

Appendix A: Background information to the instruments used

The light microscope

When viewed under a binocular microscope, mortar components' sizes and colours can be determined. A disadvantage of this method is that if the mortar samples are dirty, it may be difficult to distinguish the real colours of the mortar components and inclusions while cleaning the mortar with solvents may alter their composition. While mortar samples can be broken with a scalpel tip to expose a fresh edge, it was deemed important to try to keep the outer, exposed parts as much as possible during the sampling process. This due to the fact that by retaining the exposed parts, comparative studies could be made between the outer and core parts of the samples.

X-ray diffraction

X-rays are electromagnetic radiation of wavelength about 1 \AA (10^{-10} m), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structures at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. X-ray diffraction is in fact, one of the most important characterization tools used in solid state chemistry and materials science¹.

The X-ray radiation most commonly used is that emitted by copper. When the incident beam strikes a powder sample, diffracted beams may be detected by using a moveable detector such as a Geiger counter, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of 2θ values at a constant angular velocity. Routinely, a 2θ range of 5 to 70 degrees is sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter is usually 2θ of 2degrees per minute and therefore, about 30 minutes are needed to obtain a trace².

Nowadays most X-ray Diffraction analysis (including the one used here) is done with a goniometer, a device in which the variation of intensity of the diffracted X-radiation is measured by scanning an ionisation detector through a range of angles – usually 0 to 100° . Goniometer spectra are thus produced³.

¹ Whittingham: 1997: Xray powder diffraction

² Whittingham: 1997: Xray powder diffraction

³ IOP: Projects: Chemical composition by X rays

Scanning Electron Microscope

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, as well as its low cost. Other types of electron emitters include lanthanum hexaboride (LaB6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally-assisted Schottky type, using emitters of zirconium oxide⁴.

The electron beam, which typically has an energy ranging from a few hundred eV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion (scanning in parallel lines) over a rectangular area of the sample surface⁵.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as

⁴ Goldstein, Newbury, Echlin, *et al.*: 1981

⁵ Goldstein, Newbury, Echlin, *et al.*: 1981

variations in brightness on a cathode ray tube. The raster scanning is synchronised with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image is nowadays digitally captured and displayed on a computer monitor and saved to a computer's hard disk⁶.

Thus, scanning electron microscopes (SEM) produce an electron beam that unlike that of Transfer Electron microscopes, (TEM) does not at any time carry a complete image of the specimen. The SEM produces images by probing the specimen. The secondary electron detector is the conventional imaging mode in most SEMs. Because the intensity of the back-scattered electrons (BSE) signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. Characteristic X-rays on the other hand, are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic x-rays are used to identify the composition and measure the abundance of elements in the sample⁷.

Sample preparation

All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM (including the one used here) can examine any part of a 15 cm semiconductor wafer, and some can tilt an object of that size to 45 degrees⁸.

For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub but nonconductive specimens (as the ones in

⁶ Goldstein, Newbury, Echlin, *et al.*: 1981

⁷ Goldstein, Newbury, Echlin, *et al.*: 1981

⁸ Goldstein, Newbury, Echlin, *et al.*: 1981

question) tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultrathin coating of electrically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium and graphite. Coating prevents the accumulation of static electric charge on the specimen during electron irradiation⁹.

Two important reasons for coating, even when there is more than enough specimen conductivity to prevent charging, are to maximise signal and improve spatial resolution, especially with samples of low atomic number. Broadly, signal increases with atomic number, especially for backscattered electron imaging. The improvement in resolution arises because in low-Z materials such as carbon, the electron beam can penetrate several micrometres below the surface, generating signals from an interaction volume much larger than the beam diameter and reducing spatial resolution. Coating with a high-Z material such as gold maximises secondary electron yield from within a surface layer a few nm thick, and suppresses secondary electrons generated at greater depths, so that the signal is predominantly derived from locations closer to the beam and closer to the specimen surface than would be the case in an uncoated, low-Z material¹⁰.

