



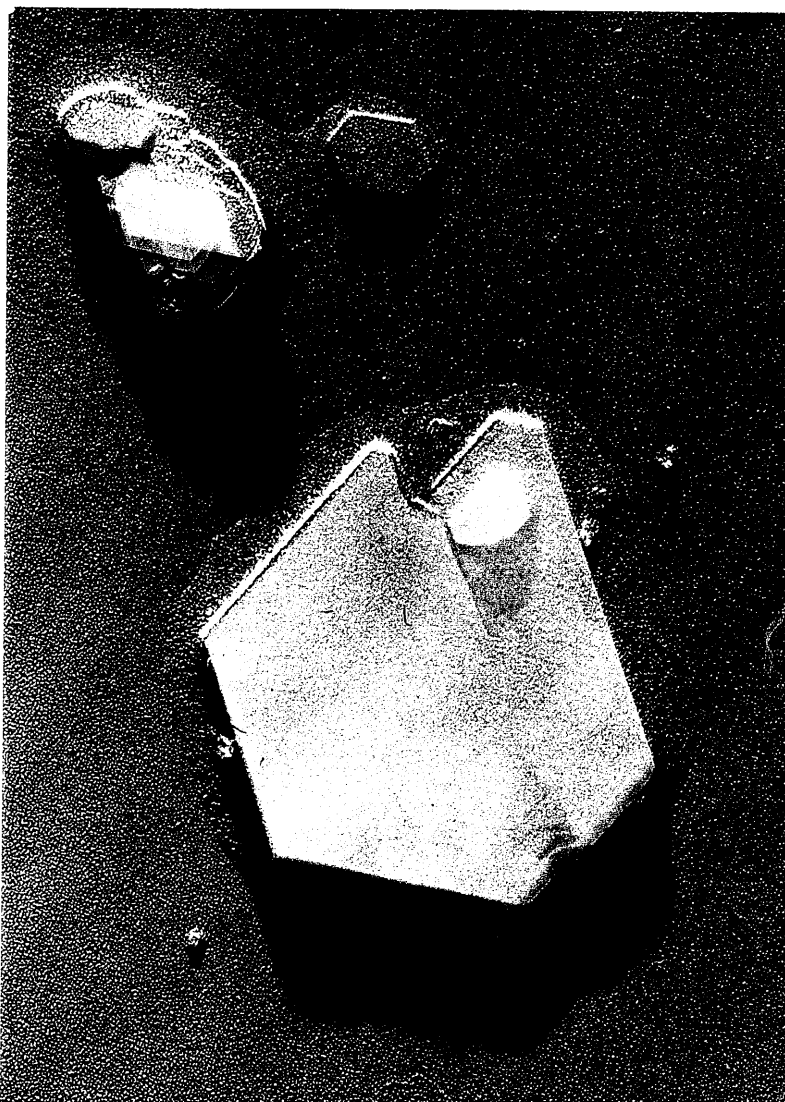
British Geological Survey

ODA

TECHNICAL REPORT WG/93/1
Mineralogy and Petrology Series

Industrial Minerals Laboratory Manual
KAOLIN

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Industrial Minerals Laboratory Manual

KAOLIN

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Transmission electron micrograph of well-formed hexagonal crystals of kaolinite from Uganda (X 75000). The crystals have been metal-shadowed to allow measurement of thickness and aspect ratio.

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Preface

Industrial mineral raw materials are essential for economic development. Infrastructure improvement and growth of the manufacturing sector requires a reliable supply of good quality construction minerals and a wide range of other industrial mineral raw materials.

Although many less developed countries have significant potential industrial mineral resources, some continue to import these materials supply their industries. Indigenous resources may not be exploited (or are exploited ineffectively) because they do not meet industrial specifications, and facilities and expertise to carry out the necessary evaluation and testwork are unavailable. Unlike metallic and energy minerals, the suitability of industrial minerals generally depends on physical behaviour, as well as on chemical and mineralogical properties. Laboratory evaluation often involves determination of a wide range of inter-related properties and must be carried out with knowledge of the requirements of consuming industries. Evaluation may also include investigation of likely processing required to enable the commodity to meet industry specifications.

Over the last 10 years, funding from the Overseas Development Administration has enabled the British Geological Survey to provide assistance to less developed countries in the evaluation of their industrial mineral resources. This series of laboratory manuals sets out experience gained during this period. The manuals are intended to be practical bench-top guides for use by organisations such as Geological Surveys and Mines Departments and are not exhaustive in their coverage of every test and specification. The following manuals have been published to date:

- Limestone
- Flake Graphite
- Diatomite
- Kaolin
- Bentonite
- Construction Materials

A complementary series of Exploration Guides is also being produced. These are intended to provide ideas and advice for geoscientists involved in the identification and field evaluation of industrial minerals in the developing world. The following guide has been published to date:

Biogenic Sedimentary Rocks

A J Bloodworth
Series Editor

D J Morgan

Kaolin

1. INTRODUCTION

Kaolin is a commercial term used to describe white clay composed essentially of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The term is typically used to refer to both the raw clay and the refined commercial product. This manual describes the laboratory assessment of 'non-plastic' kaolin (sometimes known as china clay); plastic kaolinitic clays (or ball clay) are dealt with elsewhere in this series of manuals. Although originally valued for use in the manufacture of whiteware ceramics, the principal use of kaolin is now in the filling and coating of paper. The mineral is also used to a lesser extent as a filler in paint, rubber and plastics, as well as in a wide range of other applications. Kaolins are distinguished from other clays by whiteness, and fine, controllable particle size. It is generally necessary to process kaolin from the crude state in order to optimise these highly commercial properties.

This manual is one of a series produced as part of the BGS/ODA R&D Project 'Minerals for Development'.

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2. GEOLOGICAL OCCURRENCE

Kaolin deposits are generally classified as either primary (residual) or secondary (sedimentary). The mode of formation of the kaolin may have considerable influence on the mineralogy, chemistry and morphology of the clay and may dictate the type of mining and beneficiation process employed to achieve a commercial product.

2.1 Primary kaolins

Primary deposits of kaolin are generally formed by *in situ* alteration of aluminosilicate-rich parent rock (such as granite or granitic gneiss) by weathering, hydrothermal, and, more rarely, volcanic processes. The nature of the parent rock may be critical in determining the quality of the kaolin; the abundance and nature of iron-bearing minerals is particularly important. The kaolinite content of primary kaolins may vary, though 20-30% is not untypical.

Humid tropical weathering of granitic rocks is a major process in kaolinite formation through the intense leaching of alkalis from aluminosilicate minerals. Kaolin deposits form as residual mantles at or near the surface. Occasionally they may occur in association with bauxite deposits.

Hydrothermal alteration of aluminosilicate-bearing rocks is an important kaolinisation process. The host rock must be sufficiently fractured to allow the circulation of hot groundwater. High-heat-flow granites may provide optimum thermal conditions required to drive groundwater convection cells. High-quality kaolins are produced from granitic host rocks which are relatively low in iron-bearing minerals such as biotite.

The kaolin resources of south west England are regarded as typical primary deposits (Bristow, 1987). These world class deposits are developed within high-heat-flow granites rich in radiogenic elements such as U, Th and K. High-temperature hydrothermal circulation associated with a relatively early phase of mineralisation is thought to have increased the permeability of the granite and reduced its iron content. This was followed by the main phase of kaolinisation, carried out by low-temperature convection cells of meteoric groundwater. This process was augmented by an intense period of deep tropical weathering during the Palaeogene. The intensity of kaolinisation is controlled by the joint patterns within the granite. Kaolinised zones are funnel or trough-shaped, narrowing downwards (Figure 1). Sodium feldspars are preferentially altered to kaolinite in these granites.

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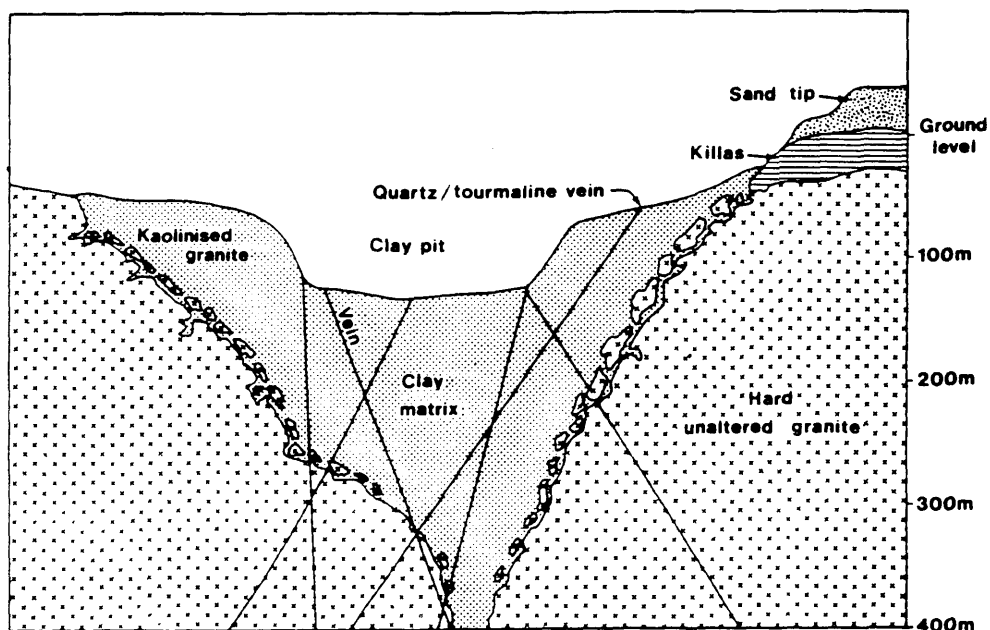


Figure 1. Idealised section of a kaolin pit in south west England (After Bristow, 1969)

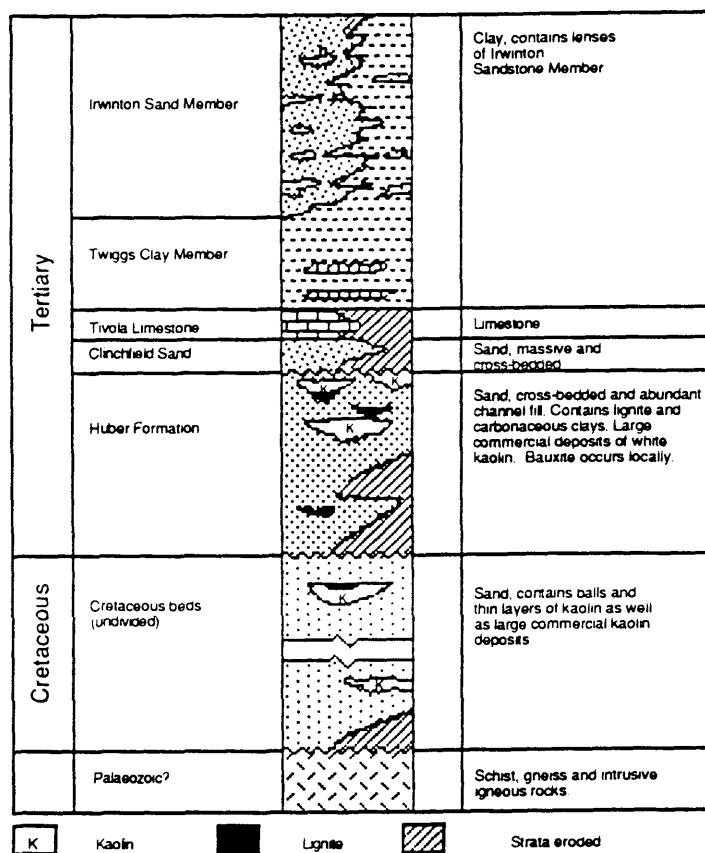


Figure 2. Generalised geological section through kaolin-bearing formations, Georgia, USA (After Patterson & Murray, 1984).

