CHAPTER 7 - CHARACTERISATION METHODOLOGIES

Both the physical and chemical characteristics of MSW incinerator residues must be evaluated to develop a proper management strategy for the various residue streams, including utilisation of the bottom ash. Information on the physical and chemical properties is also required when considering alternatives for handling, transportation and minimising occupational health risks. Since the physical properties of incinerator residues is highly variable, the following section provides an outline of the types of test methods available to determine key properties for evaluating disposal and utilisation scenarios for ash.

7.1 PHYSICAL TESTING

7.1.1 Visual Observation

Visual observation is used to define the relative quantities of recognisable materials in ash samples, coupled with parameters such as grain shape and grain size distribution. Recognisable materials in bottom ash include glass, ceramics, combustibles (char), ferrous metal, non-ferrous metals, minerals and ash. The proportion of each component provides an indication of the non-combustible fraction of material present in the waste fed to the incinerator and the potential extent of processing required to render the ash suitable for use. The data can also be used as a tool in assessing the impact on the quality and quantity of the ash resulting from recycling of ferrous, non-ferrous and glass components within the solid waste stream. Furthermore, the visually identifiable combustible content provides a gross assessment of the relative efficiency of the combustion process.

Fly ash and other flue gas cleaning residues are so fine-grained it is not possible to identify the individual particles. The noticeable parameters are colour, texture and the general appreciation of the particle size.

Method

Although, there is no specified ASTM procedure for cataloguing visual observations, the following section provides some guidelines.

Bottom Ash

Visual observation can be subdivided into two or more grain size ranges. The plus 50 mm fraction may be visually classified in the field during the sampling of the material. The material is then sieved through a 50 mm screen, and the individual components not passing through the screen are manually removed, weighed and categorised (i.e., ferrous, non-ferrous, brick, ceramic, motors, etc.). The minus 50 mm sample can be analysed in the laboratory in a dry state. Particles smaller than about 2 mm are difficult to visually identify.

The ferrous content can be determined by slowly passing a magnet over oven-dried ash. The ferrous content is expressed as a percent of removed weight related to the total dry weight of the ash prior to ferrous removal.

Visual classification of bottom ashes from two incinerator plants in Sweden is given in Table 7.1 and show the following distribution, in the 2-16 mm fraction [Jacobsson & Höbeda (1988a) and Jacobsson (1989)].

Table 7.1
Main Constituents of Bottom Ash in Malmö and Linköping

Distribution of Components in Bottom Ash by Weight (%)

Content	2-4 mm	4-5.6 mm	5.6-8 mm	8-11.2 mm	11.2-16 mm	Total
Malmö						
Metal-magnetic	18.2	16.9	9.1	14.5	5.6	10.2
non-magnetic	58.0	38.6	30.7	18.0	13.1	22.5
Glass	23.1	41.6	55.4	64.2	73.3	62.0
Ceramics	0.0	0.4	2.2	2.8	5.0	3.2
Stone	0.7	0.7	1.2	0.0	2.6	1.4
Paper	0.0	1.8	1.4	0.5	0.4	0.8
Linköping						
Metal-magnetic	10.0	4.8	11.6	2.2	5.1	8.5
non-magnetic	67.0	51.4	33.2	23.1	25.2	54.8
Glass	20.1	39.9	50.1	69.9	57.4	32.6
Ceramic	0.0	1.9	3.4	3.7	10.2	1.7
Paper	2.9	2.0	1.6	1.2	2.2	2.4

Jacobsson & Höbeda, 1988a; Jacobsson, 1989

Fly Ash and APC Residue
Visual observation primarily concerns the colour and texture. For example, the colour of fly ash can range from a light brown through grey to almost black, whereas APC residues can range between white and dark grey. Darker coloured ash generally indicates poor combustion efficiency. Textures can range from a "dusty" fine-grained powder to agglomerated chunks. It is also a good idea to check the friability of the ash, since may have implications on interpreting the grain size distribution results. For example, the grain size distribution of agglomerated materials, such as some boiler ashes, may be much finer than indicated by the grain size distribution determination, and subsequent handling of the material may break the agglomerated chunks into much smaller pieces if the material is friable.

7.1.2 Particle Size Distribution

The sieve analysis test is used to determine the size distribution of the aggregates and is a suitable method for bottom ash. The grain size distribution gives the percentage by weight of different sizes of the particles, which can also be used to assess other physical properties such as shear strength, bearing capacity, permeability, workability, dusting and frost susceptibility.

In general, well-graded materials (i.e., contain an even gradation of size fractions from coarse to fine) tend to be relatively stable, resistant to erosion, and can be readily compacted to a dense condition with a high bearing capacity. The strength generally also increases as the maximum size of the material increases. Materials deficient in fines will usually be less stable, despite compaction.

The uniformity coefficient is defined as the ratio of the diameter of the particle size at the 60% fines fraction, to the diameter of the 10% fine fraction, and is sometimes used as a measure of the relative distribution of particle sizes in a soil sample. The material becomes frost-susceptible when the content of fines reaches a level high enough for capillary sorption of water to occur. In soils, this level is reached when the percent of minus No.200 sieve fines (<0.075 mm) exceed 10-15%. Bottom ashes seem to become frost susceptible at about the same level.

Test Methods
The test method selected is dependent on the type of residue. For coarse grained material, standardised sieve tests are generally adequate. This usually involves drying, screening and weighing the ash. The quantity of material retained on each sieve is weighed to determine the fraction of the size distribution. Sometimes the grain size distribution may be incorrect as finer particles stick to more coarse-grained particles or agglomerate due to electrostatic charges, although the latter primarily occur with fly ash samples. When the content of fines is substantial, washing the ash prior to sieving can be useful, although it should be noted this may result in solubilisation of some components in the ash.

The gradation curve is a graph of the percent weight passing a specified sieve size, plotted on the ordinate, and particle or sieve size, plotted logarithmically on the abscissa. The curve can be used to compare materials to specifications or to assess the gradation characteristic of the material. A steep slope indicates a poor gradation which is unfavourable for most engineering purposes. A gentle slope indicates a good gradation. Data can also be presented in the form of frequency by particle as well as by weight.

Dry Sieve Methods

The standard test procedure (ASTM C136) is recommended for material sizes larger than the No. 200 mesh sieve (75 μm). Wet sieving, ASTM C117, is recommended for materials containing >10% particles <75 μm in size. After washing, the material is dried and sieved according to the dry sieving method. However, when a material containing high levels of salts (such as APC-residues) is washed, the grain size distribution is significantly altered, and therefore ASTM methods C136 and C117 are not recommended for APC residues or fly ashes.

Fine Particle Analyses Methods

As mentioned previously, particle size determination of fine sized particles may result in agglomeration or "balling up" of particles when sieved through smaller sieves (100-200 μm). Some of the static which causes this agglomeration can be eliminated by grounding the sieving device. For finer particles, test procedures such as sedimentation tests (ASTM D 422-63, DIN 18123, BS 1377:1975 and DIN 66115; or balance body method SS 027124) are not recommended since the ash particles can dissolve, whereas granulometric methods are appropriate for highly soluble ash matrices. Although ultrasonic devices can be used to disintegrate the agglomerated material, different solutions such as hydrogen peroxide, hexane and acetone are typically used.

Grain size distribution of grains less than 200 μm can be determined by dry methods such as the laser granulometer method used in the cement industry or by projected area diameter (Hinds, 1982).

7.1.3 Density

Density is an important parameter when considering the homogeneity, porosity of the particles, the bulk pore volume, as well as the degree of compaction. The density is also used to determine if a mass is in a loose, medium or dense state. Specific procedures are followed to measure either the loose (uncompacted) or dense (compacted) state. The uncompacted density state is measured by pouring the material gently through a funnel into a known volume and weighing the material filling the volume. The compacted density is measured by compaction (see Section 7.1.6).

The term density involves a group of parameters, such as bulk density, dry density and specific gravity.

The dry density classifies the individual aggregates as lightweight, normal weight or heavyweight. The dry density is used to evaluate the degree of compaction related to a compaction test (see Section 7.1.6).

Bulk Density

The bulk density expresses the mass per unit volume. The value includes solid particles, water (if present) and air. The dry density is defined by weight of material, divided by its original volume before drying. The dry density of a material reflects the void content and specific gravity of the particles. A test method is given in ASTM C 29. The dry density of a material is determined by drying a specified volume of a sample in 105°C in 24 hours or until constant weight is reached. The volume of the container depends upon the nominal maximum size of the material to be tested, i.e., the recommended sample size is 5 times greater than the nominal maximum particle size.

Specific Gravity

Specific gravity is defined as the ratio of the weight of a given volume of a sample to the weight of an equal volume of water. It is a dimensionless number. There are different types of specific gravity measurements. The purpose of the measurement is to evaluate the compactness (density) of the individual particles. Specific gravity provides an indication of the minerals, voids in the particles and existence of non-combusted material. It can be measured using a multi-volume pycnometer with helium gas.

Laboratory Testing

The bulk specific gravity (ASTM C 128) is a measure of the relative weight of the dry particle to the weight of a volume of water that includes the solid particle volume and the volume occupied by the internal pore space within each particle.

The specific gravity, bulk specific gravity, and saturated surface dry (SSD) measurement (ASTM C 127 and C 128) is a measure of the relative weight of a wet aggregate (i.e., absorption has been satisfied) to the weight of a volume of water which also includes the solid particle volume and the volume occupied by the internal pore space within each particle.

The apparent specific gravity (ASTM C 127, C 128), is intended to measure the actual or true specific gravity of the dry particle itself. It is the relative weight of the solid material making up the particles to the relative weight of an equal volume of water. The water volume in this measurement excludes the volume of the pore space within each particle. If there are any permeable pores in the sample, the apparent specific gravity

will have higher values than either of the two bulk specific gravities. Consequently, when evaluating the use of ash in construction applications, such as roads, it is recommended to determine the apparent specific gravity value to avoid potential problems (Eighmy et al, 1992).

Field Testing
Density often has to be controlled in the field through compaction. For example, when residues are used in road construction, the degree of compaction has to exceed a minimum value. Another example is a sealing layer of natural soil is placed at a disposal site. The density is, to a large extent, the controlling factor limiting the permeability. The lower the density, the higher the permeability, and vice versa. The in-situ density can be measured by several methods, such as the sand-cone method (ASTM D 1556), the drive-cylinder method (ASTM D 2937), the rubber balloon method (ASTM D 2167) and by nuclear methods at shallow depths (ASTM D 2922). However, these methods are generally not applicable when the material contains particles coarser than about 40 mm.

7.1.4 Absorption Test

The absorption test predicts the change in weight due to water absorbed in the pore spaces within the constituent particles. The result is based on the weight difference between the wet and dry ash. With bottom ash, those aggregate materials with higher absorptive capacity can also be expected to exhibit greater susceptibility to freeze-thaw weathering. The pores in lightweight aggregates may not satisfy the absorption potential during the period of this test (i.e., 24 h). Therefore, recorded 24 hour results for certain lightweight aggregates may be questionable.

Test Method
A test method is presented in ASTM C 127 for coarse aggregate and in C 128 for fine aggregate. Typically, the material is immersed in water for a period of 24 hours prior to measurement. The absorption is normally only applicable for bottom ash. The values can change depending on the content of fines, and it may be of value to measure the absorption of both the coarse and the fine fractions to compare the difference.

7.1.5 Water Content

Water content (moisture content) identifies the mass of free water which can be evaporated when exposed to a temperature of 105°C. The water content affects the maximum density obtained by compaction in field and thus the internal stability and stiffness. Therefore, water content is an important parameter with respect to disposal

of ash, as well as in different utilisation applications. It must also be controlled within specified limits for selected construction applications such as Portland cement concrete and asphaltic concrete applications.

For fly ash and APC residues, the water content is related to the amount of water used to limit the risk from fugitive dust emissions during transport. Normally, the water content must exceed 15% (geotechnical). On the other hand, water contents at levels higher than about 30% often results in a fluid material which may be difficult to handle. Care should be taken with the desiccation of lime scrubber residues, since they contain $CaCl_2$ which is hygroscopic and will create variable results depending on ambient humidity.

Test Methods

Moisture content is determined by measuring the weight of material before and after drying at 105°C to a constant weight (ASTM D 2216). If parameters (especially mercury) require later analysis, the temperature of 105°C may cause volatilisation of the Hg, and consequently, the sample should be discarded after testing.

The geotechnical water content (used in geotechnical engineering) is defined as the weight of the water divided by the weight of dry material, expressed as a percentage. The environmental water content (used in environmental, water quality, and solid waste management) is typically defined as the weight of water divided by the total wet weight of the sample. Thus:

Geotechnical water content

w_g=*(weight water:weight dry material)*

Environmental water content

w_e=*(weight water:total weight wet material)*

Typically, the water content of an ash/residue is dependent on the ash handling equipment at a given facility. The types of quenching, drainage and storage prior to sampling can have a significant impact on the amount of moisture retained in the ash. Water contents of 30-45% in geotechnical terms (25-30% environmental) are commonly reported for bottom ash (Schmidt, 1984; VEABRIN, 1988; Hartlén & Rogbeck, 1989; Chessner, 1990; Eighmy et al, 1992;). It is estimated that bottom ash requires a minimum of 17% moisture to prevent wind-borne fugitive dust emissions.

7.1.6 Proctor Compaction Test

The Proctor Compaction Test defines the relationship between bulk density and water content achievable within a specified compaction effort. This is achieved by

determining the moisture and compaction requirements of a soil-type material that will result in the maximum density of the material when compacted in the field. It is desirable, from an engineering viewpoint, to compact a material to a dense state to decrease future settlement, to increase shear strength and to decrease permeability. The water content in the ash affects the density that can be achieved. For example, too little water will inhibit compaction, whereas increasing water contents act as a lubricant and aids in compaction. However, too much water makes the material more fluid and elastic, preventing compaction. A greater applied compaction effort will generally result in an increase in soil density and a lowering of optimum water content.

