0.10 $cmol^+/kg$, Na 0.49 $cmol^+/kg$, Mg 1.38 $cmol^+/kg$, and Ca 16.34 $cmol^+/kg$. These values are all fairly low with the exception of Ca. The source of this Ca is likely to be the dissolution of Ca-salts, which are secondary precipitates from the pyrite oxidation reactions. The Ca released is not truly exchangeable, but rather an extractable phase. The presence of these salts make the determination of CEC in these materials quite difficult. The high Ca values also cause wide Ca:Mg ratios.

Extractable aluminum would also provide useful information, especially when planning lime requirements, however, little data on this parameter is available. Since coal refuse is low in pH it is assumed that it has a high extractable Al. This is not always the case, however. Haynes and Klimstra (1975) report a moderate mean extractable Al content of 2.8 $cmol^+/kg$ in material whose mean pH was 2.8.

Extractable H values above 20 cmol$^+$/kg in these samples indicate that the major source of acidity is active H$^+$ (Haynes and Klimstra, 1975).

Sulfur content

Sulfur content is one of the parameters that is measured in most coal refuse work, and this being the case there is a large amount of total S data available. Refuse will reflect the characteristics of its parent coal seam(s), and high S refuse will generally be associated with high S coal. Mining and cleaning methods, variability within coal seams, and weathering processes will also play a role in the S content of coal refuse. Buttermore et al., (1978) determined the S content of refuse from several mining districts. Total S values ranged from a low of 0.88% in eastern Kentucky and southwest Virginia to a high of 6.22% in northern West Virginia. Two refuse piles in Illinois had mean S contents of 2.27% and 3.00% (Medvick and Grandt, 1976). A single refuse pile near Staunton, Illinois had an average S content of 6.85% (Sobek and Sullivan, 1981). Rich and Hutchison (1990) report a prep plant operating in Nicholas County, WV usually produces refuse that is <1% sulfur, but when the Stockton seam (high S) is cleaned the S content of the refuse rises to above 1%.

Potential Acidity

Potential acidity (PA) is one of the most useful parameters of coal refuse which can be determined. The PA will estimate the extended acid producing potential of refuse. The PA is used interchangeably with lime requirement in this study. The units of PA are tons $CaCO_3$ / 1000 tons material (the classic acre-furrow-slice concept). There are several different methods for determining PA and lime requirement. These methods and their strengths and weaknesses are discussed by Caruccio et al., (1988), Caruccio and Geidel (1986), Perry (1985), and Barnhisel et al., (1982).

Two methods of determining PA will be used in this study. They are the acid-base-accounting method (ABA) and the hydrogen peroxide method. The ABA is based upon several assumptions that do not always hold true. All the S is assumed to be present in a pyritic form, and all S is assumed to react to form acidity. All bases present are assumed to be reactive and weather at the same rate of the pyrite. One problem with these assumptions is that significant amounts of S can be present in organic or sulfate forms and not react to produce acidity. This method overestimates lime requirement in many cases.

Another method of determining PA is to oxidize a finely ground sample using concentrated hydrogen peroxide. This method has been used with mixed results (Caruccio et al., 1988). This method was originally developed by Smith et al., (1974) and was the method of choice until the development of ABA in the mid 1970s. A modified version of this method has been used for at least 10 years to estimate initial lime requirements in Kentucky minespoils (Barnhisel et al., 1982). The rationale behind using this method is that it generally gives lime requirements that correlate well with reclamation success in field trials. Neither if these methods predict long term lime requirement accurately for all materials, however.

Total Elemental Analysis

The elemental content of coal refuse has been the subject of a few studies. The major elemental content of coal refuse has been examined by Robl et al., 1976, Williams et al., 1977, and Buttermore et al., 1978. The trace element content of coal refuse has also been examined by Williams et al., 1977, and Wewerka et al., (1976) present data for trace elements for coal refuse from West Virginia reported by Busch et al., 1975.

Mineralogy

The mineralogical composition of coal refuse has been determined by some researchers. In an effort to determine the packing properties of refuse, its mineralogy and elemental composition were determined by Busch et al., (1974). Quartz was found to be the major mineral species present. Clay minerals such as illite, kaolinite, and chlorite were also identified. Augenstein and Sun (1974) studied refuse from anthracite mining in Pennsylvania and found it was composed of

70-80% clay minerals (kaolinite, illite, pyrophillite) and 10-30% quartz. Small amounts of pyrite were also identified. Three refuse like materials from eastern Kentucky, were found to composed mainly of kaolinite, illite, and quartz with small amounts of pyrite and rutile (Barnhisel and Massey, 1969).

Materials and Methods

Pile Selection and Sampling

The refuse piles under study were selected on the basis of coal seam, age of the pile, accessibility, coal company co-operation, and other factors. Twenty-seven coal waste piles were sampled during the summers of 1986 and 1987. At least ten of the 24 major coal producing seams of southwest Virginia were included in this sample set. Large bulk samples (usually about 4 kg) were obtained by combining several subsamples from each sampling site. The subsamples were taken at random across the walkable surface of each pile. On the larger piles one or two different representative areas were sampled. Erosional gullies, burned areas, toeslope positions, disturbed areas, and other nonrepresentative features were avoided during sampling. When possible, stable, noneroded positions were chosen for sampling. All samples were taken from the upper 10 cm of refuse. All coarse fragments larger than 15 cm were excluded at the time of collection. In addition to the refuse sample, information on the slope, aspect, age, and seam composition was recorded at each site. After collection, the bulk samples of refuse were taken to the laboratory for chemical and physical and analysis.

Physical Analyses

All samples were air dried, sieved, and analyzed for the percentage retained on a 2 mm sieve. A subsample of the coarse fragments (> 2 mm) was retained for future analysis. The entire < 2 mm fraction was retained for detailed analyses. Moisture desorption determinations at 0.01, 0.03, 0.10, 0.30, and 1.5 MPa soil moisture tension were performed on the < 2 mm fraction of each sample using porous ceramic plates and pressure vessels. Refuse samples were placed in metal rings 12 mm in height by 48 mm in diameter on the ceramic plates and allowed to saturate by the procedure described by Richards (1965). Since most coal refuse shows limited development of soil structure, sample disturbance errors were minimal (Bruce, 1972). The soil moisture retention at each tension was then adjusted to reflect the entire refuse sample including coarse fragments, assuming the coarse fragments have negligible water holding capacity. Particle size analysis by the hydrometer method of Day (1965) was performed on all samples. Weight loss at 923 K, an estimator of carbon content, was determined by heating 5 g of < 2 mm coal refuse for 3 hr in a muffle furnace and recording the weight change.

Chemical Analyses

All chemical analyses were performed on the < 2 mm fraction only. Soil pH was determined in a 1:1 soil:water slurry with a combination glass-calomel electrode and a pH meter (McLean, 1982). Electrical conductivities were determined from a saturated paste extract using a conductivity cell referenced to standard 0.01 N KCl (Rhoades, 1982). Extractable Ca, Mg, and K were determined by atomic absorption spectrophotometry (AAS) after extraction with N NH_4OAc buffered at pH 7 (Thomas, 1982). Extractable aluminum was extracted with N KCl (Barnhisel and Bertsch, 1982). The amount of extractable acidity was determined using the barium chloride triethanolamine ($BaCl_2$-TEA) method of Peech (1965). Effective cation exchange capacity (ECEC) was estimated by the summation of the extractable cations (Ca+Mg+K+Al) (Chapman, 1965). Percent base saturation was determined by dividing the sum of the basic cations by the total CEC. A CEC determination by the double wash method of Zelazny (1987) was also made to adjust for errors due to soluble salts in these samples.

Available P was extracted using a double acid solution, (0.05N HCl and 0.025N H_2SO_4), with subsequent colorimetric analysis as described by Olsen and Dean, (1965). Sodium dithionite-citrate-bicarbonate (DCB) was used to extract free-Fe (Holmgren, 1967) which was then determined using AAS. Total-S was determined with a LECO™ furnace S-analyzer. Hot water soluble boron was extracted and colorimetrically analyzed as described by Parker and Gardner (1981). Potential acidity from a H_2O_2 digestion was determined as described by Barnhisel and Harrison (1976). This procedure was performed on a whole sample including the > 2 mm fraction.

Total Elemental Analysis

Total Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Na, P, Pb, Si, Zn was determined using ion coupled plasma emission spectroscopy (ICPES) from a total digest with HF in a pressure bomb (Bernas, 1968). Potassium was also determined from this digest by AAS. These digests were performed on the < 2 mm fraction only. As pretreatments for digestion, the samples were ground to 100 mesh in a Spex™ mixer mill and heated to 923 K to remove carbon.

Clay Mineralogical Analysis

The clay mineralogy of the < 2 mm fraction of samples CCR, JSR, and RRA were also investigated. Samples CCR and JSR were part of the S-199 toxic waste exchange project, and RRA was a part of a class project. Samples were pretreated with N NaOAc to remove soluble salts (Kunze 1965), with H_2O_2 buffered at pH 5 with NaOAc (Kunze 1965) to remove organic matter, and with DCB to remove free iron oxides (Holmgren, 1967). Sand was separated by wet sieving. Silt and clay were separated by centrifugation with subsequent decantation after dispersion with dilute Na_2CO_3 adjusted to pH 10. Oriented clay mounts were prepared by placing approximately 250 mg of suspended clay onto a unglazed ceramic tile using a suction apparatus. The samples were then saturated with Mg or K and washed free of excess salts, and the Mg saturated tiles were glycolated. X-ray diffractograms were obtained for the Mg samples at room temperature and after a 378 K heat treatment.

Diffractograms for the K saturated samples were obtained at room temperature, and after heat treatments of 378 K, 573 K, and 923 K. The diffractograms were generated using a General Electric XRD-8300 diffractometer equipped with a Digital Equipment Company L11/23 computer. The mounts were step scanned at a rate of 2° 2-Theta per minute using Cu K-alpha radiation and a graphite monochromator. The relative amounts of kaolinite, muscovite, vermiculite, and chloritized vermiculite were determined using relative peak areas.

Statistics

Descriptive statistics on each parameter, mean, standard deviation, and range were computed using the program Minitab Rel. 6.1.1 (Minitab, Inc. 1987). Minitab was also used to calculate the correlation coefficients between parameters. The computer program SAS (SAS Institute, 1985) was used for ANOVA procedures and for linear regression analysis. The Student-Newman-Keuls method of means comparison was also used (SAS Institute, 1989). This method is more conservative than Duncan's test or Fisher's LSD, but less conservative than Tukey's test (Zar, 1984). A two sample t-test was also performed as outlined by Zar (1984).

Many comparisons were drawn between the < 20 year old piles and the > 20 year old piles. These comparisons were made with the Mann-Whitney test. This test is also known as the Wilcoxon test (Zar, 1984). These comparisons were made using Minitab (1987). This is the nonparametric equivalent of the two sample t-test. The Mann-Whitney test is one of the most powerful statistical tests available. When either test applies the Mann-Whitney test is 95% as powerful as the two sample t-test (Zar, 1984). If the assumptions (normality, equal variance) of the two sample t-test are violated, the Mann-Whitney is the more powerful test (Zar, 1984).

Boxplots have been used to display the distribution of most parameters. The boxplots were plotted using Minitab (1987). Much information is contained in a boxplot. The box (Fig 1) represents the middle half of the data, or the two inner quartiles. The length of the box is called the interquartile range (IQR). The "whiskers" extend 1.5 times the interquartile range from the edge of the box. Observations which are between 1.5 and 3 IQRs away from the box are plotted as * and are mild outliers. Observations greater than 3 IQRs away are extreme outliers and plotted as O

The center (median) of the distribution is plotted as +. The relative location of the median (+) gives us information about the distribution of the data. If the data is normally distributed, then the + will be in the middle of the box. If the median lies in one end of the box it indicates skew in that direction.

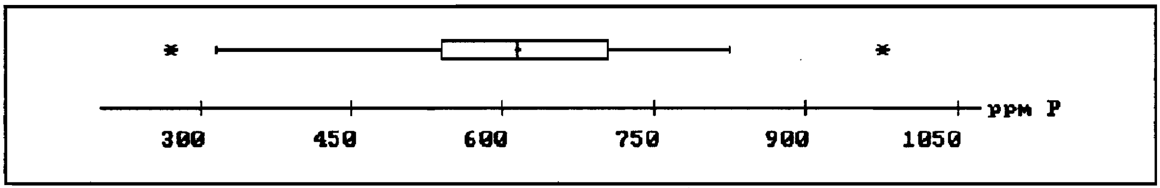

Figure 1. Example of a boxplot using total P data. * are mild outliers.

Pile Locations and Identification Codes

The names of the piles and their approximated or confirmed ages are presented in Table 1. Ages were estimated by the size of trees on the piles, by the configuration of the piles, by their locations, and by coal company information. Tree borings were usually inconclusive due to the hearts of many of the trees being rotted. All of the pre-1970s piles in this study were hillside dump type piles in which refuse was transported along a hillside, usually with some type of tram, and dumped over the edge of the slopes. It is also likely that most of the pre-1960s materials were hand picked. The run of the mine coal was placed on a belt and a number of workers (usually children) picked the refuse from the coal. The refuse was then dumped over a nearby hillside. These piles today resemble black alluvial fans descending over their hillsides. Location was also a clue to the age of the refuse. Old refuse piles are located near the portals of old mines and near the remnants of old tipples while the more recent piles are located in association with modern coal preparation plants.

Of the piles sampled, five were active piles (Table 1) at the time of sampling. Sites BMR, JSR, and RRA are currently active. Site NPB was active until 1987 and is currently in an inactive state. Site CCR is temporarily abandoned and slowly being reclaimed. This site has been inactive since 1982 but it is included with the active piles because it was produced

Table 1. The codes, names, and the ages and status of the refuse piles sampled in this study.

Site	Name	Age and status
BBR	Betty B Refuse	abandoned < 20 years
BMR	Bullit Mine Refuse	active
BWR	Blackwood Refuse	abandoned < 20 years
CCR	Crane Creek Refuse	abandoned 1980
DANTE	Dante Refuse Pile	abandoned > 50 years
DRP	Derby Refuse Pile	abandoned 1950's
DR1	Dale Ridge Pile #1	abandoned < 20 years
DR2	Dale Ridge Pile #2	abandoned < 20 years
JSR	Jewell Smokeless Refuse	active
KRP	Keokee Refuse Pile	abandoned 1927
LDR	Little David Refuse	abandoned > 20 years
LTR	Lee Town Refuse	abandoned in 1978 or 79
MRP	McComas Refuse Pile	abandoned > 50 years
NPB	New Pine Branch	Active but idle
NRP	Norton Refuse Pile	abandoned
PBRU	Pine Branch Refuse	abandoned late 1970's
PBRV	Pine Branch Refuse	abandoned late 1970's
PTH	Possum Trot Hollow	abandoned 1952
RDH	Red Dog Hill	abandoned > 60 years
RRA	Ramsey Refuse Pile	active
RRP	Roda Refuse Pile	abandoned 1957
RRR	Red Robin Refuse	abandoned > 40 years
SGR	Short Gap Refuse	abandoned > 50 years
WCR	Wise Coal Refuse	abandoned > 20 years
31H	31 Hollow	abandoned > 20 years
35P	Westmoreland Pile # 35	abandoned 1973
670A	Along Tazewell Co. 670	abandoned > 40 years
670B	Along Tazewell Co. 670	abandoned > 40 years

by a modern prep plant. Seven of the piles fell into the < 20 year old category. Site BWR is located near a coal loading facility; it is likely that refuse has been dumped here for many year and an occasional deposit of refuse may occur even today. Sites BBR, DR1, DR2, LTR, PBR, and P35 are all associated with coal preparation facilities. It is interesting to note that many of these piles were abandoned in the late 1970s which corresponds to the passage of SMCRA.

There were 10 piles between 20 and 50 years of age included in this study. Sites NRP and LDR are included in this group although their ages are not positively known. There are 5 sites in the study that were produced before 1940. This gives a wide range in ages of refuse materials represented in this study. The seam composition of the refuse materials are presented in Table 3. The Clintwood, and Imboden seams are heavily represented. At least 10 of the major coal producing coal seams are represented in the sample set. The older piles are usually single seam while the refuse from the modern preparation plants can come from many seams.

The locations of the piles are presented in Table 3. Seventeen of the piles sampled are in Wise County, VA. Four sites resided in Tazewell County, VA. Two piles each were sampled in Buchanan County, VA and Mercer County, WV. Single piles occur in Russel and Lee Counties in VA. Dickenson County, VA the largest coal producing county in the state is conspicuous by its absence from this list. The major coal

Table 2. The seam compositions for the refuse piles sampled in this study.

BBR	Upper Banner*
BMR	Dorchester, Imboden, Parsons
BWR	Load out facility, likely many seams
CCR	76% Pocahontas No. 6, 24% Pocahontas No. 12
DANTE	Clintwood possibly Blair and upper Banner*
DRP	Imboden
DR1	Clintwood and Blair*
DR2	Clintwood and Blair*
JSR	Tiller, Jawbone, Kennedy
KRP	Wilson
LDR	unknown
LTR	Upper Banner, War Eagle
MRP	Pocahontas No. 6*
NPB	Taggart Marker maybe some Taggart
NRP	Blair probably others, load out facility
PBRU	Taggart Marker maybe some Taggart
PBRV	Taggart Marker maybe some Taggart
PTH	Imboden
RDH	Clintwood, Blair*
RRA	75% Dorchester 25% Norton + Clintwood
RRP	Imboden
RRR	Clintwood, Blair
SGR	unknown
WCR	Clintwood
31H	Pocahontas No. ?
35P	Parsons
670A	unknown
670B	unknown

* = estimate

Table 3. The locations of the refuse piles sampled in this study, and estimates of their areas.

Code	Location	Size
BBR	Blackwood, Wise Co. VA	16 ha
BMR	Appalachia, Wise Co. VA	>81 ha wc
BWR	Blackwood, Wise Co. VA	3 ha
CCR	Crane Creek, Mercer Co. WV	>40 ha
DANTE	Dante, Russel Co. VA	4 ha
DRP	Derby, Wise Co. VA	2 ha
DR1	Coeburn, Wise Co. VA	8 ha
DR2	Coeburn, Wise Co. VA	6 ha
JSR	Vansant, Buchanan Co. VA	>40 ha wc
KRP	Near Keokee, Lee Co VA	8 ac
LDR	Near Cranes Nest Wise Co. VA????	<1 ha
LTR	Leetown Buchanan Co. VA	10 ha
MRP	McComas, Mercer Co. WV	2 ha
NPB	Near Pardee, Wise Co. VA	8 ha
NRP	Norton, Wise Co. VA	2 ha
PBRU	Near Pardee, Wise Co. VA	8 ha
PBRV	Near Pardee, Wise Co. VA	
PTH	Near Stonega Wise Co. VA	8 ha
RDH	North of Coeburn, Wise Co. Va	12 ha
RRA	Tacoma, Wise Co. VA	120 ha wc
RRP	Roda, Wise Co. VA	8 ha
RRR	North of Coeburn, Wise Co. Va	4 ha
SGR	Near Short Gap Tazewell Co. VA	4 ha
WCR	Dorchester, Wise Co. VA	1 ha
31H	Near Amonate, Tazewell Co. VA	1 ha
35P	Near Pardee, Wise Co. VA	1 ha
670A	Near Raven, Tazewell Co. VA	6 ha
670B	Near Raven, Tazewell Co. Va	6 ha

wc = when completed

producer in this county, Pittston Coal, would not allow us access to their property, thus we did not take samples in this area.

Results and Discussion

Physical Properties

Coarse Fragment Content

The amount of coarse fragments or material > 2mm in diameter will strongly influence many of the physical and some of the chemical properties of coal refuse. Since many processes and phenomena are surface area controlled, it is obvious that the particle size will have a large influence on the reactivity of coal refuse. The amount of soil size materials essential for plant establishment varies, but less than 20% is considered to be a limiting factor (Haynes and Klimstra, 1975).

The results of the sieve analysis are presented in Table 4. The sample set mean of 60% >2mm is similar to the coarse fragment content reported by Buttermore et al. (1978) and Delp (1975) for refuse piles in this region. It was observed that coarse fragment content increased with depth in the few piles that were sampled with depth. This trend was also observed by Delp (1975) in a study of coal refuse in central West Virginia. Boxplots of the sieve analysis data (Fig. 2a and 2b) show the data to have a near normal distribution with no outliers.

It was assumed that the coarse fragments are chemically unreactive and contribute little to water holding capacity. This is probably true in the laboratory, where the materials

Table 4. Results of the sieve analysis performed on the 27 pile sample set.

Site	% >2mm	% < 2mm
BBR	55	45
BMR	66	34
BWR	58	42
CCR	77	23
DANTE	54	46
DR1	45	55
DR2	46	54
DRP	71	39
JSR	71	39
KRP	65	35
LDR	53	47
LTR	57	43
MRP	60	40
NRP	60	40
PBRU	58	42
PBRV	72	28
PTH	66	34
RDH	63	37
RRA	56	44
RRP	55	45
RRR	48	52
SGR	72	28
WCR	64	36
31H	50	50
35P	43	57
670A	68	32
670B	72	28
MEAN	60	40

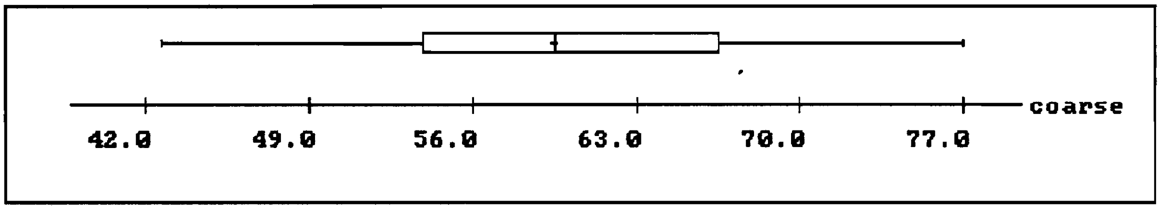

Figure 2a. Boxplot of the distribution of coarse fragments from the 27 pile sample set.