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2.2 Secondary kaolins

Kaolin deposits occurring in sedimentary rocks are generally classified as 'secondary' or 'sedimentary'. Some may have formed by the transportation and deposition of kaolinite formed elsewhere. However, diagenetic and weathering processes appear to play an important role in the *in situ* formation and modification of sedimentary kaolins. Deposits often contain in excess of 60% kaolinite. Lower concentrations occur in kaolinitic sand, formed by the *in situ* alteration of feldspathic sandstones.

The extensive sedimentary kaolin deposits of the south-eastern United States occur in a belt extending over some 400 km. Economic deposits occur within Upper Cretaceous and Palaeogene intertidal sediments as lenses and tabular bodies of kaolin (Figure 2). The clays contain 90-95% kaolinite, with quartz, ilmenite and anatase being the main impurities (Patterson & Murray, 1984).

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3. MINING AND REFINING

The techniques used in mining and refining (beneficiation) of primary and secondary kaolins are reviewed in this section. An understanding of the processing methods used in the refining of commercial kaolins is essential for effective laboratory appraisal of these raw materials. A more comprehensive discussion of commercial kaolin mining and processing techniques can be found in Highley (1984) and Pemberton (1989).

3.1 Mining

In south-west England the kaolinised granite is stripped of overburden and the clay matrix mined with high-pressure water monitors, which disintegrate the friable, kaolinised granite and disperse the kaolinite into suspension. Hard, unkaolinised granite is left behind and is removed by truck and shovel. In order to maintain a consistent blend from a variable clay matrix, up to twelve different positions may be worked simultaneously. The slurry collects in the pit bottom and is then pumped to the refining system.

The exploitation of secondary kaolins shows many differences from primary deposits. They are worked by conventional strip mining methods with overburden thicknesses of up to 45 m. In the south-eastern USA the clay is excavated from widely-dispersed pits and the clay transferred to a central refining plant. The clay may be moved in the raw state, or it may be blunged (dispersed) to produce a slurry which is then pumped to the refining plant. After degrading to remove quartz, the kaolinite content may be sufficiently high not to require further refining, subsequent processing principally being dedicated to improving the brightness and particle-size distribution of the clay.

3.2 Refining

The two principle objectives of kaolin refining are the removal of impurities and the production of the desired particle-size distribution. Air-floated kaolins are produced in the USA for low-grade applications. However, most kaolin is refined by wet classification involving the separation of fine platy kaolinite from coarser quartz, feldspar and mica using the different settling velocities associated with particle size as governed by Stokes' Law. Kaolinite is generally concentrated in the fine fraction, therefore beneficiation can be achieved by simple size separation (Figure 3). A cut at between 10 and 20 μm removes all of the quartz and most of the mica and for many years this was the only form of beneficiation used by the industry.

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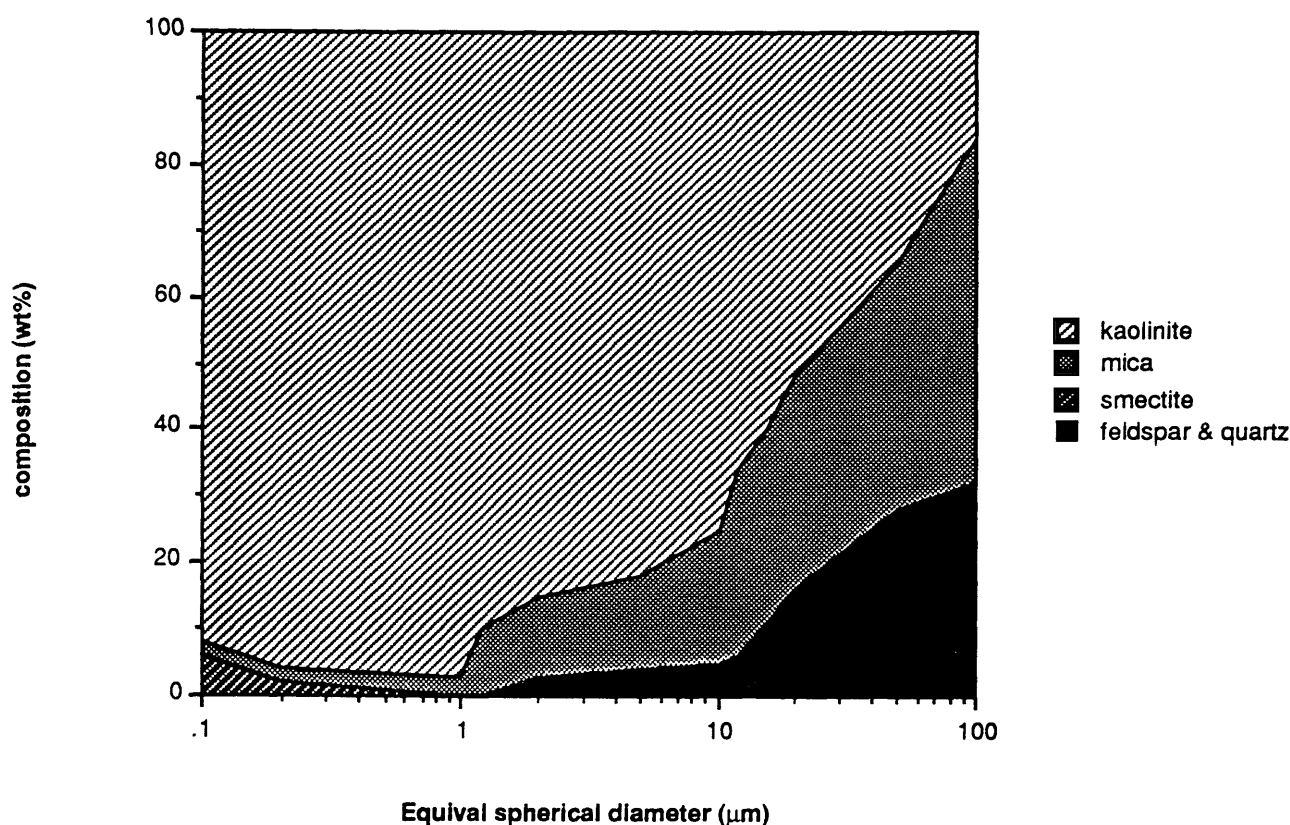


Figure 3. Variation in mineralogy of a kaolin from south-west England with particle size (After Jepson, 1984).

The wet refining of primary and secondary kaolins follows similar routes and the south-west England operations will be used to illustrate the main techniques. A generalized flowsheet of the process route followed in south-west England is shown in Figure 4.

Spiral classifiers or bucket wheel classifiers form the first stage of the separation process, the objective of which is to remove all material coarser than 250 µm (mainly quartz and feldspar). Following sand removal, the <250 µm clay slurry is pumped to hydrocyclones for the next stage of refining. The <53 µm 'overflow' (fine fraction) from the hydrocyclones is thickened prior to being fed to the hydroseparation system. This consists of circular tanks where the suspension is allowed to settle under gravity to remove the >15 µm fraction. A fine saleable product is recovered (45% <2 µm), suitable for paper filler purposes (see Section 4.2). High-performance, small-diameter hydrocyclones are now replacing hydroseparators with savings on capital costs. The use of hydrocyclones dispenses with the need to chemically deflocculate the clay.

Clays used for paper-coating purposes must have finer particle sizes (see Section 4.2). This is achieved by using continuous centrifuges that

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can separate kaolin into coarse and fine fractions. Filler grade material is used as feed to this process. A typical product will be 75% <2 μm , although some processes are capable of achieving products at 95% <2 μm and 80% <1 μm . The 'underflow' (coarse fraction) from the primary centrifuges can be either used as a coarse filler clay, or be retreated in secondary centrifuges and fed back to the primary centrifuges.

3.2.1 Flotation

The processes described so far all depend on particle size separation to beneficiate the kaolinite. Although kaolinite is concentrated in the fine fraction, the mineral also occurs in the coarser size fractions. Treatment of centrifuge underflow by ultraflotation recovers coarse kaolinite, which after sand grinding produces filler or coating grade clays depending on residence times. Operation of sand grinding in closed circuit with a hydrocyclone results in products with well controlled particle sizes.

This system is also used to treat the hydroseparator underflow. Although this material contains only 10% <2 μm , it has a kaolinite content of approximately 60%; mica, quartz and feldspar are the main impurities. After flotation, the kaolinite content can be raised to 80% and abrasive quartz and feldspar reduced to about 2%. The introduction of flotation technology has improved kaolinite recovery. This has increased reserves, and allowed the retreatment of mica waste residues into which coarse kaolinite has been lost.

In the south-eastern USA, froth flotation is used to remove fine-grained anatase and other titano-ferrous impurities. This significantly reduces the TiO_2 content of the clay and improves its brightness.

3.2.2 Other beneficiation processes

A number of other processes are used to improve or modify the properties of the clay other than those based on particle size. These processes include;

- Magnetic separation
- Selective flocculation
- Leaching
- Delamination
- Calcination

Impurities in kaolin which cause particular problems are iron-bearing minerals and fine-grained anatase. These tend to be more abundant in

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sedimentary kaolins. The removal of colouring oxides is essential if high-brightness saleable grades are to be produced. High-intensity magnetic separators are a standard processing technique used in the kaolin industry. This process uses a canister filled with fine stainless steel wool that when magnetized will remove iron- and titanium-bearing minerals from the kaolin slurry as it passes through the canister. In south-west England, this technique is used to separate mica and tourmaline from ceramic clays leading to a 40% extraction of Fe_2O_3 , and thus giving a significant gain in fired brightness.

Titano-ferrous impurities may be selectively flocculated to form aggregates by the addition of small quantities of a polymeric flocculant. The method is used to beneficiate kaolins from the deposits in south eastern USA.

Chemical leaching is also a standard beneficiation technique that is used to improve the brightness of kaolin. The addition of a strong reducing agent, usually sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), in an acid environment reduces ferric to ferrous iron. This process results in a 2 to 4% increase in brightness. The higher solubility of ferrous iron allows a small proportion of the hydrated iron oxides coating the clay to be removed in solution. Ozone and chlorine may be used to improve brightness by oxidising organic matter.

Delaminated clays with a high brightness and high aspect ratio (particle length/particle diameter) are produced by subjecting the clay to a grinding or similar attrition operation using pug mills or sand grinding units. This treatment breaks down vermicular stacks of coarse kaolinite into thin plates.

There is an increasing demand for calcined clays which exhibit strong open aggregates with improved optical properties and hardness (see Sections 4.4.1 and 4.4.2). By varying the nature and composition of the feedstock and the firing schedule (the maximum temperature achieved, time sustained and rate of temperature increase above 400°C), a range of products with different properties and uses can be produced.