The accumulation of electric charge on the surfaces of non-metallic specimens can be avoided by using environmental SEM (though not available here). In an Environmental SEM, the specimen is placed in an internal chamber at higher pressure than the vacuum in the electron optical column. Positively charged ions generated by beam interactions with the gas help to neutralize the negative charge on the specimen surface. The pressure of gas in the chamber can be controlled, and the type of gas used can be varied according to need. Coating is thus unnecessary, and X-ray analysis unhindered¹¹.

⁹ Goldstein, Newbury, Echlin, *et al.*: 1981

¹⁰ Goldstein, Newbury, Echlin, *et al.*: 1981

¹¹ Goldstein, Newbury, Echlin, *et al.*: 1981

Detection of secondary electrons

The most common imaging mode collects low-energy (<50 eV) secondary electrons that are ejected from the k-orbitals of the specimen atoms by inelastic scattering interactions with beam electrons. Due to their low energy, these electrons originate within a few nanometers from the sample surface. The electrons are detected by a scintillator-photomultiplier system. The secondary electrons are first collected by attracting them towards an electrically-biased grid at about +400V, and then further accelerated towards a phosphor or scintillator positively biased to about +2000V. The accelerated secondary electrons are now sufficiently energetic to cause the scintillator to emit flashes of light (cathodoluminescence) which are conducted to a photomultiplier outside the SEM column via a light pipe and a window in the wall of the specimen chamber. The amplified electrical signal output by the photomultiplier is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected to analog-to-digital conversion and displayed and saved as a digital image. As noted before, this process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Using this technique, image resolution less than 1 nm is possible¹².

SEM offers a wide range of magnifications from about $\times 25$ (about equivalent to that of a powerful hand-lens) to about $\times 250,000$ and exceptionally to 2 million times in the Hitachi S-5500 in-lens Field Emission. Unlike optical and transmission electron microscopes (TEM) however, image magnification in the SEM is not a function of the

¹² Goldstein, Newbury, Echlin, *et al.*: 1981

power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Thus magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x,y scanning coils, and not by objective lens power. In fact, because the SEM image relies on surface processes rather than transmission, it is able to image bulk samples up to several centimetres in size (depending on instrument design) and has a much greater depth of view, and so can produce images that are a good representation of the 3D structure of the sample¹³.

The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the electron-optical system which produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam. The spot size and the interaction volume are both large compared to the distances between atoms, so the resolution of the SEM is not high enough to image individual atoms, as is possible in the shorter wavelength (i.e. higher energy) transmission electron microscope (TEM). The SEM has compensating advantages, though, including the ability to image a comparatively large area of the specimen; the ability to image bulk materials (not just thin films or foils); and the variety of analytical modes available for measuring the composition and properties of the specimen. Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm. In general, SEM images are easier to interpret than TEM images¹⁴.

¹³ Goldstein, Newbury, Echlin, *et al.*: 1981

¹⁴Goldstein, Newbury, Echlin, *et al.*: 1981

Seperation of the samples' clay fraction

Clay minerals are made up of extremely fine solids. Most clays have a layered arrangement of sheet-like silica tetrahedrons and alumina octahedrons i.e. layered silicates or as more commonly referred to, phyllosilicates. Other clay minerals have lath/chain structures while others are allophanes i.e. non crystalline and amorphous.

Clay minerals are divided in three main groups factors as follows¹⁵;

- The T/O or 1:1 group consist of an alternating tetrahedral and octahedral layers and a spacing of 7Å.
- The T/O/T or 2:1 group that consists of an octahedral layer sandwiched by two tetrahedral layers. This group is further divided into expanding lattice and non expanding lattice mineral types. In the expanding lattice group, one finds minerals such as smectite and vermiculite, which, have a spacing of 14 to 15 Å. Illite is an example of the non-expanding lattice type with a 10Å spacing. The lath/chain-structure minerals are sometimes combined with the group as they too consist of alternating layers, this time, of hydrous-magnesian nature. Sepiolite and paygorskite are such minerals with a spacing of 12 and 10,4 Å respectively.
- The mixed layer T/O/T/O minerals are also known as micas. An example of which, is chlorite with a 14 Å spacing.