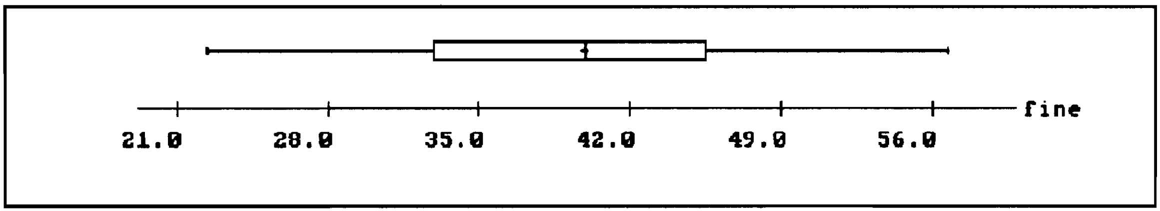

Figure 2b. Boxplot of the fine fraction content of the 27 pile sample set.

are dried, shaken, and sieved, and have no real "structural" arrangement, and to some extent in older refuse piles which are stacked loosely against hillsides. In modern refuse piles, the materials are packed to prevent erosion and spontaneous combustion. During this compaction the coarse fragments aid in tight packing of the fine material due to their incompressible nature. This may give the coarse fragments some role in water holding since the fine fraction will be tightly packed against the coarse fragments. Percolating water and rooting will often be concentrated along the faces of coarse fragments in these situations.

Examination of the coarse fragments in the refuse piles shows that the majority of the rock types are shales. There are also some sandstones present. Shale fragments that are at the surface and have bedding planes which are perpendicular to the ground surface tend to weather to smaller particles quickly. This can be observed on the surfaces of the fresh refuse piles.

There is no clear relationship between coarse fragment content and refuse age. The older piles (< 20 yrs) have a higher mean coarse fragment content (61%) than the younger piles (<20 yrs), but there is no significant difference between these means (Mann-Whitney test, $p = 0.10$). Mining and cleaning methods and rock hardness are the primary determinate factors for the wastes' initial particle size. In modern cleaning plants, the refuse from the fine coal cleaning circuit may be excluded from the refuse pile surface altogether. In older piles much of the material was handpicked and this resulted in a large proportion of coarse fragments in the refuse. The change from separate coal cutting and loading machines to continuous mining machines, which integrated these jobs into one machine, resulted in the production of finer run of the mine coal. It is speculated that this also resulted in finer refuse. Piles in which the shale fragments are hard, such as CCR and MRP tend to have a correspondingly high proportion of coarse fragments.

Particle Size

The fine (< 2 mm) fraction of these materials was used for nearly all of the chemical analyses. The fine fraction was assumed to dominate soil solution chemistry although, in most cases, it made up < 50% of the refuse by weight. Crushing the whole sample was considered, however, this procedure would expose large amounts of unweathered surfaces to the solutions used in extraction and analysis. This exposure would lead to dissolution of freshly exposed minerals, and erroneous results in many cases. The aim of this project was to analyze the properties of these materials with respect to revegetation, in a state that represents their condition in the field. For this reason analyses were limited to the < 2mm fraction. The amount of water and nutrients provided by the coarse fraction was assumed to be negligible.

The particle size distribution of the soil sized fraction is controlled by the proportion of shale to sandstone in the pile, the hardness of the materials, and the methods by which to materials were cleaned and mined. Sites CCR and MRP are derived from a hard competent shale that weathers to smaller shale fragments. These materials have a correspondingly high sand content. Sites LTR and KRP are derived from a fissile shale grading to a mudstone, and have a high clay content. At sites BMR and JSR the cleaning process includes a fine coal cleaning circuit, which results in little silt and clay sized materials in these refuses. The older piles (> 20 yrs) have coarser textures even though they have been exposed to weathering for a long periods of time. It is likely that the silt and clay sized materials were lost from the surfaces of these piles by sheet erosion. This erosion loss would result in the concentration of sand sized material and coarse fragments at the pile surface, which is evident in some piles. This is evident in both the coarse fragment content and the sand content of the soil size fraction.

The results of the particle size analysis of the soil size fraction are presented in Table 5. The mean sand (2 mm - 0.05 mm) content was 62%, the mean silt (.05 mm - 0.002 mm) content was 22%, and the mean clay content (< 0.002 mm) was 16%. Sand and silt content appear to be normally distributed as can be observed in the boxplots of the data (Fig. 3a and 3b). The mean clay content is skewed upward due to the

Table 5. Results of the particle size analyses performed on the 27 pile sample set and USDA textures.

Site	% Sand	% Silt	% Clay	Texture
BBR	57	28	15	sandy loam
BMR	78	13	9	sandy loam
BWR	60	25	15	sandy loam
CCR	67	18	15	sandy loam
DANTE	51	30	19	loam
DR1	49	27	24	loam
DR2	53	36	11	sandy loam
DRP	75	14	11	sandy loam
JSR	80	9	11	loamy sand
KRP	44	20	36	clay loam
LDR	58	33	9	sandy loam
LTR	42	16	42	clay
MRP	76	1	23	sandy loam
NRP	62	22	16	sandy loam
PBRU	52	30	18	loam
PBRV	45	36	19	loam
PTH	76	16	8	sandy loam
RDH	77	15	8	sandy loam
RRA	54	26	20	sandy loam
RRP	65	25	10	sandy loam
RRR	61	19	20	sandy clay loam
SGR	75	11	14	sandy loam
WCR	53	28	19	sandy loam
31H	66	24	10	sandy loam
35P	44	37	19	loam
670A	72	18	10	sandy loam
670B	73	20	7	sandy loam
MEAN	62	22	16	sandy loam

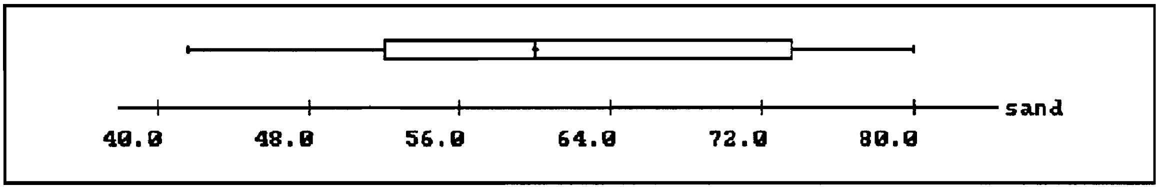

Figure 3a. Boxplot of the distribution of sand content in the 27 pile sample set.

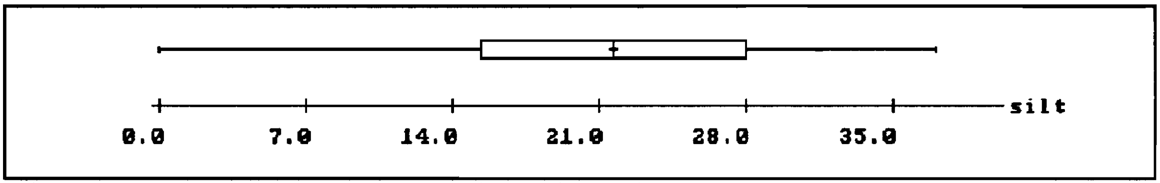

Figure 3b. Boxplot of distribution of silt content for the 27 pile sample set.

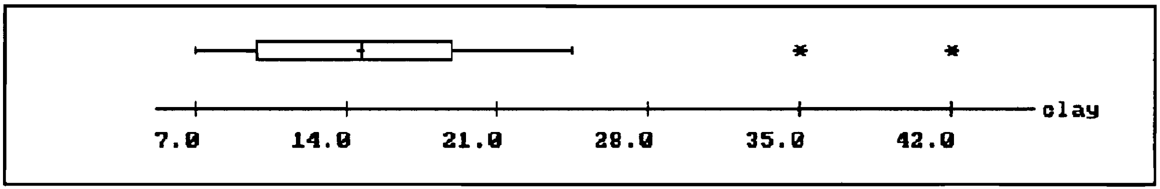

Figure 3c. Boxplot of the distribution of clay content for the 27 pile sample set.

presence of 2 samples which have high clay contents and are mild outliers in this sample set (Fig. 3c). The USDA soil texture for the sample set mean was a sandy loam. Sandy loam was also the texture of 18 out of 27 of the piles. The USDA textures are also presented in Table 5. A sandy loam texture is similar to the findings of Delp (1975) in his study of refuse in West Virginia. He pointed out that refuse has a lower specific density than the 2.65 normally used in PSA calculations. This would lead to an underestimation of sand content and a corresponding overestimation of silt and clay.

Water Holding Capacity

The determination of water holding capacity in these materials is difficult due to their high coarse fragment content. To simulate the effects of the coarse fragments, the water holding capacities of the soil size fraction were adjusted to reflect coarse fragment content by weight. It was assumed that the water holding ability of coarse fragments was negligible. Values for water retention at 0.033, 0.10 and 1.5 MPa along with water retention difference (WRD) (0.033 - 1.5 MPa) are presented in Table 6 and the data is also presented without the coarse fragment correction in Table 7. The 0.033 and 1.5 MPa measurements are usually used to approximate the water content at field capacity and the wilting point, respectively. Distributions of the values for the parameters

Table 6. Moisture retention values at 0.03, 0.10 and 1.50 MPa. Water retention difference (WRD) = 0.03 - 1.50 MPa.

Site	0.03 MPa	0.10 MPa	1.5 MPa	WRD
BBR	6.9	6.1	3.2	3.7
BMR	3.6	2.2	1.2	2.4
BWR	6.5	5.8	2.8	3.7
CCR	2.8	2.6	1.1	1.7
DANTE	8.5	6.7	2.4	6.1
DR1	11.7	10.3	5.2	6.5
DR2	5.7	8.3	3.1	2.5
DRP	5.5	2.4	1.5	4.0
JSR	6.8	2.6	0.8	5.9
KRP	8.2	7.7	3.5	4.7
LDR	5.6	4.8	1.6	3.9
LTR	10.1	9.1	3.7	6.4
MRP	4.5	4.0	1.4	3.0
NRP	5.7	4.4	2.2	3.6
PBRU	8.9	6.8	2.7	6.2
PBRV	5.5	2.8	1.6	3.9
PTH	5.0	4.6	3.1	1.9
RDH	4.7	3.9	2.1	2.6
RRA	8.6	7.2	4.2	4.4
RRP	5.8	4.9	2.6	3.2
RRR	6.3	5.7	2.4	3.9
SGR	2.3	2.2	0.9	1.4
WCR	8.2	6.0	2.6	5.6
31H	6.6	5.3	2.8	3.8
35P	7.9	7.1	2.2	5.7
670A	3.5	2.9	1.0	2.5
670B	2.8	2.4	1.4	1.4
Mean	6.2	5.2	2.4	3.8

Table 7. Moisture retention values at 0.03, 0.10 and 1.50 MPa. Values are not corrected for coarse fragment content as in 6. Water retention difference (WRD) = 0.03 - 1.50 MPa.

Site	0.03 MPa	0.10 MPa	1.5 MPa	WRD
BBR	15.4	13.5	7.1	8.3
BMR	10.5	6.6	3.6	6.9
BWR	15.4	13.9	6.7	8.4
CCR	12.1	11.2	4.8	7.3
DANTE	18.6	14.5	5.3	11.3
DR1	21.4	18.8	9.5	10.9
DR2	10.5	15.3	5.8	4.7
DRP	19.1	8.3	5.3	13.8
JSR	23.4	8.9	3.0	20.4
KRP	23.5	22.0	10.0	13.5
LDR	11.8	10.3	3.5	8.3
LTR	23.4	21.1	8.6	14.8
MRP	11.3	10.0	3.7	7.6
NRP	14.5	10.0	5.5	9.0
PBRU	21.1	16.1	6.3	14.8
PBRV	19.5	10.0	5.7	13.8
PTH	14.6	13.6	9.2	5.4
RDH	12.6	10.6	5.7	6.9
RRA	19.5	16.3	9.6	9.9
RRP	12.8	11.0	5.7	7.1
RRR	12.1	11.0	4.6	7.5
SGR	8.5	8.0	3.4	5.1
WCR	22.9	16.8	7.2	15.7
31H	13.2	10.6	5.6	7.6
35P	13.9	12.5	4.0	9.9
670A	11.1	9.2	3.2	7.9
670B	10.1	8.6	5.0	6.1
Mean	16.9	13.1	5.8	13.6

in Table 6 are shown graphically in boxplots (Fig 4a - 4d). The distributions appear to be normal with no outliers and little skew.

The low water holding capacity of refuse is one of the major factors limiting plant growth on these materials. The water retention at 0.01, 0.1, and 1.5 MPa, of 2 refuse materials, are compared in Figure 5. The sample set mean and the water retention data for a Groseclose silt loam, are also included in this figure for comparison. There is wide variability in the water holding capacity of refuse, but it is much lower than that of a natural soil.

Several factors contribute to the low water holding capacity of refuse, with high coarse fragment content the major factor. It is likely that assuming negligible water holding capacity for the coarse fragments results in an error on the conservative side. Another factor is the hydrophobic nature of the carbonaceous surfaces in these materials. These surfaces repel water due to the presence of long chain hydrocarbons. The coarse texture of the soil size fraction also results in low water holding capacity. As would be expected, there is a correlation between silt + clay content and water holding capacity (r = 0.63). This suggests that, as these materials weather and the coarse fragments and sand sized shale particles are reduced to silt and clay, the water holding capacities of refuse will improve with time. This

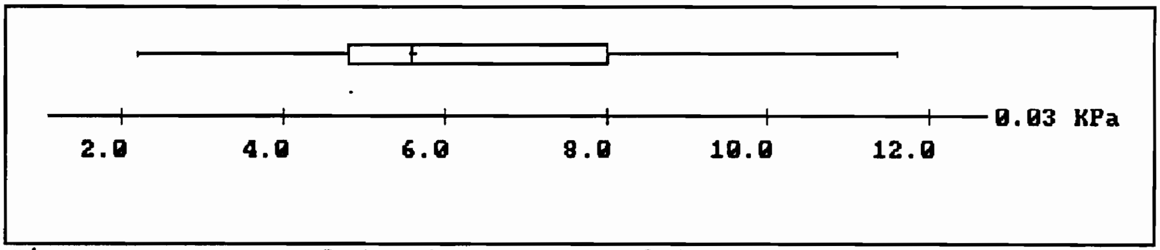

Figure 4a. Boxplot of 0.03 MPa data.

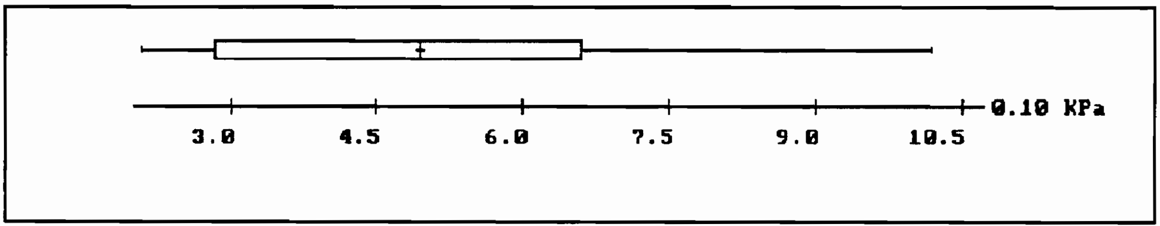

Figure 4b. Boxplot of the 0.10 MPa data.

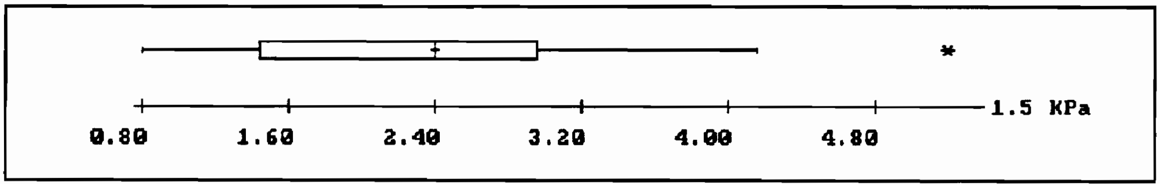

Figure 4c. Boxplot of the 1.5 MPa data.

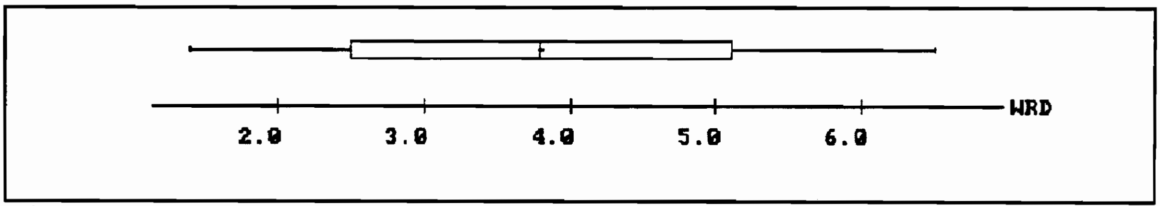

Figure 4d. Boxplot of the WRD data.

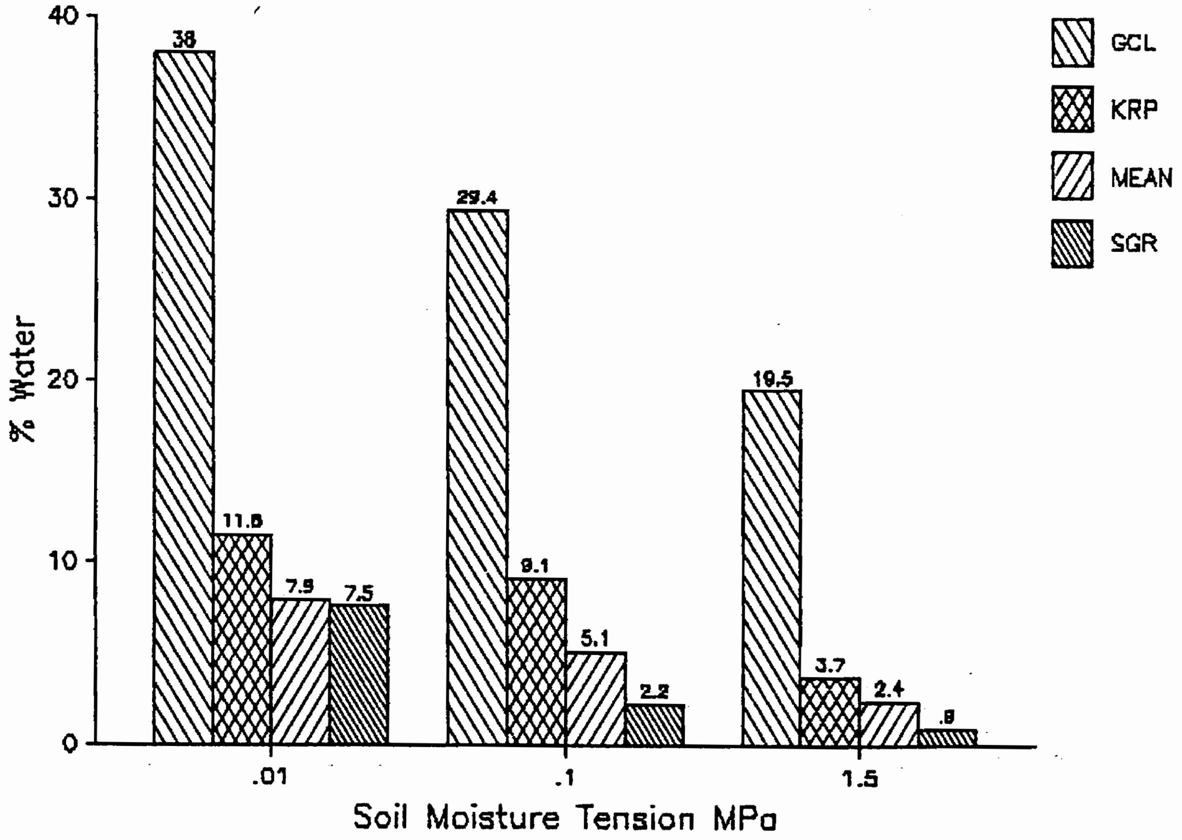

Figure 5. Comparison of WRD between 2 refuse materials, the sample set mean and a natural soil (GCL).

improvement in water retention will only occur if the fine particles are not allowed to erode from the pile surfaces.

A Mann-Whitney comparison of the water retention at 0.03 and 0.10 MPa of the older piles (>20yrs) (5.7% and 4.5% respectively) with the younger piles (<20 yrs) (7.1% and 5.9% respectively) shows that the older piles have a significantly lower water retention at the given pressures ($p = 0.10$). This lower water retention is likely due to the higher coarse fragment content and the higher coal content of the older piles. Whether or not these statistical differences in water retention have any affect on plant growth is questionable.

Weight Loss at 923 K

The weight loss of these materials after heating to 923 K was used as an estimator of the amount of coal or oxidizable C remaining in these samples. This method will overestimate the actual coal content due to other weight losses in this temperature range. These include dehydroxylation losses from kaolinite and Fe and Al oxyhydroxides, and losses of CO_2 from carbonate minerals. This parameter does provide a rough estimator of the coal content, however, and may possibly be used as an indicator of the potential for remining of a given pile. Processing the older piles through a modern prep plant would reduce their volume, and would also allow smaller piles, which are typically perched precariously on stream banks, to be incorporated into modern refuse piles which have improved environmental erosion controls.

The weight loss at 923 K on a percent basis for the sample set is presented in Table 8. A boxplot of the data is presented in figure 6, and reveals two mild outliers. These are piles 31H and RDH; both are old piles which contain significant amounts of coal. Site RDH may not be a candidate for remining due to the large volume of red dog (burned coal refuse) in this pile. The median weight loss of the < 20 year old piles was 26%, while the median weight loss of the > 20 year old piles was 37%. These medians are significantly different (Mann-Whitney test p = 0.10). This difference is attributable to the improvement in coal cleaning technology over time.

Table 8. Values for the weight loss at 923K.

Site	% weight loss*
BBR	21.0
BMR	36.9
BWR	31.9
CCR	23.1
DANTE	47.7
DR1	26.7
DR2	37.1
JSR	28.0
KRP	18.9
LDR	20.2
LTR	17.0
MRP	43.4
NPB	18.8
NRP	26.6
PBRU	18.9
PBRV	18.9
PTH	62.6
RDH	47.7
RRA	30.8
RRP	53.8
RRR	26.4
SGR	35.4
WCR	36.8
31H	64.4
35P	20.4
670A	18.7
670B	22.7
Mean	31.7

* after 3 hr at 923 k in a muffle furnace.