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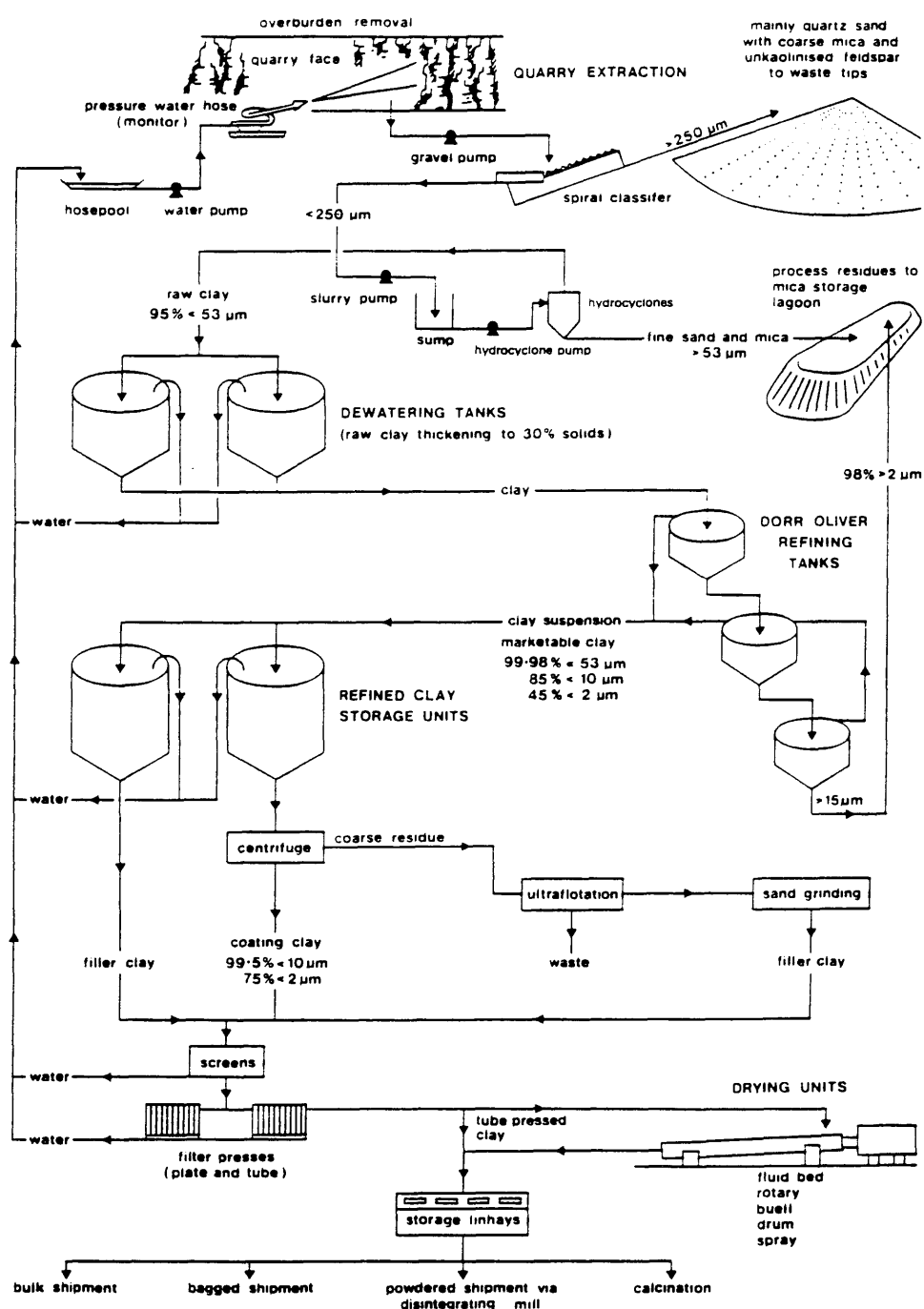


Figure 3. Processing flowsheet used to refine the kaolin deposits in south west England (from Highley, 1984).

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4. INDUSTRIAL APPLICATIONS

Kaolin forms the basis of an industry of worldwide importance with output being in excess of 20 Mt in 1990 valued at about \$2000 million. In terms of value, about 75% is used in papermaking, 10% in ceramics and 15% in the paint, rubber and plastics industries; the latter category also includes a range of miscellaneous applications.

4.1 Critical properties

The industrial applications of kaolin are based largely on a combination of physical characteristics, different applications demanding distinct combinations of functional properties. Specific grades are therefore rarely suitable for all applications. With the exception of kaolin for use in ceramics, chemical composition is not generally a critical property.

The commercial value of kaolin depends on whiteness and fine particle-size. The latter property also has a bearing on viscosity, colour, abrasiveness and ease of dispersion. Other important properties include its lamellar particle shape (which increases opacity or hiding power), its soft and non-abrasive texture (due to the absence of coarser impurities), and its chemical inertness over a wide range of pH. The presence of surface charges leads to properties which ensures that the mineral is flocculated at low pH and deflocculated at high pH, a feature that is utilised during processing and application. Kaolins have desirable rheological properties, allowing them to be easily dispersed in water to produce slurries of low viscosities, both at low and high shear values and at high solids content, a factor of critical importance in the paper industry.

Increasing demands are being placed on kaolin quality. Process technology is now required not only to purify the mineral, but also to modify particular functional properties.

4.2 Paper

Kaolin is the dominant white mineral used by the paper industry, over 10 Mt/y being consumed worldwide. In the manufacture of paper and board it performs two quite separate functions. As a **filler** it is incorporated into the paper web to reduce cost and improve printing characteristics. It is also used as a **coating** pigment to enhance surface properties of the paper such as brightness, smoothness, gloss and ink receptivity. This allows accurate reproduction of colour printing. The percentage of kaolin used in various papers is given in Table 1. Lightweight coated papers can contain up to 40% kaolin both as a filler and coating medium.

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Table 1. Percentage kaolin used in different paper types.

Paper type	Kaolin wt%
Newsprint	3 - 10
Uncoated	10 - 20
Coated	35 - 40
Lightweight coated	up to 40

Kaolin has a number of desirable properties as a paper filler including a fine, uniform and controllable particle size, ready dispersal in water, softness and low abrasiveness (so that wear on papermaking machinery is reduced), a high brightness giving high light reflectance and increased opacity, and chemical inertness. The incorporation of kaolin between the fibres also gives a smoother paper with good ink receptivity, improved printing characteristics and dimensional stability. Moreover, kaolin reduces the overall cost of the paper by replacing expensive wood pulp. However, whilst it may be desirable to increase the level of filler addition on the grounds of cost, high loadings have an adverse effect on paper strength by interfering with the fibre bonding, the strength-giving component of the paper. Similarly, although finer particle sizes increase brightness, opacity and gloss, their larger surface area interferes with fibre bonding, thereby reducing paper strength. Finer particles also have poorer retention. Control parameters for filler kaolins are particle size, powder brightness and abrasiveness.

For coating purposes kaolin is applied to the surface of the finished paper as a thin film of finely divided mineral suspended in water with an adhesive mixture. Machine-made paper has a relatively rough substrate which can be masked to produce a smoother, brighter, glossier surface, more receptive to ink transfer and ideal for high-quality printing. Particle size exerts the most influence on coating performance, contributing not only to the smoothness, gloss and printability of the coated sheet, but also to the rheological properties of the coating slurry. Coating clays are mainly controlled in terms of particle size, powder brightness and rheology. Gloss, brightness, opacity and smoothness all generally improve with decreasing particle size, although very finely-sized kaolins may give other problems.

Combinations of properties required for filler and coating grades of kaolin are significantly different. Properties of filler and coating grade kaolins are contrasted in Table 2. Coating demands the highest qualities of clay which are brighter and whiter with better glossing properties than filler grades. Since finer kaolinite particles have improved

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brightness, gloss characteristics and superior hiding power, coating grades are much finer than filler grades, with typically >75% -2 μm compared with >30% -2 μm for filler grades. As a general rule the relative cost of kaolin pigment increases as pigment brightness increases and particle size decreases. As a result coating clays command a higher price than filler grades.

Table 2. Typical properties of paper filler and coating kaolins

	Filler clays	Coating clays
Raw ISO* brightness %	76 - 82	81.5 - 90.5
Yellowness%	5.7 - 8	4 - 6.5
% <2 μm	25 - 60	75 - 95
% >10 μm	6 - 25	0 - 6
% >53 μm	0.05 max	0.02 max
Viscosity concentration (% solids at 5 poise at 22°C)	61.2 - 71.5	64.2 - 74.5

* International Standards Organisation (ISO)

Typical particle-size distribution curves for filler and coating clays are given in Figure 5. Particle-size distribution of kaolin products is generally measured using a gravity sedimentation technique such as Andreasen pipette or X-ray sedigraph.

Brightness is defined as the ratio, expressed as a percentage, of the radiation reflected by a body to that reflected by a perfectly reflecting ISO (International Standards Organisation)-approved BaSO_4 standard measured at an effective wavelength of 457 nm with a Carl Zeiss photoelectric reflection photometer. Yellowness is expressed as the difference between the percentage reflectance at 570 nm and 457 nm. ISO standard brightness is widely used in Europe although elsewhere in the world other systems may be used. For reconnaissance studies of kaolin deposits, such as those which might be carried out by a Geological Survey or Mines Department, apparatus is available which provides a low-cost alternative to the more sophisticated equipment used for brightness measurement by large kaolin producers and consumers (see Section 5.2.5 of this manual). Brightness can be improved by fine grinding, magnetic separation, froth flotation and chemical bleaching.

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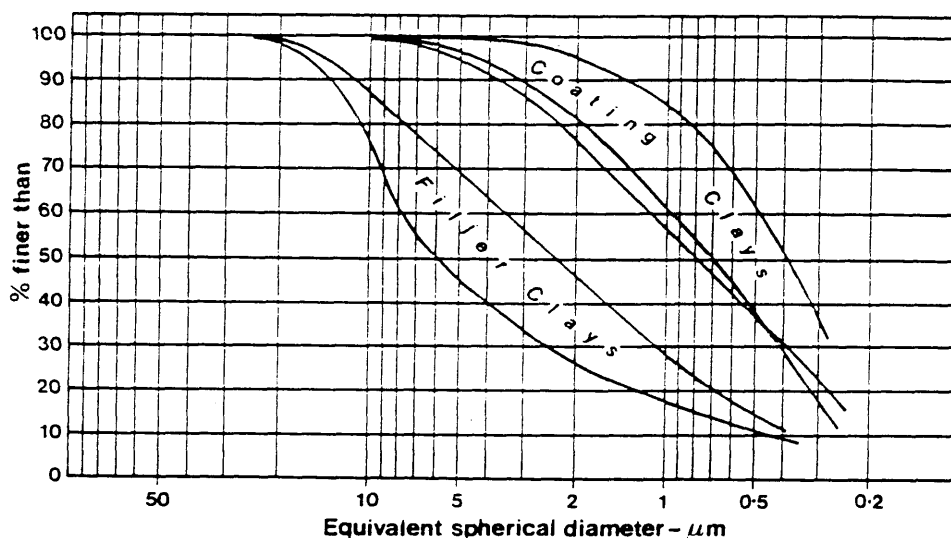


Figure 4. Particle-size distribution of typical coating and filler grade kaolins (from Highley, 1984).