Data analysis generally includes a graphical plot of the water content versus the dry density. The density at the peak of the dry density curve is called the maximum dry density, and the water content at the peak density is termed the optimum water content.

Many compaction specifications require a percent of the maximum density be achieved in field applications. The degree of compaction is the ratio of the density required in the field to the maximum density determined in the laboratory, expressed as a percentage. The required degree varies from 85 to 100% for granular soils as well as fine grained silts and clays.

Standard Proctor

The Standard Proctor method (ASTM D 698) specifies the use of a 5.5 lb. (2.49 kg) rammer, dropped from a height of 12" (305 mm) onto a sample contained in a collared soil test mold. The rammer is dropped on the sample 20 times in a series of 3 "lifts" of the sample.

Modified Proctor

The more commonly used Modified Proctor method (ASTM D1557) is similar to the standard method, but uses a 10-lb. (4.54 kg) rammer with an 18" (457 mm) drop. A series of samples is then prepared with increasing weight of water. After the sample is compacted in the mold, the dry density and the water content of the sample is determined.

Widely varying compaction curves have been obtained for the same residue streams from different incinerator facilities, even though the configuration of the system is the same. This is probably a function of waste feed composition and the type of operating conditions. Consequently, this test should be conducted not only on samples from separate facilities, but also on series of samples from the same facility.

It is often difficult to perform compaction tests on fly ashes. This is often revealed by the compaction curve, which may not show a defined maximum value. Moreover, the

powder-like nature of fly ash makes it impossible to compact at low moisture contents. Moisture contents below about 10-15% tend to result in the ash simply being driven out of the mold during compaction.

The Standard Proctor test will result in lower maximum densities and higher water contents achieved at optimum compaction, due to the lower compaction energy. In addition, the modified proctor may crush ash particles due to the extra force exerted by the heavier rammer. Comparisons between laboratory and field compaction results indicate the standard laboratory proctor test is the most applicable test to estimate field compaction curves (Hartlén & Rogbeck, 1989).

7.1.7 Strength and Strength Development

Strength parameters are used in different circumstances, such as determining the maximum inclination of a landfill slope, the bearing capacity of a fill built up with ash, or the durability of cementitious material. The strength of coarse grained materials is dependent upon the friction between the particles, whereas the strength in fine grained materials primarily builds up by cohesion and cementation forces. This means different test methods should be used for bottom ash than those for APC residues and stabilised residues.

The strength of aggregates, such as bottom ash, can be determined by direct shear tests or triaxial tests to evaluate the cohesion and angle of friction of the material. This type of test is not often made on bottom ashes as the knowledge of the grain size and its distribution may be enough to determine the strength. The angularity of the bottom ash particles results in a rather high angle of friction (35 to 50). However, the angle decreases with increasing stress level. Hence, ash subjected to high stresses (above 200 kPa) should be tested in the laboratory. In special cases, there may be a need to determine the shear strength parameters in detail. In these cases, the tests are performed using standard geotechnical equipment. As mentioned earlier, it is important to use a sample diameter five times the maximum particle size.

It is also important to determine the strength of cementitious materials. Cementitious reactions that could occur are not only complex, but can change the character of the ash material with time. The most commonly used test is the uniaxial compression test (ASTM D 1633) on compacted samples. By performing the tests at different time intervals after compaction, the strength development can be determined. The pozzolanic type of reaction can be evaluated following test procedures allocated for "real" pozzolanic materials (ASTM C 311). Sometimes the tests are made on samples immersed in water (ASTM C 109 mod.).

A test method to evaluate probable cementitious reactions is outlined in ASTM D 1557. The sample is compacted, sealed in plastic bags, stored and tested for compressive strength at intervals up to 28 days, in accordance with procedures outlined in ASTM 1633.

The uniaxial compression strength of a well-compacted sample can, under favourable conditions, reach 1 MPa. After stabilisation with additives, such as cement, it may be several MPa. It is important to record any swelling activity, since this generally indicates the ash strength will decrease over time.

7.1.8 Bearing Capacity

The Californian Bearing Ratio (CBR) test is a special test used to evaluate the ability to meet road base specification criteria and to assist in defining the bearing capacity. The CBR test is a measure of the shearing resistance of a sample or aggregate material to that of a standard sample. CBR values of base, sub-base and sub-grade materials have been correlated to pavement performance. These correlations have resulted in criteria permitting the use of CBR as a strength and stability measurement. These correlations have been converted to design curves that can assist in the determination of requisite pavement thickness as a function of anticipated traffic and CBR values.

The test procedure is outlined in ASTM D 1863. The sample is initially molded to the maximum density and optimum moisture content as determined from the compaction test (i.e. ASTM D1557). The molded CBR sample is subsequently soaked in water for a period of 4 days. The initial soaking is intended to simulate a condition of high water content encountered during the spring season. After 4 days, the soaked sample is taken from the water and placed into a load testing machine. A square loading piston is mechanically pushed into the sample at a defined rate, and the load at specified penetration distances are monitored. The CBR is usually selected at a 0.1" (2.54 mm) penetration, however, the highest CBR value is used, whether it is a 0.1" (2.54 mm), 0.2" (5.08 mm), or higher.

The limited data base on CBR values for bottom ash generally show higher values than those of most natural soil materials, and hence fulfill the minimum specifications for use of the material as a road base. However, more laboratory data on ash are required to ensure the comparison of natural soil and ash is statistically valid.

Another test to measure bearing ratios is the Swedish Earth Bearing Method (SEB). It was developed by the Swedish Road and Traffic Research Institute (VTI), and is outlined in their Report No. 31, 1973. The SEB method is similar to the CBR method, however, the load is only 0-500 kPa and is, according to Swedish experience, more relevant to incinerator residues.

7.1.9 Durability

Durability testing is used to estimate the physical resistance of an aggregate to various weathering conditions. Soundness and freeze-thaw tests define freeze-thaw resistance, where as the LA abrasion test defines durability of ash particles.

Soundness Tests

The sodium or magnesium sulphate test is a used method of soundness testing. The test procedure may follow ASTM C88 and involve testing for 5 cycles. After drying, salt crystals grow in the permeable pores and cause particles to disintegrate. After the last cycle, the sample is washed to remove all the salt and screened dry. The average loss of material from each specified sieve is used in calculating the soundness loss.

This test is considered very aggressive and may reject materials that in fact will perform well. Aggregates that readily break down during the test must therefore be carefully evaluated based on the deposition environment before being rejected.

Typical results suggest most bottom ashes are not susceptible to freeze-thaw cycle breakdowns. ASTM C33 prescribes a maximum of 12 % loss when sodium sulphate is used and a maximum of 18 % when magnesium sulphate is used.

The wet/dry weathering test covers procedures determining material loss caused by repeated wetting and drying of monolithic samples. It also covers the visual observation of disintegration of solid samples.

The following test procedure is suggested by Stegemann (1991) for solidified ashes. Samples should be molded in disposable plastic molds, each having a 44 mm inner diameter and a 74 mm length, and then vibrated on a vibrating table or tamped/compacted with a compaction hammer to provide adequate settling in the mold. Samples molded for these tests require curing in a moisture chamber for 28 days.

Reporting of data should include the water content of the specimens, the average cumulative, corrected relative mass loss after 12 cycles, the number of cycles survived (if the specimens did not survive 12 cycles of testing), and the results of visual observations after each cycle (physical deterioration).

LA Abrasion Test

The Los Angeles Abrasion Test measures the degradation of aggregates resulting from a combination of actions including abrasion, impact and grinding in a steel drum. The test method recommended is ASTM C131.

A 5000 g sample is placed in a drum with a charge of 6 to 12 steel balls which is tumbled for 500 revolutions. The percentage of wear is the percentage loss in weight during the test, and is that measured weight of material which will pass a standard No.12 sieve (1.70 mm).

Ash tested to date exhibit losses ranging from 10 (extremely hard) to 90 % (very soft). In the US the maximum acceptable loss for a material to be used in a road base course is 60 %. Eighmy et al (1992) considers this test to be overly aggressive for pavement applications.

Freeze-Thaw Tests
This test covers procedures for determining material loss produced by repeated freezing and thawing of monolithic samples. It also covers the visual observation or disintegration of solid samples.

Stegemann and Cote (1991) proposed a test procedure for solidified/stabilised waste material which was used during the solidification trials of APC residues under NITEP (Sawell & Constable, 1993). The test involved exposing cylindrical shaped samples to repeated cycles of freezing and thawing. Sample preparation is similar to the one used for wet/dry tests. The Swedish Traffic and Road Institute (VTI) has developed a modified freeze-thaw test procedure for residues (Höbeda & Jacobsson, 1988b) in which the sample (diameter of 50mm and height of 100mm) is stored for a specified time, then saturated with water under a vacuum. Swelling is recorded based on a uni-axial compression test.

Reporting of data should include the water content of the specimens, the average cumulative, corrected relative mass loss after 12 cycles, the number of cycles survived (if the specimens did not stand 12 cycles of testing) with the results of visual observations after each cycle (physical deterioration).

7.1.10 Permeability

The coefficient of water conductivity (coefficient of permeability) is a parameter that explains how pervious a material is to water. It is essential to know the permeability when predicting the leachate flow in a disposed ash and forecasting the frost susceptibility and the drainage properties of an ash.

The coefficient of conductivity, k, is defined as the ratio between the speed of transport and the hydraulic gradient. When the coefficient is higher than about 10^{-4} m/s the material is considered self-draining, whereas coefficients lower than 10^{-9} m/s are considered impervious (Sjöholm et al, 1994).

Parameters that influence the coefficient of permeability are (Head, 1982): particle size distribution, particle shape and texture, mineralogical composition, void ratio, degree of saturation, fabric, nature of fluid, type of flow and temperature. To these factors, effects as cementation and specimen size may be added.

Test Methods
Testing can be performed in the field or in the laboratory. Different types of laboratory equipment exist and the choice is dependent primarily upon the permeability. In low permeable material, the equipment shall have flexible walls to prevent leakage and to admit a procedure to saturate the sample. This pertains specifically for self-hardening residues. The test can be performed with falling or constant water pressure head.

It is important to ensure the permeability of the filter stones used is more than 10 to 100 times higher than that of the material tested.

Tube Permeameter

The tube permeameter utilises a sample with e.g. a diameter of 101 mm and a height of 124 mm contained within a rigid wall. This equipment is used primarily for granular materials, which are compacted in the cell, normally to a 90% degree of compaction.

The following parameters are normally chosen: a gradient of 15, water saturation with back pressure for up to 1 day, an upward flow direction during testing and preferably a constant head. The total experimental time is about 48 hours (Sjöholm et al, 1994).

This type of equipment is sensitive to coefficients of permeability between 10^{-2} - 10^{-9} m/s.

Triaxial Cell Permeameter

Triaxial cell with flexible membrane is used to limit the risk of seepage along the circumference of the sample due to channelling. (Figure 7.1) The diameter is normally 50 mm and the height 30-200 mm. Larger diameters, up to 150 mm, can be used. This test type is especially suited for fine-grained, cohesive or stabilised material. The cell pressure to be used depends on the material tested, but may never be more than 200 kPa.

It is recommended the gradient not be more than up to 30 and an upward flow direction be used. The time for saturation under back pressure is 1 to 10 days and the total experimental time will be 2 to 13 days. Saturation is an important consideration, since unsaturated samples will generate widely variable results. This is especially true for low permeable ashes, not the least for solidified samples (Sjöholm et al, 1994).

This method is sensitive to coefficients of permeability between 10^{-6} - 10^{-11} m/s.

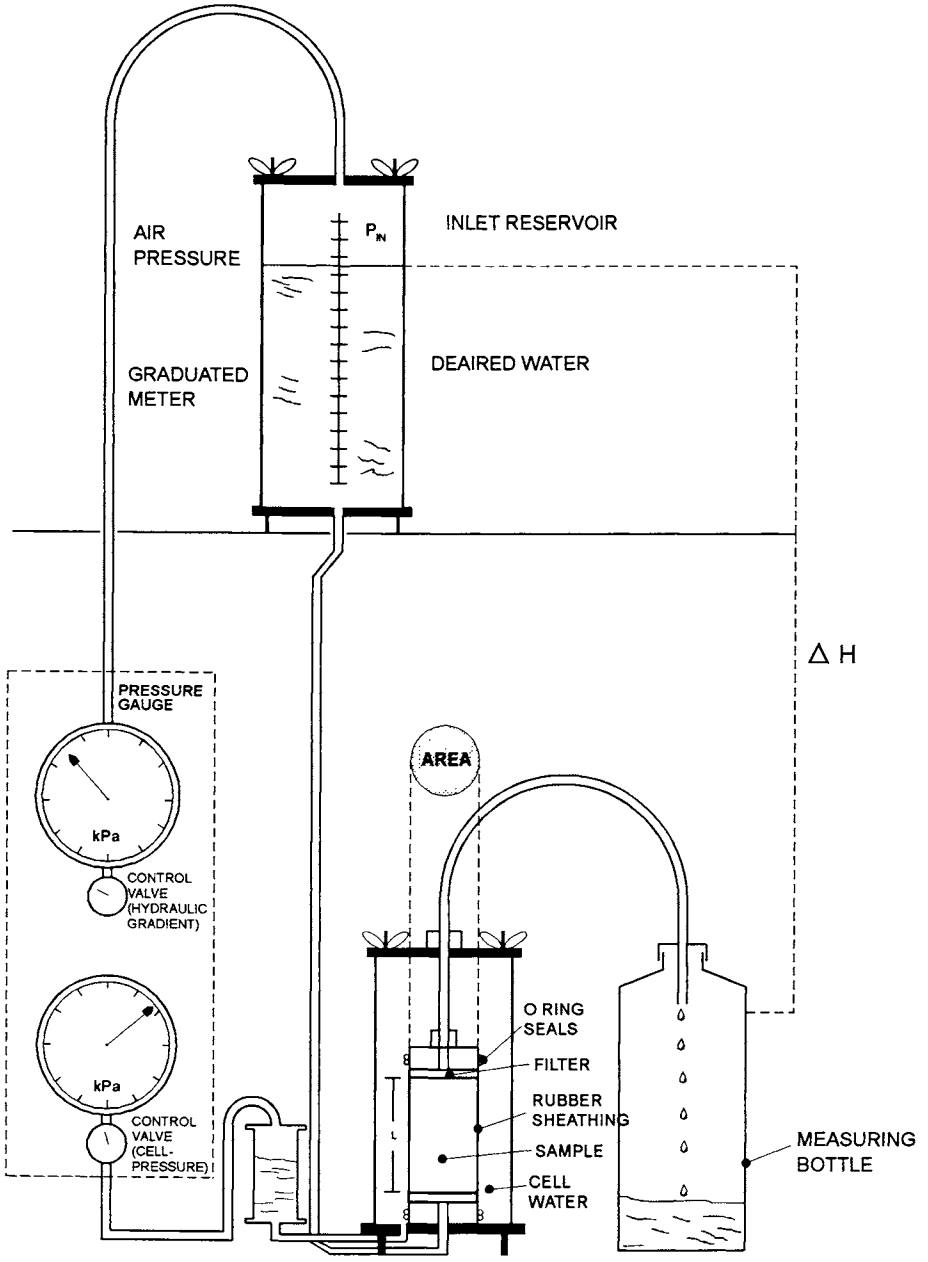
If a solidified waste is not monolithic, ASTM D2434 is recommended for determining the hydraulic conductivity of granular soils by a constant-head method.