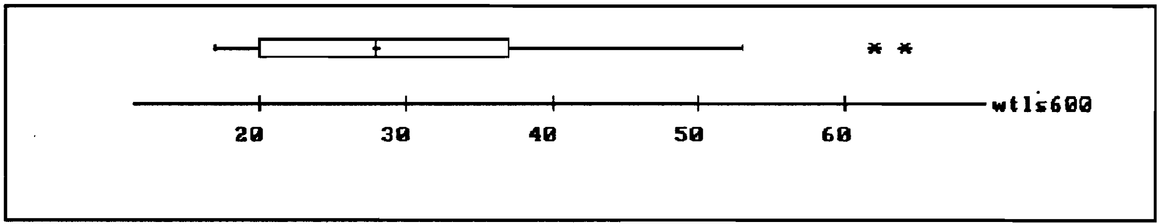

Figure 6. Boxplot of the weight loss at 923 K data.

Chemical Properties

pH

One of the most severe problems in the stabilization and revegetation of coal refuse is low to extremely low pH. Weathering of pyrites and low alkalinity content are the main factors contributing to the low pH values of these materials. When refuse is fresh, it usually has a near-neutral pH. This condition reflects the depositional environment of coal refuse. These materials were deposited in shallow swamps, which provided a reducing environment. Under these conditions electron acceptors other than oxygen began to function. Some of the reactions that take place are as follows; reduction proceeds to the right.

$$2NO_3+12H^++10e^-\rightleftharpoons N_2+6H_2O$$

$$MnO_2+4H^++2e^-\rightleftharpoons Mn^{+2}2H_2O$$

$$Fe(OH)_3+e^-\rightleftharpoons Fe(OH)_2+OH^-$$

$$SO_4^{-2}+H_2O+2e^-\rightleftharpoons SO_3^{-2}+2OH^-$$

$$SO_3^{-2}+3H_2O+6e^-\rightleftharpoons S^{-2}+6OH^-$$

(Foth 1984)

Acidity is consumed and OH^- is produced in these reactions, therefor, under reducing conditions pH values will be near neutral. When coal refuse materials are brought to the surface the pyrite and other minerals begin to oxidize.

Sulfur and iron oxidation is an acid producing process, and the pH begins to decrease. Since one of the end products of pyrite weathering is H_2SO_4, the pH drop can be very rapid. The pH can drop from near neutral into the high threes in a matter of months (Daniels et al., unpublished data 1990). The amount of pH drop depends upon the amount of pyrite present, the reactivity of the pyrite, and the amount and reactivity of the alkaline materials in the refuse.

The relative amounts of acid and alkaline producing materials are the basis of the acid-base accounting method of predicting mine spoil quality. This method does not account for the reactivity and kinetics of the materials and reactions involved, however. The reactivity of pyrite is largely determined by its grain size. Fine grained, framboidal pyrite is very reactive, and is often the major source of acidity in these materials (Caruccio, 1970).

The data for exchangeable and total Ca and Mg content for these materials, which will be presented later, demonstrates the low base status of these materials. Due to their low base status and pH, the exchange complex is saturated with Al. As the pyrite weathers protons are produced, which attack the mineral surfaces and Al is liberated. This Al is then hydrolyzed and is adsorbed onto the exchange complex.

The pH values for the 27 pile sample set are presented in Table 9. There is a wide range of pH values from a low of 3.0 to a high of 8.3. Only three of the samples exhibited pH

Table 9. The pH values for the 27 pile sample set. The pH values were taken in a 1:1 deionized water/refuse slurry.

Site	pH
BBR	3.0
BMR	4.2
BWR	3.0
CCR	3.8
DANTE	6.0
DR1	3.7
DR2	3.4
DRP	5.5
JSR	5.8
KRP	3.6
LDR	5.9
LTR	3.2
MRP	5.6
NRP	4.0
PBRU	3.7
PBRV	4.0
PTH	4.0
RDH	4.2
RRA	7.1
RRP	7.6
RRR	4.8
SGR	4.5
WCR	3.6
31H	3.9
35P	8.3
670A	5.2
670B	4.7
MEAN	4.7

values higher than 7. Sample 35P was mined from the Parson's or "limestone seam" (Prescott, 1946) which could be responsible for its high pH. Sample RRP comes from a pile located adjacent to and now covering an old bank of coke ovens. It is speculated that the flyash from these ovens may have influenced the pH of this refuse. Samples DRP and PTH are from the same coal seam and these samples have pH values of 5.50 and 4.20 respectively. Sample RRA is a fresh refuse sample from pile which has displayed very little acid producing ability. The other refuse samples from active piles all have pH values below 5 indicating that these samples had weathered some before they were collected, and that the S reactions can occur very quickly.

The boxplot illustrating the distribution of the pH data (Fig. 7a) indicates that P35 is a mild outlier. The mean is skewed upward due to the 3 high pH samples. There is a difference (Mann-Whitney test $p = 0.09$) between the median pH of the > 20 yr old piles (4.7) and the median pH of the < 20 yr old piles (3.8). This difference is probably due to the efficiency of modern coal prep plants in putting a higher proportion of pyrite into the refuse piles. The pH of the older piles may also have increased after most of the pyrite contained in them oxidized. The pH in these piles is no longer controlled by active pyrite oxidation, and the pH rises to the Al buffering range (about pH 5).

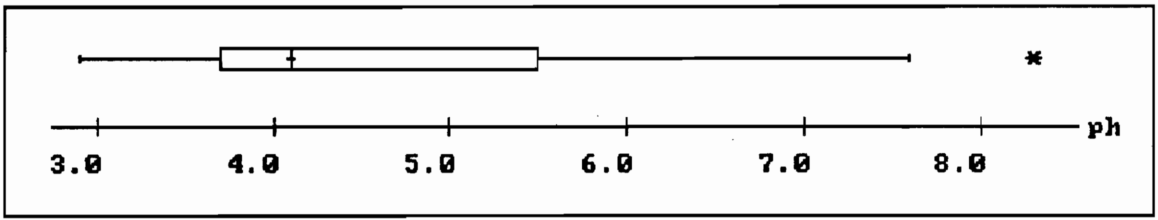

Figure 7a. Boxplot of the pH data.

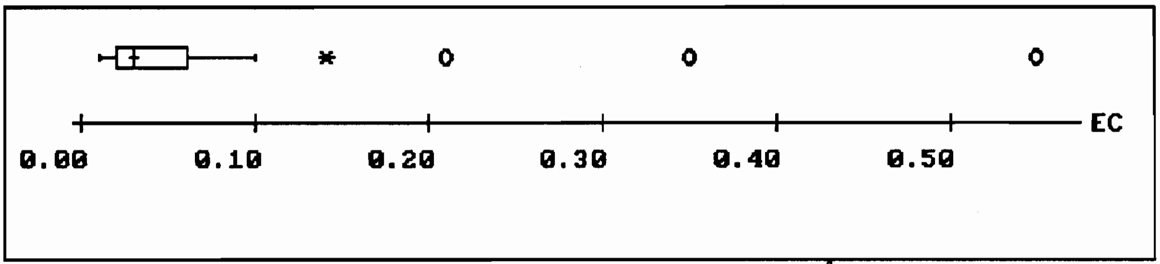

Figure 7b. Boxplot of the EC data in S m^{-1}.

Plant growth is uniformly inhibited when pH values are < 4. Bacteria important to the breakdown of organic matter, and in the nitrification process also do not function well below pH 5.0. Also, since available P is one of the major growth limiting factors in these materials, the pH should be adjusted to at least 5, in order to make P more available. At low pH values metal toxicities of Al, Fe, and Mn, may also occur. Molybdenum forms insoluble compounds with Fe at low pH, and thus, plants susceptible to Mo deficiency, such as legumes, may have reduced growth. Adjustment of the pH through liming is essential if vegetation is to be established, especially if the pH is <4.5. Materials with pH values <4.5 with high amounts of potential acidity, or extractable Al and Fe may require at least 30 cm of topsoil with lime applied at the refuse/soil contact to be successfully revegetated.

Soluble Salts

The dissolution of primary and secondary minerals are the primary sources of salts in these materials. Acid-sulfate weathering is the driving force behind this mineral dissolution. Many of the secondary minerals are the sulfate and bicarbonate salts of Al, Fe, Ca, and Mg and more complex minerals such as jarosite. Information on the soluble salt toxicity levels for plants of the humid region is limited due to the fact that these toxicities are not usually encountered.

Saturation extract electrical conductivity (EC) values of < 0.2 Sm^{-1} are generally thought to indicate negligible salt problems, however, some of the plant species, such as white clover, used in reclamation of these areas show salt sensitivity at EC values of 0.15 Sm^{-1} or greater.

The saturated paste extract EC values are presented in Table 10. The sample set mean of 0.09 Sm^{-1} is well below the 0.2 Sm^{-1} threshold level. The distribution of the EC data is presented in a boxplot (Figure 7b). Samples BMR, JSR, and RRA are all strong outliers. These are all active piles. This suggests that high salt contents are only a problem in < 10 year old refuse. The majority of the data is in a tight cluster near the sample set mean. There is an obvious association between EC values and pile age. The mean EC value of the piles < 20 years old is 0.17 Sm^{-1}, while the mean EC of the >20 year old piles is 0.03 Sm^{-1}. This difference is significant at the $p = 0.001$ level (Mann-Whitney test). Further examination of the data reveals that the 4 active piles have a mean EC value of 0.44 Sm^{-1}. Salt concentrations at this level may result in reduced plant growth. The salt concentration decreases with age as the salts are leached away, and acid-sulfate weathering in the surface is completed. Eventually the salts will be leached out of the surface layer of a refuse pile, except those areas associated with acid leachate seeps. The amount of time needed to leach the salts away will be dependent upon the salt producing

Table 10. The electrical conductivity (EC) values for the 27 pile sample set.

Site	EC Sm^{-1}
BBR	0.14
BMR	0.55
BWR	0.22
CCR	0.04
DANTE	0.02
DR1	0.04
DR2	0.11
DRP	0.03
JSR	0.35
KRP	0.03
LDR	0.01
LTR	0.07
MRP	0.02
NRP	0.03
PBRU	0.06
PBRV	0.03
PTH	0.02
RDH	0.03
RRA	0.36
RRP	0.04
RRR	0.04
SGR	0.02
WCR	0.04
31H	0.03
35P	0.04
670A	0.02
670B	0.03
MEAN	0.09

characteristics of the pile, the water infiltration characteristics, and the amount of precipitation a pile receives. No information is available about the time it takes for the salts to leach from a pile. It appears that a reduction in EC to nontoxic levels will occur within 10 years in most refuse, in the study area.

Estimation of EC

The results of a study evaluating water to soil ratios in the determination of EC in coal refuse are presented in this section. The objective of this study was to examine the relationship between the ECs of saturation extracts and higher water to soil extraction ratios (WSR) on coal refuse. Saturated paste extracts are the standard technique, but they require large amounts of sample and are quite laborious to prepare. It takes a day and a half to prepare, extract and analyze a batch of saturated paste extracts, while it takes less than 3 hours to prepare and analyze samples using WSRs of 1:1 to 1:5.

Because of the fresh geologic nature of the refuse materials it was hypothesized that a regression relationship could be developed to relate the EC values of higher WSRs to the EC values of saturated paste extracts. The reproducability of the EC measurement of the various WSRs was also evaluated. The cation (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) concentration in the various extracts used was also evaluated to see if any dilution/solution trends could be observed, which might indicate the solid phase source of the salts.

In all cases the EC was inversely related to water:soil ratio as was expected. The mean saturated paste EC values for the seven samples ranged from 5.48 to 0.37 dS/m, while the EC for the 5:1 WSR ranged from 1.25 to 0.10 dS/m. The statistical analysis of the conductivity data set is presented in Table 11. The 5:1 WSR had a lower EC value than the other WSRs. The WSRs of 1:1, 2:1 and 2:1 by volume showed no differences. These data indicate that no direct comparison can be made between the EC values from a saturated paste extract and the various WSRs. This is consistent with the findings of the U.S. Soil Salinity Lab (1954) for soils.

The reproducability of the data was also evaluated. The coefficient of variation (CV) for each replicate pair was calculated by dividing the standard error by the mean and multiplying by 100. The CV was then analyzed using a randomized complete block design without replication. Refuse type was the blocking variable. The mean CV values were compared using the LSD procedure on SAS. These values are presented in Table 12. There were no significant differences in the mean CV values of 5 WSRs used. The saturated paste had the highest mean CV value. This was expected since the proportions of water to soil used in this procedure are not constant. The procedure says to add water and mix and continue adding water until the soil just glistens, but has no

Table 11. The comparison of mean EC values for the 5 WSR treatments. The mean EC value of each treatment is being compared.

Treatment	Mean EC value
paste	2.47[a]
1:1	1.73[b]
2:1	1.34[b]
2:1 volume	1.17[b]
5:1	0.69[c]

[1] means with the same letter are not significantly different at the alpha= 0.05 level using the Student-Newman-Keuls procedure.

Table 12. The comparison of mean CV values for the 5 WSR treatments. The variability (expressed as a CV) of each each treatment is being compared.

Treatment	Mean CV value[1]
Paste	4.79[a]
1:1	4.37[a]
2:1	2.07[a]
2:1 volume	2.96[a]
5:1	4.60[a]

[1] means with the same letter are not significantly different at the alpha= 0.05 level using the Student-Newman-Keuls procedure.

free water (Rhoades, 1984). The paste also should not stick to a spatula or stirring rod. This rather subjective description should lead to some variability in water content and therefore EC. This variability was not observed in this experiment, however. The 2:1 by volume WSR had a lower CV than was anticipated. Differences in packing in the measuring of the soil volume could lead to variability in the WSR. The CV determined here suggests that this is not a problem. Based on the reproducability demonstrated here, there is no reason not to use the saturated paste extract. The relationship between WSR and EC was evaluated for each sample. The slope, intercept, r-square, and CV values for each of the samples are presented in Table 13. The relationship for all samples is shown graphically in Figure 8a. Each of these relationships has a negative slope as expected. Samples PAA, WCR, and CCR have slopes that are nearly zero (Figure 8c). These samples are weathered older samples that have had most of the soluble salts leached from them and therefore have low EC values at all WSRs. The data for these older weathered samples show similar slopes and could probably be grouped together.

Four samples analyzed had relatively high soluble salt levels. Samples NPB, BMR, and JSR are samples from active refuse piles that could still contained salts from the coal cleaning process and are still undergoing pyrite oxidation. Sample BWR is from an older refuse pile that had a relatively

Table 13. The slope, intercept, r-square, and CV values of the EC = WSR relationship for the 7 refuse materials tested.

site	slope	Intercept	r^2	CV
BWR	-0.29	1.83	0.73	25.2
JSR	-0.53	3.13	0.81	22.3
BMR	-0.76	4.61	0.73	26.7
CCR	-0.04	0.29	0.62	31.0
NPB	-0.59	4.33	0.71	21.6
WCR	-0.04	0.31	0.88	9.6
PAA	-0.05	0.50	0.92	7.0

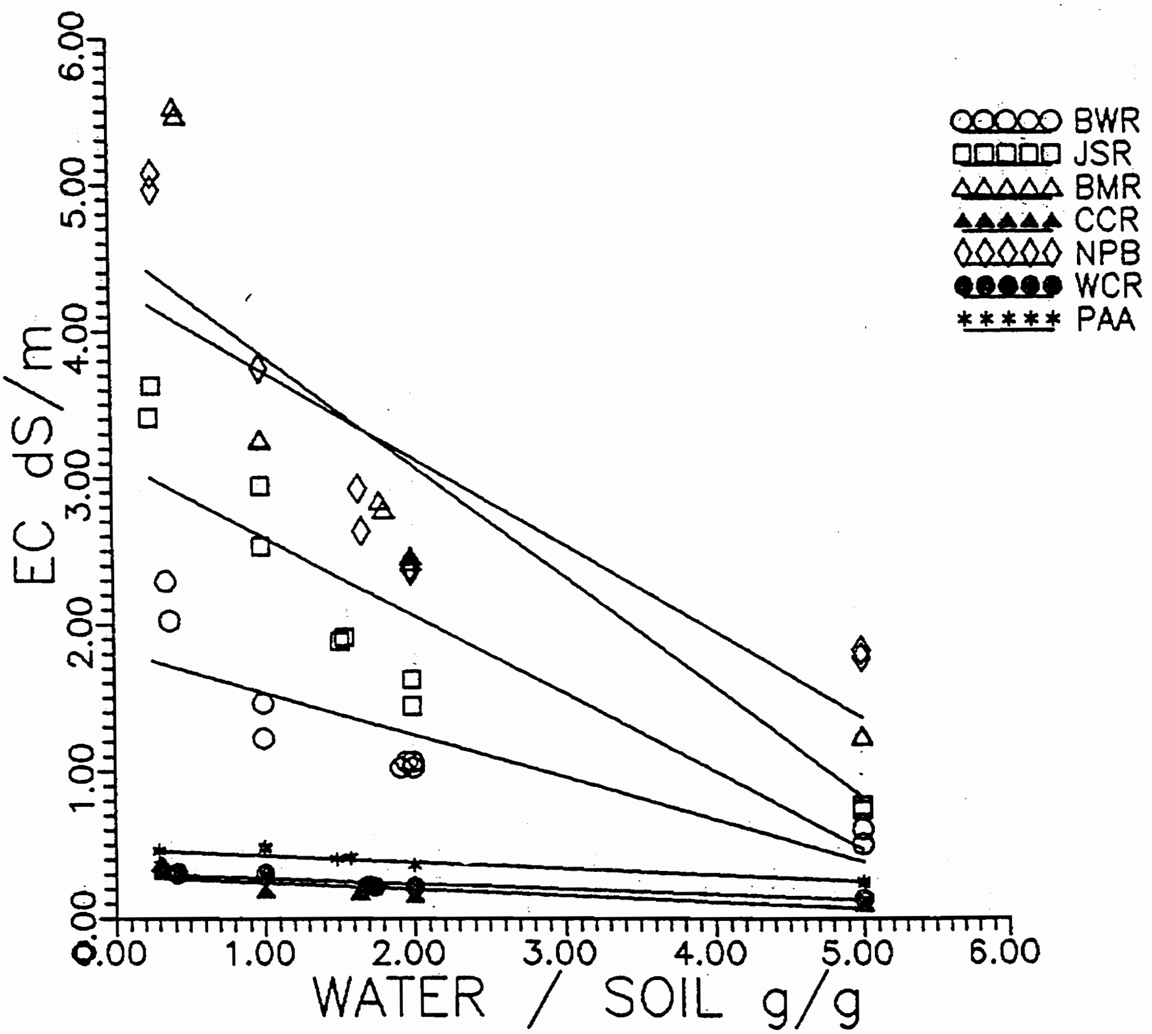

Figure 8a. EC vs WSR at all sites.