Using Stockes law (see below), it is calculated that for natural sedimentation of the clay fraction to occur (i.e. particles <2µm), 1h35min and sampling at 2cm above the suspension are needed or after 8hours and sampling at 10cm above the suspension formed.

$$t = (190 \cdot x) / D^2$$

Where;

¹⁵ Lecture notes simplified after Brindley: 1966

t = time of sedimentation in minutes (min)

x = distance of particle drop in centimetres (cm)

D= diameter of the particles in micrometers (μm)

In order to speed up the natural sedimentation process and make sure that rinsing from the acid takes place, centrifugation is used.

The parameters used for the centrifugation process are shown below as well as a sketch showing centrifuge distances [Fig. 75].

$$t = \frac{63 * 10^8 * \eta * \log_{10}(R/S)}{N^2 * D^2 * \Delta d}$$

Where;

t = time of centrifugation in minutes

η = dynamic viscosity of the liquid (in this case, water) in poises (P) i.e. a centimeter-gram-second unit of dynamic viscosity equal to one dyne-second per square centimeter¹⁶

R = radius of the rotary container into which the solutions are placed in centimetres (cm)

S = distance of the rotation at the surface of the liquid (cm)

N = speed of turns of the centrifugation rotary containers per minute (tr/min)

D = diameter of the particles in micrometers (μm)

Δd = the difference in density between the liquid and that of clay particles (an average of 2.65 is taken for the latter)

¹⁶Answers.com: 17/12/2008

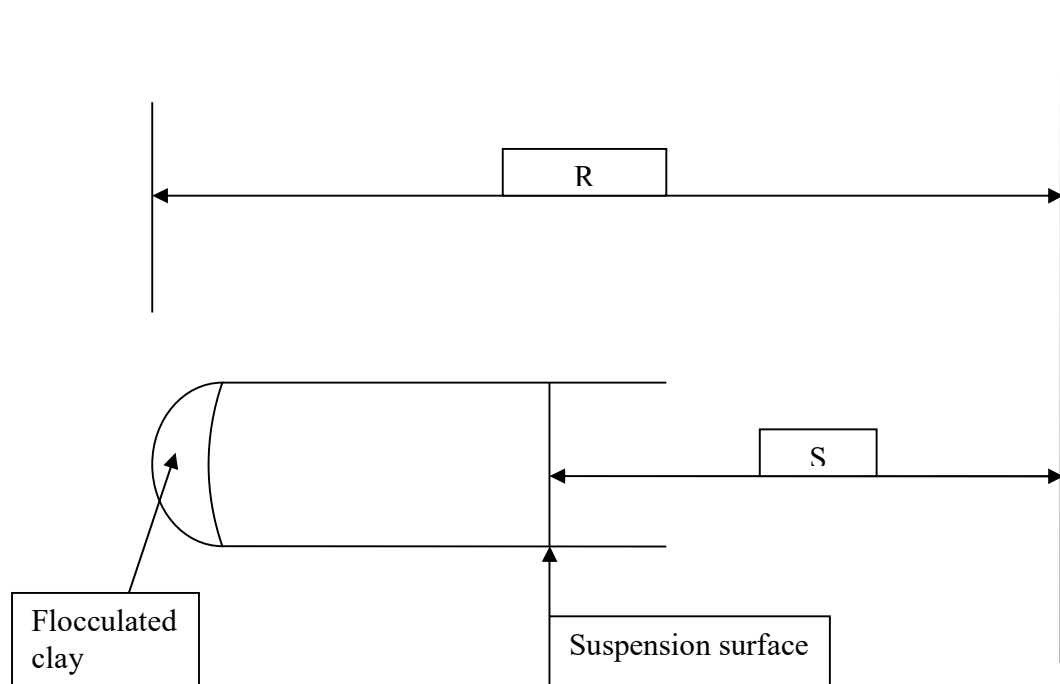


Figure 1: Sketch showing centrifuge distances that determine the time of centrifugation

Once separated, the clay fraction can be identified by XRD which, determines the distance between the layers (d_{001})

- after exposure to normal conditions (i.e. free air)
- after exposure to different pre-treatments i.e. saturation in ethylene glycol atmosphere for 12 hours, saturation in hydrazine for 12 hours and to heat (490° for 4 hours).