Stegemann (1991) has proposed the following procedure for monolithic samples. A triaxial cell is used which will accommodate a 3" (76.2 mm) high, 3"-inch (76.2 mm) diameter sample with a rubber membrane to enclose the sample. The test is carried out 28 days after sample preparation, using a monolithic cylindrical sample. The flow direction is downwards.

Rigid Cell Permeameter with Varying Sample Diameter

Undisturbed samples are taken by drilling in field for performance control. The sample is then enclosed in a rigid tube. In the laboratory, the same tube is used to reduce

Figure 7.1 Triaxial Cell Permeameter



disturbance. The diameter of the sample may vary due to sampling disturbance. Any space between the sample and the wall should be filled with sealing material, such as bitumen or silicon-caoutchouc. Sample diameter may be 50-200 mm and height 30-300 mm. The same procedure given above for triaxial cell permeameter can be used.

In Situ Methods

Laboratory testing of samples normally underestimates the permeability due to heterogeneities, variation in degree of compaction and variation in water content. Moreover, there is a need for field testing to monitor in-situ quality, using a double ring infiltrometer (ASTM D 3385-88) which is limited in application to materials with a coefficient of conductivity between 10^{-7} - 10^{-8} m/s.

However, there is a need for methods that can be used for impervious material. Because of that, methods such as "The two staged borehole" have been developed (Boutwell & Tsai, 1992). In this method, the measurements are made in a 100 mm diameter borehole.

Single ring infiltrometers have been developed. The problem is the flow is not very well defined and one has to consider both the vertical and the horizontal permeability. At the Swedish Geotechnical Institute, a test procedure has been developed, Figure 7.2. The equipment consists of one cylinder (inner infiltrometer ring) with stiff walls and with lid and stand pipe attached. The ring is placed on the surface of the material to be tested and loaded by weights. Outside this inner ring an outer ring is placed. Between the two rings, bentonite is placed and also loaded to utilise the swelling pressure of the bentonite. Water is filled into the infiltrometer ring and the stand pipe. The equipment is suitable for material with a hydraulic conductivity in the range of 10^{-5} - 10^{-10} m/s.

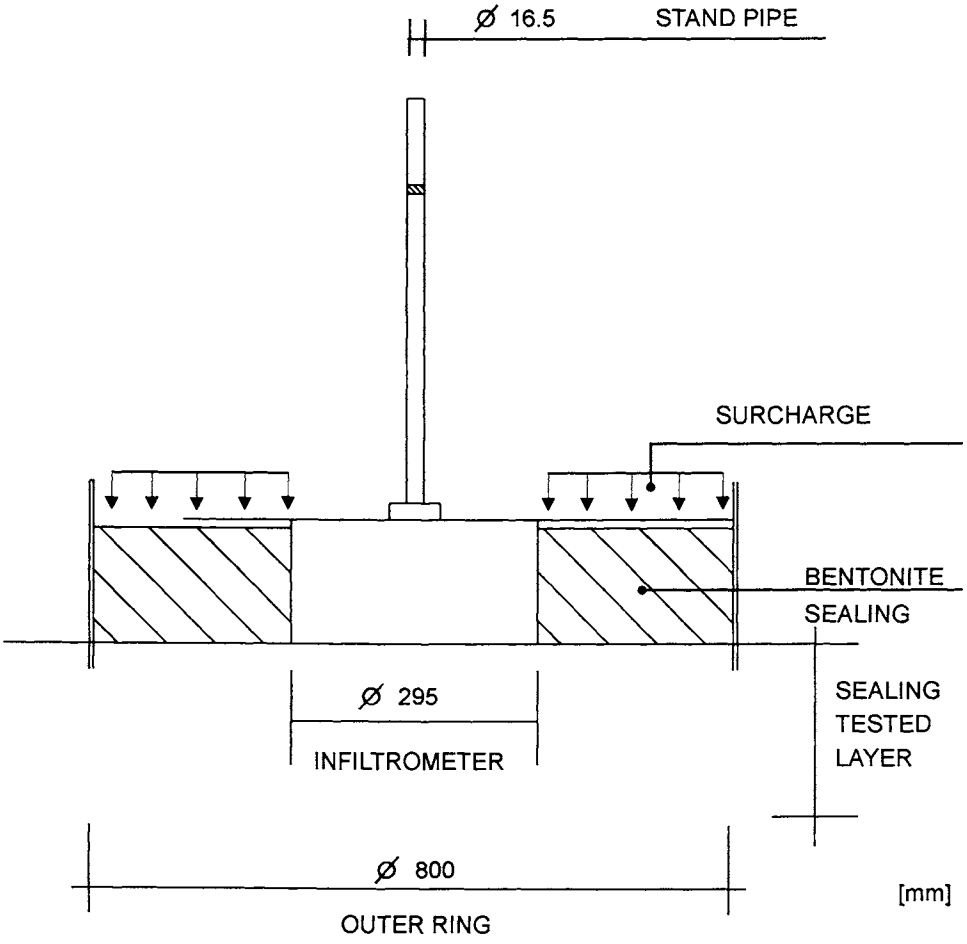
The calculation assumes full saturation. The hydraulic coefficient, K (m/s), can be calculated using the following two different equations. Assuming one dimensional flow according to Darcy modified to consider horizontal flow gives:

$$K = F\frac{A_R L}{A_I(t_{(n+1)} - t_n)}\ln\left(\frac{H_{t_n} + L}{H_{t_{n+1}} + L}\right) \qquad (7.1)$$

where

F = correction factor, see Figure 7.3
A_R = area of stand pipe
A_I = area of infiltrometer
L = thickness of layer
H_t = pressure head at time t (m)
t = time (s)

Figure 7.2 Single Ring Infiltrometer



Sjöholm et al., 1994

An evaluation following Hvorslev (1949), assuming a half spherical flow, the equation becomes:

$$K = \frac{\pi d^2}{8D(t_{(n+1)} - t_n)} \ln\left(\frac{H_{t_n}}{H_{t_{n+1}}}\right) \qquad (7.2)$$

where

d = stand pipe diameter (m)
D = area of infiltometer (m^2)
H_t = pressure head at time + (m)
t = time (s)

Both these equations should be used parallel until further experience is achieved. Normally, they give results in the same order of magnitude.

Remarks

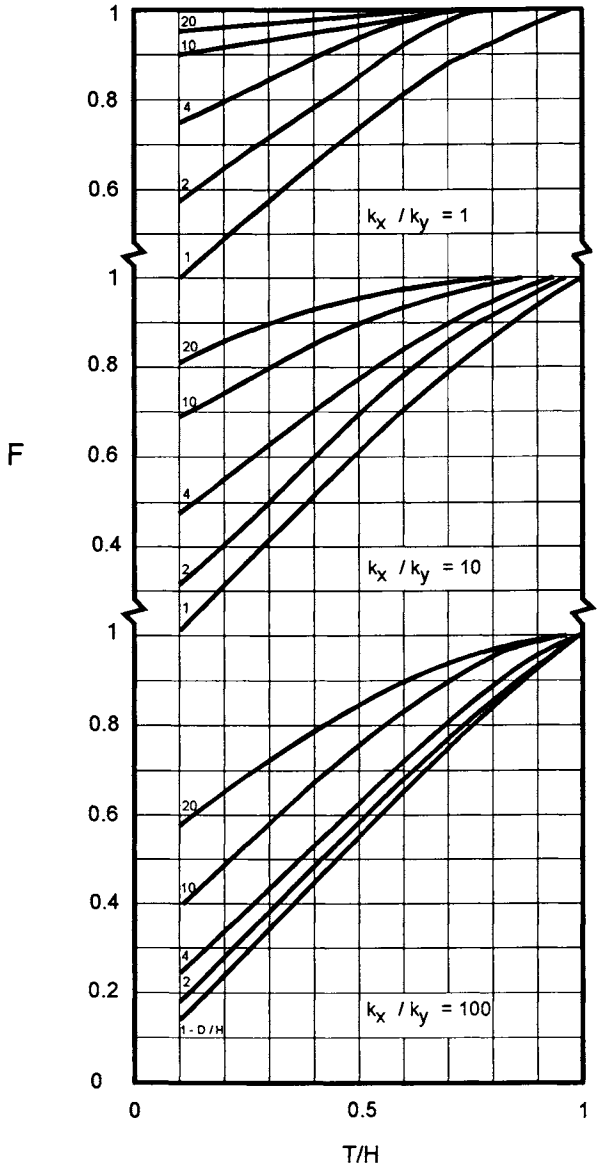
There are potential concerns to be aware of when carrying out permeability tests. The most important factor is to ensure the sample is saturated. In a triaxial cell permeameter, this can be done by using back pressure. Back pressure means both cell pressure and pore pressure inside the sample are increased to a high level simultaneously to solve the air. When using rigid wall permeameters, this procedure cannot be followed and the saturation not checked. This means rigid cells should not be used for ashes with a coefficient of conductivity lower than 10^{-8} m/s.

There is always a risk plugging or clogging may occur due to migration of small particles into interstitial pores, hence reducing the apparent hydraulic conductivity. To counteract this effect, the water shall have an up-flow direction. If the permeability decreases over time, the reason should be investigated to see if clogging or cementation are responsible.

The coefficient of permeability decreases with increasing content of fines. This means heavy compaction may change the properties. Thus the compaction must reflect the compaction method to be used in field.

Fly ashes, as well as APC-residues (fly ash mixed with flue gas cleaning residues), often show strength increase with time. As the strength increases, the permeability decreases. On the other hand, if the APC-residue is mixed with water and stored for some time before compaction, the permeability may be higher (Fällman et al, 1989).

Figure 7.3 Correction Factor F



Day and Daniel, 1985

The coefficient of conductivity is, as mentioned earlier, very dependent on the degree of saturation and thus of the water content. In field it is difficult to control the water content. This might be the main reason why large differences have been noticed when comparing field and laboratory data (Bryant & Daniel, 1985).

7.2 CHEMICAL COMPOSITION

Some of the controversy over MSW incinerator ash characteristics is based on the variable chemical data generated on the different residue streams. In Chapter 6, the importance of exercising sound sampling practices to obtain representative samples was emphasised as a means to minimise the effects of the heterogeneity. In this section, the importance of following sound laboratory procedures to determine the chemistry of the residues is stressed as a key to better defining the characteristics of ash.

7.2.1 Sample Preparation

With the exception of loss on ignition, all of the chemical tests covered in this section require particle size reduction of the various residue streams prior to testing and analyses. Reduction to less than #100 mesh sieve size (<149 μm) is a minimal requirement for most analyses, whereas less than #200 mesh (74 μm) is preferable. The reason for recommending the finer particle is to facilitate more efficient chemical reactions by increasing the surface area to volume ratio of the ash particles, and minimise the sample heterogeneity by finely dividing and mixing the samples. In the case of the bottom ash and grate siftings residue streams, the mineral and silica content of the ash presents some unique problems.

Size Reduction Techniques

Selection of size reduction techniques are highly dependent on the type of ash being processed and to a minor degree, perhaps the type of incinerator system generating the ash. The particle size data given in Figure 6.1 indicates bottom ash and grate siftings streams generally contain much larger sized particles than the heat recovery or air pollution control system residues and hence require a greater degree of processing than the finer sized residue streams. Bottom ash from RDF combustion facilities may contain a greater proportion of moderately sized particles, however, good laboratory practice dictates proceeding with the same sample preparation techniques used for the coarser bottom ash.

After the samples of bottom ash or grate siftings have been sieved through a 7.5 mm mesh to screen out the reject material, it is recommended the sample be examined to remove ferrous (e.g., nails, paper clips, etc.) and non-ferrous metals (e.g., foil wrap, coins, etc.) since these materials typically cannot be size reduced. After removing

these malleable materials, the samples should be partially size reduced by passing the ash through a commercial grade laboratory jaw crusher or hammer mill.