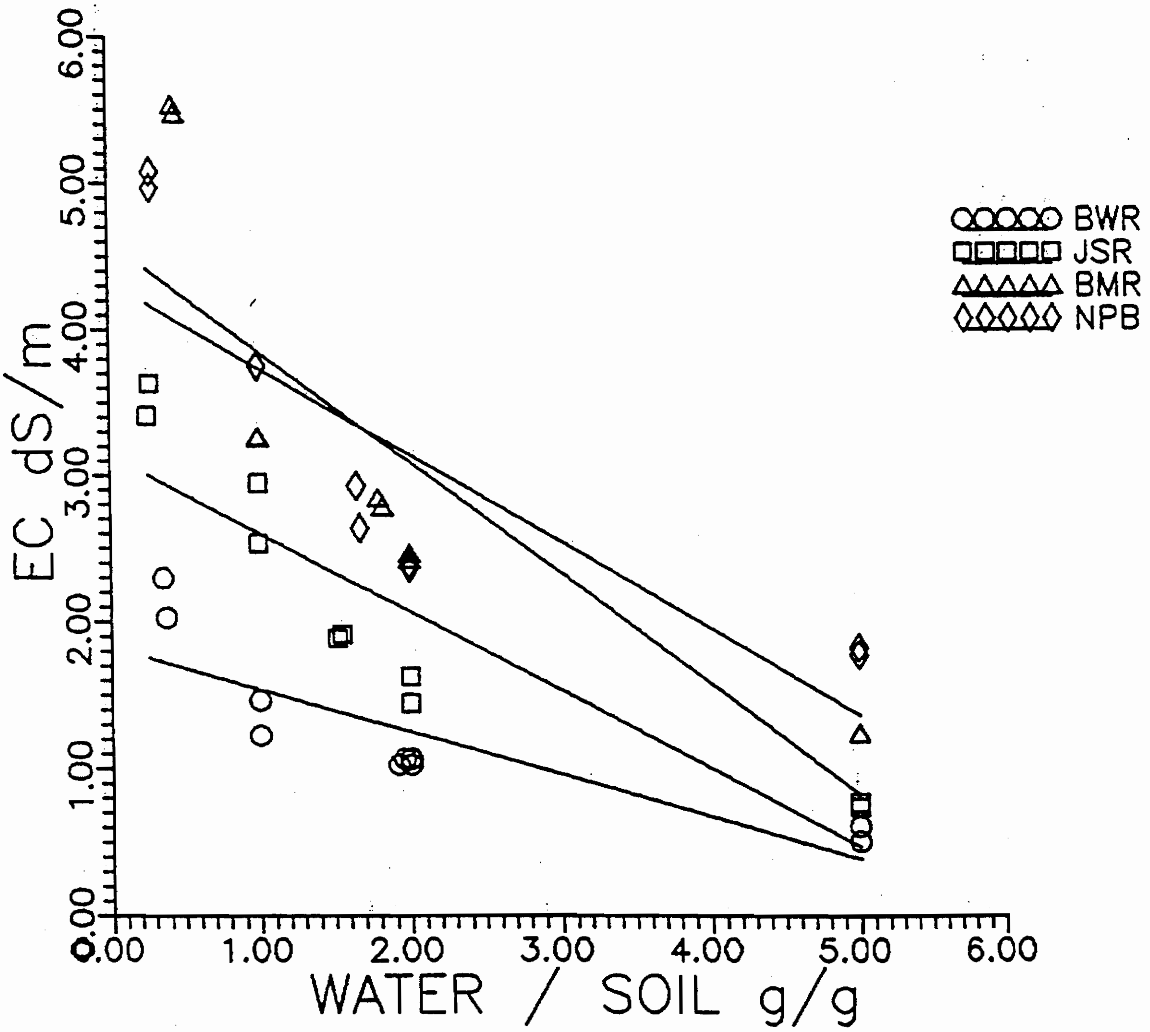

Figure 8b. EC vs WSR at the high conductance sites

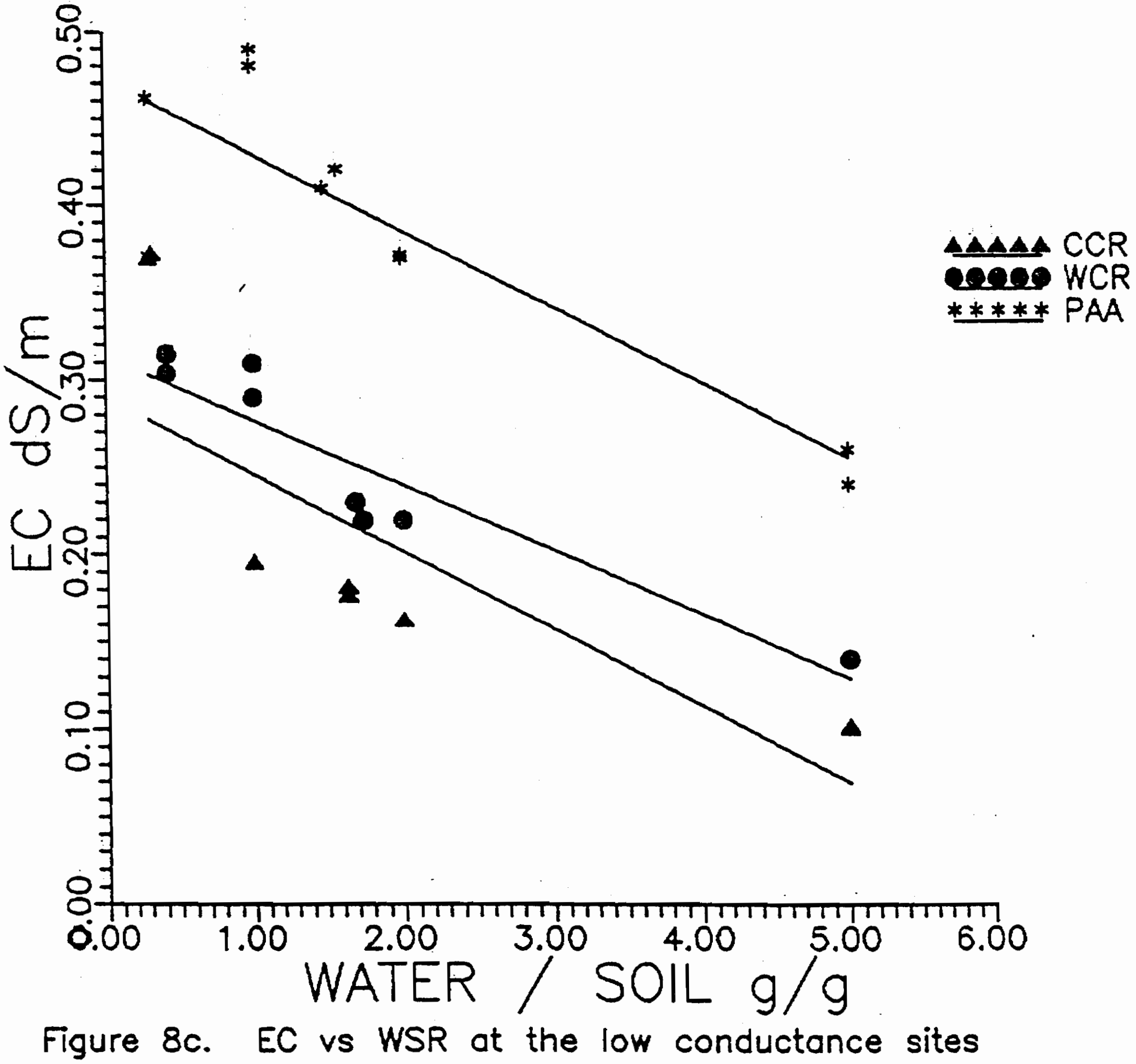

Figure 8c. EC vs WSR at the low conductance sites

high (0.8%) sulfur content indicating that it still had reactive pyrite remaining. As this pyrite oxidizes soluble salts will be produced. Each of the samples with a high EC has a unique slope (Figure 8b, Table 13) and therefore it is and doubtful that these data can be grouped to form a general conclusion. The r^2 values for these linear models are fairly high ranging from 0.62 to 0.88. It is not suggested to use these regressions as predictors, but they do indicate significant trends in the data. The CV values are high; however this is due to the small (only 2 replications) sample size. If more replications were included I believe the CV values would decrease significantly.

These data suggest that if the 5:1 WSR EC value is less than 0.5 dS/m then it is safe to assume that the paste conductivity will be less than 2 dS/m. More work needs to be done to verify this finding, however. The 5:1 WSR extract would be much easier to perform in the lab. In fact, the 5:1 extract is fluid enough that it can be filtered without the aid of a vacuum pump. The 5:1 extract could therefore be used as a screening test to see which samples actually need to have a saturated paste extract performed.

The relationship between the natural log of the EC and the WSR was also evaluated for the 4 high EC samples. This seems to offer an improvement over the straight regression method, since the r^2 values are higher and the CV values are lower. One CV value (sample BWR) actually increased but this was due to the decrease in the mean of the data when the natural log was taken (Table 14, Figure 9). It is also interesting to note that three of the samples had similar slopes. With more testing on high conductance samples a predictive relationship between the 5:1 WSR and the paste conductivity might be developed.

The fresh refuse samples had conductivities high enough to cause yield reductions in reclamation seedings. This problem can probably be alleviated with time. If the refuse is allowed to weather, without efforts to mitigate the low pH, then the pyrite will oxidize and the salts will be generated and then leached away with time. This may not be a solution, however, because these areas must have a plant cover to counter erosion, and runoff. Reclamationists must manage these areas with the level of soluble salts in mind. These areas also present a somewhat unique situation because they are usually high in soluble salts and low in pH. Samples NPB and CCR would actually classify as sodic soils. This is much different than the arid regions of the world where high salt areas are also high in pH. Reclamation species selection for refuse piles must be made with salt tolerance in mind, especially for the first several years after seeding. After the initial salt load is leached away long term tolerance to acidity will be important.

Table 14. The slope, intercept, r-square, and CV values of the ln EC = WSR relationship for the 4 refuse materials tested which had high conductivities.

site	slope	Intercept	r^2	CV
BWR	-0.29	0.66	0.90	133.9
JSR	-0.32	1.23	0.95	22.0
BMR	-0.29	1.61	0.92	15.2
NPB	-0.82	1.48	0.82	15.6

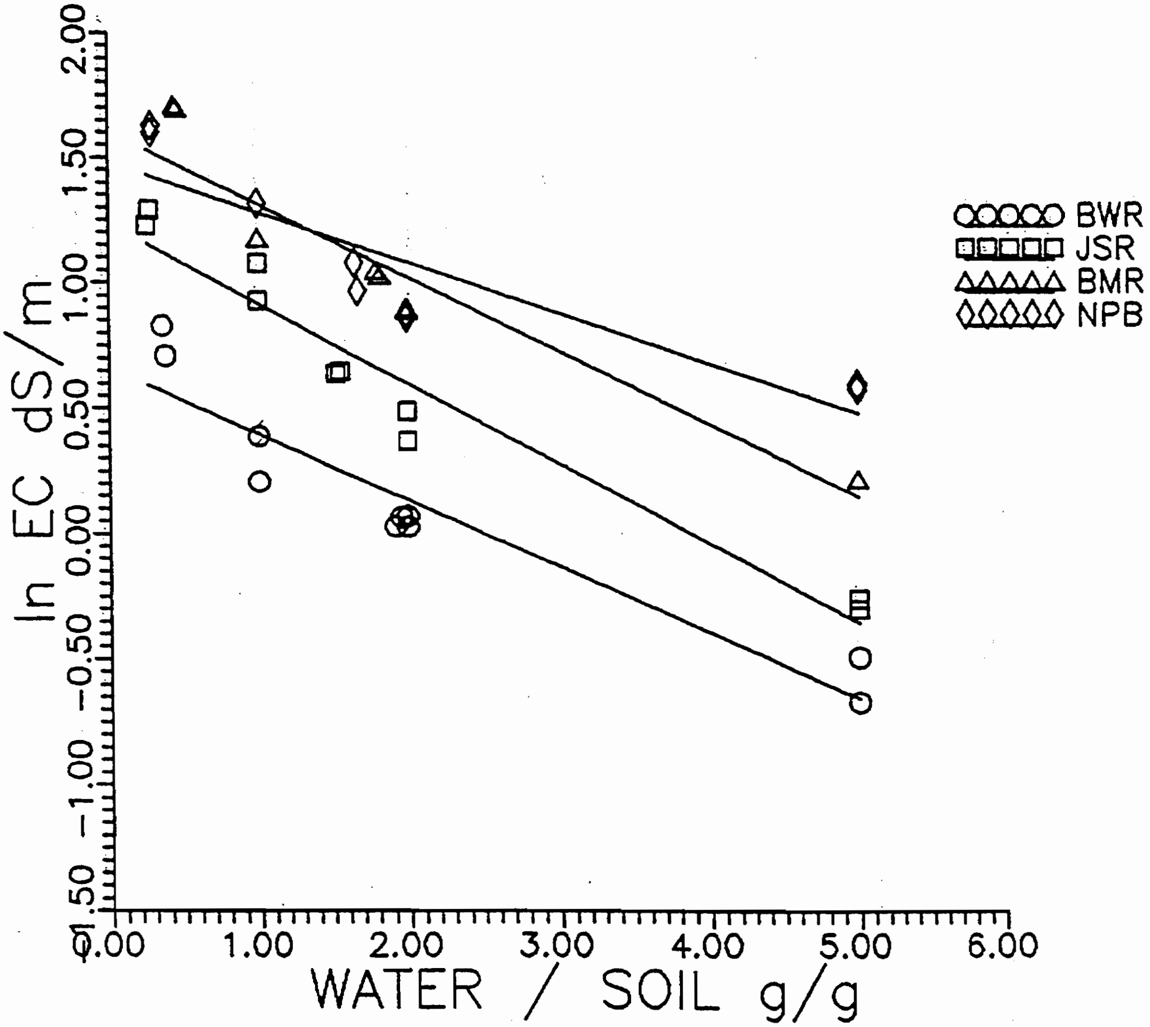

Figure 9. ln EC vs WSR at the high conductance sites

The relationship between WSR and cation concentration in the various extracts for selected samples is presented graphically in Figures 10a through d. The reader is advised to note the differences in the scale before interpreting these figures. Figure 10a presents the dissolved Ca, Mg, Na, and K concentrations at site BMR at 1:1 and 5:1 WSR. The amount of cations extracted increase with increasing WSR. The increases in each element are slight, with the exception of Ca, which increases two fold.

Samples from BMR and NPB were tested for their gypsum content using the method of Hesse, (1972). The sample BMR contained 0.8 mEQ of gypsum/100g while sample NPB contained only a trace of gypsum. The NH_4OAc extracts were also tested with the same method and neither sample showed the presence of gypsum. This indicates that either the NH_4OAc does not dissolve appreciable amounts of gypsum or the test does not work in a salt matrix. Dissolved gypsum was surmised to be the source of the high conductivity in sample BMR. Site NPB also had a high conductance, but this was surmised to be the result of the high amount to Na salts in this sample (Fig. 10d). These could be remnants of the cleaning process, or secondary minerals formed from weathering.

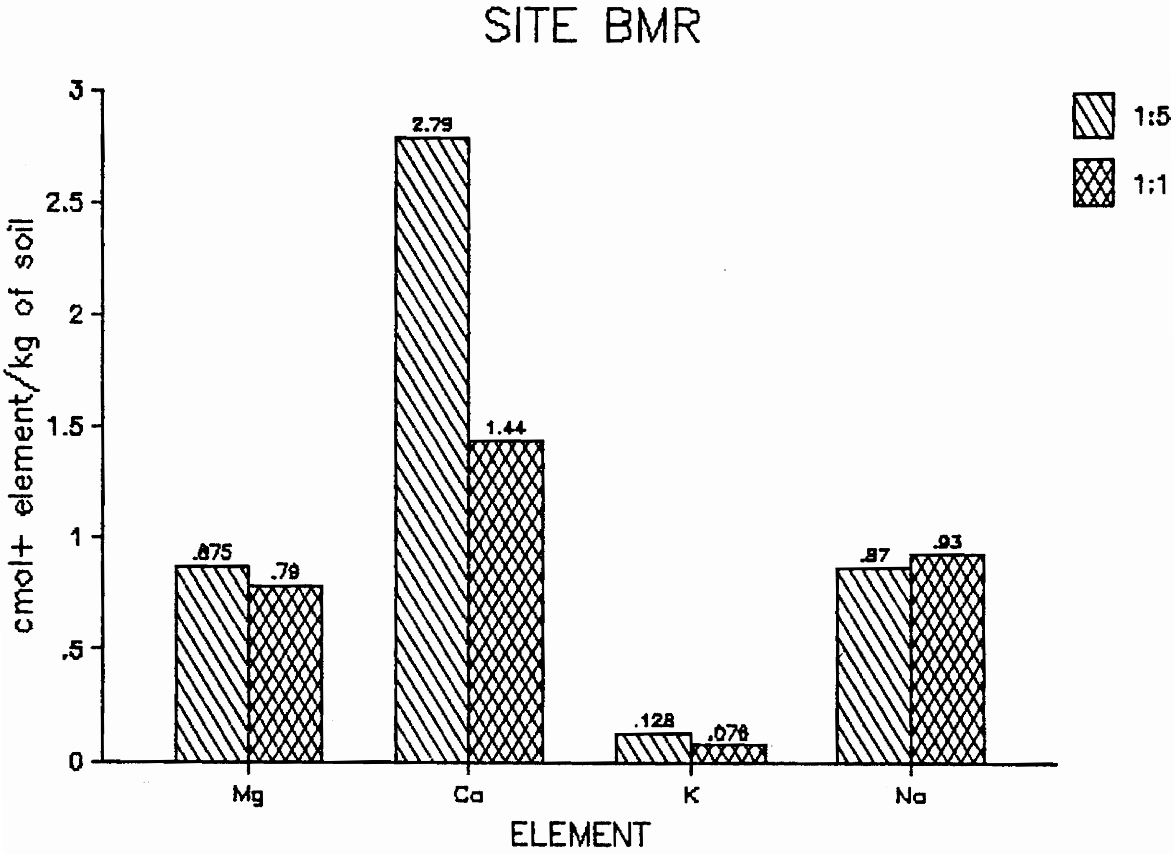

Figure 10a. Soluble cations at site BMR.

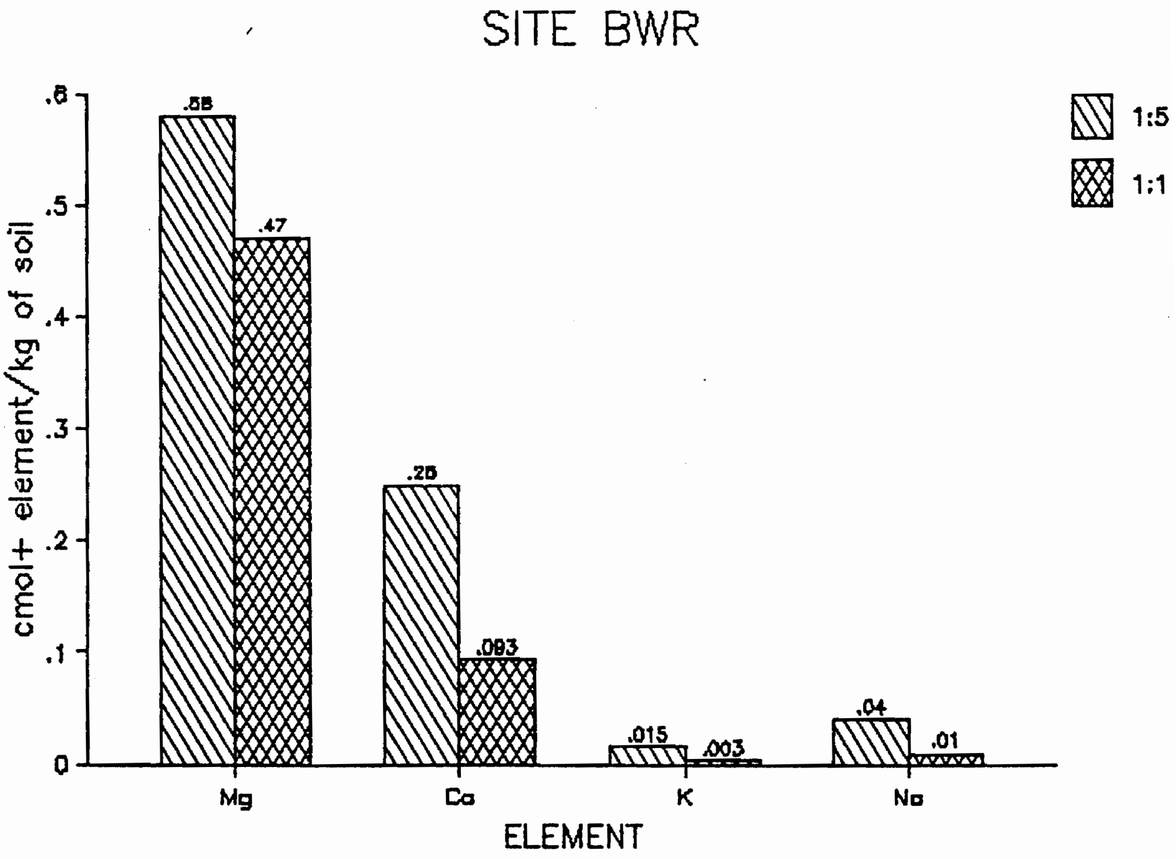

Figure 10b. Soluble cations at site BWR.

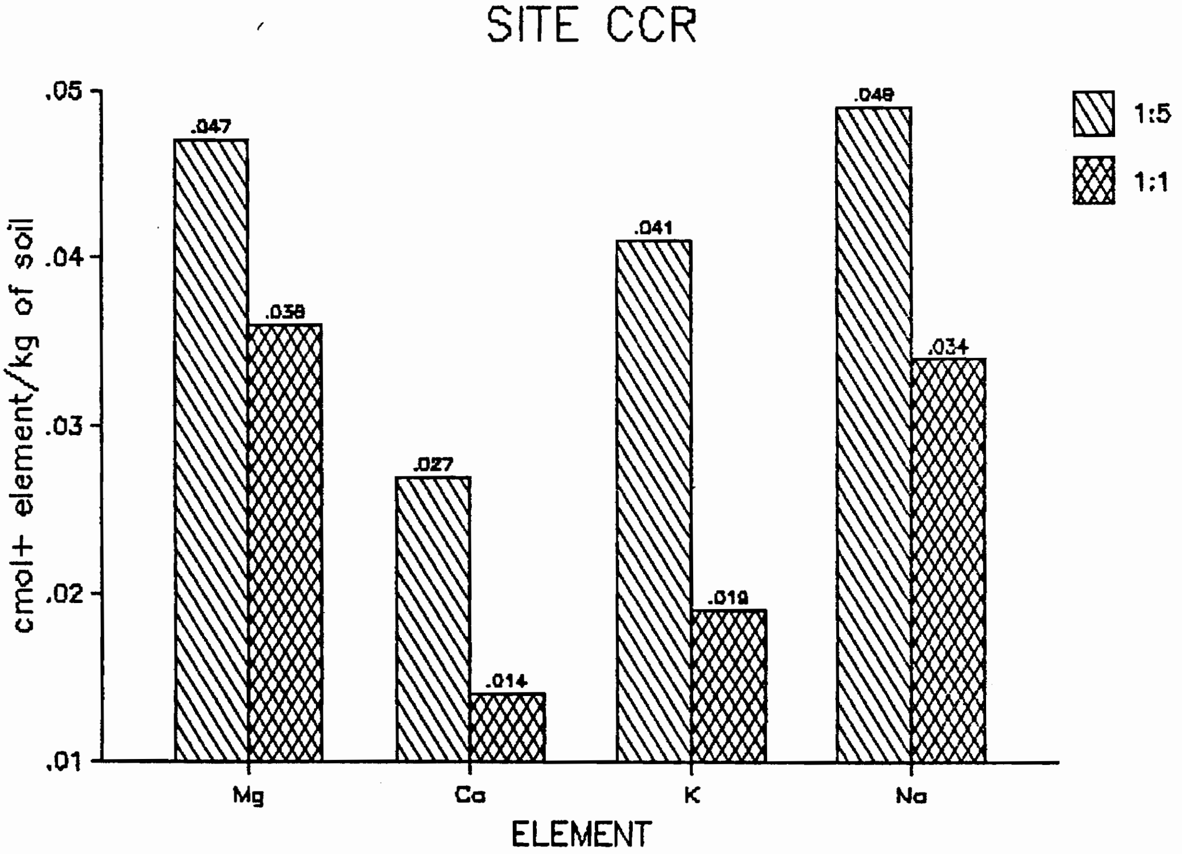

Figure 10c. Soluble cations at site CCR.