The abrasiveness of kaolin for papermaking is important, although rarely expressed in specifications. The principal focus of wear is on the bronze or plastic papermaking wire and on the coating blade. Although kaolinite is soft (Mohs hardness 2-2.5), other minerals present in the clay such as quartz and feldspar may significantly contribute to abrasiveness. Particle size of the mineral is critical along with hardness, since abrasiveness reduces with particle size. A variety of apparatus may be used to measure abrasiveness. These highly specialised techniques generally measure the abrasiveness of a clay via the weight change in a standard bronze wire abraded by a clay slurry over a specified period of time. Commonly quoted abrasion values include those obtained using the 'Valley' clay abrasion tester or Breunig test values obtained using an 'Eihnehner' machine. Typical values for coating clays and filler clays are 30 and 60-70 g/m² respectively. Apparatus for measurements of this kind is rarely seen outside the specialist laboratories of major kaolin producers and consumers.

Since the coating pigment is applied to the surface of the paper at high speeds as a suspension of high solids content (70%), the rheology of the kaolin slurry is also of critical importance to give a smooth and even coverage of the web. Failure to flow would result in a streaky and blotchy appearance and perhaps breakage of the paper. The physical properties of clay-water suspensions are complex with dilatancy and thixotropy providing the two extremes. Many kaolins are unacceptable for paper-coating purposes because of a high viscosity in suspension which cannot be easily improved by processing. Viscosity is affected by

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contaminant minerals such as smectite and halloysite, as well as particle shape and packing of the kaolinite. Viscosity also increases with specific surface area. The principal rheological specification for paper-grade kaolins is the viscosity concentration value. This is equivalent to the percentage by weight of a chemically deflocculated pigment in an aqueous suspension which has a viscosity of 5 poise at 22°C when measured with a Brookfield RVF 100 viscometer. Typical viscosity concentrations for coating clays vary from 64 - 74 wt%.

Powdered calcium carbonate, sometimes known as 'whiting', is the main alternative to kaolin in the paper industry both for filler and coating applications. The introduction of alkaline and neutral papermaking systems, together with improved technology for producing finer grades, has led to calcium carbonate becoming a significant competitor to kaolin in this market.

4.3 Ceramics

Until the end of the 19th century, kaolin was used almost exclusively in the manufacture of ceramics. Although the tonnages used in this application are now greatly exceeded by those consumed in paper making, whiteware ceramics and refractories remain a major market for kaolin. Kaolin forms an important constituent of a number of ceramic body formulations (Table 3).

Table 3. Typical body compositions for whiteware ceramics (Jepson, 1984)

	Weight % total solids				
	Kaolin	Ball clay	Flux ¹	Quartz ²	Others
Earthenware	25	25	15	35	-
Porcelain	60	10	15	15	-
Bone china	25	-	25	-	50 (bone ash)
Vitreous-china sanitaryware	20-30	20-30	15-25	30-40	0-3 (talc)
Electrical porcelain	20	30	30	20	-
Wall tiles	20	30	-	30-35	10-12 (limestone)

¹ Usually K-feldspar, nepheline-syenite or china stone.

² Silica sand, calcined sand or flint.

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By definition, non-plastic kaolins have low plasticity and low dry strength (due mainly to their relatively coarse particle size). Kaolinitic ball clay is added to most ceramic bodies to confer both plasticity and green/dry strength. The main function of non-plastic kaolin in ceramics is to confer whiteness on the body, therefore fired (as distinct from natural) brightness is the critical property in kaolins intended for this application. A low iron content (<0.9%) is necessary in order to achieve fired brightness values in excess of 83% at 1180°C (Highley, 1984). The absence of iron-bearing minerals such as biotite and tourmaline is also important to prevent specking on the surface of the fired product.

As in kaolins intended for paper manufacture, the rheological properties of ceramic-grade kaolins are an important consideration. The main controls on these properties are the particle-size distribution of the clay and the presence of smectite. The overall effect of increasing smectite concentration on the rheological behaviour of ceramic grade kaolin may be summarized as follows:

- Reduction in casting concentration (maximum amount of clay added to produce a standard slip).
- Reduction in casting rate (rate of clay build-up in the plaster mould).
- Increase in deflocculant demand (amount of deflocculant required to produce a slip of a standard viscosity at the casting concentration).

Particle-size distribution and the presence of small amounts of smectite also influences properties such as modulus of rupture (strength) and shrinkage of the clay. Dry strength of the kaolin component is important in bone china and some porcelain bodies where ball clay is absent. These bodies utilise fine grades of kaolin which exhibit a higher dry strength. Coarser grades are used in sanitaryware bodies where a considerable thickness of clay must dewater quickly into the plaster mould.

The range of physico-chemical and ceramic properties against which ceramic grade kaolins are assessed is summarised in Table 4; typical values are given for commercial products. The table shows the relationship between particle size, rheological properties, dry strength, and fired shrinkage. The influence of iron content on fired colour may also be seen.

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Table 4. Composition and properties of ceramic-grade kaolins

	(a)	(b)	(c)
SiO ₂	47	48	48
Al ₂ O ₃	38	37	37
Fe ₂ O ₃	0.39	0.70	1.00
TiO ₂	0.03	0.02	0.05
CaO	0.10	0.06	0.07
MgO	0.22	0.30	0.30
Na ₂ O	0.15	0.10	0.10
K ₂ O	0.80	1.85	2.00
LOI	13.0	12.2	12.1
% kaolinite	93	81	83
% micaceous material	4	15	13
% feldspar	1	1	2
% other minerals	2	3	2
% <2 μ m	85	57	40
% >10 μ m	1	10	20
Modulus of rupture (Kgf/cm ²) ¹	55.0	25.7	11.0
Casting conc. (weight % solids)	58.0	62.5	64.5
Deflocculant (5 poise [0.5 Pa.s]) ²	1.5	0.65	0.55
Casting rate (mm ² /min)	0.35	0.80	1.5
% Brightness (1180°C) ³	95	86	82
% Shrinkage (1180°C)	10	9	7.5

(a) ECC Super Standard Porcelain; high quality tableware, porcelain and bone china.

(b) ECC Grolleg; Earthenware, tableware.

(c) ECC Remblend; Sanitaryware.

1: Dried at 110°C.

2: Amount of P84 sodium silicate required for 5 poise slips.

3: At 457 nm wavelength.

Source: English China Clays technical literature.

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4.4 Paint, rubber and plastics

Natural and calcined kaolins are used as functional fillers and extenders in the paint, rubber and plastics industries. Clay is used both to enhance the properties and reduce the cost of the final product. Attributes such as shape, size and surface properties of kaolin are important in these applications. The mineral can also be reacted with certain organic chemicals to give surface layers designed to be compatible with the polymer. This leads to improvements in mechanical properties of the product.

4.4.1 Paint

Because of its high oil absorption, kaolin is mainly used in undercoats and water-based paints. In addition to reducing the overall cost of the paint, it also contributes to the optical properties of the product by improving opacity or hiding power. Specifications for kaolin for inclusion in paint are given in Table 5.

Table 5. Specifications for kaolin for paint

Grades	a	b	c
Sieve residue % >45 μm	0.5	0.1	0.05
particle size %			
<20 μm	90	95	99.5
<10 μm	70	80	99.0
<2 μm^*	15	35	70
Volatile matter at 105°C	-----2%-----		
Loss on ignition	-----10-14%-----		
Matter soluble in water	-----0.5%-----		
pH aqueous suspension	-----4.5 - 9.5-----		

* given for guidance only

Normal oil absorption values 30 to 60 g/100g

There are no British or International standards of brightness for fillers for paint.

Source: BS 1795: Extenders for paints and International Standard

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Fine particle size, good dispersibility, lamellar structure and presence of electrostatic charges on the faces (negative) and edges (positive) of the kaolinite particles also impart useful rheological properties to the paint. These properties enable kaolin to function as a suspension aid, preventing pigment settling in the can. Increasing quantities of calcined clays are being used in paint formulations. Enhanced brightness (~90%) improves opacity and allows this material to replace part of the more expensive TiO₂ pigment. Calcination also produces harder particles which impart greater durability to the paint film. Control parameters are particle size and brightness. Kaolin grades used in paint are comparable to those used for filling paper.

4.4.2 Rubber

Kaolin is the most extensively used non-black reinforcing filler in the rubber industry. Critical properties of kaolin for use in rubber are particle shape, particle-size distribution and surface properties. Kaolins used in rubber are categorised as either semi-reinforcing 'hard' clays, or as non-reinforcing 'soft' clays. Fine grades of kaolin (75-80% 2 µm) have valuable reinforcing properties. These give high tensile strength and abrasion resistance to the product. High brightness allows these materials to be used in coloured compounds. Coarser grades (20-45% <2 µm) make a smaller contribution to reinforcement, but can be used at high loadings and thus contribute to cost savings. Kaolins with specific surface areas above 10 m²/g have measurable reinforcing properties whilst those below do not. Calcined kaolin shows marked differences in properties to the natural clay, including improved brightness and increased electrical resistivity, and the most common application for this material is in cable insulation compounds.

4.4.3 Plastics

In plastics, kaolin is commonly used in PVC flooring compounds. Clays calcined at relatively low temperatures have important applications in the cable industry as a filler in PVC for sheathing and insulation purposes. Because of its high volume resistivity, calcined clay is particularly suitable for high-voltage insulation compounds where high electrical resistance is required. Quality requirements for the polymer industries are comparable to those for paper filling.

4.5 Other uses

Kaolin has a wide range of other applications for which quality requirements are normally not so demanding, the notable exception being in pharmaceutical products. The mineral is used as an anti-caking

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agent in the manufacture of fertilizer prills, as a carrier for pesticides, in the manufacture of white cement, where it contributes alumina without iron, and in the production of glass fibre where again it is used as a low-iron, low-alkali source of alumina.

5. LABORATORY ASSESSMENT OF KAOLIN

The laboratory assessment of kaolins may involve a variety of mineralogical, chemical and physical techniques. The investigation process may also include small-scale beneficiation trials and the analysis of subsequent products to determine properties relevant to a specific application. The extent to which these further investigations are carried out will depend on the outcome of a preliminary characterisation of the raw ('head') sample.

It must be stressed that the evaluation scheme and techniques described in this manual are considered appropriate for a reconnaissance appraisal of a deposit or deposits, such as might be carried out by a Geological Survey or Mines Department. Highly-specialised use-related test methods providing data required by consumers in the paper/ceramics/polymer industries are not covered here. Results from the tests discussed below will give the geologist information on the likely quality, processing characteristics, and potential application(s) of a kaolin. This in turn will provide vital basic information to enable mining companies and potential consumers to reach a decision on whether further evaluation of the deposit is warranted.

An idealised assessment scheme for kaolin-bearing rocks is given in Figure 6. The scheme covers most of the potential stages in preliminary characterisation, beneficiation, and product evaluation. In a 'real' investigation, this scheme would be modified according to the character of the raw material and the likely market for the kaolin.