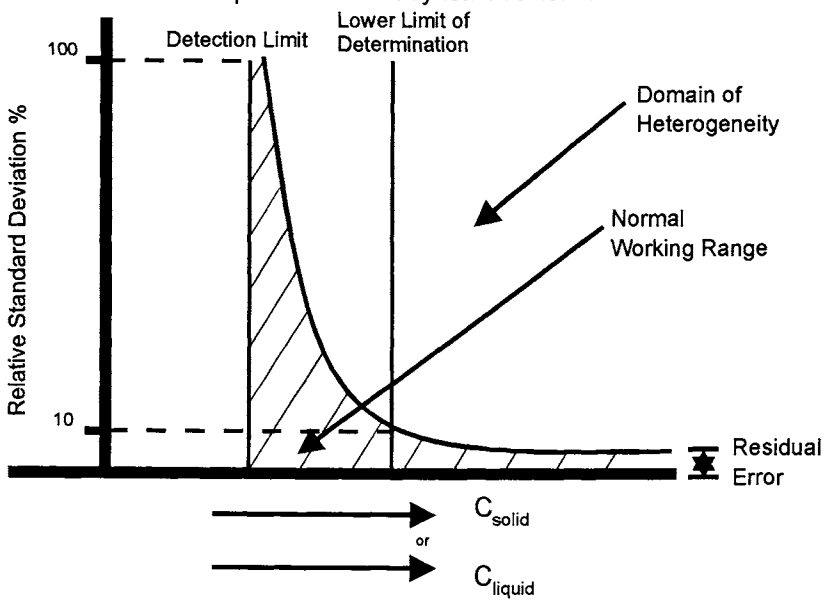
The crushing plates of the jaw crusher should be manufactured of a material which is capable of handling the tenacious mineral/silica based matrix of the two ash streams. Another sound laboratory practice is to avoid placing too much stress on the crushing device. Samples should be passed through the unit in succession, stepping down the aperture size after each pass to achieve the lowest particle size.

After the ash has undergone the initial particle size reduction, final size reduction can be achieved by milling the ash in a motorised mortar and pestle. The mortar and pestle should be made from a suitably hard substance, such as agate or other such mineral, to be able to withstand the abrasive nature of the mineral matrix of the ash. Ceramic, or other types of material can be used, however, they tend to wear more easily and thus are not as effective as agate mills and may result in contamination of the sample. Furthermore, it is recommended the ash be ground in small batches. During the grinding procedure, processed ash should be screened through the required sieve size. Ash not passing the required sieve should be returned to the mill and ground. This should be repeated until all of the sub-sample will pass the proper sieve size.

Of the remaining types of ash/residues (heat recovery and APC residues), the heat recovery ashes and perhaps residues from the early stages of the APC system should be ground in a motorised mortar and pestle. Conversely, APC system residues, especially fabric filter residues from mass burn or two-stage systems typically do not require grinding prior to testing and analyses, since the bulk of the particles are sized well below #100 and even #200 mesh sieve sizes. However, the type and age of incinerator should be taken into account, since older incinerators and RDF systems may carry over substantial quantities of larger sized particles than two-stage or modern mass burn systems, and hence should be processed accordingly.

It should be noted careful sample preparation will only minimise potential variability due to the heterogeneity of the sample. Results from a Dutch study on carefully prepared bottom ash samples indicated reproducibility between sub-samples of prepared ash was difficult to achieve for trace elements such as lead, copper, cadmium and tin (Mammoet Project, 1990). It was speculated the analysis could be greatly influenced by fine metallic particles of these elements. One means of evaluating the reproducibility of results is to plot the concentration of a measured parameter versus the percent relative standard deviation of the results (% RSD). By overlaying the residual error created by the detection limit of the procedure, and the lower limit of determination (level of 10% precision), data falling outside the residual error zone indicates heterogeneity, whereas those falling inside the zone are reproducible results (Figure 7.4). The position of the DTL and the LLD can shift along the X-axis depending on the complexity of the matrix of the sample tested.

Figure 7.4 Statistical Interpretation of Analytical Precision



7.2.2 Inorganic Analyses

Digestion Techniques

In an attempt to verify results, researchers compare their own data with data from other studies. As discussed in Chapters 9 - 11, total metal concentration results can vary widely, sometimes even between sub-samples. Typically, the inconsistencies are attributed solely to sample heterogeneity, especially in view of the fact that a very small quantity of residue is used for analytical purposes, perhaps as low as 0.1 grams. However, another factor which can strongly influence results is the sample digestion technique used. Although the US EPA provides a guidance document for choosing the best procedure for various types of samples (Chapter 2 of EPA's Test Methods for Evaluating Solid Waste, 1986), extra care must be taken in selecting the most appropriate procedure for digesting incinerator residue samples.

One good example of how different digestion techniques can influence total concentrations is the experience gained during the first two NITEP studies. Sub-samples of residues were submitted to two different laboratories for total metal analyses using two different digestion techniques (Environment Canada, 1985 and 1986). The results are presented in Table 7.2 in the form of a ratio of the concentration measured after an aqua regia digest versus the concentration measured after hydrofluoric acid/aqua regia/peroxide digestion (HF/AR/P) (see descriptions given below). The arithmetic mean values and standards deviations are provided. Values less than 1 indicate greater yield from the HF/AR/P digestion, values close to 1 indicate no difference and values greater than 1 indicate potential volatilisation of the metal during the HF/AR/P digestion.

Table 7.2
Comparison of Concentration Ratios Generated by Two Different Digestion Techniques on 24 Sub-samples of Ash

			Applicability	
Metal	Mean	Std Dev	Aqua regia	HF/AR/P
Aluminum	0.72	0.13		*
Barium	0.31	0.29		**
Boron	0.65	0.67		*
Calcium	1.09	0.35	*	*
Cadmium	0.98	0.44	*	*
Chromium	0.52	0.47		**
Cobalt	1.14	0.78	*	
Copper	0.77	0.41		*
Lead	0.57	0.32		**
Nickel	0.49	0.17		**
Sodium	0.85	0.38		*
Tin	2.68	2.19	**	
Vanadium	321.05	241.66	**	
Zinc	0.91	0.37	*	*

* = suitable method ** = recommended method
Adapted from Environment Canada, 1985 and 1987; Bridle and Sawell, 1986; Sawell et al., 1987

Based on these results, it is evident the type of digestion method should be chosen according to the type of metal and matrix being analysed. For example, it appears better recovery was achieved through an HF/AR/P digestion for metals associated with the silicate matrix such as B, Ba, Cr, Cu, Pb, V, and Ni. Both types of digestion methods work equally well for calcium, cadmium, sodium and zinc, whereas cobalt, tin and vanadium requires less rigorous digestion to achieve better recovery. Similar results were observed during the Mammoet Project (1990) and the EPA study of stabilised incinerator residues (1993).

There are several methods routinely used for digestion of MSW incinerator residues. The following discussion includes a brief description of the method and the qualification factors surrounding the interpretation of the data generated by the specific digestion method:

EPA Method 3050 - Acid Digestion of Sediments, Sludges and Soils (US EPA, 1986)

This method involves a nitric acid and hydrogen peroxide reflux followed by a hydrochloric acid reflux for those elements compatible with hydrochloric acid. It is considered a strong acid leach and although it is moderately aggressive, it should not be expected to produce analyses considered "true total" concentrations for MSW residues. It provides limited dissolution of metals bound in the silica matrix of these materials and is limited in its ability to dissolve stable oxides (refractory materials) formed during incineration. The hydrochloric acid step is applied mainly for the adjustment of oxidation state of arsenic and selenium, thereby making it an appropriate digestion prior to analysis by hydride reduction.

Aqua-Regia Digestion

This method involves reflux of the solid in a mixture of $HCl:HNO_3$ at a ratio of 10:3. It is very commonly used for the digestion of MSW incinerator residue samples. Although it is considered more aggressive than the EPA 3050, it is still only classified as a strong acid leach and as such will not likely produce "true total" analyses of these residues.

APHA Standard Method 3030I

This method is widely used for "total" type digestions of solid materials. It involves a nitric acid/perchloric acid/hydrofluoric acid medium. This highly reactive combination should provide total dissolution of MSW wastes. Certain metal species however, may not be recovered quantitatively when subjected to this digestion. Silica will be lost through volatilisation. Chromium may also be volatilised due to the highly oxidative nature of this digestion. Either chlorochromate ion (CrO_3Cl^-) or chromyl chloride (CrO_2Cl_2) may form and be driven off at the temperatures used during the digestion. These losses may be exacerbated in high chloride content solids such as incinerator residues. Other elements which may be lost during this digestion are: Ag, As, B, Ca, K, Mo, Sb, Se and V (see Table 7.4).

Wastewater Technology Centre (WTC) Hydrofluoric Acid/Aqua-regia/Peroxide Method

This method is also commonly employed by other laboratories and has a similar performance to SM 3030I (WTC, 1993). The major difference is the use of hydrogen peroxide which helps to keep the chromium in the reduced +3 state thereby preventing the losses described above.

Specialty Methods for Specific Elements

Silica

For refractory elements such as silica, fusion techniques are recommended to obtain a "true total" analysis. Two common methods exist. The first method involves using

lithium metaborate as the flux agent mixed at a solid to flux ratio of 1:9, then heated to 950°C in a graphite crucible for 30 minutes. The molten "glassy material" is then dissolved in 4% nitric acid. This method is also acceptable as a digestion method for most metals with the exception of As, B and Se.
The second method is an alkaline fusion using a mixture of sodium hydroxide or potassium hydroxide, which is effective for preparing ash samples for As and Se. The sample is mixed with the salt base (12:1 salt:sample) in a Zirconium crucible and heated to 1000°C or until the mixture is completely molten. After cooling, the residue is dissolved in hot 10% HCl.

The analyses generated by using either of these fusion techniques are limited by the fact that the amount of the sample that can be used is minimal, consequently the detection limits become elevated and analytical precision suffers.

Mercury
The quantitative recovery of mercury from incinerator residue samples is highly dependent on maintaining oxidising conditions throughout the sample preparation step. EPA method 7471 is perhaps the most commonly applied method and involves digesting the sample with aqua-regia in a heated bath at 95°C, followed by the addition of potassium permanganate. The potassium permanganate is added primarily to oxidise chloride to free chlorine which must be removed before the analysis step. This method has generally provided good recoveries, although in samples with relatively high carbon content, there is a tendency towards lower recoveries. This digestion protocol is designed for sample weights up to 0.2 grams.

WTC developed another digestion method for mercury to permit using a greater mass of sample (up to 0.5 grams) and thereby enhancing the reproducibility of the data. The method is significantly more reactive than the EPA method since it involves subjecting the sample to a nitric acid/sulphuric acid/vanadium pentoxide digestion medium at 160°C. At the present time, it appears the data generated by either method on low carbon content ashes are comparable.

7.2.3 Analytical Measurement

The chemical matrix of MSW incinerator residues is very complex, and the measurement of the individual elements within the matrix can be equally complicated. Analysis can be divided into two major categories, 1) Destructive Methods and 2) Non-destructive Analytical Techniques.

Destructive Methods
Metal species contained in the digestates generated from the digestion techniques mentioned above may be quantified through instrumental analysis. Either atomic

absorption or atomic emission spectroscopy can be used for the analysis. The methods under each type of analytical technique are summarised in Table 7.3 along with a list of suggested elements for which the method is suitable.

Table 7.3
Summary of Destructive Spectroscopic Analytical Techniques

Absorption		Emission	
Method	Application	Method	Application
Flame AAS	Transition and alkaline elements	ICAP	Most elements
Graphite Furnace	Sb, As, Be, Cr, Cd, Pb, Se, Tl	DCP	Most elements
Cold Vapour	Hg	Hydride Generation	As, Se, Sb, Sn
Hydride Generation	As, Se, Sb, Sn		

Flame Atomic Absorption Spectroscopy (Flame AAS)
Flame AAS is commonly used to measure most of the transition and alkaline elements in digestates. However, there are two areas of concern which must be considered when analysing a sample using this technique:

1) The choice of flame conditions (i.e., nitrous oxide/acetylene or air acetylene) on a per element basis is extremely important. Even the same sample run on the same instrument will produce widely variable results. Since some elements, such as Al, Ca, Mo and Si, have relatively low ionisation potentials, they are likely to undergo ionisation in the flame, thereby lowering the measured value. This is generally corrected by the addition of a concentrated element which has a lower ionisation potential than the element being analysed.

2) Most MSW incinerator residue streams contain high concentrations of salts, especially combined bottom/fly ash and air pollution control system residues. The high salt concentrations increase the viscosity of the sample and can potentially cause severe problems with aspiration of the sample into the flame. One way of remedying the problem is to dilute the sample, although this entails raising the method detection limit, perhaps beyond acceptable levels. Anion exchange can also be used to overcome the high salt concentrations, however, this approach requires extra QA/QC including analyte spiking checks.

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

GFAAS is a method of quantification which is preferred in some instances since the detection limits are significantly lower than flame AAS, although the increased precision is gained at the expense of time. Typically, it is used for a limited number of trace elements, such as those listed in Table 7.3 (recommended under EPA Method 1620). Similar to flame AAS, analysis by GFAAS requires careful attention to the sample matrix, either through matrix modification, anion exchange, dilution or matrix duplication with standards. Another way of increasing the accuracy of the analysis is to use low porosity graphite tubes.

There are a number of interferences encountered when using GFAAS to measure certain elements. Table 7.4 summarises the problem encountered with a number of metals and the corrective measure required to eliminate the interference.

Table 7.4
Summary of Interference Problems and Correction Measures for Specific Elements

Element	Interference Problem	Corrective Measure
Sb	High chloride content produces losses prior to atomisation	Add an excess of 5mg of ammonium nitrate to the sample in the graphite tube prior to drying and ashing
As	Deuterium arc background correction insufficient compensation for high levels of Al and Fe	Conduct background correction with Zeeman or Smith-Hieftje correction
Be	Potential gas phase interaction with nitrogen	Do not use nitrogen as purge gas
Cr	Oxidation state may change	Add hydrogen peroxide to the acidified sample to ensure Cr is in trivalent state, or add 500 mg/L of Ca to reduce volatilisation (may cause further problems due to high TDS of sample)
	CN band broadening interference	Do not use nitrogen as purge gas
Pb	Sulphate interference	Add lanthanum nitrate to sample to suppress the effect of sulphate
Se	Same as for As	Same as for As

Cold vapour AAS is another application of flameless AAS. It is used in the analysis of mercury with a primary working range of 0.1 to 5.0 ppb. Major interferences are from

gaseous species that also absorb at the 253.7 nm mercury wavelength. Chlorine and water vapour are the two main contributors to this type of error. After the rigorous digestions required for the MSW residues there is little chance of having free chlorine present and water vapour can be removed by passing the post reacted gas stream over concentrated sulphuric acid or other moisture trap.