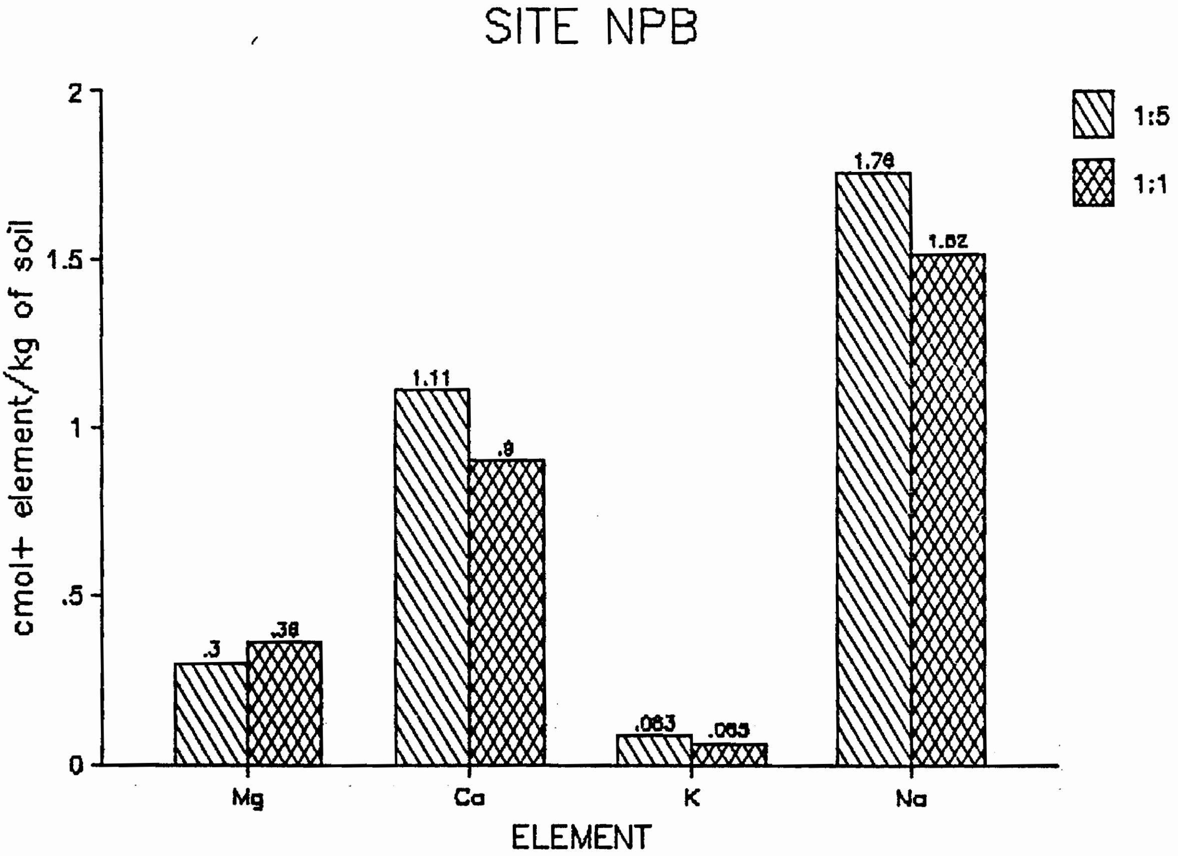

Figure 10d. Soluble cations at site NPB.

Sites BWR and CCR had moderate to low EC values and had lower values for soluble cations (Fig. 10b and c). Site BWR did have an elevated level of Mg, however, and sulfate salts were assumed to be the source of the moderate EC value for this sample. Site CCR had the lowest EC and a correspondingly low soluble cation content.

The soluble cation data suggest that in the low EC samples the soluble cations are being liberated from sparingly soluble carbonate and sulfate minerals. The evidence for this is the large, 2 fold or greater, increase in soluble cations as the WSR increases. The high EC samples contain true "soluble" salts. The amount of soluble cations increase only slightly on dilution of these samples. I believe that this indicates there could be a weathering sequence in these materials. The sodium salts are the initial source of high EC. The sodium salts leach and the pH drops as the pyrite weathers. Gypsum and Mg sulfate precipitate as the carbonate minerals dissolve and release Ca and Mg to the system. In time the slowly soluble gypsum is leached and the EC drops to low levels shown in the older refuse samples.

The paste extract proved to have no disadvantages as far as reproducibility was concerned. Since most recommendations salt tolerance are based on paste EC it will continue to be the standard method. A 5:1 WSR extract may prove effective in the screening of samples which need to have paste ECs performed on them. Low conductance samples had low slopes for the EC vs WSR relationship, and it was concluded that if a sample had a 5:1 EC of <0.5 dS/m it was unlikely that the paste extract would have an EC of >2 dS/m. More observations are needed to evaluate the validity of this relationship.

Extractable Cations

The cations extracted from a soil, usually with 1.0 N NH_4OAc for Ca, Mg, K, and sometimes Na, and 1 N KCl for Al, are usually referred to as "exchangeable cations". In weathered soils in which the salt content is negligible there is likely to be very little difference in exchangeable and extractable cations. In samples such as these, which have appreciable amounts of soluble salts, cations are exchanged from the exchange complex, but are also the product of salt dissolution during extraction. The cations extracted will heretofore be referred to as extractable cations and not as exchangeable cations.

Extractable Calcium

The amount of extractable Ca shows a large amount of variability. The values range from 0.20 to 17.1 $cmol^+/kg$ extractable Ca (Table 15). This variability is due to the varying Ca content in the parent rocks of the refuse. The distribution of the Ca data (Fig. 11a) is skewed with a long tail on the high end. This extends the mean extractable Ca value of 3.23 $cmol^+/kg$ well above the median value of 1.23

Table 15. Extractable cation data for the 27 pile sample set.

Site	Ca	Mg	K	Al
	cmol+/kg			
BBR	0.52	0.84	0.07	7.37
BMR	14.05	1.78	0.24	1.36
BWR	0.98	1.08	0.05	6.74
CCR	0.65	0.60	0.16	6.55
DANTE	6.36	1.78	0.22	0.12
DR1	0.72	0.54	0.13	5.92
DR2	1.23	0.82	0.10	5.24
DRP	2.42	1.35	0.28	0.32
JSR	9.00	1.39	0.23	0.15
KRP	0.54	0.36	0.17	7.03
LDR	4.15	1.83	0.17	0.05
LTR	0.64	0.46	0.09	7.90
MRP	2.80	1.84	0.12	0.34
NRP	0.75	0.75	0.18	6.94
PBRU	0.73	0.87	0.22	6.55
PBRV	0.78	0.59	0.12	6.35
PTHR	0.20	0.08	0.12	6.40
RDH	0.88	0.64	0.18	3.93
RRA	5.64	1.75	0.33	0.17
RRP	6.49	0.73	0.10	0.10
RRR	4.02	1.77	0.22	1.14
SGR	1.34	1.34	0.17	4.03
WCR	0.75	0.31	0.12	5.72
31H	0.45	0.17	0.09	3.54
35P	17.10	1.18	0.22	0.05
670A	2.65	1.49	0.21	3.38
670B	1.40	0.85	0.15	1.99
MEAN	3.23	1.01	0.17	3.58

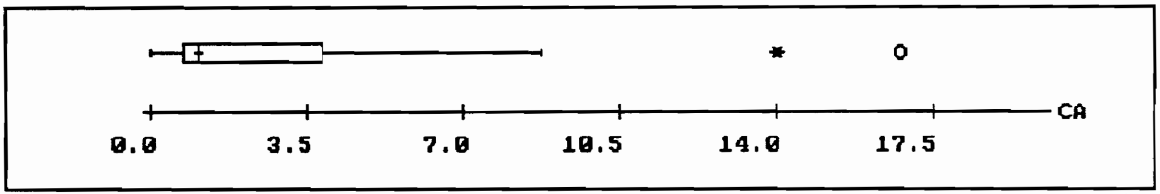

Figure 11a. Boxplot of the extractable Ca data. Data is presented in cmol⁺/kg.

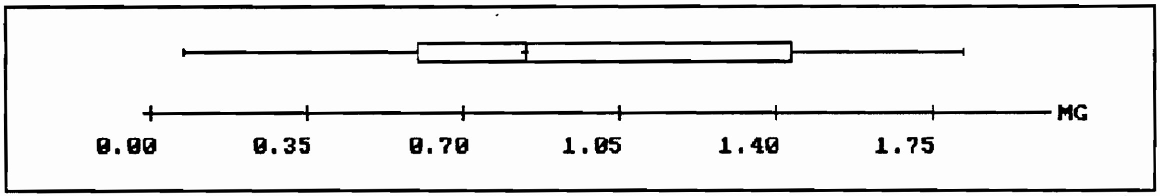

Figure 11b. Boxplot of the extractable Mg data. Data is presented in cmol⁺/kg.

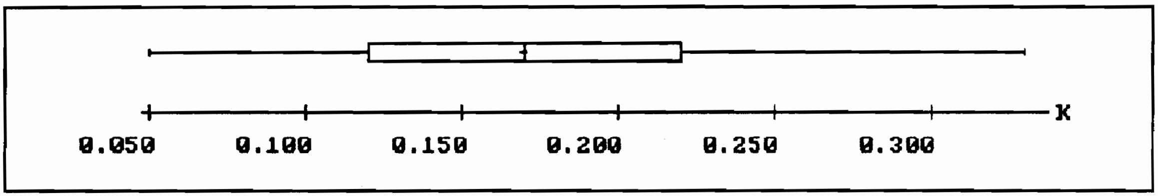

Figure 11c. Boxplot of the extractable K data. Data is presented in cmol⁺/kg.

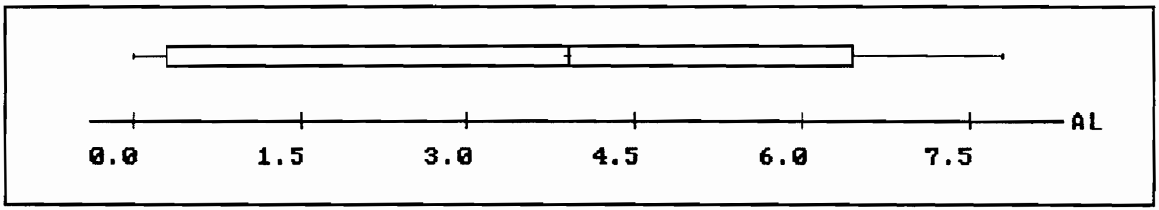

Figure 11d. Boxplot of the extractable Al data. Data is presented in cmol⁺/kg.

cmol$^+$/kg. Thirteen of the samples have less than 1 cmol$^+$/kg extractable Ca. There is some correlation between pH and extractable Ca (r = 0.69). The samples with high pH values tend to have high Ca values, however there are exceptions such as site BMR which has a pH of 4.2 and a high extractable Ca content.

Little difference in extractable Ca was found in the < 20 year old materials and the > 20 year old materials. This also suggests that extractable Ca content is related to the Ca content in the parent rocks and changes little in a 20 year time period. The sources of the Ca in these materials are Ca-carbonates and secondary gypsum. Those samples that have a pH above 6 and high levels of Ca are likely to contain Ca-carbonate cements especially in their sandstone component. Those samples with pH values < 6 and large amounts of extractable Ca are to likely to contain gypsum. The gypsum is a secondary precipitate formed as the Ca-carbonates react with the sulfate weathering products of iron pyrite.

Since lime will be added to most of these materials during reclamation, adequate Ca for normal plant growth should be available in most situations.

Extractable Magnesium

The amount of extractable Mg shows less variability than does Ca. The extractable Mg values ranged from 0.08 to 1.84 cmol$^+$/kg (Table 15). The distribution of the data appears to be fairly normal (Fig. 11b). The mean value of 1.01 cmol$^+$/kg is skewed slightly above the median of 0.85 cmol$^+$/kg. There is a cluster of six samples with extractable Mg values > 1.7 cmol$^+$/kg which causes this skew. The distribution of extractable Mg could be bimodal, but requires a larger sample set for complete evaluation. Extractable Mg is less strongly correlated with pH ($r = 0.52$) than is Ca. This correlation reflects the fact that Mg levels are usually lower than Ca levels. The sources of Mg are carbonate minerals, secondary sulfate precipitates, and biotite micas. If dolomitic limestone is used in the reclamation of these materials no plant deficiencies of Mg should occur.

Extractable Potassium

The amount of extractable K shows very little variation and fell into a relatively narrow range. The distribution of extractable K (Fig. 11c) is similar to that of total K which will be presented later. Extractable K ranged from 0.05 to 0.33 cmol$^+$/kg (Table 15). The data is evenly distributed throughout the range. The extractable K data is normally distributed and the mean and median are both 0.17 cmol$^+$/kg. The mean extractable K of the < 20 year old piles was 0.16 cmol$^+$/kg, while the > 20 year old pile mean was 0.17 cmol$^+$/kg. These values are obviously not statistically different. The sources of K in these materials are micas, mainly muscovite, and feldspars. As these materials weather, K is released.

Under acid conditions the weathering of these materials can be very rapid. The micas probably weather to kaolinite.

Potassium fertilization is not likely to be needed on these materials. The sample with the lowest extractable K value would still supply about 42 kg K/ha. This is a moderately low amount, but it should be sufficient since most of the systems established will be closed systems in which no fodder is removed from the site. In a study of minesoils, Roberts (1986) noted that exchangeable K increased annually for the first three years after plant establishment due to biological weathering. On sites, with low extractable K fertilization may improve stand vigor and winter hardiness especially in the legume component of the stand.

Extractable Aluminum

The amount of extractable Al, like Ca is quite variable. The values ranged from 0.05 to 7.90 cmol^+/kg (Table 15). The distribution of extractable Al data appears to be bimodal (Figure 11d). The mean extractable Al value is 3.6 cmol^+/kg, which is slightly lower than the median value of 3.9 cmol^+/kg. Nine of the extractable Al values are < 1.0 cmol^+/kg, while 12 samples have values > 5 cmol^+/kg. The major difference in the distributions of Al and Ca is that high levels of Ca can occur throughout the range of pH values, while high levels of Al are only encountered at low pH values. All samples (12), with the exception of sample WCR, that have a pH value of < 4 have extractable Al contents of > 5.5 cmol$^+$/kg. Haynes and Klimstra (1975) used the criteria of Lindstrom (1948) to classify spoil banks in Illinois as toxic if they had a pH of <4.0 over 75% of their surface areas. If this criteria is correct then 5 cmol$^+$/kg of Al probably is a toxic level of Al. The threshold level of Al toxicity may be lower than this. All samples with pH values of < 5 had 1.14 cmol$^+$/kg or more of extractable Al. Conversely all samples which had pH values of > 5 had < 1.0 cmol$^+$/kg extractable Al.

The < 20 year old piles have a median extractable Al content of 6.14 cmol$^+$/kg, while the > 20 year old piles have a median of 1.99. The difference in these values is significant at the p = 0.20 level (Mann-Whitney test). This is a weakly significant difference, however it brings up a point. As pyrite weathers, Fe^{3+} and sulfuric acid, control the pH of the system. After the pyrite has weathered out, Al controls the pH of the system and it is buffered up to around pH 5. The pH values encountered in active pyrite weathering are generally less than 4.5. Under these conditions Al is present mainly as the Al^{3+} form. This species is free to form salts with the other weathering products of pyrite. These salts then dissolve in the extraction process and give high Al values. With time these salts are leached or eroded from the surface layers of a refuse pile and the amount of extractable Al decreases. Acidity and the associated Al and Fe toxicities are the major chemical factors that limit plant growth in the reclamation of coal refuse. Low nitrogen level are assumed, but it is also correct to assume that nitrogen fertilization will be part of the reclamation soil amendments. If these materials are limed to a pH of 5.5, and that pH is maintained, many of the problems associated with acidity are corrected. The question is what is the best way to control the pH in these materials. Does one try to control the pH from the outset and therefore also control pyrite oxidation, or does one let the pyrite weather from the surface of the pile and then attempt to adjust the pH?

Cation Exchange Capacity

By evaluating the CEC of a soil, it is possible to ascertain its ability to buffer a system against changes in the cation makeup of soil solution. If the nature of the cations occupying the exchange complex can be determined, it is also possible to determine the ease with which the base saturation and pH of soil could be changed. There are many methods by which CEC can be determined. The problem is that few methods give the same result for a given sample.

In this study CEC was determined by 2 methods. The first method used was to sum the 1N NH_4OAc (pH 7) extractable Ca, Mg, and K, and 1N KCl (pH 7) extractable Al. This method will overestimate the CEC in these materials due to dissolved salt errors, hydrolysis errors, and errors due to the high ionic strength of the solutions. A double wash low salt content method was also used. This method will slightly overestimate CEC due to hydrolysis errors involved with the divalent-divalent exchange used. This method did correct for entrained salt errors and for salt dissolution errors, however, and gave lower CEC values for all samples and in some samples gave considerably lower values. The summation method will be referred to as CEC1 and the double wash method will be referred to as CEC2.

The CEC1 values ranged from 4.75 to 18.6 $cmol^+/kg$ (Table 16). The mean value was 8.0 $cmol^+/kg$, which was slightly higher than the median of 7.4. The mean is skewed upward due the presence of 2 extreme outliers on the high end (Fig. 12a), i. e. samples BMR and 35P. These samples have high levels of extractable Ca, which occurs due to the dissolution of Ca salts and carbonates contained in these samples. With the exception of the 2 extreme outliers, the data appears to be normally distributed.

The CEC2 values range from 1.92 to 6.32 $cmol^+/kg$ (Table 16). The mean value of 3.84 $cmol^+/kg$ is only slightly higher than the median 3.65 $cmol^+/kg$. The CEC2 values appear to be normally distributed with no outliers and little skew (Fig. 12b). There is little correlation between the values obtained from the 2 methods $r = 0.06$. This suggests that we are not measuring the same quantity with the two methods. The CEC2 method provides a better estimate of the actual magnitude of

Table 16. Results of two methods for the measurement of cation exhange capacity (CEC). CEC1 = sum of cations method; CEC2 = double wash method

Site	CEC1 cmol$^+$/kg	CEC2 cmol$^+$/kg
BBR	8.80	4.95
BMR	17.43	3.97
BWR	8.85	2.96
CCR	7.96	4.95
DANTE	8.48	2.62
DR1	7.31	4.69
DR2	7.39	4.59
DRP	4.37	1.92
JSR	10.77	2.82
KRP	8.10	3.65
LDR	6.20	3.60
LTR	9.09	3.65
MRP	5.10	4.41
NRP	8.62	6.32
PBRU	8.37	5.34
PBRV	7.84	5.21
PTH	6.80	3.56
RDH	5.63	2.26
RRA	7.89	4.39
RRP	7.42	4.60
RRR	7.15	4.75
SGR	6.88	3.02
WCR	6.90	4.29
31H	4.25	2.36
35P	18.55	2.61
670A	4.88	3.24
670B	4.39	2.92
Mean	7.98	3.84

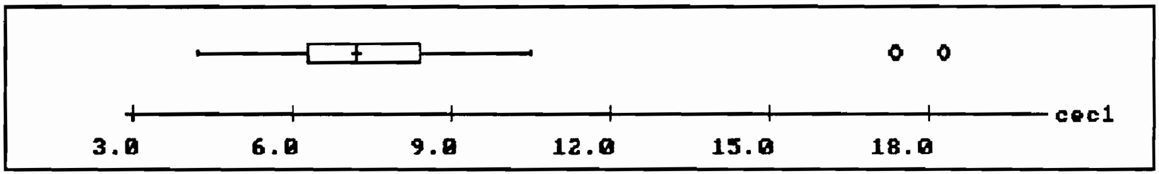

Figure 12a. Boxplot of the CEC1 data.

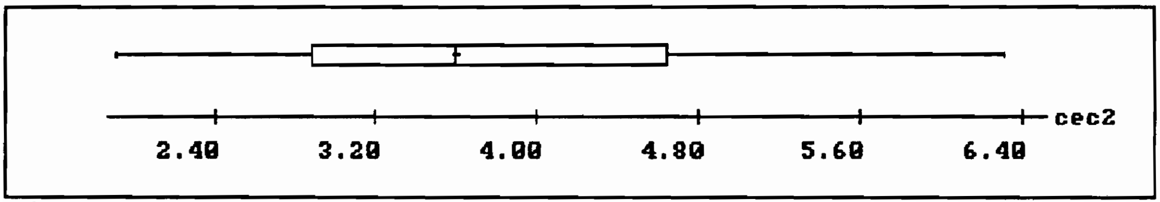

Figure 12b. Boxplot of the CEC2 data.

the CEC, at an ionic strength, and at a pH that somewhat resemble field conditions.

In examining the difference in the data from CEC1 and CEC2 we find that CEC1 is always larger than CEC2. The difference was found to be strongly correlated with the sum of extractable Ca and Al (r= 0.96). This high correlation is somewhat due to the influence of samples BMR and 35P, which are extreme outliers in the CEC1 data set and exert a large influence on the correlation coefficient. If these data are removed from the set the correlation is still fairly strong (r= 0.70). This is a further indication that these materials contain Ca and Al salts which are dissolving during the CEC1 procedure.

These materials have low CEC values. This is due to the general lack of organic matter, and the clay mineralogy dominated by muscovite and kaolinite, which are low CEC minerals. It also should be considered that these materials are roughly 60% coarse fragments by weight, so the actual CEC values of the materials in the pile would be approximately 1.5 $cmol^+/kg$. This indicates that these systems are not highly buffered and that they should be responsive to liming. Of course this assumes that the potential acidity generated by the weathering of pyrite is neutralized. The addition of organic amendments such as sewage sludge will increase the CEC of these materials. This would be beneficial if the pH was maintained at or above pH 5 and a favorable base status was also maintained.

Available Phosphorus

The importance of P lies in the fact that it is the universal energy carrier for metabolic processes in cells. The energy is stored in the high energy P bonds in ATP, and energy is released when this bond is broken. Phosphorus is inadequate to support plant growth on many minewastes. Addition of P fertilizers is needed to establish vegetation on most minespoils and coal refuse. Additions of P may also be effective in slowing pyrite oxidation by removing Fe^{3+} from solution.

The amount of plant available P was analyzed using the dilute double acid procedure of Olsen and Dean (1965). This method was used because the double acid extractant extracts some P from Al and Fe phosphates. This extractant has been found to be well correlated to plant response in low pH systems, where P is bound by Al and Fe. The amount of double-acid-extractable P (AP) is presented in Table 17. Of the 26 samples analyzed, 15 fell into the low (<10 mg kg^{-1}) classification (Olsen and Dean, 1965). Three of the samples, 670A, 670B, and LDR are in the very high (> 56 mg kg^{-1}) category. The rest of the samples fall in the medium (11-31 mg kg^{-1}) category of P availability. The distribution of the AP data is displayed in a boxplot Figure 13a. There are two mild outliers on the high end of the data. These are samples

Table 17. Double-acid-extractable P and total P data.