5.1 Preliminary characterisation

In addition to observation of normal geological parameters, examination of potential kaolin-bearing rocks in the field should take particular account of the colour of the clay. Since brightness is the critical property in most high-value applications of kaolin, there is little point in wasting effort collecting samples which are not white or near white in colour. Kaolin-bearing rocks in tropical and sub-tropical latitudes are commonly heavily stained with ferric iron, resulting in a red or deep pink coloration. This coloration may be evenly spread through the clay, mottled, or as stringers or veins. If the staining is widespread, then it is very unlikely that the clay has any potential in high-value applications. It is generally not economic to chemically treat clay to remove staining of this type. Small-scale mining techniques may permit pockets of white clay to be worked amongst stained material, whilst larger scale mechanised operations will require a raw material of consistently high brightness. The field geologist must, therefore, use colour as a primary consideration in selecting samples of kaolin-bearing rock for laboratory assessment.

Kaolin

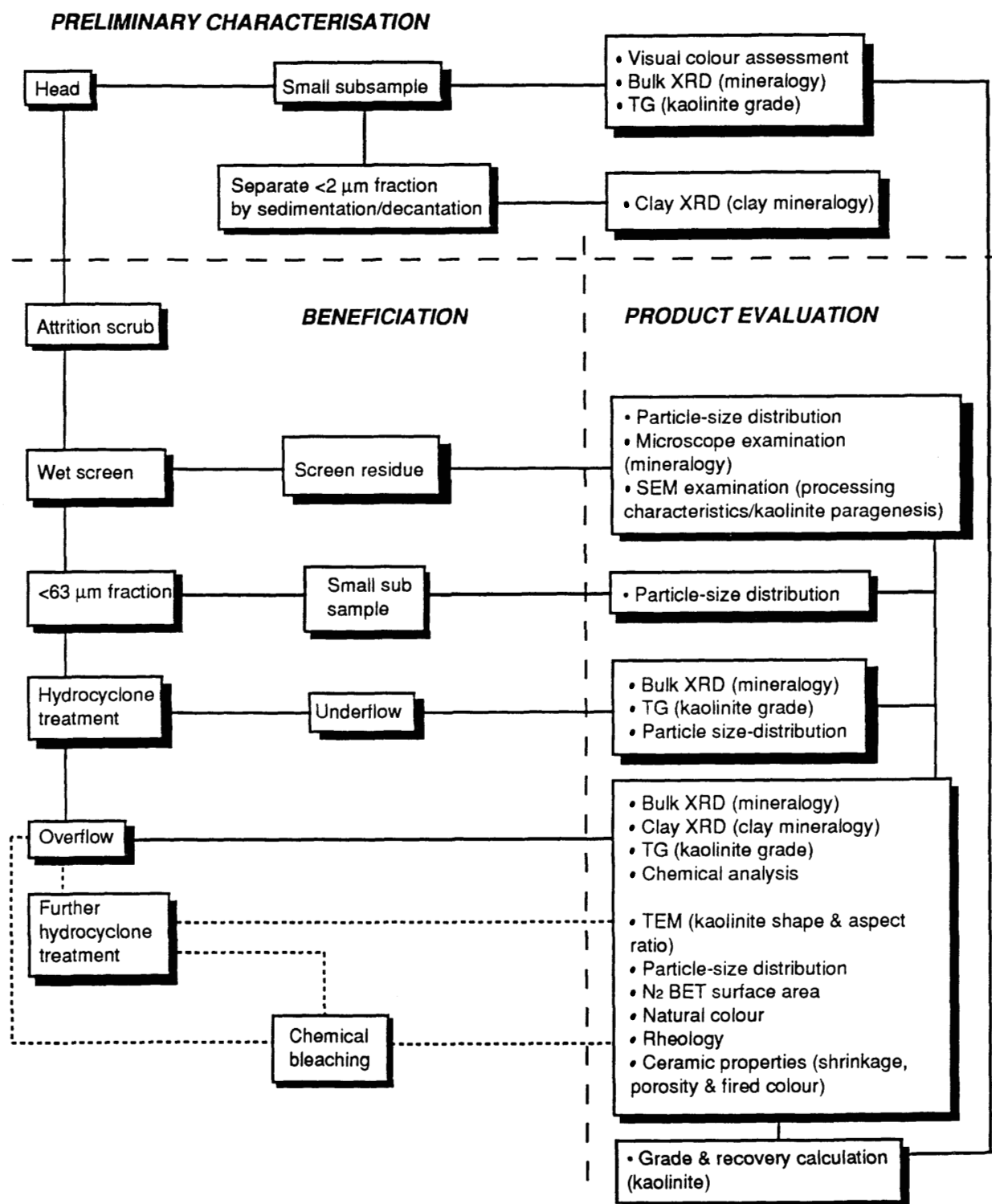


Figure 6. Idealised laboratory assessment scheme for kaolinite-bearing rocks.

Kaolin

This initial stage in the laboratory assessment of a potential kaolin will generally be carried out on all samples received from the field. Relatively rapid mineralogical analysis, coupled with a visual assessment of colour, should allow samples to be prioritised. Subsequent beneficiation trials and product evaluation are both expensive and time consuming. The preliminary characterisation stage will ensure that inferior samples are 'screened out' so that resources can be directed toward investigation of those samples with most commercial potential.

5.1.1 Mineralogy

The primary aim of mineralogical analysis of potential kaolins is to confirm the presence of kaolinite. As with all clay-bearing rocks, effective mineralogical analysis must be carried out by X-ray diffraction (XRD). Analysis of 'whole-rock' randomly-oriented mounts will allow identification of the main clay and non-clay components in the rock. Although commercial kaolins are generally considered as monomineralic clays, small amounts of other minerals are invariably present. The quantity and nature of these minerals exert a strong influence on colour, abrasiveness and viscosity which may have a deleterious effect on the end product for particular applications. Examination of oriented <2 μm material separated from the rock will provide more detailed information on the clay mineral species present.

Figure 7 shows an XRD trace of a randomly-oriented whole-rock mount of a kaolinite-bearing rock from Zambia. Also shown are 'stick patterns' corresponding to the component minerals in the rock. These are taken from the Joint Committee for Powder Diffraction (JCPDS) index. The trace shows kaolinite, together with significant amounts of mica, K-feldspar and quartz.

In contrast, Figure 8 shows an XRD trace of an oriented mount prepared from a <2 μm fraction separated from the same Zambian clay. This shows a <2 μm assemblage dominated by a poorly-ordered kaolinite. Small amounts of quartz and gibbsite are also present. The abrasion value of this material may be relatively high due to the presence of very fine-grained quartz. Gibbsite was not detected in the whole-rock XRD analysis of this material. In samples with more complex clay mineralogy, standard diagnostic treatments such as those set out in Brindley & Brown (1980) or Moore & Reynolds (1989) may have to be applied in order to identify the clay mineral species present. The presence of mica may affect the chemistry and processing characteristics of the kaolin. Relatively small quantities of smectite group minerals may significantly modify the rheological properties of kaolin products.

Kaolin

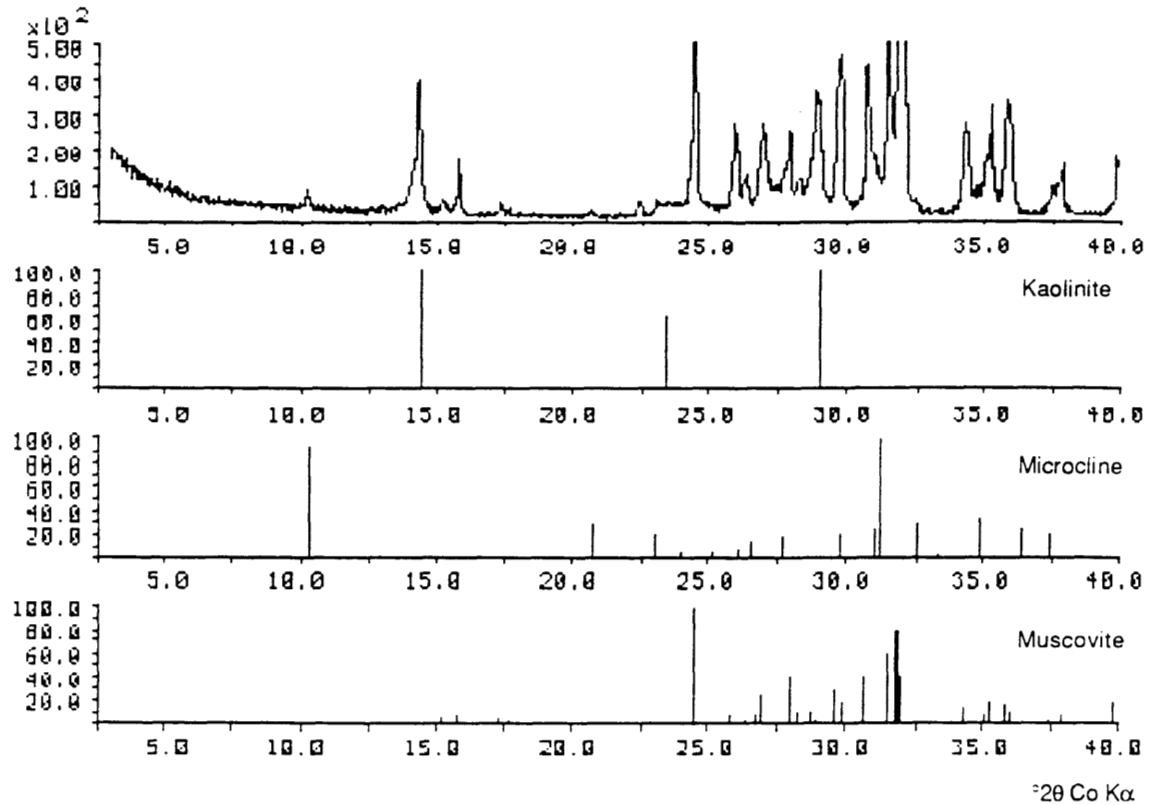


Figure 7. Whole-rock, randomly-oriented XRD trace ($\text{Co-K}\alpha$) of a kaolinite-bearing rock from Zambia.

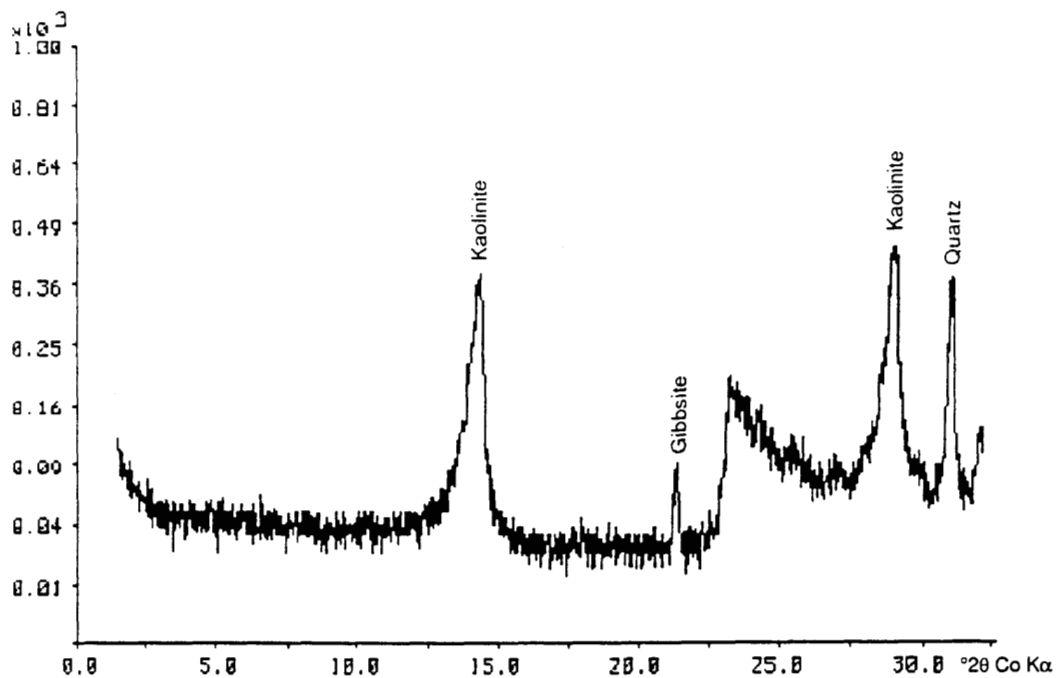


Figure 8. XRD trace ($\text{Co-K}\alpha$) of oriented $<2 \mu\text{m}$ material separated from a kaolinite-bearing rock from Zambia.