Hydride generation is another form of analysis that quantifies the analyte in the gaseous phase. Elements such as, Se, Sb, and Sn are routinely analysed by this method. It is adaptable to both absorption and emission spectroscopy. Detection limits as low as the part per billion range can be attained with good accuracy and precision.

Interferences can occur in the generation of the hydride species which are due to high concentrations of metals such as copper, chromium, iron and nickel. Increasing the borohydride:sample ratio is an approach generally used to overcome this problem. It is also necessary to ensure the analyte species are in the proper oxidation state prior to the hydride reduction. This may be accomplished by heating the digested sample in hydrochloric acid before analysis.

Atomic emission analysis can be performed by using either an inductively coupled argon plasma spectrometer (ICAP) or a direct current argon plasma spectrometer (DCP).

ICAP is routinely used for metal analysis since it has the potential of being accurate and efficient with Method Detection Limits (MDL's) of 1 to 2 orders of magnitude lower than that of flame AAS. This is due to the very high operating temperature of the plasma. In addition, the sample is pumped into the flame rather than being aspirated, therefore less physical interference is generally encountered than during atomic absorption spectrophotometry. Similar arguments for DCP are also true.

There are two main categories of interference which can occur with ICAP or DCP analyses, namely, spectral and physical interferences. These interferences are summarised in Table 7.5 along with the specific corrective measures required to eliminate or minimise the interference.

There are trade offs which much be considered when choosing ICAP or DCP for analysis. Although the detection limits for DCP are higher than ICAP, DCP will handle the high total dissolved solids content of MSW incinerator digestates or leachates better than ICAP. Consequently, the choice of instrument is highly dependent on the requirements for a detection limit on specific elements.

Non-Destructive Analytical Methods

Instrumental Neutron Activation

In principle, Instrumental Neutron Activation (INA) measures primarily gamma radiation emitted by the radioactive isotopes produced by irradiating samples in a nuclear

reactor. The MDL's are generally higher than those associated with either AAS or DCP/ICAP, however, the technique has some advantages depending on parameter choices:

1) There is no chemistry required, hence the difficulties and limitations of trying to dissolve the sample do not exist;

2) It is a multi-element technique, capable of determining 35 elements simultaneously; and

3) A much larger sample mass (up to 30 grams) can be used thereby further minimising the effects of sample inhomogeneity.

Table 7.5
Summary of Interferences and Corrective Measures for ICAP/DCP Analysis

Category	Interference	Correction
Spectral	Overlap of different elemental spectral lines	Install software packages designed to analyse the raw data and add further resolution
	Unresolved overlap of molecular band spectra	Choose an alternate operational wavelength
	Background contribution of stray light caused by line emissions from high concentration elements	Apply background correction adjacent to the analyte line
Physical	High dissolved solids content of the sample matrix causing fouling of equipment	Dilute the sample or ensure peristaltic pump lines are clean and free flowing
	Salt accumulation at the tip of nebuliser and torch causing plasma drift, hence inaccurate readings	Constantly rinse the system with distilled water between readings and replace fouled parts

X-Ray Fluorescence

X-Ray Fluorescence (XRF) is another non-destructive mode of analysis that may be applied to MSW incinerator residues, however, the detection limits are generally higher than any of the aforementioned methods of analysis. This method is discussed in more detail in Chapter 7.3.

Since the detection limit required during analysis is quite often the determining factor when selecting analytical instrumentation, Table 7.6 provides a summary of the potential detection limits which can be achieved by the various methods. In addition, Table 7.6 provides a summary of acceptable methods for quantifying specific elements in the sample matrices of MSW incinerator residues.

Table 7.6
Summary of Achievable Detection Limits by Different Analytical Instruments

	ICAP		INA	XRF
Element	Wavelength (nm)*	MDL (ppm)**	MDL (ppm)	MDL (ppm)
Al	308.215	0.045		
Sb	206.833	0.032		5.0
As	193.696	0.053	2.0	5.0
Ba	455.403	0.002	100	5.0
Be	313.042	0.0003		
B	249.773	0.005		
Cd	226.502	0.004		
Ca	317.933	0.010	10,000	
Cr	267.716	0.007	10	5.0
Co	228.616	0.007	5	5.0
Cu	324.754	0.006		5.0
Fe	259.940	0.007	200	
Pb	220.353	0.042		5.0
Mg	279.079	0.030		
Mn	257.610	0.002		5.0
Mo	202.030	0.008	5	5.0
Ni	231.604	0.015	50	
Se	196.026	0.075	5	
Ag	328.068	0.007	5	
Na	588.995	0.029	500	
Th	190.864	0.040	0.5	
Sn	189.989+	0.030	100	5.0
Ti	334.941	0.003		
V	292.402	0.008		5.0
Zn	213.856	0.002	50	5.0

* = Recommended for sensitivity and overall acceptance. Use of alternate wavelengths should be reported with data.

** = Source: "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines" (EPA-600/4-79-017).

+ = nitrogen purge used at this wavelength

7.2.4 Loss on Ignition

"Loss on ignition" (LOI) data has typically been used to provide an indication of the degree of "burnout" achieved during combustion or the "combustion efficiency". LOI is usually defined as the weight loss of a solid sample (previously dried for 24 hours at 105°C) after exposure to 550°C in a muffle furnace for sufficient time to achieve a constant weight. Typically the results are expressed as a percentage of the dried sample weight.

$$LOI = \frac{W_{DA} - W_{MA}}{W_{DA}} \ (x\ 100\%)$$

where; W_{DA} = weight of ash dried at 105°C in grams
W_{MA} = weight of ash muffled at 550°C in grams

Although the use of LOI values is an acceptable surrogate parameter for measuring "burnout" in bottom ash and grate siftings samples, the interpretation is not accurate when used in context with heat recovery system and APC residue streams. Since the temperature in the flue gases exiting the boiler are much lower than 550°C, any flue gas reaction products which condense out or sorb onto particles, will be re-volatilised during muffling. In addition, a portion of the volatile material from lime-based APC residue is attributable to the loss of water of hydration from the excess lime ($CaOH_2$ to CaO and water). A further bias which prevents direct comparison of LOI values between APC residues from different facilities can be attributed to the fact the stoichiometric ratio of lime addition varies from facility to facility. Hence, if the content of excess lime in the residue varies, so will the amount of water of hydration. Other methods, such as particulate carbon, should be used to determine the content of "combustible" material remaining in heat recovery and APC system residues.

Much of the LOI data quoted in the literature are used to define combustion efficiency, however, caution should be used when attempting to compare LOI data from some sources. LOI data can also be administratively defined as a function of the total weight of ash leaving the facility, which includes accounting for the ferrous, non-ferrous and other non-combustible materials in the ash removed prior to testing (which were originally non-combustible). Consequently, comparison of laboratory LOI values and administrative values would generally indicate lower administrative values than the laboratory LOI values (by a factor equal to the proportion of reject material).

The most commonly used methods of determining LOI are the APHA Standard Method 209E (1981) and ASTM Standard Method C25-88. Some of the different modifications incorporated into these methods include:

1) Reduction in Particle Size of Bottom Ash Samples - prior to muffling bottom ash, the samples are ground to minimise the potential for material loss due to

displacement via "popping" or violent cracking of particles which has been noted with some unprocessed bottom ashes. This phenomenon has been noted mostly on quenched bottom ash samples, not on those samples collected prior to quenching. Since there are blind pores or "pockets" within some ash particles and hydrogen can be liberated upon hydration of bottom ash, it is speculated quenched samples may contain small pockets of hydrogen gas or water trapped within clinker-like particles which are not liberated during drying at 105°C, but exert sufficient pressure to escape when heated to 550°C. Reducing the particle size also helps to minimise variations between bottom ash samples by acting to "homogenise" the sub-samples, thereby enhancing reproducibility. Consequently, it is recommended ground bottom ash and grate siftings samples be used for LOI determination.

2) Variations in the Quantity of Sample - the quantity of sample used in the determination varies (usually between 10 and 50 grams), and is typically based on the precision of the weigh scale being used and/or the quantity of sample available for testing. Generally, the less sensitive the scale, the larger the sample size required to provide an adequate degree of precision. For example, a minimum of 50 grams of sample should be used when employing a scale capable of sensitivity to a milligram in order to achieve a precision of at least 0.1% $\pm$0.05%. Weigh scales with the capability to measure to the 1/10 of a milligram will permit using sample sizes down to 10 grams.

3) Typically, the length of time for muffling the sample varies between 1 to 2 hours. However, the volume of the sample is a factor to be considered in deciding upon the length of time required for muffling. Since the density of some residue streams is less than 1 g/cm^3 (e.g., APC residues), a relatively large volume of low density ash (hence, increased insulating properties) will require more time to reach 550°C, than a similar weight sample of a relatively high density ash (e.g, bottom ash >1.5 g/cm^3). Consequently, it is recommended the time required for muffling should be increased to permit sufficient heating of the less dense residues (mixing the sample part way through the muffling process is also recommended). A period of two hours is recommended to ensure sufficient time for the temperature of most samples to reach 550°C. This should also ensure adequate time for volatile material to escape the solid matrix.

4) The procedures stipulate the determination should be conducted to achieve constant weight. Although the ASTM method indicates precision of $\pm$4% difference between consecutive readings, experience indicates this level of precision will be difficult to achieve without weight sensitivity to 1/10th of a milligram. One repetition of the procedure should be sufficient to ensure constant weight has been achieved.

5) As an additional or alternate QA/QC procedure, it is recommended the test be conducted on triplicate sub-samples and the LOI values compared. If there is less than a $\pm$5% difference in values, the average of the triplicate values should be used.

There are other aspects of the procedure which require special attention to ensure generation of accurate data, namely, cooling and desiccation of the sample. Experience has shown MSW incinerator residues are hygroscopic, and hence are very sensitive to changes in humidity in the laboratory. Some precautions that should be taken to ensure better reproducibility include:

1) Employ the use of a vacuum vented drying oven for moisture content determination prior to muffling. This avoids the potential for a build up of humidity which can often occur in passive drying ovens, and can result in moisture being held in the "so called" dry sample for muffling.

2) After muffling, the samples should only be allowed to cool in the open air for a short period of time before being placed in a desiccator. Steps should also be taken to ensure the desiccant material is fresh and active.

7.2.5 Total Carbon, Carbonate, Sulphur and Ammonia

Analysis of total carbon and total sulphur are generally conducted using the Leco induction furnace method. Since the sample mass used for the analysis can be relatively small (0.02 - 0.5 grams), a well homogenised sample plays a critical role in generating good data. Sulphate content is typically determined by analysing distilled water leachates of the residue samples, although this method will only detect the soluble sulphate compounds. It should also be noted sulphate solubility is limited, and several water extractions may be required to ensure most of the sulphate has been released from the solid sample. Sulphides can be measured by an iodometric method using Method 4500 S^{-2} E (Standard Methods for Examination of Water and Wastewater (SMEWW). The speciation of sulphur-based compounds can be determined by chromatographic methods given in Streudel et al., (1989), and by the potentiometric procedures given in Satake et al., (1981). Examples of the achievable detection limits for the various sulphur compounds are given in Table 7.7.

Table 7.7
Achievable Detection Limits for Sulphur Based Compounds

Parameter	Detection Limit for Solid Sample (µg/g)	Detection Limit for Liquid Sample (µg/mL)
SO_4	100	0.15
S^{2-}		0.10
SO_3^{2-}		0.10
$S_2O_3^{2-}$		2.00
S_x^{2-}		6.00

Methods also exist to distinguish the different types of carbon present in a sample (i.e., total organic carbon and degradable organic carbon versus total carbon), which are given in VGB Arbeitsgruppe (1992). A further distinction between the specific organic carbon substances may also be warranted. For example, Method 5560 (SMEWW) provides for determination of organic and volatile acids, whereas Method 5510 (SMEWW) outlines the determination of sugars, humic and fulvic compounds.

A precise method for determining carbonate contents in ash is important when evaluating the carbonation of bottom ash for utilisation purposes. Carbonate is often measured as total alkalinity based on Method 2320 (Standard Methods for Examination of Water and Wastewater). A more accurate value is obtained by quantitatively converting the carbonate to carbon dioxide via acidification. The carbon dioxide is then trapped in a NaOH solution which is subsequently titrated with HCl for the determination (Vogel, 1961).

Several methods are available for the determination of ammonia which are described in Method 4500 NH_3 Nitrogen (Standard Methods for the Examination of Water and Wastewater). These include the Nessler method, a phenate method, a titrimetric method and ammonia selective electrode method, although the latter method is less accurate for ammonia in the high salt content matrix of incinerator residue leachates.

7.2.6 Acid Neutralisation Capacity

Acid neutralisation capacity (ANC) is defined as the capacity of a material to resist changes in pH. The ANC results are typically used to assist with determination of the potential for trace metal mobility, based on the variation in pH over time.

The test is generally performed using one of either two methods. One method is a titration method based on the ASTM Standard Method C400-64. It typically involves slurrying a 1 gram sample of ground ash with distilled water at a 20:1 liquid-to-solid ratio and titrating to an end point pH with an acid solution, usually HNO_3. Although this can be done either manually or by using an automatic titrator, there are some precautions which need to be taken to ensure generation of reproducible results. The ash should be ground to at least 150 µm (#100 mesh) particle size to hasten the chemical reactions. Experience has shown manual titration of ash can be very time consuming. When acid is added to the ash slurry, the pH may drop quickly, then slowly increase over a wide pH range. As the slurry moves closer to the end point pH, care must be taken to add the acid in drop-wise increments to avoid "overshooting" the target pH. Consequently, the length of time required to reach equilibrium at the end point pH is generally considerable (hours to days). Use of an automatic titrator saves on personnel time.