Site	AP mg kg^{-1}	Total mg kg^{-1}
BBR	3.4	692
BMR	24.0	604
BWR	3.1	775
CCR	4.2	605
DANTE	11.7	280
DR1	7.6	657
DR2	6.0	627
DRP	32.0	not run
JSR	25.4	653
KRP	5.0	984
LDR	64.5	668
LTR	2.3	837
MRP	24.8	445
NPB	not run	655
NRP	2.5	642
PBRU	2.5	724
PBRV	7.6	741
PTH	5.2	325
RDH	11.7	535
RRA	26.8	405
RRP	2.7	352
RRR	14.8	553
SGR	17.0	629
WCR	10.0	626
31H	2.2	620
35P	1.8	579
670A	82.8	729
670B	55.0	811
Mean	17.0	609

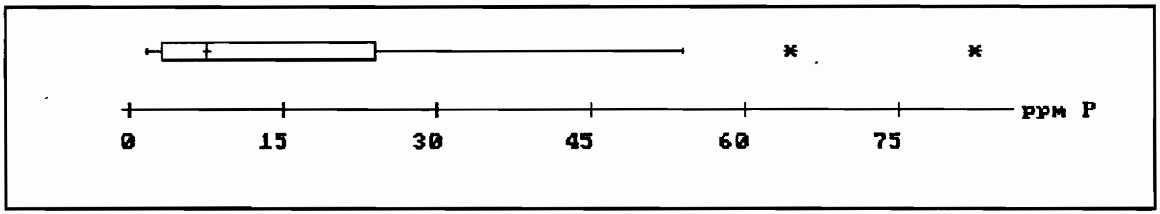

Figure 13a. Boxplot of the AP data.

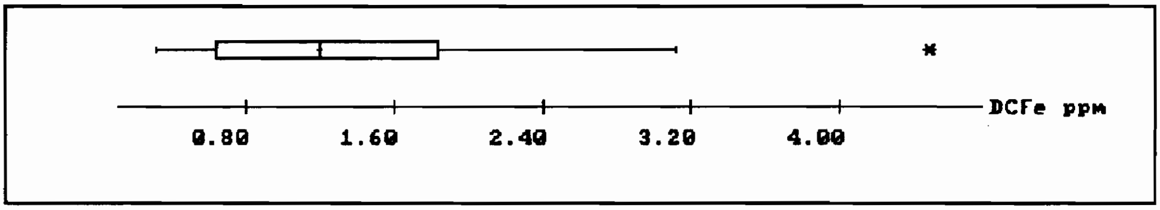

Figure 13b. Boxplot of the DCB-Fe data. Site KRP is the mild outlier.

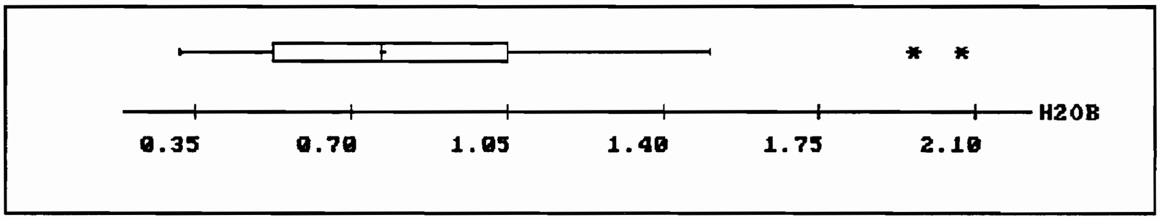

Figure 13c. The distribution of the HWS-B data.

670A and LDR. Sample 670B is also a mild outlier. The factor responsible for the high levels of P in these samples is not known, but is speculated to be geologic in nature. Samples 670A and 670B do have higher than average total P values. The sample set mean, 17.0 ppm, is skewed upward from the median value of, 7.6 ppm this reflects the influence of the outliers on the high end. The extractable P levels in these materials underscores the need for P fertilization in most situations. Care should be taken in P application, however, due to the high runoff potential and close proximity to streams of most refuse piles. Total P is also presented in Table 17. There is little correlation, r = 0.05, between total P and AP. As with many nutrients only a small portion of the P that is present is in a plant available form.

Extractable and Total Iron

The amount of free Fe and its oxidation state is often used as a weathering index in soil genesis studies. Iron extracted by dithionite-citrate-bicarbonate (DCB-Fe) is mainly in the form of Fe-oxide coatings on mineral surfaces. These coatings are precipitates that are generated as Fe is weathered out of primary minerals such as pyrite and biotite. Soils high in DCB-Fe are anticipated to have low P availability due to P fixation by Fe-oxides. These oxides and oxyhydroxides are also important in the binding of some heavy metals such as Mn and As which can occur as anionic species.

As Fe oxidation takes place, precipitates of Fe hydroxides and oxyhydroxides, such as geothite and ferrihydrite, form. These are the main constituents of the orange and yellow slimes, known as "yellow dog" or "yellow boy", found in the drainage streams of refuse piles. These precipitates also form rapidly when the pH of the drainage is raised using strong caustics. An example of these precipitates can be observed in Figure 15.

Extractable iron (DCB-Fe) ranged from 0.4 to 4.5% with a mean of 1.45% in this sample set. The per cent DCB-Fe data is presented in Table 18. A boxplot plot (Figure 13b) illustrates the distribution of these data. Sample KRP is a mild outlier on the high end. This sample also contained the highest total iron content. The Mann-Whitney test was again used to test the differences in the < 20 year old piles and the > 20 year old piles. The < 20 year old piles were found to have a significantly higher DCB-Fe content ($p = 0.06$) than the > 20 year old piles. This is an indicator of Fe oxidation and precipitation that is occurring, at the surface on the more recently deposited piles. In the older piles these processes have slowed or stopped at the surfaces and the precipitates have been translocated into the pile or eroded away. A band of these precipitates can usually be found beneath the surface in older piles. We observed that the piles which had a yellowish cast had high levels of DCB-Fe. Samples with yellow casts, BBR, BWR, KRP, and LTR all have DCB-Fe contents > 2%. This yellow cast is hypothesized to be

Figure 15. Photo of iron precipitates in drainage from a refuse pile.

Table 18. DCB-Fe, Total FE (TFE), and DCB-Fe/TFe values.

Site	% DCB-Fe	% TFe	DCB-Fe/TFe
BBR	2.59	4.64	0.56
BMR	0.54	5.00	0.11
BWR	2.46	4.22	0.58
CCR	1.42	2.95	0.48
DANTE	1.20	3.78	0.32
DR1	2.50	4.51	0.55
DR2	1.94	3.87	0.50
DRP	0.55	not run	n/a
JSR	0.36	4.83	0.07
KRP	4.49	6.66	0.67
LDR	0.74	2.99	0.25
LTR	3.18	4.83	0.66
MRP	0.85	3.00	0.28
NRP	1.38	4.27	0.32
PBRU	1.84	4.05	0.45
PBRV	1.66	3.65	0.45
PTH	1.10	4.27	0.26
RDH	0.88	3.27	0.27
RRA	2.76	4.76	0.58
RRP	0.38	3.38	0.11
RRR	0.46	2.74	0.17
SGR	1.04	4.49	0.23
WCR	1.37	3.29	0.42
31H	1.37	4.26	0.32
35P	0.40	3.77	0.11
670A	0.67	4.32	0.16
670B	1.00	4.73	0.21
MEAN	1.45	3.95	0.35

due to jarosite or other Fe-sulfate minerals.

The data for percent Fe on a total basis are also presented in Table 18. (These data will be presented on an oxide basis in a later section). The ratio of DCB-Fe to total Fe (DCB-Fe/TFe) has also been included. This ratio is being used as an indicator of weathering. The older piles (>20 yrs) have a lower DCB-Fe/TFe ratio than the more recent piles. The difference in this parameter for the two groups is significant at the $p = 0.05$ level (two-sample t test). This reflects the active weathering of Fe minerals at the surface of the more recent piles.

We originally hypothesized that the older piles would have higher DCB-Fe/TFe ratios. This hypothesis did not account for the erosion and translocation of Fe-precipitates form the surfaces of the piles. Due to these processes, the surface samples from the older piles have lower DCB-Fe/TFe ratios than the more recent piles, which have been weathering for a shorter period of time. More investigation is needed to determine if this is due to the presence of more pyrite in the more recent piles. The high amounts of DCB-Fe in these materials indicate the need for careful nutrient management of elements, such as P, that are bound by Fe-oxides and oxyhydroxides.

Iron itself is also a plant micronutrient. Iron toxicities and deficiencies could both occur on refuse piles during reclamation. The reactions of Fe are largely determined by the EH-pH system and by the oxidation state of the Fe compounds involved. In general, oxidizing and alkaline conditions promote the precipitation and immobilization of Fe, whereas acid and reducing conditions promote the solution of Fe compounds. Soluble Fe is at a minimum in the alkaline pH range. These are likely to be the conditions immediately after a lime application to refuse, and a short term Fe deficiency may occur. Toxic amounts of Fe are likely to be present in very acid refuse piles ($pH < 4.0$) and in refuse under reducing conditions. In the more recent refuse piles, in which refuse is deposited in a wet state and compacted to exclude air, pockets of reducing conditions are likely to occur. In refuse materials with $pH < 4.5$, the hydrolysis of Fe is the major reaction that is buffering the system pH. If the pH of these materials is adjusted and maintained above 5.5 the problems of iron toxicities and to some degree high Fe drainage can be mitigated.

Hot Water Soluble Boron

Total B could not be determined from the total digests because the final analyte matrix contained boric acid. Total B content in soils has little bearing on the status of available B in soils anyway (Bingham, 1982). Hot-water-soluble B (HWS-B) has been found to be a fairly reliable indicator of B status is soils. Many workers have found HWS-B to be a good predictor of plant uptake of B, but not necessarily a predictor of response to B fertilization. However, HWS soluble B has been found to be a good indicator of soils which do not require fertilization. Three categories of HWS-B were defined by Reisenauer (1979). They are:

1) Less than 1.0 mg kg^{-1} B soils that may not supply sufficient B for plant growth.

2) 1.0 to 5.0 mg kg^{-1} B soils that supply concentrations of B which usually allow normal plant growth.

3) Greater than 5.0 mg kg^{-1} B soils that may supply toxic amounts of B.

These categories are wide due to the influence of other parameters, such as pH and soil texture on B uptake.

The HWS-B values for the 27 pile sample set are presented in Table 19. Eighteen of the samples fell into category 1, soils that may not supply sufficient B for plant growth. Of the eight samples that fell into category 2, only 1 sample, site RDH had a HWS-B value higher than 2 mg kg^{-1}. The distribution of the HSW-B data is presented in Figure 13c. The data appears to be normally distributed with 2 mild outliers, samples RDH and KRP. The samples which high amounts of carbon in them also seemed to have higher levels of HWS-B. This could be due to the yellow tinge that was imparted on the analyte solution by these samples. The double blank method used in this procedure should have corrected for this problem, however. Perhaps some B is associated with the carbonaceous materials in these samples. Regardless of the slight

Table 19. The hot-water-soluble-B (HWS-B) values for the 27 pile sample set.

Site	HWS-B mg kg^{-1}
BBR	0.99
BMR	1.03
BWR	1.13
CCR	0.67
DANTE	1.47
DR1	0.46
DR2	0.79
DRP	0.49
JSR	0.46
KRP	1.99
LDR	0.50
LTR	0.77
MRP	0.52
NRP	0.94
PBRU	0.58
PBRV	1.14
PTH	1.52
RDH	2.08
RRA	0.33
RRP	0.94
RRR	0.64
SGR	0.56
WCR	0.84
31H	1.15
35P	0.57
670A	0.38
670B	0.79
MEAN	0.88

analytical problems, the data suggests that B fertilization is needed on these materials. Boron is especially important in the establishment and maintenance of legumes, and legumes are the backbone of any good reclamation strategy.

Total S and Potential Acidity

The percent total S data are presented in Table 20. The mean percent total S value is 0.44. Many miners would be happy to have coal this low in S. Coal refuse from the Virginia coal field has much less S than the refuse from neighboring states. Refuse with as much as 6% S has been reported in West Virginia (Buttermore et al, 1978). The distribution of the data is presented in a boxplot (Fig. 15a). The data are skewed high by 2 mild outliers in the high end. Sample BMR has the highest S content; it comes from Westmorland Coal Company's Bullit Processing Facility which is a modern prep plant. Sample KRP is from the Wilson seam which is known to be high in S. This pile has been idle since 1927, so it would be interesting to know the initial S content. With a few exceptions, the older piles seem to have less S than the piles from modern prep plants.

Potential acidity

Total S data is used in the acid-base-accounting (ABA) method of determining potential acidity. The percent S is multiplied by 31.24, to generate the net stoichiometric

Table 20. % total S as determined by a Leco™ S analyzer.

Site	% S
BBR	0.49
BMR	1.43
BWR	0.78
CCR	0.22
DANTE	0.25
DR1	0.43
DR2	0.45
JSR	0.88
KRP	1.04
LDR	0.10
LTR	0.52
MRP	0.27
NPB	0.76
NRP	0.24
PBRU	0.28
PBRV	0.14
PTH	0.53
RDH	0.47
RRA	0.54
RRP	0.28
RRR	0.11
SGR	0.29
WCR	0.53
31H	not run
35P	0.11
670A	0.11
670B	0.18
Mean	0.44

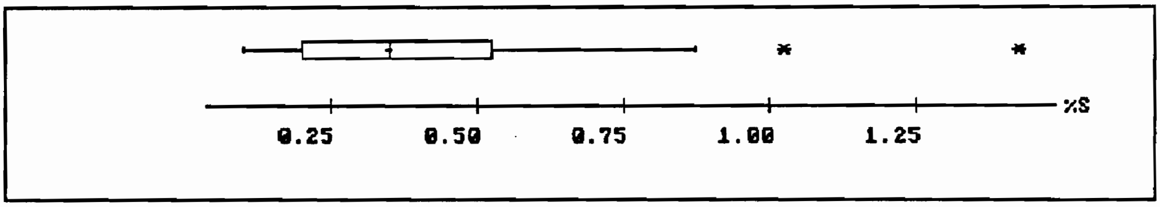

Figure 15a. The boxplot of the per cent total S data.

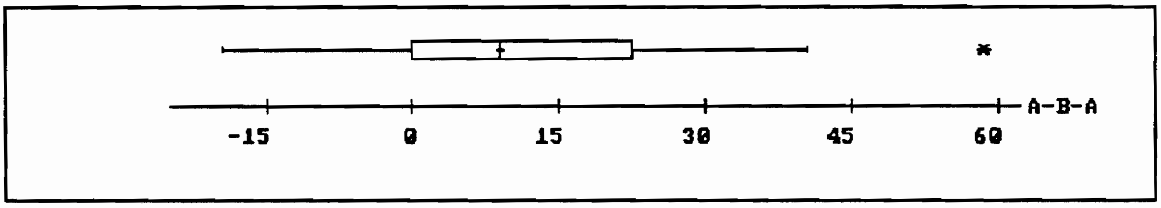

Figure 15b. The boxplot of the acid base accounting potential acidity data. Data is in tons $CaCO_3$/1000 tons of refuse.

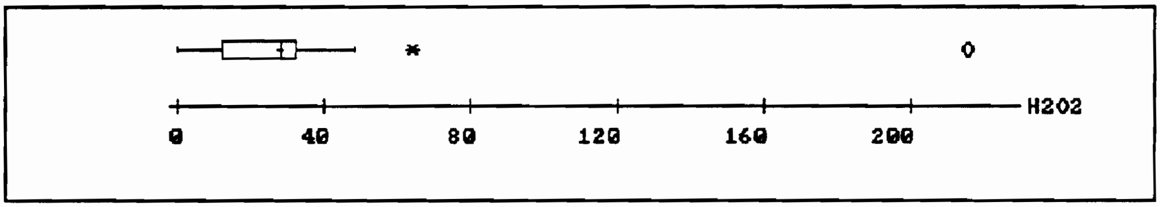

Figure 15c. The boxplot of the H_2O_2 potential acidity data. Data is presented in tons $CaCO_3$/1000 tons of refuse.

potential acidity in a material. This assumes all the S is in a pyritic form, and that it all reacts to form acidity. A crushed sample is also analyzed for its net basicity. The net basicity and acidity are summed and this represents the net acid-base balance of the material. The assumptions that the S is 100% pyritic and totally reactive are usually not completely valid, however. This method is still widely used due to its simplicity and history of good results, which may be due to the fact that this method generally overestimates lime requirement.

The ABA data are presented in Table 21. The most acid material had a potential acidity of 59.3 tons of $CaCO_3$ / 1000 tons of material. That is, 59.3 tons of calcium carbonate are needed to neutralize all the acidity potentially produced by 1000 tons of this material (or the classic acre furrow slice). The lowest potential acidity was - 19.3 tons / 1000 tons. This material P35 therefore, could be used as a liming agent, and appears to be unique in many ways among this sample set. Five of the samples tested were net basic. The mean potential acidity by ABA for this sample set was 13.7 tons / 1000 tons. These data are skewed slightly high, but they appear to be fairly normal (Fig 15b).

Another method of estimating the potential acidity of pyritic materials uses H_2O_2 to oxidize the pyritic material in a sample. The acidity generated is then free to react with the minerals in the sample. This allows the whole sample to

Table 21. Values for potential acidity using the acid-base-accounting method and H_2O_2 method.

Site	total acid	total base	net acidity*	H_2O_2
BBR	15.3	-8.5	-23.8	46.8
BMR	44.7	3.0	-41.7	21.1
BWR	24.4	-14.8	-39.2	27.3
CCR	6.9	-16.6	-23.5	9.4
DANTE	7.8	16.1	8.3	20.6
DR1	13.4	6.7	-6.7	28.2
DR2	14.0	-9.4	-23.4	not run
JSR	27.5	6.6	-20.9	28.2
KRP	32.5	-26.8	-59.3	28.8
LDR	3.2	2.8	-0.4	31.8
LTR	16.2	-8.9	-25.1	49.9
MRP	8.4	3.4	-5.0	18.8
NPB	18.8	16.2	-7.5	38.0
NRP	7.5	-17.7	-25.2	64.4
PBRU	8.7	-16.2	-24.9	32.3
PBRV	4.4	-15.4	-19.8	10.7
PTH	16.6	-9.3	-25.9	215.8
RDH	14.7	-3.5	-18.2	28.6
RRA	16.9	6.7	-10.2	13.5
RRP	8.7	21.7	13.0	10.4
RRR	3.4	2.5	-0.9	1.9
SGR	9.1	-14.5	-23.6	35.4
WCR	16.6	10.3	-6.3	33.2
35P	3.4	22.7	19.3	0.5
670A	3.4	6.2	2.8	21.8
670B	5.6	3.1	2.5	9.1
Mean	6.2	5.2	2.4	3.8

* total acid - total base

be accounted for in the neutralization of the acidity generated. This method has been used successfully in Kentucky for a number of years (Barnhisel et al., 1982), however it is an "arty" technique, and it is slow and laborious.

The data for the H_2O_2 potential acidity are presented in Table 21. The values ranged from an exceedingly high 215 tons $CaCO_3$ /100 tons of material, to 0.5 tons / 1000 tons. The high sample contains a large amount of weathered coal, i. e. the C content of the sample was 63%. I believe we were titrating functional groups on this sample, such as COOH and COH, on the coal surfaces. Khan et al (1984) report that as coal weathers, many functional groups form as the unsaturated long chain hydrocarbons in the coal are oxidized. Weathered coal surfaces were found to have a ZPC near pH 2, with negative charge increasing with increasing pH. Some of the other samples with high coal content also have high potential acidities by this method. The use of this method is not recommended with samples containing large amounts of weathered coal.

The mean potential acidity value for the H_2O_2 analysis was 25.4 tons / 1000 tons. This mean does not include the 215 value, and is about 2 times that of the ABA method. The distribution of the H_2O_2 data is presented in Figure 15c. If the extreme outlier is removed the data appears to be normal with a slight skew to the high side.

The H_2O_2 method shows some potential for giving insight into the nature of the acidity in a sample. A potentiometric analysis of the H_2O_2 digest may be used to quantify the acidity in different forms. It is hypothesized that there would be plateaus corresponding to Fe, Al, and possibly organic matter in the titration curve.

Total Elemental Analysis

Total elemental analysis allows us to examine the nature of the basic structural building blocks of these materials. The data generated does not necessarily have any bearing on how much of an element is in a plant available or leachable form, however. Plant availability/leachability is determined by many factors other than the shear quantity of the element present. These factors include pH, Eh, solubility, reactivity, the presence of chelating agents, and the presence of ions which will cause an element to precipitate.

The methodology I used was a standard method (Bernas, 1968), which is designed to dissolve silicates so their elemental content can be determined. I had hoped to also be able to accurately determine the amount of trace elements such as Pb, Cu, Zn, Cr, Ni, Cd, Se, and As. Due to the large amounts of Si, Al, and Fe in these digests the accuracy of the data for the trace elements is somewhat questionable (Table 22). The Si, Al, and Fe produced a large amount of background "noise" on the ICAP and when the peaks of the trace elements are scanned, some of this "noise" is included in the peak.

Table 22. The NBS certified values and the values obtained for the elemental analysis of NBS SRM 1633a coal fly ash.

Element	NBS certified value	experimental value
	%	
Si	22.8 +- 0.8	23.2
Al	14.3 +- 1.0	12.0
Fe	9.4 +- 0.1	8.5
K	1.88 +- 0.06	1.83
Na	0.17 +- 0.01	0.41
Mg	0.45 +- 0.01	0.36
Ca	1.11 +- 0.01	0.95
	mg kg^{-1}	
Cu	118 +- 3	130
Cr	196 +- 6	356
Mn	179 +- 8	264
Ni	127 +- 4	151
P	not available	0.25
Pb	72.4 +- 0.4	397
Zn	220 +- 10	227
Cd	1.00 +- 0.15	14.2

The "noise" pads the peak area and the element in question is overestimated. Background subtraction was attempted, but this cut down on sensitivity. The analysis of cadmium is a good example of this problem. The original Cd data was found to overestimate the Cd content by 14 fold. When background correction was attempted most of the samples fell below the detection limit of the instrument. Due to these difficulties the Cd data is not presented. A hydride generator is needed for the accurate determination of Se and As. Since this equipment was not available, analysis of these elements was not attempted. The HF-aqua-regia-boric acid matrix used may also cause difficulties with the hydride generator (D.R. Parker, personal communication, 1990).