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XRD analysis of $<2 \mu\text{m}$ material will also give an indication of the degree of order-disorder of the kaolinite (sometimes known as 'crystallinity'). Figure 9 illustrates two kaolinites from Pugu in Tanzania which show contrasting degrees of crystal order. The prominent basal spacings 001 and 002 near 14 and $29^\circ 2\theta$ (Co $K\alpha$) in sample S are relatively sharp and intense compared to sample H. The sequence of 021, 111 reflections in the 22 to $30^\circ 2\theta$ region is distinct in sample S, contrasting with the diffuse 'tailed' reflections in sample H which is characteristic of poorly-ordered kaolinites. The degree of order-disorder of the kaolinite component may influence the potential end-use of the kaolin. Generally, though not always, well-ordered kaolinites are coarser-grained and have better crystal morphology than more poorly-ordered varieties. These differences in physical characteristics will be reflected in the rheological and forming behaviour of products derived from these clays. Commercial non-plastic kaolins generally contain kaolinites which are well-ordered compared to those found in plastic kaolinitic clays (ball clay).

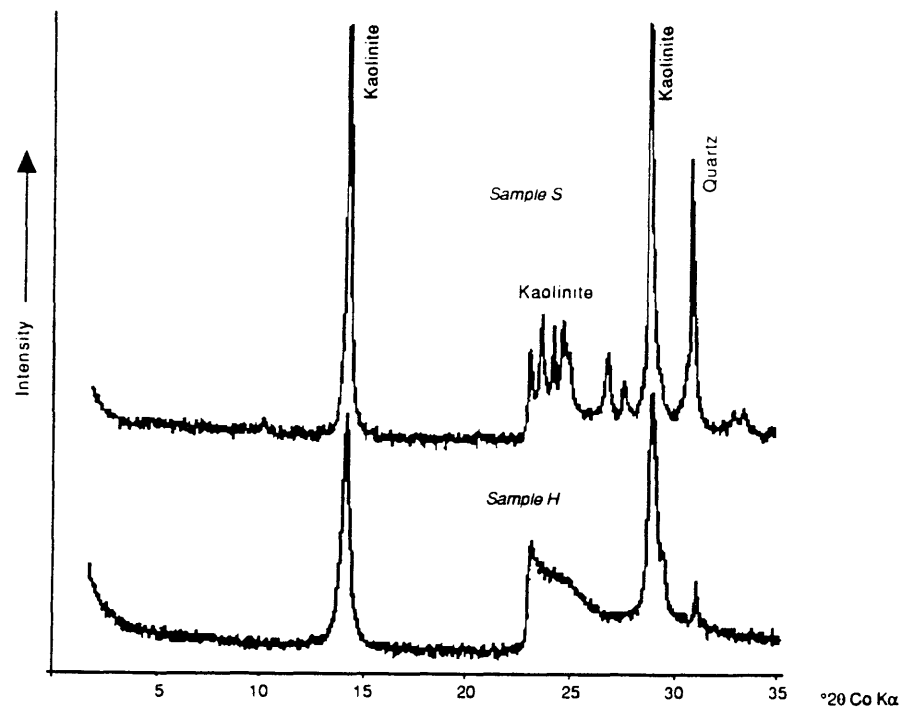


Figure 9. XRD traces (Co- $K\alpha$) of kaolinites from Tanzania showing contrasting degrees of order/disorder.

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A high degree of kaolinite disorder may indicate the presence of halloysite in a sample. Halloysite is a kaolin-group mineral which may exist in two forms: a variety which has a layer of water between the 7 Å layers to give a distinctive 10 Å spacing, and a dehydrated 7 Å variety. The interlayer water in 10 Å halloysite is easily driven off by gentle heating. As a consequence, by the time a sample from the tropics reaches the laboratory it has generally dehydrated to the 7 Å form. For all practical purposes, 7 Å halloysite is indistinguishable from highly disordered kaolinite by XRD and chemical analysis (Brindley & Brown, 1980). However, the fibrous or rolled habit generally shown by halloysite crystals has a major influence on its behaviour and potential applications. Its particle shape precludes use in paper manufacture and restricts applications in the ceramic industry. Although the presence of halloysite may be inferred from rheological and forming behaviour (see Section 5.2.6), transmission electron microscopy provides the only definitive method of confirming its presence by examination of crystal morphology (see Section 5.3.1). Some primary deposits of kaolin formed by deep tropical weathering of granitic rocks have been found to contain a significant proportion of halloysite. Halloysite should therefore be suspected if highly-disordered kaolinite is found in this type of deposit.

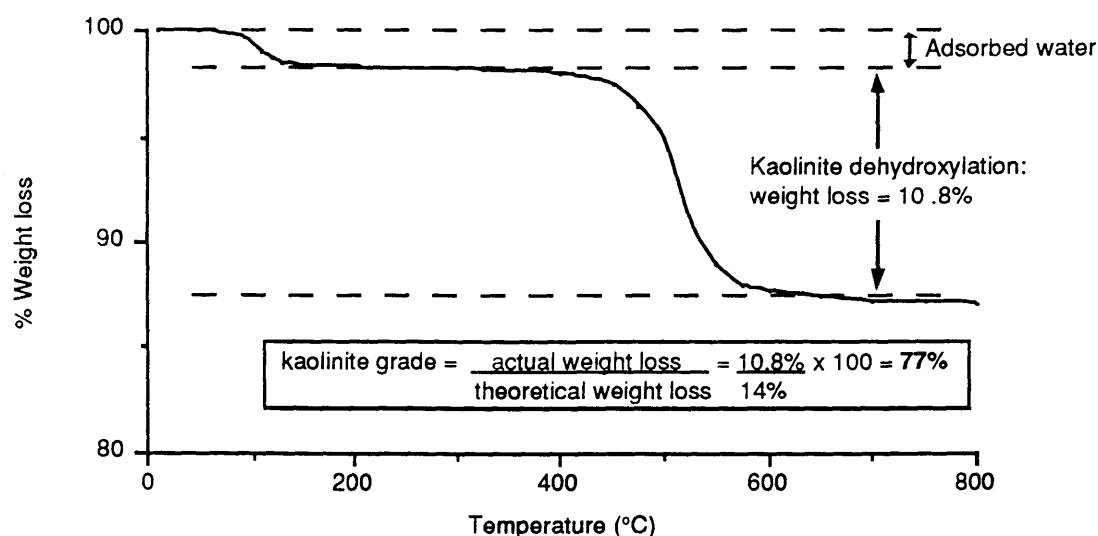


Figure 10. Thermogravimetric (TG) curve of a kaolinite-bearing rock from Zambia.

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In addition to the qualitative mineralogical analysis carried out by XRD, determination of kaolinite content provides useful information in the preliminary assessment of a suite of kaolin samples. In BGS laboratories, kaolinite content (assay or grade) is generally determined by thermogravimetric (TG) analysis. A typical TG curve for a kaolinite-bearing rock is shown in Figure 10.

This procedure measures the change in mass of a sample as it is heated at a controlled rate. Pure kaolinite loses approximately 14 weight % between 500 and 600°C due to dehydroxylation. The percentage kaolinite in an unknown sample can therefore be calculated by dividing the weight loss of the unknown by the weight loss of the pure mineral. This determination depends on the kaolinite weight loss being free from interference from weight losses associated with the breakdown of other minerals.

5.1.2 Colour

In addition to mineralogical analysis, visual colour assessment provides a rapid means of categorising a suite of kaolinite-bearing samples. Clays which are whiter in appearance should be given a higher priority for more detailed laboratory investigations. Although colour may be assessed by simply comparing different samples 'by eye', the use of a Munsell Soil Colour Chart (Munsell Color Company, 1954) will ensure a more objective approach. Colour assessment is best carried out on dry samples, since moisture can significantly affect whiteness. Munsell notation consists of separate notations for hue, value and chroma. Although the hue of unprocessed kaolins may vary from 5YR (yellow red) through to 5Y (yellow), figures for value are not likely to be below 8, with a chroma between 0 and 4. Fully quantitative spectrophotometric methods of colour measurement used in the assessment of kaolin products are not appropriate for the characterisation of unprocessed 'head' material.

5.2 Beneficiation trials

As discussed in Section 3.2, almost all commercial kaolins require some form of beneficiation in order to produce a marketable product. The type and amount of processing required depends on several factors, including the nature of the raw material, specifications of consuming industries, amount of investment available and local conditions (availability of water etc.). Small-scale beneficiation trials in the laboratory should take as many of these factors as possible into account. The aims of the laboratory trials are to assess the processing characteristics of the kaolin and to determine potential applications and likely quality of kaolin products. Rapid evaluation of products from the

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beneficiation trials enables processing to be adjusted to optimise kaolinite grade and recovery.

Both laboratory beneficiation and commercial processing are essentially size fractionation processes which utilise the tendency of kaolinite to concentrate in the fine fraction. 'Wet' processing is generally preferred since this method is more efficient in concentrating kaolinite and is much more commonly used commercially. A suggested flowsheet for laboratory beneficiation trials of kaolin is given in Figure 11.