The extended length of slurrying time may also be detrimental to the quality of data being generated. The longer the test takes, the greater the potential for uptake of CO_2

from the air, which biases the measured ANC value. This can be avoided by running the titration in a covered vessel, or "closed" system, to limit the exposure of the slurry to the air.

Another drawback to a titration is the difficulty in obtaining sufficient data to generate a pH/ANC curve, which can then be used in models to help estimate the potential for trace metal solubility over time. Even with an automatic titrator, obtaining a titration curve is difficult because the time required to reach equilibrium with these types of highly buffered materials is not conducive to a continuous titration process.

The second method is a modified procedure which involves mixing individual 5 gram samples of ash in 30 millilitre acid solutions of varying strength. The solutions range in strength over 10 equal increments from distilled water to either 2.0 N HNO_3 or 4.0 N HNO_3. The respective ash and acid solution slurries are mixed for 48 hours in a rotary extractor before centrifuging and monitoring of the pH of each sample.

This method is generally more cost effective since it is less time consuming than the straight titration. It also provides a closed system for the test, which reduces the potential for CO_2 uptake to bias results. In addition, more pertinent information is derived, since a pH/ANC curve can be developed from the incremental analysis, which in turn can be used to assist with modelling of potential trace metal solubility. Furthermore, the filtered extracts from each increment can also be analysed for dissolved trace metal content to develop a pH/solubility curve which can also be used for modelling.

One of the drawbacks to this method is it requires a rotational device and high speed centrifuge to conduct the determination, both of which can be costly. Another drawback is if the extracts are to be analysed for trace metals, the quantity of ash and acid solutions must be scaled up to accommodate analytical requirements. Scaling the quantities up may also require the containers to be "burped" during the mixing process to bleed off the build up of excess hydrogen generated by slurrying the ash.

Based on the discussion above, it is recommended the incremental method of performing the ANC determination be used instead of the titration method. The benefits of the extra data generated from this procedure far outweighs the capital cost requirements, and is generally less susceptible to error caused by CO_2 uptake.

7.2.7 Organic Analyses

Sample Preservation

The prominence of the issues surrounding polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) compounds in MSW incinerator ash warrants a brief discussion on the importance of proper sample collection and preservation prior to extraction.

It is suggested that due to the potential dynamic nature of organic compounds, all samples collected for organic analyses should be cooled as quickly as possible after collection, and a storage temperature of 4°C should be maintained until extraction. This is especially true for quenched ash samples.

Samples submitted for analyses are typically processed on an "as received" basis and results should be specifically expressed either on a wet weight (give % moisture) or a dry weight basis. Should it be deemed necessary to dry and grind the sample prior to extraction, it is suggested the samples be either air dried or dried at temperatures less than 50°C to minimise potential volatilisation of some organic compounds.

Extraction

The extraction of ash samples is generally facilitated by decomposition of the matrix using hydrochloric acid. After digestion, the mixture is neutralised and lyophilised. The remainder of the extraction is conducted in a similar manner to air emission samples. Generally, standard solutions of organic compounds are then added to the digest solutions prior to extraction with toluene.

Chlorophenols

Potassium dichromate is mixed into the toluene extracts to extract the chorophenol fraction. The chlorophenols are then acetylated using acetic acid anhydride and further extracted using dichloromethane and concentrated by evaporation. The fractionate is then analysed using GC/MS.

Chlorobenzenes

Chlorobenzenes must be fractionated from the dioxins and furans prior to analysis. The toluene extract must be cleaned up removing the chlorophenols, alcohols and organic acids by treatment with potassium dichromate. The cleaned extract is then concentrated and fractionated by column adsorption chromatography in a aluminum oxide column. The fractionate is then eluted with benzene to generate chlorobenzenes as the first fraction, then with dichloromethane/hexane to give a dioxin/furan fractionate.

Analysis

Analysis of trace organic compounds can be conducted using gas chromatography/mass spectroscopy (GC/MS) preferentially, or a high resolution GC and MS (HRGC/HRMS). The HRGC/HRMS instrument provides lower detection limits and is considered state-of-technology at the present time. The actual analysis requires the skill of a highly trained technician to run the equipment and interpret the data being generated.

7.3 CHEMICAL SPECIATION METHODS

The nature of the solid phase is very important when evaluating leaching phenomena, utilisation, and management of MSW combustion residues. As discussed in Chapter 13, the nature of the solid phase has a profound impact on fundamental leaching behaviour. It is therefore important to describe methods that can be used to characterise the morphology of solid phases, the mineralogy of the solid phases, elemental associations in the solid phases (particularly in less crystalline, more amorphous material), and valence states of elements in the solid phase. These issues comprise the nature of the chemical speciation of elements in ash particles.

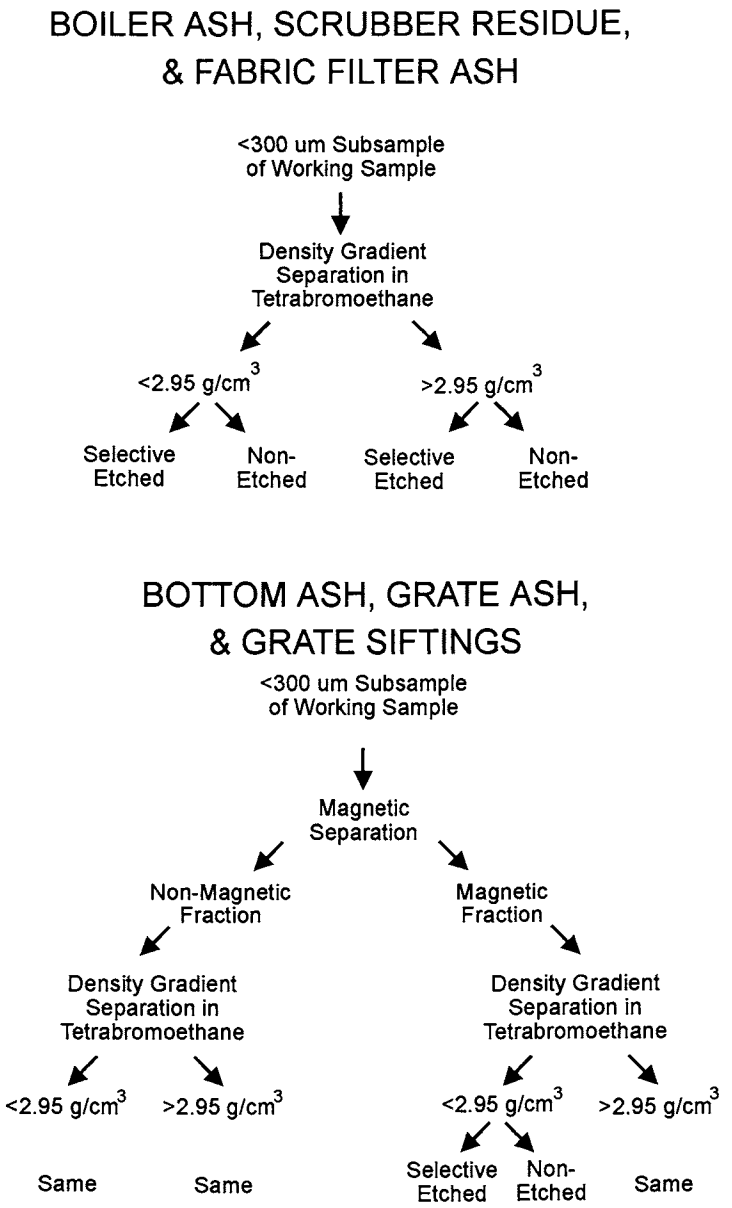
Elements at the surface of an ash particle (top atomic layer) exist in a markedly different environment than atoms situated just below the surface (near-surface environment), which in turn differ from elements situated in the bulk of the sample (bulk environment). These differences arise because the top atomic layer can have at least one bond direction where the coordination chemistry differs from bulk elements (Hochella, 1990). Additionally, external gases, liquids, or solid phases can react with the top atomic layer, causing disruption in bond strength among adjacent atoms in minerals and between crystal lattices. This disruption can extend into the near-surface environment but it dissipates with depth (Hochella, 1990), hence caution should be used when describing the type of solid phase analytical method employed to characterise bulk, near-surface, and surface elements for characterising their speciation.

By drawing on the extensive experience used by metallurgists and by geochemists the mineral surfaces and mineral phases can be characterised, particularly for basaltic rock, evaporites, and sedimentary rock, since these minerals are close in composition to certain MSW ashes. Readers are directed to the recent reviews of Whan (1986), Hochella (1990), Coyne, McKeever and Blake (1990), and Hawthorne (1988) for very detailed reviews of all the spectroscopic methods available to characterise solid phases. The methods described in this section therefore are not considered to be inclusive of all the methods available for use.

7.3.1 Separatory Techniques

The goal of this section is to discuss methods of "disassembling" the complex, heterogeneous constituents in ash samples so the resultant fractions can be better characterised for their solid phase chemical speciation. Disassembling can help to concentrate phases of similar magnetic or density characteristics. By concentrating the phases, problems with detection limits can be avoided. In one study on bottom ash, disassembly and subsequent concentration resulted in over a 500 fold increase in the concentration of chromium (Eighmy et al., 1993). Figure 7.5 depicts the type of sample processing to be discussed. Such schemes have been used in part or in total to characterise ash (Eighmy et al., 1992, Eighmy et al., 1993).

Figure 7.5 Schematic Showing the Type of Sample Processing that can be Employed to Disassemble Incinerator Residue for further Analysis



Sample Drying

It is sometimes advantageous to analyse ash particles in their native states. Almost all the described analytical methods discussed in this section require the use of dried samples. Additionally, some methods require fine powders, polished flat specimens, or particle thin sections. However, processes that dehydrate the ash samples or reduce the size of particles to unit mineral grains can have a profound impact on chemical speciation. Bulk specimens become so fractured that internal grain boundaries become atmosphere-exposed. The presence of oxygen or carbon dioxide can react with and alter these surfaces. Consequently, some of the efforts used to analyse solid phases have inherent compromises in them. A balance must be struck in the use and selection of analytical methods. Invariably, multiple methods should be used.

Sample drying can arrest aging reactions that can occur in hydrated ash samples. Hydration, carbon dioxide uptake, and biological activity can be stopped. It is possible to use drying as a means of arresting aging reactions during a time course to look at "snapshots" of the aging progression. Drying methods, as outlined in Section 7.2.1, are sufficient. Care should be taken that temperatures are maintained at 60 to 70°C to prevent phase changes in some of the more heat-sensitive minerals or amorphous phases. Labile waters of hydration can also be removed from gels or crystal phases that may alter phase morphology or properties.

Particle Size Reduction

Ideally, investigations of the bulk particle can focus on the properties of all the particle constituents or the particle can be size-reduced into its component grains or phases. The latter provides the opportunity to better characterise its components. Thorough size reduction can even allow us to examine monophasic particles, provided fracturing occurs at grain or phase boundaries. In any case, questions can be investigated regarding the chemical speciation of the bulk, the component phases, the near surface environment, and the top atomic layer of particles or their component phases, keeping in mind the original ash particle size and the size of its constituent phases. This is more important for bottom ash and grate siftings than for all the other incinerator residues.

Jaw crushing can be used to break apart bottom ash into smaller size material. Hutchinson (1974) details crushing methods. Jaw spacing can be adjusted to select for final particle size. Final sizes can range down to 1 mm. The use of a jaw crusher provides for more systematic final sizes than impact crushing. Riffle sampling can then be used to select subsamples.

Further size reduction of all types of ash specimens can be accomplished using a number of devices. Caution should be used here. Further size reduction can help to produce a more homogeneous material. The degree of homogenisation also depends on the final particle size. In order to reduce fine-grained fly ash into its component

monophases, extensive grinding may be needed and a high degree of homogenisation may be obtained. Overgrinding introduces the risk of sample contamination from the grinder. Component monophases of a coarse bottom ash can be examined with less grinding and hence a low degree of homogenisation may be obtained.

Grinding may be accomplished using hand-held mortar and pestles made of agate, mullite, corundum, or tungsten carbide. Porcelain or iron mortars can be too soft for certain ashes. Mechanised mortars and pestles can be used to provide more systematic grinding procedures.

Grinding may also be accomplished using mechanised grinding plates, ball mills, or hammer mills. The use of tungsten carbide grinding surfaces is preferred; however, contamination from these surfaces is possible with certain bottom ash samples. The lower limit of particle size reduction using these mechanised method is about 10 μm. Micronising mills reportedly can produce this size range (Bish and Reynolds, 1989). For some fine grained ESP boiler, and fly ashes, it may be difficult to size-reduce to monophasic material.

Extensive grinding can generate high quantities of heat. Alcohols and acetone can be used as lubricants for certain grinding processes (Bish and Reynolds, 1989); however, these solvents may have slight solubilising effects on certain highly soluble metal salts in ash residues. Control of temperature may be quite important for hydrated phases, but evaluation of potential solvent dissolution should be done.

Magnetic Separation Techniques

Incinerator residues, particularly bottom ash, grate siftings, and ESP ashes contain magnetic materials. Magnetic separation can be used to remove these fractions. This can allow for the more careful study of these fractions, or other phases intimately associated with these fractions. The non-magnetic residue can then be more carefully studied without the diluting effect of the magnetic fractions. Magnetic separation techniques have worked well with coal fly ash (Hansen et al., 1981) and with municipal solid waste ashes (Eighmy et al., 1992; Stämpfli, 1992).

Two types of magnetic separation can be employed. The first involves the use of either a hand-held magnet or a rotary ferromagnetic separator. The hand-held magnet can be covered with glycine weighing paper or done through a glass petri dish to facilitate separation of particles from the magnet. The rotary separator is a more systematic method (Hutchinson, 1974). Both methods remove hematite (Fe_2O_3), magnetite (Fe_3O_4) and iron metal fragments. These are routinely found in bottom ash at concentrations up to 35% on a dry weight basis.

Isodynamic or barrier separators are available that can adjust the amperage applied to an inclined vibrating plate. The amperage is used to control the intensity of the magnetic field. More than sixty types of minerals can be diverted (Hutchinson, 1974).