In order to check our technique a duplicate sample of NBS standard reference material (SRM) 1633a, coal fly ash, (NBS, 1990) was included in the sample set. The NBS certified values, and the experimental values from my digests are presented in Table 22. The experimental values for Si, K, and Zn fall with the limits of the certified values. The values for Al, Fe, Mg, Ca, Cu, and Ni are reasonably close to their certified values. There is no comparison value for P so I will assume that its values are also accurate. Elements Pb, Cr, Mn, and Na vary considerably from their certified values. As points of reference, Pb was overestimated by a factor of 5, Cr and Mn by a factor of 2, and Na by a factor of 2.5.

Silicon

The data for the percent SiO_2 in the refuse samples are presented in Table 23. The distribution of this data is presented in Figure 16a. The data are skewed low. This is due to the large range of values in the weight loss at 923 K parameter. Those samples which had a high weight loss have low Si contents ($r = 0.94$). Examination of the data for the ash that was digested reveals a distribution of Si content that appears to be normal. The mean of this data is 55.9% and the median is 55.8%, and there are no outliers. This trend holds true in all the major elements i.e. those expressed as oxides. This suggests that the basic noncoal elemental backbone is similar in these samples. Silicon is the backbone of the silicate minerals hence its high content in refuse which is largely made of silicate minerals (Barnhisel and Massey, 1969; Busch et al., 1974).

Aluminum

The data for the percent Al_2O_3 content are also presented in Table 23. The boxplot of the data is presented in Figure 16b. Again the data are skewed a bit low. Again the mean is below the median indicating skew to the low side. There is a mild outlier at each end of the boxplot. The high sample is sample 35P, which was associated with the "limestone seam". The low sample is 31H which had a coal content of > 60%.

Table 23. Total Si, Al, and Fe content. Values are expressed on a whole sample basis (pre-ashing weight).

Site	%SiO_2	%Al_2O_3	%Fe_2O_3
BBR	43.5	15.3	5.24
BMR	33.2	14.2	3.81
BWR	42.4	13.1	5.01
CCR	40.8	17.2	3.24
DANTE	30.2	8.77	2.83
DR1	39.0	14.5	4.79
DR2	34.6	11.9	3.44
JSR	37.2	14.7	4.98
KRP	48.3	14.2	7.72
LDR	44.1	13.8	3.41
LTR	48.9	13.9	5.74
MRP	32.6	8.11	2.43
NPB	47.7	13.3	3.62
NRP	41.2	14.4	4.49
PBRU	45.3	14.7	4.70
PBRV	46.5	14.0	4.25
PTH	20.2	8.88	2.45
RDH	32.2	11.0	2.44
RRA	38.0	14.7	4.72
RRP	24.5	7.75	2.24
RRR	42.0	12.8	2.88
SGR	37.8	11.5	4.15
WCR	38.3	12.6	4.70
31H	22.4	6.19	2.17
35P	55.2	19.6	5.39
670A	43.8	13.3	5.02
670B	46.4	12.2	5.23
Mean	39.1	12.8	4.11

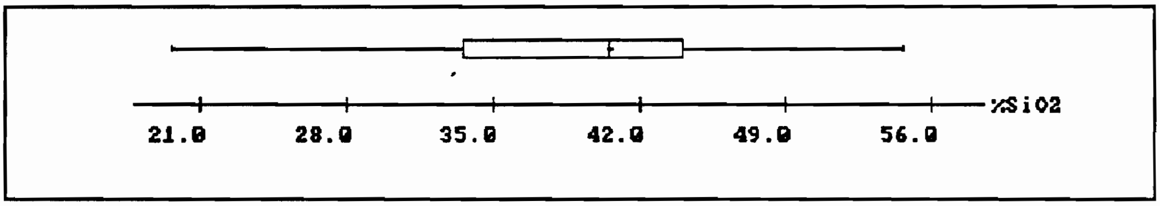

Figure 16a. The boxplot of the SiO_2 data.

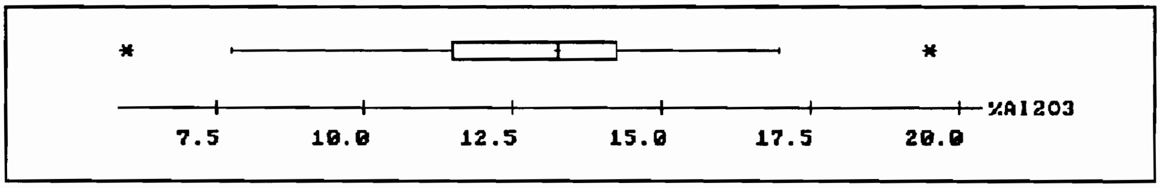

Figure 16b. Boxplot of the Al_2O_3 data.

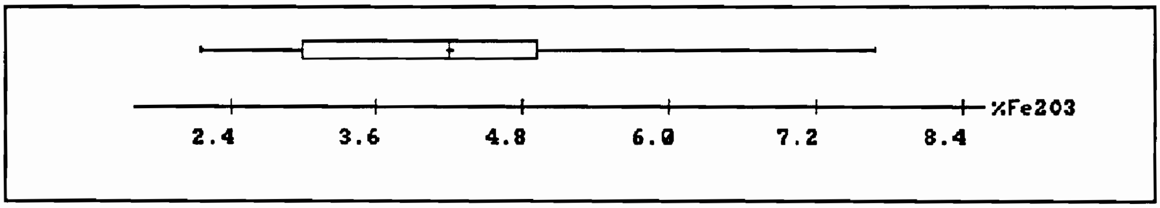

Figure 16c. The boxplot of the Fe_2O_3 data.

Aluminum is a structural component of the layer silicate minerals, the feldspars, and many other minerals.

Iron

The data for the percent Fe_2O_3 content is also presented in Table 23. The boxplot of the data is presented in Figure 16c. The mean Fe_2O_3 content was 4.1%, while the median value was 4.2%. There are no outliers revealed by the boxplot. The CV of the Fe data is 32, this is slightly higher than the CV values for Si and Al which are 21 and 23, respectively. The main sources of Fe in these materials would be the pyrite minerals, and Fe-oxides and oxyhydroxides. The iron sulfate salts were likely washed away when these materials were saturated with NH_4^+ prior to digestion.

Potassium

The data for the percent K_2O in these materials are presented in Table 24. A boxplot of the data is also presented (Fig. 17a). The distribution of the data is nearly normal (Fig. 17a). Because of the spread of the data about the mean the slight difference between the mean of 2.89% and the median 3.00% graphically appears as a larger difference than is actually present. There are mild outliers on each end of the boxplot. The high outlier is sample 35P, and the low outlier is sample PTH which had >60% coal. The K

Table 24. Total K, Na, Mg, and Ca content. Values are expressed on a whole sample basis (pre-ashing weight).

Site	%K_2O	%Na_2O	%MgO	%CaO
BBR	3.36	0.30	0.31	0.02
BMR	2.79	0.33	0.94	0.40
BWR	2.40	0.29	0.30	0.03
CCR	2.35	0.38	0.26	0.06
DANTE	1.90	0.20	0.50	0.18
DR1	3.25	0.22	0.38	0.02
DR2	3.00	0.23	0.37	0.03
JSR	3.31	0.43	0.94	0.34
KRP	3.22	0.59	0.44	0.03
LDR	3.48	0.36	0.38	0.05
LTR	3.45	0.45	0.68	0.03
MRP	2.47	0.24	0.48	0.09
NPB	2.83	0.30	0.32	0.08
NRP	3.01	0.35	0.75	0.03
PBRU	3.31	0.42	0.74	0.02
PBRV	3.63	0.29	0.35	0.01
PTHR	0.99	0.07	0.15	0.04
RDH	2.45	0.27	0.52	0.08
RRA	2.39	0.24	0.97	0.33
RRP	1.88	0.24	0.57	1.53
RRR	2.98	0.35	0.62	0.07
SGR	3.08	0.30	0.80	0.07
WCR	2.72	0.22	0.36	0.03
31H	1.12	0.16	0.19	0.05
35P	4.88	0.42	1.77	1.97
670A	4.20	0.29	0.47	0.03
670B	3.51	0.41	0.50	0.04
Mean	2.89	0.31	0.56	0.21

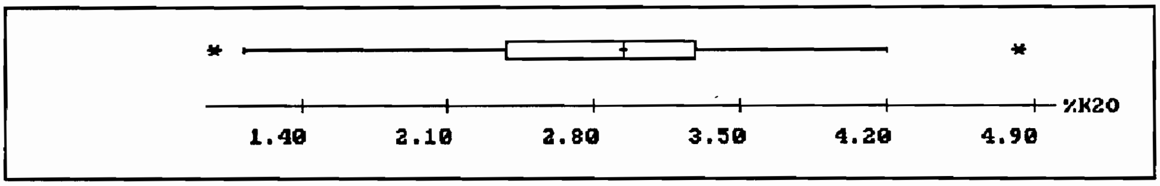

Figure 17a. The boxplot of the K_2O data.

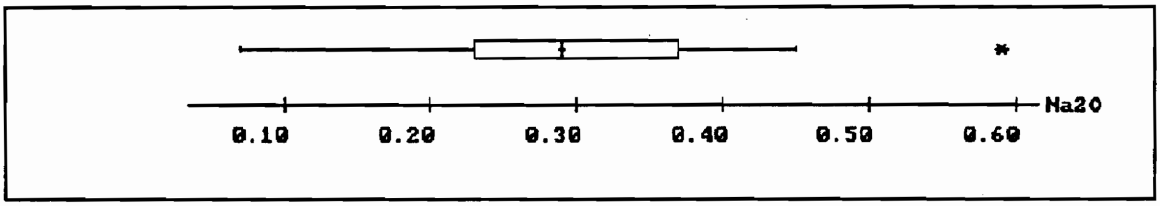

Figure 17b. The boxplot of the Na_2O data.

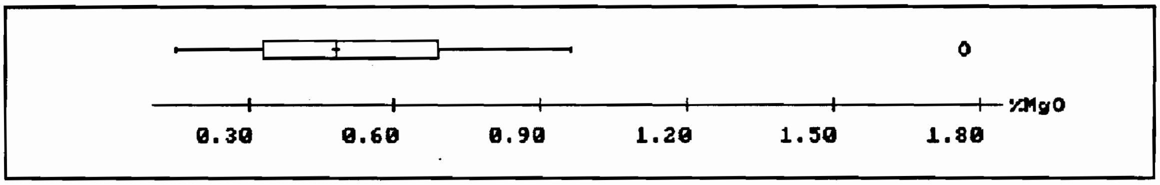

Figure 17c. The boxplot of the MgO data.

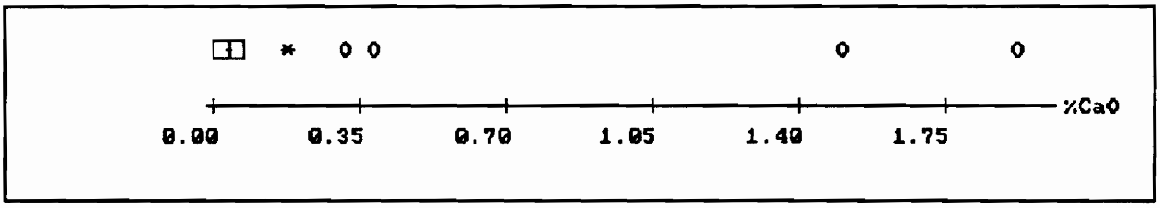

Figure 17d. The boxplot of the CaO data.

is present in the interlayers of micas and as a structural component of some feldspars.

Sodium

The data for the percent Na_2O content are also presented in Table 24. A boxplot of the data is also presented (Fig. 17b). The distribution is nearly normal with one mild outlier on the high end (Figure 17b). Sodium was overestimated by a factor of 2.5. Sodium is a very difficult element to run cleanly due to problems with contamination. Sodium also has a relatively high detection limit on the ICPES. The Na in refuse is probably present in Na-feldspars such as albite.

Magnesium

The data for percent MgO are presented in Table 24. A boxplot of the data is also presented (Figure 17c). The plot reveals on extreme outlier on the high end (Figure 17c). Again this is sample 35P, which has nearly twice as much Mg as any other sample. Magnesium is likely to be present as a carbonate in the high pH samples or as a component of many of the opaque minerals.

Calcium

The data for the percent CaO content are also presented in Table 24. The mean CaO content is 0.21%, which is significantly higher than the median value of 0.05%. The CV is a very large 217. The boxplot of the data (Figure 17d) reveals that the distribution is not normal and there aré several extreme outliers. Working inward form the most extreme outlier the extreme samples are 35P, RRP, BMR, JSR, and RRA respectively. The mild outlier is sample Dante. These samples are all either high pH samples or samples from recent refuse piles. As a rule, Ca content is low in these materials. The extreme outliers presented here would not be outliers if calcareous soils were being considered. In most soil, systems the Ca:Mg ratio is 1:1 or greater, in some cases much greater. These materials have a Ca:Mg ratio of 1:10 or less. Since large amounts of limestone will be added to these materials during reclamation it is not likely that the low Ca:Mg ratio will be a problem. These data do suggest that in their native state most acid refuse piles may be Ca deficient.

Phosphorus

The P data are presented in Table 25. The distribution of this data is presented in a boxplot (Fig. 18a). This plot reveals a near normal distribution with 2 mild outliers (Fig. 18a). Sample KRP is the high outlier and sample Dante is the low outlier. Calcium, Al and Fe phosphates and coal are the likely sources of P in these materials. At high pH values P is most likely present in the form of Ca and Mg

Table 25. Total P, Cu, Zn, and Ni content.

Site	P mg kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}	Ni mg kg^{-1}
BBR	692	51.2	64.6	35.9
BMR	604	64.4	126	49.6
BWR	775	37.0	55.1	38.7
CCR	605	48.8	70.7	45.0
DANTE	280	54.0	37.0	35.1
DR1	657	55.5	74.0	32.5
DR2	627	49.5	55.9	29.7
JSR	653	52.8	89.8	48.7
KRP	984	38.8	59.6	43.8
LDR	668	36.9	89.2	39.7
LTR	837	41.8	73.9	33.3
MRP	445	55.8	60.8	36.1
NPB	655	49.0	89.5	43.7
NRP	642	47.8	60.6	38.8
PBRU	724	46.7	75.7	38.9
PBRV	741	54.3	81.2	39.4
PTH	325	90.4	21.6	24.5
RDH	535	73.4	59.4	34.9
RRA	405	61.6	62.1	35.0
RRP	352	47.9	57.1	31.1
RRR	553	49.9	97.4	40.5
SGR	629	46.0	64.9	35.5
WCR	626	79.1	65.2	48.2
31H	320	84.1	23.0	17.6
35P	579	84.1	83.5	55.8
670A	729	64.4	111	50.7
670B	811	64.2	88.5	55.5
Mean	609	55.0	70.3	39.2

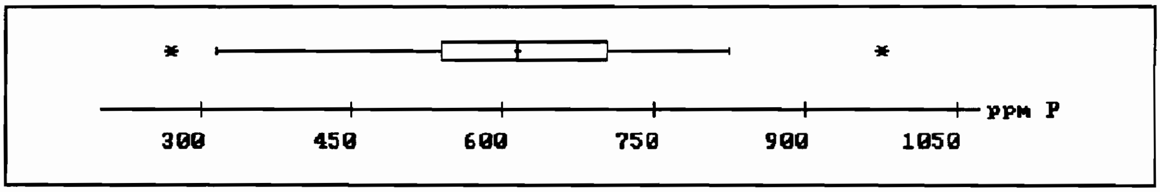

Figure 18a. The boxplot of the P data.

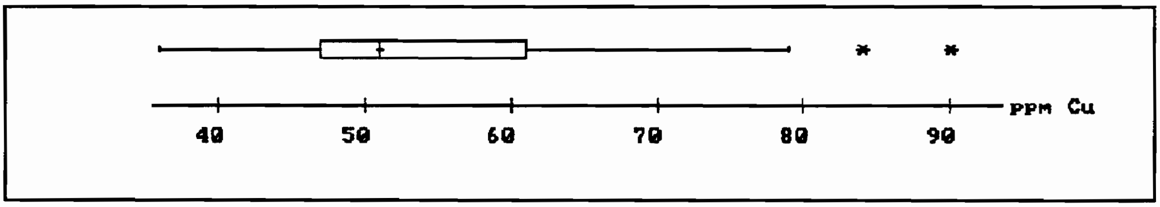

Figure 18b. The boxplot of the Cu data.

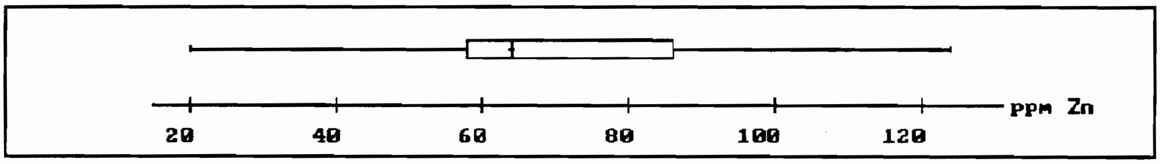

Figure 18c. The boxplot of the Zn data.

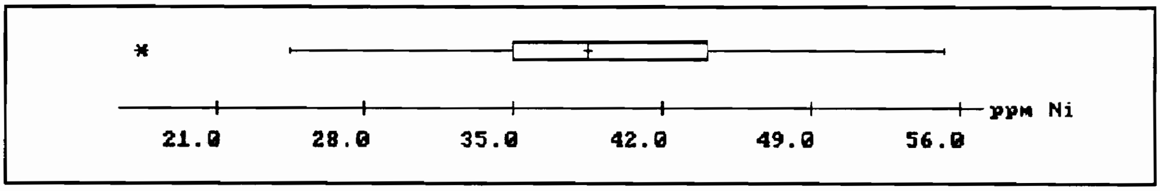

Figure 18d. The boxplot of the Ni data.

phosphates, while at low pH P is most likely present as Fe and Al phosphates.

Copper

The Cu data are also presented in Table 25. The distribution of this data is presented a boxplot (Fig. 18b). There are 2 mild outliers, which are associated with high C samples, and the mean is also skewed high. Most high C samples are also generally high in Cu. This suggests that the Cu is associated with the coal in the refuse. The correlation between Cu and wt loss at 923 K is fairly strong (r = .83). This correlation appears much more significant when one considers that Ni is the next most highly correlated element with wt loss at 923 K (r = .34). The correlation of Cu with coal is logical since Cu has been found to be strongly bound by organic substrates (Martens, 1986). Bland et al (1977) hypothesized that Cu was associated with pyritic materials.

Zinc

The Zn data are also presented in Table 25. The distribution of this data is presented a boxplot (Fig. 18c). There are no outliers, however the mean is skewed high. The source of the Zn in these materials may be the mineral sphalerite (Bland et al, 1977), which is a Zn-sulfide mineral which weathers to form Zn sulfate.

Nickel

The Ni data are also presented in Table 25. The distribution of this data is presented a boxplot (Figure 18d). There is one mild low outlier representing sample 31H, however the mean is skewed high. Bland et al (1977) hypothesized that the Ni was associated with the pyrite in refuse. The high %S samples tend to have higher Ni contents, however, this is not a consistent trend.

Lead, Manganese, Chromium

The data for the Pb, Mn, and Cr contents are presented in Table 26. The distributions of these elements of are presented in Figures 19a-19c, respectively. These parameters have similar distributions, they are skewed slightly low with no outliers. It must be remembered that these elements are overestimated by 2 to 5 times. Lead is likely present as galena, a sulfide mineral. Manganese is likely to be present as Mn-oxides.

Summary of Elemental Data

The elemental values generated by this study are compared with the data from a similar study in Table 27, and are similar to other elemental data for coal refuse from this region. The exceptions are the elements Ca, S, Pb, and Cr. Calcium is about half the value reported by Rose et al (1976)

Table 26. Total Pb, Mn, and Cr content.

site	Pb mg kg^{-1}	Mn mg kg^{-1}	Cr mg kg^{-1}
BBR	227	142	173
BMR	223	207	196
BWR	287	131	200
CCR	221	124	181
DANTE	158	121	87
DR1	208	169	149
DR2	213	140	136
JSR	222	243	167
KRP	343	166	186
LDR	214	305	154
LTR	290	181	149
MRP	169	213	108
NPB	285	159	176
NRP	259	148	170
PBRU	287	174	177
PBRV	288	168	182
PTH	110	74	74
RDH	216	123	138
RRA	201	68	115
RRP	141	145	92
RRR	209	170	158
SGR	228	250	133
WCR	212		194
31H	139	49	84
35P	293	228	157
670A	220	311	159
670B	299	277	200
Mean	228	173	152

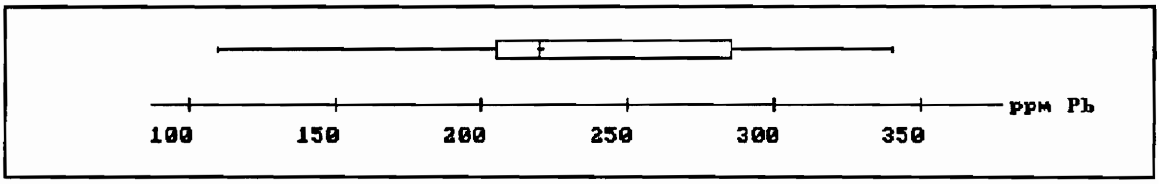

Figure 19a. The boxplot of the Pb data.

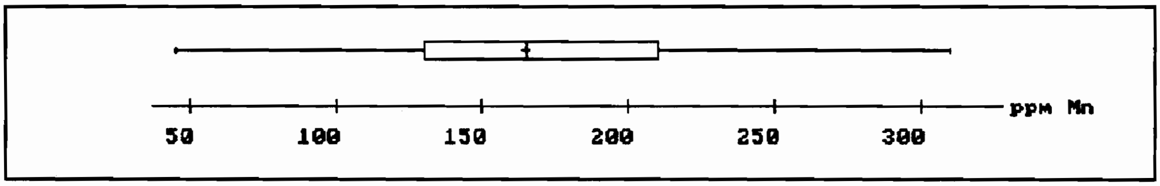

Figure 19b. The boxplot of the Mn data.