Kaolin

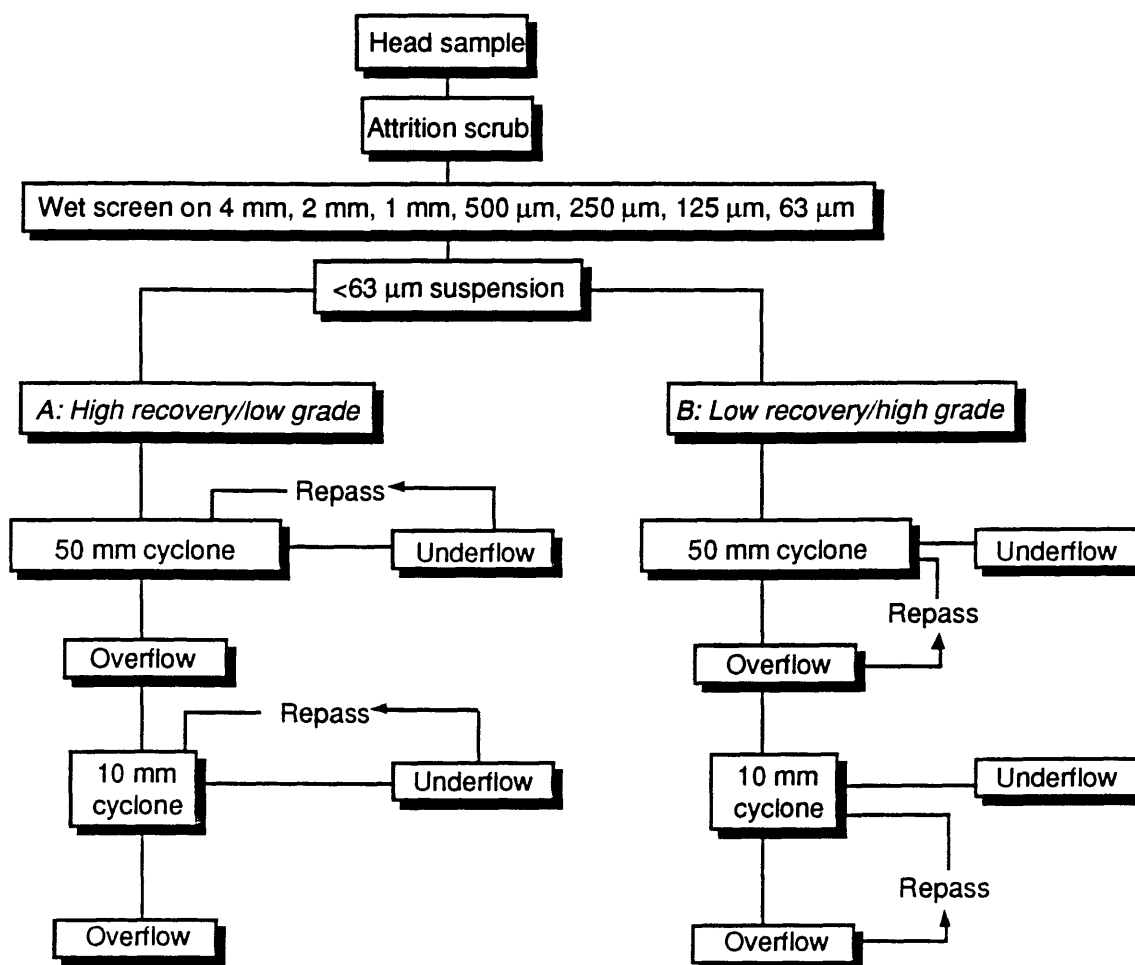


Figure 11. These alternative hydrocyclone processing schemes are intended to maximise either grade or recovery. By repassing the underflow product through the cyclone (Scheme A), more material will be recovered to overflow. If the overflow fraction is repassed (Scheme B), then less material will be recovered. However, the final product of B is likely to be higher in kaolinite and have a finer particle-size distribution than the final product of A.

Scheme A is more likely to be used on a head material with a low kaolinite grade. A high kaolinite grade head sample might be processed using Scheme B, since overall kaolinite recovery is likely to be less critical and the final product of higher quality.

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5.2.1 Attrition and wet screening

In the BGS laboratories, 'wet' processing of kaolin begins with the dispersion of the kaolinite-bearing rock sample in water in an attrition cell. This is generally carried out using a heavy duty laboratory stirrer rotating at a known rate for a given period of time. This method has been found to be very effective in breaking up aggregates and liberating kaolinite to suspension, whilst minimising the production of non-clay fines. This is followed by wet screening through sieves ranging from 500-63 μm to produce a kaolinite-rich <63 μm suspension. A method for attrition and wet screening of kaolinite-bearing rocks is given in Appendix 1.

5.2.2 Hydrocyclone treatment

Kaolinite is further concentrated by size fractionation of the suspension using a laboratory hydrocyclone in combination with a suitable pump. A number of laboratory hydrocyclone/pump combinations may be used to process kaolin. Selection depends on the amount of suspension available and the desired cut point (the particle size at which the hydrocyclone splits the feed into the coarser 'underflow' and the finer 'overflow'). If <63 μm suspension volumes exceed 20 litres, then a pilot scale test rig fitted with a relatively large 50 mm cyclone (Figure 12) will effectively concentrate kaolinite by removing >15 μm material to underflow. The effect of this treatment on the particle-size distribution of a kaolinite-bearing clay from Zimbabwe is illustrated in Figure 13.

If required, the fine overflow fraction from the 50 mm hydrocyclone can provide suitable feedstock for a multiple 10 mm hydrocyclone (Figure 14). This unit allows very fine cut points (down to 2 μm) and is particularly suited to fractionation of kaolins to give products with similar size distributions as commercial filler and coating grades (Bloodworth, 1989). Figure 15 shows the effectiveness of this unit in concentrating the <2 μm fraction of a kaolin from Pugu, Tanzania.

Pilot-scale hydrocyclone test rigs are unsuitable for treating small suspension volumes (>20 litre is required to fill the sump and allow the monopump to work effectively). Volumes as low as 1 litre have been separated using a small glass hydrocyclone linked to a suitable rotary or diaphragm pump (Figure 16). This unit will generally give a similar cut point to the larger 50 mm cyclone.

Kaolin



Figure 12. 50 mm hydrocyclone in operation.

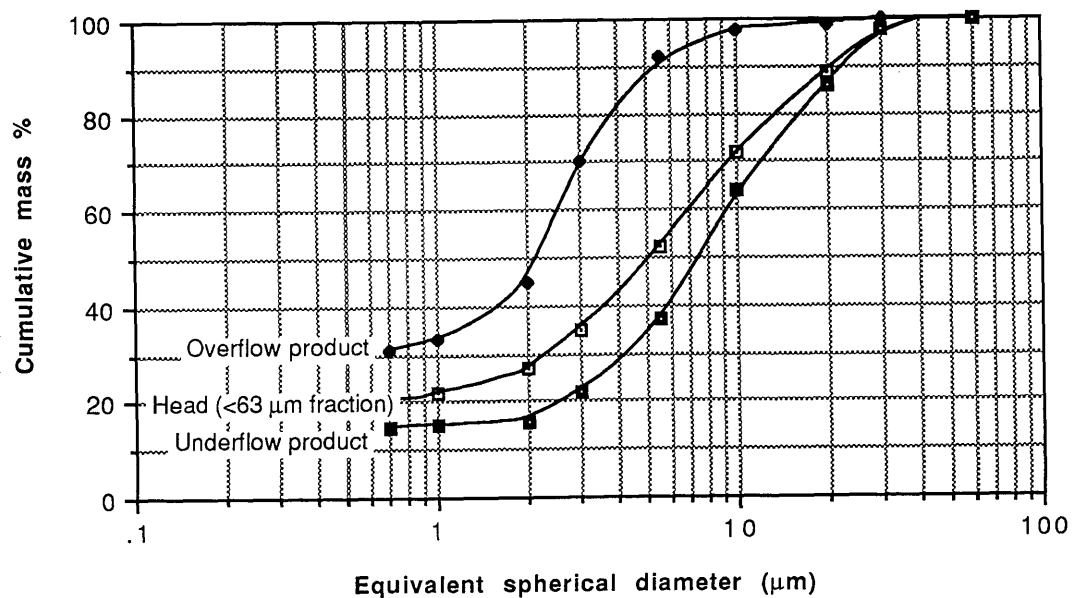


Figure 13. Particle-size distribution curves showing the effect of 50 mm hydrocyclone treatment on a Zimbabwe kaolin.

Kaolin



Figure 14. 10 mm hydrocyclone in operation.

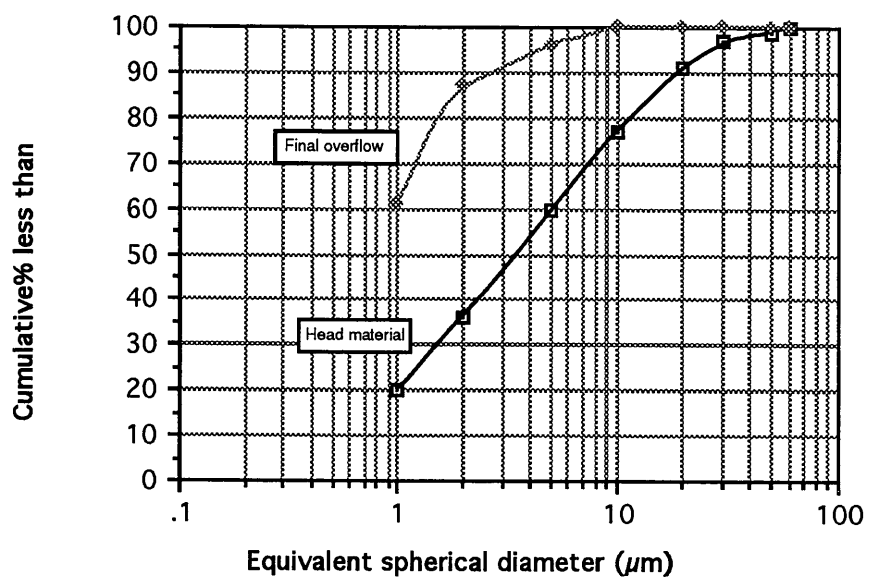


Figure 15. Particle-size distribution curves showing the effect of 10 mm hydrocyclone treatment on a kaolin from Tanzania.

Kaolin

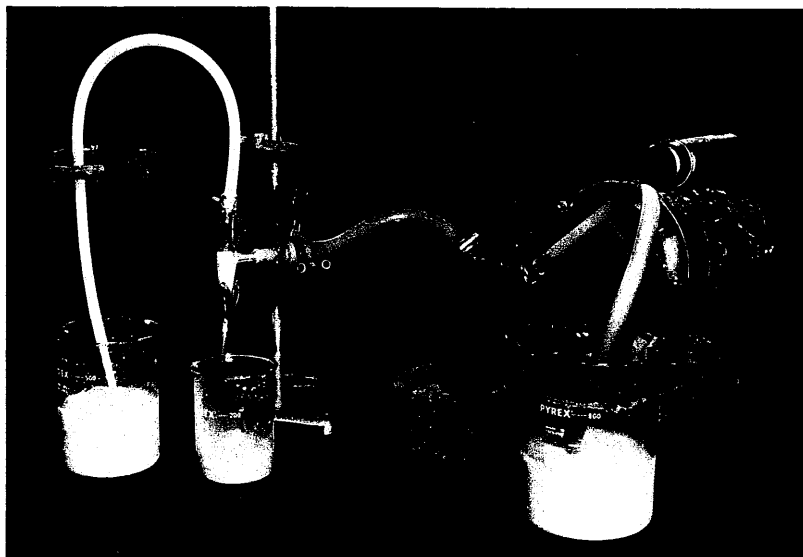


Figure 16. Bench top glass hydrocyclone and pump unit.

Typical schemes for the hydrocyclone treatment of kaolin suspensions are given in Figure 11. Re-passing over- and/or underflow products through the cyclone will 'sharpen-up' cut-points and (depending on the scheme implemented) improve grade or recovery of both kaolinite and $<2 \mu\text{m}$ particles.

The beneficiation process is monitored throughout by carrying out particle-size analysis and kaolinite assay on selected products. Rapid analysis by X-ray sedigraph and thermogravimetry (see Section 5.3) allows the processing scheme to be modified to optimise grade and recovery of kaolinite at fine particle sizes.