A sample is run through the apparatus after setting the amperage. The passed through nonmagnetic materials are saved and the magnetic fraction is then collected. The passed through materials are then run through the apparatus again at a higher amperage. The process is repeated until the applied amperage is about 1.5 amps. Repetitive separations at the same settings can also be used to effect a very thorough separation. This method has been used on bottom ashes (Eighmy et al., 1992; Stämpfli, 1992) and on ESP ashes (Eighmy et al., 1993). A fine particle size should be used. Dry particles less than 150 μm and greater than 90 μm in size are most readily processed (Hutchinson, 1974). The schemes in Figure 7.5 are also applicable for particles between 225 μm and 50 μm.

Density Separation Techniques

Density separation can be an extremely useful technique, particularly if it is performed on samples previously separated by magnetic separation methods (although the procedure could be reversed). Mineral grains can range in density from about 1.6 to 22.5 g/cm^3 with typical values of aluminosilicates below 3.0 cm^3 and heavy metal salts above 3.0 g/cm^3 (Carmichael, 1989). Other phases in the ash can also vary in density. The method can further concentrate materials by density and remove materials that can dilute the sample during analysis. The principle behind separation is mineral grains less dense than the separating liquid will be buoyant and mineral grains more dense will sink through the liquid. Density gradient separation has worked well with coal fly ash (Furuya et al., 1987), and MSW ashes (Eighmy et al., 1992).

Hutchinson (1974) and Zussman (1967) discuss methods for selection of dense liquids and use of various separatory apparatus. Typical liquids used are 1,1,2,2-tetrabromethane (2.967 g/cm^3 @ 20°C) and diiodomethane (3.325 g/cm^3 @ 20°C). These solutions are both toxic and expensive and very careful procedures for use in safety hoods are needed (Hutchinson, 1974). Diluents such as acetone and N,N-dimethyl formamide can be used to adjust fluid densities to lower values (Zussman, 1967). Detailed methods are described for separating coarse-grained material and fine grained materials (Hutchinson, 1974). Depending on the type of separatory process (separatory funnel, centrifuge tube, density gradient column), low particle settling velocities can be a concern. There are also lower limits on particle size that approach 10 μm (Zussman, 1967) because of particle aggregation. Procedures have also been established to process larger volumes of samples (Hutchinson, 1974). Riddick et al. (1986) provide specific gravities of organic solvents. Carmichael (1989) lists the grain densities of elements, alloys, and minerals.

Selective Phase Dissolution Methods

After magnetic separation into magnetic and nonmagnetic fractions and further separation by density, selective dissolution techniques can be used to partially solubilise phases within a fraction to further concentrate the non-solubilised phase and remove phases that contribute to dilution effects. Many of the techniques that can be

used here are similar to the ones used for the sequential chemical extraction leaching procedure discussed in Chapter 15.

The principle behind selective dissolution is certain phases can be removed by dissolution through the use of extractants. Such techniques have worked well for removing amorphous glassy phases from coal fly ash (Hulett and Weinberger, 1980), or surface phases from a variety of coal ashes, scrubber solids or oil ashes (EPRI, 1985) or surface phases from sewage sludge ash (Theis et al., 1984).

Reviews by Theis et al. (1984), EPRI (1987), and Tessier and Campbell (1988) discuss the relative merits of selective dissolution. Some controversy exists in the use of sequential selective extractions (Nirel and Morel, 1990; Tessier and Campbell, 1991). Principle problems include the lack of exhaustive validation of the procedures (Nirel and Morel, 1990), validation with doped artificial phases that do not resemble natural solid phases (Tessier and Campbell, 1991), and post-extraction adsorption phenomena which can cause an underestimation of element mass association with specific phases (Nirel and Morel, 1990). More careful design of spiking experiments with natural materials suggests the adsorption problem is not as severe as the other issues (Belzile et al., 1989).

Table 7.8, adapted from Theis et al. (1984), depicts the types of extracting agents that can be used to remove selective phases from a sample. Some methods remove surface soluble phases, others dissolve insoluble precipitates, others oxidise reduced phases, others reduce highly oxidised phases, and some can very selectively extract glassy phases or adsorbed metal species. Caution should be used to evaluate the efficacy of the desired extraction. Quantification of dissolved constituents in the extraction fluid, coupled with careful solid phase characterisation before and after the extraction, are usually needed to assess the efficacy of the extraction, as well as its selectivity to the desired phases in the solid. The work of Hulett and Weinberger (1980) has shown the utility of this method in dissolving the amorphous glassy phases from coal fly ash with hydrofluoric acid so mullite and quartz phases could be characterised for chemical speciation.

7.3.2 Impregnation, Thin-Sections, and Thin-Foil Methods

As discussed in Section 7.3.1, it is possible to disassemble combustion residue particles into more defined fractions. Many of the chemical speciation analytical techniques that can be used require the use of fine powders. Some techniques can be used on the intact ash specimen. Frequently, both powders and intact ash particles must be further processed to make them amenable for analysis.

Impregnation with a polymer so the samples can be polymerised, hardened, thin sectioned and polished to produce a petrographic thin section is frequently done. Fine powders can be manufactured into highly polished thin foils. Ion bombardment

techniques can then be used to ion-etch the particle surface to remove the top atomic layers.

Table 7.8
Commonly Used Extracting Agents

Extracting Agent	Primary Chemical Interaction	Major Application
H_2O	Hydration	Mild Dissolution
Acetic Acid	Acidic	Mild Dissolution
H_2CO_3	Acidic	Mild Dissolution
H_3PO_4	Acidic	General Metal Recovery
Citric Acid	Acidic	General Metal Recovery
Dilute Strong Mineral Acids (e.g. HNO_3, H_2SO_4, HCl, HF)	Acidic	General Metal Recovery HCl-Dissolution of Metal Oxides
Conc. Strong Mineral Acids (e.g. HNO_3, H_2SO_4, HCl, HF)	Acidic	Dissolution of Major Mineral Forms (except silica) General Metal Recovery
HNO_3-HCl-HF	Acidic	Complete Dissolution
NaOH	Basic	Dissolution of Polar Organic Fraction, Dissolution of Fe, Al Oxides
$BaCl_2$, $MgCl_2$, $CaCl_2$ KNO_3, KF, NH_4Ac	Solvating Power due to high ionic strength	Exchangeable and Physically Adsorbed Species
EDTA	Complexometric	Exchangeable and More Strongly Bound Metals, Dissolution of Carbonate, Recovery of Metals from Organic Phases
$Na_4P_2O_7$	Complexometric	Recovery of Metals from Organic Phases
Ammonium Oxalate (acid)	Complexometric	Dissolution of Amorphous Oxides of Al and Fe
Citrate-Dithionite-Bicarbonate	Reductive	Dissolution of Fe and Al Oxides
Hydroxylamine Hydrochloride	Reductive	Dissolution of Mn Oxides
H_2O_2	Oxidative	General Metal Recovery Organic Digestion

From Theis et al., 1984 with permission of the author

Petrography and optical mineralogy frequently make use of thin slices of rock material that are subsequently glued to a glass slide, ground, and then polished to a 30 μm thickness for subsequent analysis (Nesse, 1991). Usually, specimens must be impregnated with a heat-activated polymerising resin that solidifies the specimen. Intact ash particles or powders can be imbedded in a mold, polymerised, and then thin sectioned with a thin sectioning machine prior to grinding and polishing. Hutchinson (1974) describes two methods for ash-like material. The polymerising solution is added to the dry ash specimen, and then placed in a vacuum. Under a vacuum, pores loose gas and non-viscous epoxy infiltrates the pores. Eventually all pores are filled and the specimen can be hardened to produce a monolith. The second method uses a pressurisation technique to cause complete impregnation. These methods have been used for various ashes (Eighmy et al., 1992). Similar methods have been used for bottom ash (Lichtensteiger, 1992).

A number of techniques are available to cut the polymerised monolith. Usually a micro-trimming machine provides good samples. A diamond hand saw can be used to trim specimens. Hutchinson (1974) describes methods for sawing and lap grinding with corrudum or alumina powders or silicon carbide abrasive papers. An epoxy resin is usually used to mount the ground specimen to a glass slide. Finally the specimen is polished to very thin thicknesses using alumina or diamond pastes. A final specimen thickness of 30 μm is required; it is a standard thickness for petrographic analysis and evaluation of refractive properties of light require this thickness. Grinding and polishing can heat the sample and cause debonding between the epoxy polymer and the specimen in the thin section.

A number of methods are available to make thin foils. Tighe (1976) presents methods where petrographic thin sections are cored to collect small circular flat specimens for use in transmission electron microscopy. Powders can also be embedded in an epoxy amalgam that contains conductive silver (Eighmy et al., 1992). The molds used are the same size as transmission electron microscopy (TEM) grids. This allows direct insertion into the TEM microscope. The samples are ground with a dimpler that abrades through the centre of the specimen. After ion milling, the margins can be examined.

7.3.3 Analytical Methods for Solid Phase Chemical Speciation

Table 7.9 depicts a variety of analytical methods used to look at element speciation in the bulk phase of intact particles, in the bulk phase of particle cross sections (e.g. thin sections or thin foils), in the near surface environment of intact particles, and in the top atomic layer of particles. Here it is assumed the specimens are, for the most part, particle size-reduced with fracturing at grain or phase boundaries so the analysed particles are mostly monophasic. In some instances, entire ash particles are analysed. Care will be taken to identify differences where appropriate.

Table 7.9
Analytical Methods for Examining Solid Phase Chemical Speciation

Element Location	Type of Analysis: Morphology	Mineralogy	Element Association/ Composition	Element Bonding and Valency
Bulk (Intact Particle)	-Transmitted Light Microscopy (TLM) -Scanning Electron Microscopy (SEM)	-X-ray Powder Diffraction (XRPD) -Differential Thermal Analysis (DTA)	-Scanning Electron Microscopy/X-Ray Microprobe (SEM/XRM) -X-Ray Fluorescence (XRF)	-Electron Energy Loss Spectroscopy (EELS) -Extended X-Ray Adsorption Fine Structure (EXAFS) -Nuclear Magnetic Resonance (NMR)
Bulk (Particle Thin Section)	-Petrography	-Petrography	-Scanning Electron Microscopy/X-Ray Microprobe (SEM/XRM) -Scanning-Transmission Electron Microscopy/X-Ray Microprobe (STEM/XRM) -X-Ray Fluorescence (XRF)	-Electron Energy Loss Spectroscopy (EELS) -Infrared Spectroscopy (IRS) and Raman Spectroscopy (RS)
Near Surface (Intact Particle, Particle Thin Section, Thin Foil)	-	-	-Auger Electron Spectroscopy (AES) -X-Ray Fluorescence Spectrometry (XFS) -X-Ray Photoelectron Spectroscopy (XPS) -Secondary Ion Mass Spectroscopy (SIMS)	-Electron Energy Loss Spectroscopy (EELS) -Infrared Spectroscopy (IRS) and Raman Spectroscopy (RS) -Extended X-Ray Adsorption Fine Structure (EXAFS)
Top Atomic Layer (Intact Particle, Particle Thin Section, Thin Foil)	-Scanning-Tunnelling Microscopy (STM)	-	-	-Extended X-Ray Adsorption Fine Structure (EXAFS)

The methods in Table 7.9 provide information on particle morphology. This can include identification of crystal facets, twinning, and crystal structures. The methods in Table 7.9 also can identify minerals and estimate mineral formula which again work well for crystalline phases. Other methods in the table give elemental abundance or phase association where interrogating beams impinge the sample. Such methods can show elemental composition of mineral grains that have been characterised by other mineralogical methods. Finally, some methods are provided, that can infer an element's valence state or the nature of the bonding environment about an atom. The methods shown in Table 7.9 are not exhaustive, all have been used in matrices similar to combustion residues. Each method is briefly described; their relative advantages and disadvantages are discussed where appropriate. References are provided describing each method in detail.

A number of the techniques used for quantitation and surface microanalysis are comparatively evaluated in Table 7.10. The table discusses radiation sources, emissions, depth of analysis, resolution, detection limits, and some relative advantages and disadvantages for each method.

Transmitted Light Microscopy (TLM)

Transmitted light microscopy (TLM) can be used to view the morphology of small ash particles or powders as individual grains on spindle stages or as mounts on microscope slides. This method provides morphological information on intact bulk powders; it can be used to obtain cross-sectional morphology of particles in thin section. Reviews by Zussman (1967) and Nesse (1991) provide details of these methods.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) can also be used to examine the morphology of ash particles. Like TLM, it provides morphological information on intact particles; however, it can be used to obtain cross-sectional morphology of particles in petrographic thin section.

SEM utilises the secondary and backscattered electrons to derive a reflected energy beam picture of the sample. The beam penetrates the sample to a depth of 2 to 3 μm. Frequently specimens must be sputter coated with gold or palladium to make them electron dense or reflective. Precise detail can be observed up to magnifications of 5,000X. Reviews by Wenk (1976) and Blake (1990) provide further details about this method.

Petrography (Morphology)

Petrography can be used to examine phase morphology of intact ash particles imbedded in epoxy resins in 30 μm thin sections. The method can give exterior particle morphology by examination of the particle outline. It can also be used to look

at phase twinning, alteration, and association in the particle (Nesse, 1991). This method can also be coupled with modal analysis to quantify the relative abundance of phases in a particle cross section (Hutchinson, 1974).