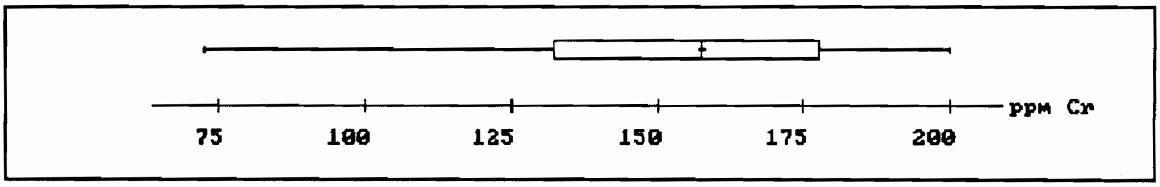

Figure 19c. The boxplot of the Cr data.

Table 27. Averages and ranges of major element chemistry for Virginia Appalachian Coal Basin (VACB), and Kentucky Appalachian Coal Basin (KACB).

	VABC	KABC
% SiO_2	55.9	55.0*
	(38.2-65.1)	(47.8-61.4)*
% Al_2O_3	18.3	26.2*
	(12.6-24.4)	(20.8-37.6)*
% Fe_2O_3	5.84	7.07*
	(3.9-10.4)	(2.3-18.7)*
% K_2O	4.07	3.94*
	(2.4-5.2)	(1.0-4.8)*
% Na_2O	0.44	0.38*
	(0.14-0.87)	(0.1-0.8)*
% MgO	0.80	1.53*
	(0.31-1.81)	(0.5-2.7)*
% CaO	0.32	0.66*
	(0.0-3.4)	(0.09-5.63)*
% S	0.44	0.93*
	(0.10-1.43)	(0.20-3.7*
Mn mg kg^{-1}	172	142+
	(49-311)	(29-1200)+
Pb mg kg^{-1}	228	26+
	(111-343)	(12-51)+
Cu mg kg^{-1}	55	53+
	(37-90)	(16-190)+
Zn mg kg^{-1}	70	56+
	(22-126)	(0.3-190)+
Ni mg kg^{-1}	39	33+
	(18-56)	(7-79)+
Cr mg kg^{-1}	152	98+
	(74-200)	(52-154)+

* Rose et al. (1976) + National Academy of Sciences (1978)

for Kentucky refuse. Sulfur content is also significantly lower than the values report for Kentucky refuse reported by Rose et al (1976). Virginia has the lowest S coal mined in the Appalachian region (EIA, 1984). Lead and Mn are also higher than those values reported by other researchers, but these value are known to be erroneously high in this data set.

Mineralogy

Sand fraction

The mineralogy of the sand fraction was not determined. Since the silt fraction of the samples analyzed was found to be dominated by quartz, it is hypothesized that the sand fraction is also mainly quartz. This is in agreement with the findings of Barnhisel and Massey (1969) who found the sand fraction of some eastern Kentucky samples to be mainly quartz.

Silt mineralogy

The silt mineralogy of the 3 samples analyzed is presented in Table 28. Quartz was found to be the dominant mineral in these materials. Kaolinite and mica also make up a significant portion of the silt fraction. There is also a recognizable feldspar component in the silt fraction. In sample JSR a peaks at 0.32 nm and 0.404 nm were identified indicting the presence of albite a Na-plagioclase mineral. It is likely that this mineral is responsible for some of the higher than expected Na values in the total elemental digests.

Table 28. The silt mineralogy for 3 represenatative samples.

Site	relative mineralogy
CCR	quartz>>kaolinite≡mica>feldspar
JSR	quartz>>kaolinte≡mica>feldspar*
RRA	quartz>>mica≥kaolinite>feldspar

*contained albite

Clay mineralogy

The clay mineralogy of the 3 samples analyzed is presented in table 29. The clay fraction of these samples is composed mainly of mica and kaolinite. A large amount of smectite was also identified in sample CCR. The mineralogy of these samples is that reported by Barnhisel and Massey (1969) for eastern Kentucky refuse like spoils. The suite of minerals in coal refuse is characterized by low charge minerals, which are largely responsible for the low CEC values of these materials. The micaceous nature of these materials may provide a source of plant available K if the weathered edges do not become clogged with Al polymers.

Table 29. The clay mineralogy of 3 representative samples.

Site	Mica	KaO	Smec	Chl	Qz	RIMV
	%mineral					
CCR*	25	25	25	10		10
JSR	45	30		10	5	10
RRA+	55	20		5	5	10

*also contained 5% chloratized vermiculite
+also contained 5% vermiculite
KaO = kaolinite Smec = smectite Chl = chlorite
Qz = quartz RIMV = Regularly interstratified mica/vermiculite

CONCLUSIONS

Little information was available about the physical and chemical properties of coal refuse from the southwest Virginia coalfield. This information is needed to allow reclamationists to make better decisions in the reclamation of these problem areas. The need for this information led to the development of this study. The objectives of this study were:

1.) To provide a full chemical and physical analysis of a broad range of coal refuse piles from southwest Virginia.

2.) To determine the effects of weathering/aging on refuse with respect to reclamation potential.

In order to accomplish these goals random surface samples were taken from 27 refuse piles. These piles represented a broad range of coal seams and over 60 years of coal refuse disposal. The samples were subjected to analysis for a number of physical and chemical parameters. The analysis of the data from these analyses have led to the following conclusions.

1. The physical factor most limiting to plant survival is the low water holding capacity of these materials. The water holding capacity of these materials is much like that of washed sand, which also has problems supporting a vigorous vegetative cover. The addition of an organic amendment would likely be beneficial in improving the water holding ability of coal refuse.

2. The chemical factor most limiting to plant survival in these materials is low pH, and its associated toxic levels of Fe and Al.

3. In the reclamation of fresh refuse, plants are established on media whose characteristics are changing. The amendments added before reclamation should not necessarily be based on the present refuse conditions, but rather on the likely conditions after 5-10 years of weathering.

4. In the reclamation of old abandoned piles, the weathered surface zone should be saved and used as the cover material. Simple regrading, which would bring unoxidized materials to the surface would likely open more wounds than it closes.

5. It may be beneficial to allow the salt evolution processes in these materials to slow before a reclamation effort is attempted. The salt production may slow after 3-5 years, and if erosion can be controlled, it may be beneficial to let the salts evolve and be leached away before revegetation is attempted.

6. The WSR of 5:1 has some potential as a screening test to determine which samples need to have a saturated paste conductivity determined. If the WSR 5:1 is < 0.5 dS $m^{-1,}$ it is

unlikely that the saturated paste EC will exceed 2.0.

7. Acid base accounting offers a rapid estimate of the acid producing potential of these materials. The peroxide digest may give a better prediction of the actual lime requirement because the Fe and Al generated by pyrite oxidation and subsequent acid attack on silicate minerals are accounted for in the titration of the digest.

8. These materials have low CEC values and are dominated by low charge surfaces. This being the case, coal refuse is poorly buffered against changes in pH.

9. Refuse materials are usually deficient in available P. Fertilization with adequate levels of P during reclamation is highly recommended.

10. An application of B which raises HWS-B to the 1-5 ppm range may be beneficial for plant growth on these materials.

11. The elemental backbone of these materials is similar across the sample set. The amount of coal remaining in the samples causes much of the variability in the major elemental values.

12. Calcium content is quite variable in these materials and

is generally low. This should not be a problem since limestone will be part of the reclamation amendments used on most refuse.

13. No heavy metal determined was shown to be in an inordinately high concentration in these materials. The control of metal toxicities depends on the maintenance of a pH above 6.0

14. The use of the total elemental digest for the determination of trace elements may not be accurate for some elements, such as Pb, Mn, Cr, and Cd, due to interferences caused by the large amounts of Si, Al, and Fe in these digests.

Based on my study, I believe some refuse piles are suitable for direct seeding. The largest problem is controlling pH. On a weakly acid (< 20 tons net acidity by acid base) pile, with high Ca content, I believe that direct seeding may work, especially with the use of an organic surface amendment. An organic amendment such as composted sewage sludge or manure would be quite beneficial since it would increase CEC, water holding, and provide nutrients to the system. I would also speculate that any pile with < 5% available water and > 1.5% total S needs at least 2 feet of a suitable topsoil cover to be reclaimed.

What lies down the road in the reclamation of these areas? I believe the results of the VA TECH direct seeding experiments at the Ramsey Refuse area will start the ball rolling toward the direct seeding of some of the less acid materials. Will a pile that has met 5 year bond release look good after 10 years? The jury is still out on this question. I don't believe that it is possible to add all the materials needed to jump-start an ecosystem at one time. Perhaps the five year bond with no augmentation is a bit severe on refuse. Maybe a longer bond period, with the opportunity to adjust the reclamation practices if the refuse conditions change more drastically than expected, is needed.

References

Augenstein, D. A., and S. C. Sun. 1974. Characterization of coal refuse by low temperature ashing. Trans. Soc. Mine Eng. AIME 256 (2), p 161-166.

Barnhisel, R. I. and P. M. Bertsch. 1982. Aluminum. *In* A. L. Page (ed.), Methods of soil analysis, Part 2, Agronomy 9:275-300.

Barnhisel, R. I.,J. 1. Powell, G. W. Akin, and M. W Ebelhar. 1982. Characteristics and reclamation of "acid sulfate" mine spoils. *In* J.A Kitterick, D. S. Fanning, and L. R. Hossner (eds.) Acid Sulate Weathering. SSSA Special Pubilcation 10. SSSA Madison WI. pp 225-234.

Barnhisel, R. I. and J. Harrison. 1976. Estimating lime requirement by a modified hydrogen peroxide total potential acidity method. (Unpublished method for KY. Agr. Exp. Sta., Soil Testing Laboratory).

Barnhisel, R. I, and H. F. Massey. 1969. Chemical, mineralogical and physical properties of eastern Kentucky acid-forming coal spoil materials. Soil Sci. 108:367-372.

Bernas, B. 1968. A new method for decomposition and comprehensive analysis of silicates by atomic absorbance spectrophotometry. Anal. Chem. 40:1682-1686.

Bingham, F. T. 1982. Boron *In* A. L. Page (ed.), Methods of soil analysis, Part 2, Agronomy 9:411-436.

Bland, A. E., T. L. Robl, and J. G. Rose. 1977. Evaluation of interseam and coal cleaning effects on the chemical variability of past and present Kentucky coal refuse. Trans. AIME. 262:331-334.

Bower, C. A., and L. V. Wilcox. 1965. Soluble salts. *In* C. A. Black (ed.). Methods of soil analysis, Part 2, Agronomy 9:933-951.

Brady, N. C. 1984. The nature and properties of soils. Macmillian Publishing Co. New York, NY.

Bruce, R. R. 1972. Hydrualic conductivity evaluation of the soil profile from water retention relations. Soil Sci. Soc. on Am. Proc. 36:555-561.

Busch, R. A., R. R. Backer, and L. A. Atkins,. 1975.

Physical property data on fine coal refuse. U. S. Bureau of Mines, Rept. Invest. 8062.

Busch, R. A., R. R. Backer, and L. A. Atkins,. 1974. Physical property data on coal waste embankment materials. U. S. Bureau of Mines, Rept. Invest. 7964.

Buttermore, W. H., E. J. Simcoe, and M. A. Malloy. 1978. Characterization of coal refuse. Technical Report No. 159, Coal Research Bureau. West Virginia University, Morgantown, WV.

Caruccio, F.T., L.R. Hossner, and G. Geidel. 1988. Pyritic materials: acid drainage, soil acidity, and liming. p. 159-189. In L.R. Hossner (ed.) Reclamation of suface-mined lands. Vol 1. CRC Press, Boca Raton, FL.

Caruccio, F. T., and G. Geidel. 1986. An evaluation of mine waste overburden analytical techniques. p147-153. *In* 1986 National Symposium on Mining, Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY. Dec. 8-11.

Caruccio, F. T. 1970. The quantification of reactive pyrite by grain size. *In* Reprints, Third Symposium on Coal Mine Drainage Research, Monroeville, PA. Natl. Coal Assn. and Bituminous Coal Research Inc, Washington D.C.

Chapman, H. D. 1965. Cation-exchange capacity. *In* C. A. Black (ed.). Methods of soil analysis, Part 2, Agronomy 9:891-901.

Day, P. R. 1965. Particle fractionation and particle size analysis. *In* C. A. Black (ed.). Methods of soil analysis, Part 1, Agronomy 9:545-556.

Davidson, W. A. 1974. Reclaiming refuse banks from underground bituminous mines in Pennsylvania. *In* Proceedings, First symposium on Mine and Prepartation Plant Refuse Disposal, Louisville, KY, 22-24 Oct. 1974. Natl. Coal Assn. and Bituminous Coal Research Inc, Washington D.C.

Delp, C. H. 1975. Soil morphology characteristics, genesis and classification of West Virginia coal mine refuse. M. S. Thesis. West Virginia University. Morgantown, WV.

Energy Information Administration. 1984. Coal production 1984. DOE/EIA-0118(84).

Foth, H. D. 1984. Fundamentals of Soil Science, 7th Ed. John Wiley and Sons. New York, NY.

Grove, J. H., and V. P. Evangelou. 1982. The role of lime in saltly spoil genesis. *In* D. H. Graves (ed.), Proceedings 1982 Symposium on Surface Mining Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY.

Haynes, R. J., and W. D. Klimstra. 1975. Some Properties of Coal Spoilbank and Refuse Materials Resulting from Surface-mining Coal in Illinois. State of IL, Institute for Environmental Quality.

Hesse. P. R. 1972. A textbook of soil chemical analysis. Chemical Publishing Co. New York, NY. p 74-75.

Holmgren, G. G. S. 1967. A rapid citrate-dithionite extractable iron procedure. Soil Sci. Soc. Am. Proc. 31:210-211.

Keystone Coal Industry Manual. 1988. Robert Lick Publisher. Maclean Hunter Puablishing Co. Chicago, Il. pp 530-537.

Khan, L. A., S. B. Bhagwat, and J. W. Baxter. 1986. Economics of secondary recovery of coal. *In* D. H. Graves (ed.) Proceedings, 1986. Symposium on Surface Mining Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY.

Khan, L. A., D. J. Berggren, and R. E. Hughes. 1984. Effects of weathering on coal and its sulfur constituents in refuse piles. p. 455-462. In D. H. Graves (ed.) Proceedings, 1984. Symposium on Surface Mining Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY. Dec. 2-7.

Lindstrom, G. A. 1948. Extent, character, and forestation potential of land stripped for coal in the central states. U. S. Dept. Ag. For. Ser., Cent. States. For. Exp. Sta. Tech. Pap. 109. 79pp.

Kunze, 1965. *In* C. A. Black (ed.) Methods of soil analysis, Part 1, Agronomy 9:128-152.

Martens D. C. 1986. Class Notes. Soil Chemistry. Agronomy Dept. VPI&SU. Blacksburg, VA.

McClean, E. O. 1982. Soil pH and lime requirement. *In* C. A. Black (ed.). Methods of soil analysis, Part 2, Agronomy 9:128-152.

Medvick, C., and A.F. Grandt. 1976. Lime treatment experiments--gob revegetation in Illinois. p. 48-62. In Proceedings, Illinois Mining Institute. 21-22 Oct. 1976. Springfield, IL.

Minitab. 1987. Release 6.1.1. Minitab Inc.

Moulton, L. K., D. A. Anderson, S. M. Hussain, and R. K. Seals. 1974. *In* Proceedings, First symposium on Mine and Prepartation Plant Refuse Disposal. Natl. Coal Assn. and Bituminous Coal Research Ind.

Nawrot, J. R., D. B. Warburton, and W. B. Klimstra. 1986. Coarse refuse reclamation: alkaline enhancement for direct vegetation establichment. *In* Proceeding of the National Mined Land Recalamation Conference. St. Louis, MO. Oct. 28-29.

National Academy of Sciences. 1979. Redistribution of Accessory Elements in Mining and Mineral Processing. Part I: Coal and Oil Shale. The National Research Council.

National Bureau of Standards. 1990. Standard reference material 1633a, coal fly ash. National Bureau of Standards. Gaithersburg, MD.

Olsen, S. R. and L. A. Dean. 1965. Phosphorus. *In* C. A. Black (ed.). Methods of soil analysis, Part 2, Agronomy 9:1035-1049.

Parker, D. R., and E. H. Gardner. 1981. The determination of hot-water-soluble boron in some acid Oregon soils using a modified azomethine-H procedure. Commun. Soil Sci. and Plant Anal. 12:1311-1322.

Peech, M. 1965. Hydrogen-ion activity. *In* C. A. Black (ed.). Methods of soil analysis, Part II, Agronomy 9:914-926.

Perry E. F. 1985. Overburden analysis: an evaluation of methods. In Proceedings 1985 Symposium on Surface Mining Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY.

Prescott, 1946. The History of the Virginia Iron Coal and Coke Co. 1888-1946. Published by Virginia Iron Coal and Coke Co.

Reisenauer, H. M., L. M. Walsh, and R. G. Hoeft. 1973. Testing for sulfur, boron, molybdenum, and chlorine. *In* L. M. Walsh (Ed.) Soil Testing and Plant Analysis. Soil Sci. Soc. of Am. Inc. Madison, Wi.

Rhoades, J. D. 1982. Soluble salts. *In* A. L. Page (ed.), Methods of soil analysis, Part II, Agronomy 9:167-179.

Rich, D. and J. Hutchison. Nuetralization and stabilization of combined refuse using lime kiln dust at High Power Mountain. p. 55-60. In Proceedings, Mining and Reclamation Conference. Vol 1. Charleston, WV. 23-26 Apr. 1990. West Virginia Univ., Morgantown, WV.

Richards, L. A. 1965. Physical condition of water in soil. *In* C. A. Black (ed.). Methods of soil analysis, Part 1, Agronomy 9:128-152.

Roberts, J. A. 1986. Mine Soil Genesis and Tall Fescue Nutrient Status as a Function of Overburden Type and Cultural Ammendment. M.S. Thesis, Virginia Polytechnic Institute and State University. Blacksburg, VA.

Robl, T. L, A. E. Bland, and J. C. Rose. 1976. Kentucky coal refuse: a geotechnical assenssment of its potential as a metals source. *In* Reprints, Second Symposium on Coal Prepartion. Natl. Coal Assn. and Bituminous Coal Research, Inc.

Rose, J. G., T. L. Robl, and A. E. Bland. 1976. Compostion and properties of refuse from Kenttucky preparation plants. p122-131. *In* Proceedings, Fifth Mineral Waste Utilization Symposium. U.S. Bureau of Mines and IIT Research Institute. Chicago, IL.

SAS Institute Inc. 1985. SAS User's Guide: Basics. SAS Institute Inc., Cary, NC.

Sencindiver, J. C. 1974. Classification and genesis of mine soils. Ph. D. diss. West Virginia University. Morgantown, WV.

Singer, P. C. and W. Stumm. 1970. Acid mine drainage: the rate determining step. Science 167:1121-1123.

Smith, R. M., W. E. Grube Jr., T. Arkle Jr., and A. Sobek. 1974. Minespoil potentials for soil and water quality. EPA-670/2-74-070. EPA Indust Environ. Res. Lab., Cincinnati, OH.

Sobek, A. A. and P. J. Sullivan, 1981. Staunton 1 reclamation demonstration project. Minesoil characterization: final report. Argone National Lab. LRP 15. Argonne Natl. Lab. Argonne, IL.

Thomas, G. W. 1982. Exchangeable cations. *In* A. L. Page (ed.), Methods of soil analysis, Part 2, Agronomy 9:167-179.

Thomas, G. W. and L. W. Hargrove. 1974. The chemistry of soil acidity. *In* F. Adams (ed.) Soil acidity and liming. American Society of Agronomy, Madison, WI.

U. S. Soil Salinity Lab. 1954. Diagnosis and improvement of saline and alkali soils. L. A. Richards (ed.) Handbook No. 60.

Van Breemen, N. 1982. Genesis, morphology, and classification acid sulfate soils in coastal plains. p. 95-108 *In* J.A Kitterick, D.S. Fanning, and L.R. Hossner (eds.) Acid sulfate weathering. SSSA Special Pubilcation 10. SSSA Madison WI.

Wagner, D. P., D. S. Fanning, J. E. Foss, M. S. Patterson, and P. A. Snow. 1982. Morphology and mineralogical features related to sulfide oxidation under natural and disturbed land surfaces in Maryland. p109-126. *In* J.A Kitterick, D.S. Fanning, and L.R. Hossner (eds.) Acid sulfate weathering. SSSA Special Pubilcation 10. SSSA Madison WI.

Wewerka, E. M., J. M. Williams, P. L. Wanek, and J. D. Olsen. 1976. Environmental contamination from trace elements in coal preparation wastes. Los Alamos Scientific Lab. EPA-600/7-76-007.

Williams, J. M., E. M. Werweka, N. E. Vanderborgh, P. Wagner, P. L. Wanek, and J. D. Olsen. 1977. Environmental pollution by trace elements in coal preparation wastes. *In* Reprints, Seventh Symposium on Coal Mine Drainage Research. Natl. Coal Assn. and Bituminous Coal Research, Inc.

Zar, J. H. 1984. Biostatistical Analysis. Prentice-Hall Inc. Inglewood Cliffs, NJ.

Zelazny, L. W. 1987. Determination of Cation Exchange Capacity. Class Handout, Clay Mineralogy II. VPI&SU. Blacksburg, VA.

VITA

Barry Robert Stewart was born on March 1, 1963 in Madison, Wisconsin. He and his family lived in Mount Horeb, Wi until he was 5, when his family moved to his great grandfather's farm near Cameron, WI. He attended Cameron Elementary, and Junior and Senior High, Schools. He excelled in tuba playing and pizza eating and graduated with high honors in 1981.

He attended the University of WI River Falls in 1981-82. In 1982-83 he attended the University of WI Center Barron County and worked at home. He returned to River Falls to pursue a B.S in Plant Science in 1983. In pursuit of that degree he came under the influence of Dr. Larry Meyers, who got him interested in soils and onto the soil judging team. An internship at a sweet corn disease nursery convinced him to pursue a career in soils. He graduated with a B.S. in Plant Science, Agronomy option in March, 1986.

He was decided to pursue an M.S in the Agronomy department at Virginia Tech, due in a large part to the good treatment he received when he visited there. Dr. W. Lee Daniels offered him a project working with coal refuse. He was selected as an National Science Foundation Fellow in 1987. Mr. Stewart plans to stay on at Virginia Tech to pursue a Ph. D. in reclamation/waste disposal.

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