These processes ensure good orientation of the clay particles for a good reading of the X-ray diffraction while the different treatments help to distinguish between different types of the clay minerals present.

Water adsorption and desorption tests

Two types of water condensation can take place in a porous system – adsorption and capillarity

Adsorbed water refers to that layer of water molecules condensed on the surface of the solid particles of the sample. The quantity of this adsorbed layer is determined by the specific surface area of the sample material, the hygrothermal ambient conditions (i.e temperature and vapour pressure) and the degree of affinity between the solid particles and the vapour. Thus adsorption of a fluid by a solid is generally represented by curves that indicate the development of the water adsorbed at equilibrium in relation to a given relative humidity while the temperature is kept constant¹⁷.

¹⁷ Merouani : 1987 : 33-4

Porosimetry is a technique is based on the capillary law governing liquid penetration into small pores i.e. the Washburn equation;

$$D = - (4\gamma \cos\phi / P)$$

Where D = Pore diameter, P=applied pressure, γ =surface tension, ϕ = contact angle.

The technique thus involves the intrusion of a non-wetting liquid (often mercury) by means of applying pressure into a material through the use of a porosimeter. The pore size can be determined based on the external pressure needed to force the liquid into a pore against the opposing force of the liquid's surface tension.

Since mercury has a high surface tension and is non wetting to most materials, its angle of contact and radius of curvature are used to calculate the pore diameter into which it intrudes at a given pressure.

Since the technique is usually done under vacuum, the gas pressure begins at zero. The contact angle of mercury with most solids is between 135° and 142°. The surface tension of mercury at 20 °C under vacuum is 480 mN/m. With the various substitutions, the equation becomes:

$$D_p = \frac{414}{P_L}$$

As pressure increases, so does the cumulative pore volume. From the cumulative pore volume, one can calculate the pore diameter and when 50% of the total volume has been added, the median pore diameter can also be calculated¹⁸.

The fact that mercury extruding from pores upon reduction of pressure is not always in accord with the above equation i.e. pore diameters are always offset toward larger

¹⁸ Washburn: 1921: 273–283

diameters and equivalent volumes of mercury extruding at pressures lower than those at which the pores were intruded. This is attributed to pore irregularities giving rise to enlarged chambers and 'ink-well' structures as well as the hypothesis that receding contact angles are less than advancing ones.

This calculation is thus in reality taken as an approximate way of calculating pore space as to know the actual shape of pores would otherwise be a most complex problem. It is also to be pointed out that the surface tension of mercury varies with purity. Thus a general value of 485 dynes/cm is usually taken. The contact angle between mercury and the solid containing the pores used here was taken as 130 degrees.

The analysis/ system process

As pointed to above, the analysis consists of injecting with mercury a previously dried sample of the material to be investigated¹⁹.

The first phase of the low pressure analysis consists of the evacuation of gases from the penetrometer which is then backfilled automatically with mercury. The second phase of the low pressure analysis is the collection of data at pressures up to the last pressure point specified in the pressure table.

As pressure increases, mercury moves into the sample's pores, vacating the stem as a result (i.e. intrusion). Intrusion of different sized pores occurs at different pressures. It is taken that the greater the pressure, the smaller the pore diameter into which mercury can be forced.

The volume of mercury in the penetrometer's stem is in turn measured by determining the penetrometer's electrical capacitance. Capacitance is the amount of electrical charge stored per volt of electricity applied. The penetrometer's capacitance varies with the length of the penetrometer stem that is filled with mercury.

¹⁹ Merouani: 1987: 19

When the penetrometer is initially backfilled with mercury, the mercury extends the entire length of the penetrometer. As increasing pressure causes the mercury to intrude into the sample's pores, the volume of mercury in the penetrometer stem decreases by an amount equal to the volume of the pores filled. This decrease of mercury in the length of the penetrometer stem causes a reduction in the penetrometer's capacitance. The software of the mercury porosimetry machine converts measurements of the penetrometer's capacitance into data points showing the volume of mercury intruding into the sample's pores.