Table 7.10
Comparison of Surface and Bulk Microanalysis Methods

	XRF	XRM	XPS	AES	SIMS
•Interrogating Beam	x-ray	electron	x-ray	electron, x-ray	ion
•Emitted Radiation	x-ray	x-ray	photoelectron	Auger Electron	ion
•Sample Prep[b]	D,G,P	D,P,C	D,CS	D,CS	D,G
•Typical Analysis Diameter	20-30 mm	3-5 μm	1-5 mm	1-5 μm	1-5 μm
•Diameter (minimum)	(-)	(1-2 μm)	(150 μm)	(0.03 μm)	(1-2 μm)
•Depth of Analysis	10-30 μm (1000 μm)	1-3 μm	10-50 Å	10-50 Å	Varies
•Detectable Elements	Na to U	Be to U	Li to U	Li to U	Li to U
•Detection Limits	ppm	ppm	high ppt	high ppt	ppm
•Data Reduction for Quantitation	Established	Established	Improving	Improving	Established
•Dot Mapping Capability	No	Yes	Yes	Yes	Yes
•Specimen Damage	Some	Some	Some	Some	Yes
•Advantages	-Bulk Analysis	-High Resolution	-Surface Sensitive	-Surface Sensitive -High Resolution	Depth Profiling
•Disadvantages	-Low Resolution -Not Surface Sensitive	-Not Surface Sensitive -Destructive	-High Vacuum -Poor Resolution	-High Vacuum -Destructive	Charging

[a]Compiled from Hochella (1988), Bancroft and Hyland (1990) with permissionfrom the Mineralogical Society of America
[b]D = dried, G = ground, P = polish, C = sputter coat, CS = clean surface

Scanning Tunnelling Microscopy (STM)
Scanning tunnelling microscopy (STM) is one of the few analytical tools that can look at the microtopography of a surface down at the atomic layer (Hochella, 1990). The method has recently been developed and utilised for examining geological specimens. This method must be applied to smooth surfaces of intact particles, it may also be considered for looking at exterior surfaces or phase boundaries in particle thin-sections. The reader should refer to Hochella (1990) for additional details of this method.

X-Ray Powder Diffraction (XRPD)
X-ray powder diffraction (XRPD) is a very important tool for characterising the mineralogy of crystalline phases in incinerator residues. Detailed principles of this method are given in Zussman (1967), Reynolds (1989), Bish and Post (1989), and Whan (1986).

Care should be taken in selection of the target element to generate the characteristic monochromatic Kα x-ray because of the potential for adsorption of x-rays of certain wavelengths. Copper is usually used, but cobalt can be used when samples contain a high percentage of iron.

Powder preparation is very important. Bish and Reynolds (1989), Hutchinson (1974), and Zussman (1967) discuss preparation methods. Particle sizes too large cause problems such as extinction and microabsorption. They can also interfere with the underlying assumptions of random orientation. For very coarse-grained or coarse-phased crystals in ash, particle size production will create a particle size equal to a phase size. For very fine-grained or fine-phased crystals in ash, particle size may exceed phase size. It is best if powders are ground close to 10 μm in diameter or that phase size is less than 10 μm. Larger particle sizes give qualitative information, smaller particle sizes can be used for quantification (Snyder and Bish, 1989). Bish and Reynolds (1989) also discuss methods of sample mounting (smears, packed tubes, thin films), requisite sample thickness, characteristics needed for the sample surface, and procedures for optimising intensities.

Because ash specimens contain numerous major mineral constituents as well as numerous minor mineral constituents, the identification of mineral phases can be quite complex using typical Hanawalt procedures. Computer-aided methods are available (Smith, 1989). However, verification of information from the computer search routines should be done using standard identification methods.

XRPD can also be used for semi-quantitative analysis of crystalline phases in solids. This can increase sample analytical times from one to two hours to up to fifteen hours. Additional details are provided in Whan (1986). XRPD has been used successfully in characterising combustion residues (Vehlow et al., 1992; Eighmy et al., 1993; Stämpfli, 1992; Kirby and Rimstidt, 1993).

Petrography (Mineralogy)
When light is transmitted through mineral grains or mineral thin sections, a number of characteristic properties of the mineral can be ascertained depending on the behaviour of the light. This is the basis of petrography or optical mineralogy. Light wavelengths can be shortened and slowed down. Light can be reflected, refracted, dispersed, and adsorbed. For isotropic minerals, polarised light will be adsorbed when the polarising filters are cross polar. Mineral identification of isotropic materials can be made by examining grain structure and comparing this information to data bases of isotropic minerals (Nesse, 1991). Anisotropic minerals exhibit characteristic uniaxial or biaxial nature using interference microscopy. Birefringence can also be used to characterise the mineral. Such properties are characteristic of anisotropic minerals. Coupled with refractive index measurements of mineral grains, such information can be used to identify minerals (Nesse, 1991).

This procedure has been used to characterise the crystalline component of bottom ash (Lichtensteiger, 1992; Eighmy et al., 1993). It holds promise when coupled with XRPD and x-ray microprobe analysis (see below).

Scanning Electron Microscopy/X-Ray Microprobe Analysis (SEM/XRM)
As discussed in the scanning electron microscopy section, primary excitation beams can cause characteristic x-rays to be emitted. Using SEM, the technique can be coupled with x-ray microprobe analysis (SEM/XRM). Samples can be characterised visually and then quantified using microprobe analysis. The probe is calibrated with primary standards, and elemental quantification of surface material can be accomplished (it can also be done with petrographic thin sections) by counting the number of x-rays in discrete channels over a continuum of x-ray energies. Dot maps showing the location of emission of the characteristic x-ray can be used to spatially locate elements. There are techniques that use standardless calibrations. The technique must be used with caution given the beam spreading that occurs, however it does provide very useful analysis of element associations particularly if it is coupled with petrography. Kevex (1989), Wenk (1976), Blake (1990), and Whan (1986) provide detailed methods.

Scanning-Transmission Electron Microscopy/X-Ray Microprobe Analysis (STEM/XRM)
It is possible to expand upon the principles of SEM/XRM to make use of transmission electron microscopy analysis of thin foils. This is termed scanning-transmission electron microscopy (STEM) and it can be coupled with x-ray microprobe analysis to be able to quantify elements in thin foils (STEM/XRM). The excitation beam width in transmission systems is only 30Å wide compared to 500Å in SEM. Thus, greater resolution is obtained.

The use of a thin foil is critical to STEM/XRM. The thin specimen means characteristic x-rays are emitted without absorption or fluorescence. As with SEM/XRM, dot maps can be generated. Electron diffraction patterns can also be analysed. One utility is transmitted electrons can be imaged to examine phase microstructure. Wenk (1976), Blake (1990), and MacKinnon (1990) provide detailed methods.

Auger Electron Spectroscopy (AES)

The emission of Auger electrons of specified energy is characteristic of the elements emitting them. Auger electron spectroscopy (AES) can be used to quantify elements in the surface of a sample. It can be used on powders or polished specimens. The reader is referred to Hochella (1988, 1990), Browning and Hochella (1990), Mogk (1990), and Whan (1986) for further details. It has been used successfully in characterising coal fly ash (Farmer and Linton, 1984) and MSW combustion residues (Eighmy et al., 1992, Eighmy et al., 1993).

AES is a relatively rapid method (10 to 15 minutes per sample). Its accuracy is limited to ± 30% for most elements with published sensitivity factors. Electron beam charging can be a problem. Embedding particles in indium foil can overcome this problem. Typical sensitivities are 0.1 to 1.0 atomic percent. This method can also do depth profiling.

X-Ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy (XRF) is a sensitive qualitative and quantitative analytical technique. The method can be used on bulk solids, powders, or fused material. Characteristic X-rays in the 1 to 60 KeV range are emitted from samples after excitation with an external energy beam, usually an x-ray.

The interrogated sample depth may range from a few microns to millimetres depending on the x-ray energy of the impinging beam. Analytical times are relatively fast, in the order of 15 minutes per sample.

The advantages of this method are its applicability to many types of solids (powders, polished specimens, fused specimens), the method is rapid, and the instrumentation is inexpensive. The disadvantages are detection limits in the part per million range and elements of lower atomic number than sodium cannot be readily quantified. More detailed information can be found in Whan (1986).

X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), formerly known as electron spectroscopy for chemical analysis (ESCA), is a sensitive surface analysis technique. In XPS, X-rays are directed at a sample where ionisation of the surface atoms in the sample occurs (Bancroft and Hyland, 1990). As an atom ionises, a photoelectron is emitted from the

atom. The ejected photoelectron has an energy that is in part characteristic of its binding energy. Over a range of binding energies, emitted photoelectrons can be counted in discrete channels. Usually at least one peak or doublet appears for each element (except hydrogen). Peak intensity is used for quantitative analysis (Bancroft and Hyland, 1990). Peak shift, or chemical shift, is also an extremely valuable tool for documenting valency, nearest neighbour affects, and speciation. Detailed reviews are given in Hochella (1988; 1990) and Perry et al. (1990).

XPS is usually conducted with an ion sputtering apparatus to allow for removal of adventitious carbon and oxygen. It can also allow for removal of the top atomic layers of a sample. The method is very slow, quantitative and chemical shift analysis can take many hours. Charging can be a problem with insulated samples. The large beam size means individual particles cannot be analysed. The method is, however, extremely valuable in identifying the relative abundance of elemental species in a sample (Eighmy et al., 1993). Whan (1986) provides more detail on the method.

Secondary Ion Mass Spectroscopy (SIMS)

Secondary ion mass spectroscopy (SIMS) is an excellent near-surface analytical technique. Elements can be quantified to trace levels. High degrees of spatial resolution are obtainable (Hochella, 1990). The method works by bombarding a specimen with an ion beam (Cs^+, O_2^+, or O^-) which sputters atomic and molecular ions from the sample into the vacuum of the instrument. The sputtered ions are then extracted into a mass spectrometer where they are quantified with magnetic and electrostatic sector analysers. Detailed methods are provided by Metson (1990). The method has been used to characterise coal fly ash (Farmer and Linton, 1984) and MSW combustion residues (Eighmy et al., 1993).

Analytical times can be long (a few hours). Charging by insulated specimens is very problematic. Indium foil-mounted powders can be used to avoid this problem (Eighmy et al., 1993). It is sometimes difficult to quantify sputtering rate. Nevertheless, it is the most sensitive depth profiling method. Whan (1986) provides more detail.

Electron Energy Loss Spectroscopy (EELS)

Electron energy loss spectroscopy (EELS) is one tool to look at element valency and bonding, it is based on the principles of studying the effects of primary electron beam elastic scattering. The method is used with very thin foils. A spectrum of energy of the transmitted electron ranges from high energy loss to low energy loss. The energy loss spectrum has characteristic edges and x-ray emissions that describe the valency of an element and the bonding environment of an element. Krishnan (1990) provides details about the method.

X-Ray Adsorption Spectroscopy (XAS) and Extended X-Ray Adsorption Fine Structure (EXAFS)

X-ray absorption spectroscopy (XAS) is another analytical tool to characterise the bonding environment of an element. The method is rather new and requires a synchrotron radiation source that provides huge and energetic X-ray fluxes (as compared to fluxes seen in XRM or XRPD target bombardment). The method works at the 1000 ppm level and can provide detailed information of bond distance, number, and type of nearest neighbour. It works for almost all elements in crystalline or amorphous solids, liquids, and gases. It works both in bulk specimens and at interfaces.

The X-rays of precise incident energy from the synchrotron are absorbed by a sample with various degrees of absorbitivity. Very large absorption edges occur when an inner orbital electron is excited. This absorption occurs when the energy of the incident x-ray photon equals the energy required for excitation of the inner orbital electron. As x-rays of increasing energy are applied, absorption is a smooth function until a characteristic edge is encountered. Usually, multiple edges are seen, one occurring at high x-ray energy when a K-level (1S) electron is excited and at lower x-ray energy when L-level electron excitations occur. The energy of these absorption edges is very precise. Subtle differences in the location of this edge occur because of element oxidation state, nearest-neighbour bonding, and geometry. After the absorption edge, absorbance decreases and shows modulation that is characteristic and comprises the extended component of XAS or extended x-ray absorption fine structure (EXAFS). Brown et al (1988) provide a detailed description of this complex method.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) can be used to evaluate the speciation of silicon-29 and aluminum-27 in solids. Kirkpatrick (1988) describes the method in detail, it has been used to examine the degree of hydration of silicon and aluminum in Portland cements (Ortego et al. 1991, Cartledge et al., 1990).

The chemical shift of a ^{29}Si nucleus in five silicate speciated states; e.g. SiO_4^{4-} (Q°), $Si(OSi)O^{3-}$ (Q^1), $Si(OSi)_2O_2^{2-}$ (Q^2), $Si(OSi)_3O^-$ (Q^3), $Si(OSi)_4$ (Q^4), can be used to look at the change in condensation of silicon-oxygen tetrahedra and formation of chains of Q^1 and Q^2 from Q° units during hydration. Chemical shifts are also seen as hydration of the four-coordinate to the six-coordinate aluminate phase occurs for $^{27}A1$. These techniques hold promise for evaluating aging reactions in bottom ash.

Analytical times range from 30 minutes to 48 hours. Care must be taken to remove magnetic material from the sample. Whan (1986) provides more details about the method.

Infrared Spectroscopy (IRS) and Raman Spectroscopy (RS)
Infrared spectroscopy (IRS) and Raman spectroscopy (RS) involve the use of light to probe the vibrational behaviour of molecules in solid phases (McMillan and Hofmeister, 1988). Vibrational energies of molecules and crystals, in the range of 0-60 kJ/mole (or 0-5,000 cm^{-1}), correspond to the wavelength of infrared light. The absorption of infrared light to promote vibration can be characteristic and is thus termed an infrared absorption measurement. Molecular vibrations can be evaluated with light scattering techniques. Changes in the energy of scattered visible light, caused by inelastic interactions with vibrational modes, promote Raman scattering. Both infrared and Raman spectroscopes generate absorption or scattering spectra as a function of energy. The spectra produced are vibrational spectra. It is dependent on interatomic forces and is therefore sensitive to microscopic structure and bonding. The methods work well for crystalline or amorphous solids, liquids, gases, and for elements of low atomic weight (McMillan and Hofmeister, 1988).

Gas cells and cuvettes are used to hold gas or liquid specimens, though thin polished surfaces can be used. Packed capillary techniques can also be used for powders. Detailed preparation methods as well as interpretation of complex spectra are outlined in MacMillan and Hofmeister (1988). The method has been successfully applied to MSW fly ash (Henry et al., 1983).

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