5.2.3 Chemical bleaching

Chemical bleaching is a standard industrial technique used to improve the brightness of kaolins intended for high-value applications (see Section 3.2.2). Depending on the degree of coloration and the intended markets for a kaolin under investigation, it may be useful to assess in the laboratory the extent to which the brightness of a clay product can be improved by chemical treatment. Bleaching is carried out by the addition of a strong reducing agent (generally sodium dithionite,

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Na₂S₂O₄) which reduces ferric iron coating the surfaces of the kaolinite particles to the ferrous form. The process whitens the clay and allows a small proportion of the total iron to be removed in solution. Figure 17 show the effect of this treatment on the brightness of a kaolin from Zimbabwe. A laboratory method for chemical bleaching of kaolin products is given in Appendix 4.

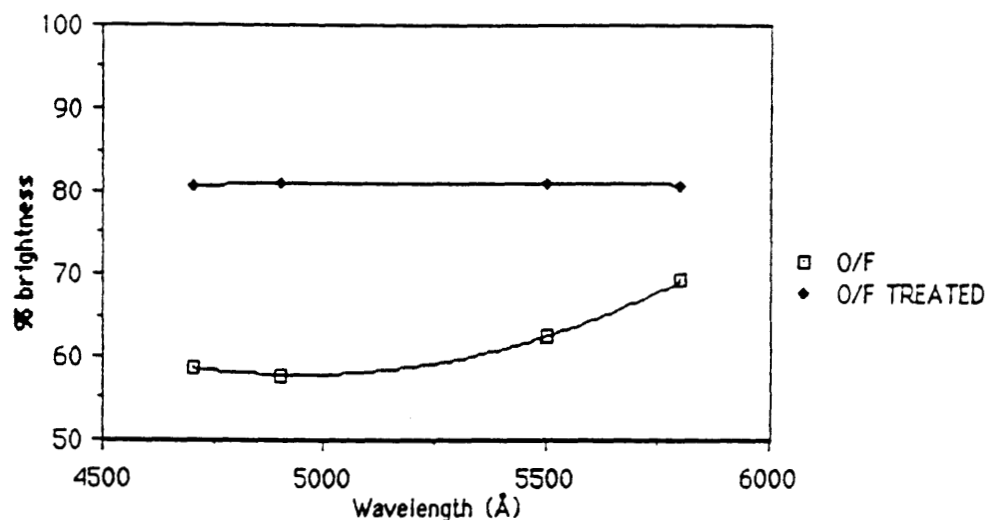


Figure 17. Spectrophotometric curves showing the effect of chemical bleaching on the brightness of a kaolin from Zimbabwe (sample 'O/F treated' bleached with sodium dithionite).

5.3 Product evaluation

Kaolin product evaluation involves determination of mineralogical, physical, and chemical properties relevant to the potential applications of the clay. Some of these data will be gathered as the beneficiation trials take place and may be used to assess and improve the efficiency of this process. A wide range of analysis techniques may be applied to the various products of the beneficiation process, although most will be applied to the fine hydrocyclone overflow products in which kaolinite concentrates. The use-related testing scheme undertaken depends on the likely markets for the kaolin, although fundamental properties such as mineralogy, particle-size distribution and brightness will also indicate likely applications. For example, products with a high proportion of <2

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μm particles and high natural brightness might warrant further investigation for applications in the paper industry, whereas tests relating to ceramics applications could be applied to coarser material.

Some of the tests described below are directly comparable to those used by manufacturers and consumers of kaolin products. Others are modified versions of commonly-used tests, or are procedures which were developed in BGS laboratories using less sophisticated equipment more appropriate to reconnaissance studies of kaolins. The likely quality of 'unknown' kaolins is therefore best assessed in this type of study by direct comparison with the behaviour of samples of commercial products which have been analysed using the same procedures.

5.3.1 Mineralogy

Examination of sieve residues by binocular microscope provides a simple method of identifying the coarse-grained components of the kaolinite-bearing rock, as well as monitoring the efficiency of the attrition-scrub dispersion process. This technique might also be used to identify any potential commercial 'by-products' in the coarse fraction such as K-feldspar or silica sand. Table 6 presents the composition of the coarse fraction of two contrasting kaolinite-bearing rocks from Kenya.

The coarse fraction of the first sample is typical of deeply-weathered granitic rock, with abundant quartz, as well as unaltered mica, and feldspar which has not yet been kaolinised. The presence of kaolinite aggregates in sieve residues from the second sample shows that the attrition process was ineffective in dispersing the clay.

Transmission electron microscopes (TEM) can provide useful data on size, shape, and aspect ratio of kaolinite crystals in fine-grained products from beneficiation trials. TEM imaging also allows the positive identification of halloysite.

Samples for TEM analysis are generally taken from hydrocyclone overflow products. Some typical images are shown in Figures 18 to 21. Crystals of kaolinite showing characteristic hexagonal form are shown in Figure 18. Metal shadowing provides quantitative data on plate thickness and aspect ratio (Figure 19). Aggregates or 'books' of undispersed kaolinite (Figure 20) indicate that further processing might be necessary to delaminate the clay and increase the proportion of fine-grained material. This figure also shows the presence of halloysite along with kaolinite. Halloysite may dominate the clay assemblage (Figure 21).

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Table 6. Composition of the >63 μm fraction of kaolinite-bearing rocks from Kenya. Minerals are listed in approximate order of abundance.

Size fraction (μm)	Mineralogy
<i>ELD 2 (Weathered granitic rock)</i>	
>4000	quartz
4000-2000	quartz, white feldspar
2000-1000	quartz, white feldspar, opaques
1000-500	quartz, white feldspar, opaques
500-250	white feldspar, quartz, opaques
250-125	white feldspar, quartz, biotite, opaques
125-63	white feldspar, quartz, biotite, opaques
<i>EBBURU 1 (Hydrothermally-altered tuff)</i>	
>4000	kaolinite aggregates (some Fe-stained)
4000-2000	kaolinite aggregates
2000-1000	kaolinite aggregates, clear prismatic quartz, milky quartz
1000-500	kaolinite aggregates, clear prismatic quartz, milky quartz
500-250	kaolinite aggregates, clear quartz, opaques
250-125	kaolinite aggregates, opaques, clear quartz
125-63	kaolinite aggregates, opaques, clear quartz

Scanning electron microscopy (SEM) is a less useful tool than TEM in the evaluation of kaolinites, although it can provide data on the effectiveness of processing. Figure 22 shows the surface of a partially-kaolinitised feldspar grain coated with tubular halloysite crystals. The presence of clay intimately associated with feldspar taken from a sieve residue indicates that the attrition scrubbing process has not been totally effective in concentrating this material in the fine fraction. SEM studies also provide data on the petrography and paragenesis of the kaolinite-bearing rock, although this is not a high initial priority in an economic study.

XRD provides basic mineralogical data on the fine-grained products from beneficiation trials. The distribution of clay and non-clay minerals between different hydrocyclone under- and overflow products can be monitored and the process adjusted if necessary. Techniques used are identical to those used to characterise the raw material (Section 5.1.1). Figure 23 shows contrasting XRD traces of randomly-oriented mounts prepared from hydrocyclone under- and overflow products. The effectiveness of the hydrocyclone in removing feldspar, mica and quartz from the fine fraction can clearly be seen. XRD is particularly important in identifying potentially abrasive mineral impurities in products from

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processing trials. The presence of fine quartz in a product which otherwise has a high kaolinite grade and a high proportion of $<2\ \mu\text{m}$ particles will significantly reduce its potential as a high-value paper coating clay.

Thermogravimetry (TG) is used to provide the quantitative data needed to assess the efficiency of the beneficiation process. Kaolinite grade of the various products of the beneficiation trials is determined by TG analysis. These data are combined with the kaolinite grade of the raw material, and the weight percentage distribution of material between the different beneficiation products to produce product grade and recovery data. A 'worked example' of a kaolinite grade and recovery calculation is given in Appendix 2.

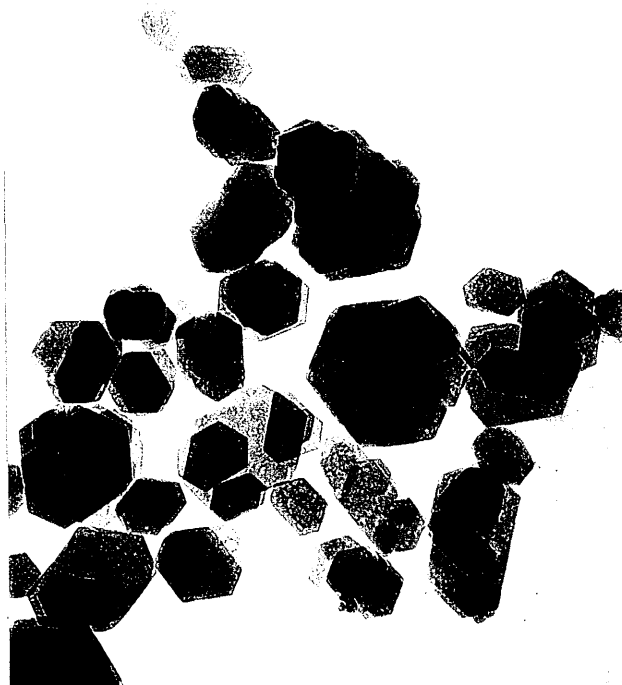


Figure 18. Transmission electron micrograph of well-formed hexagonal crystals of kaolinite from Tanzania (X 54000).

Kaolin

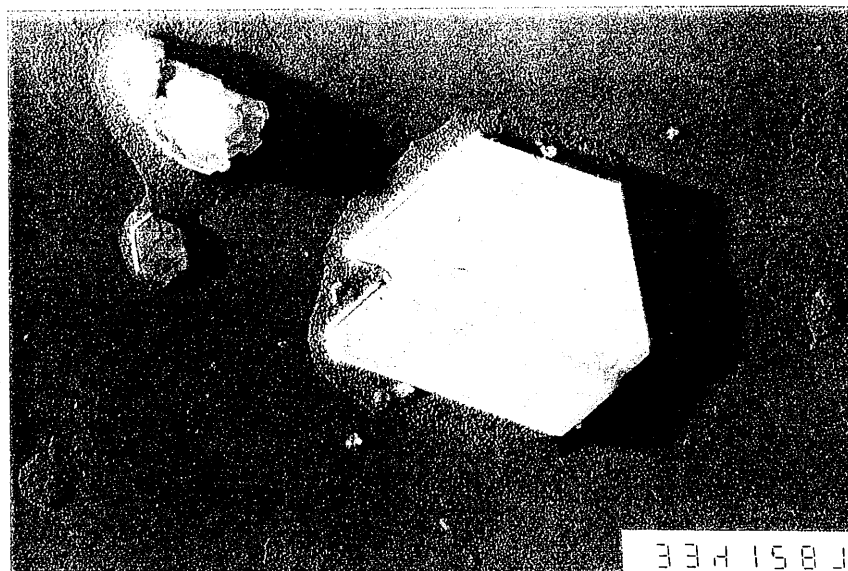


Figure 19. Transmission electron micrograph of well-formed hexagonal crystals of kaolinite from Uganda (X 50000). The crystals have been metal-shadowed to allow measurement of thickness and aspect ratio.

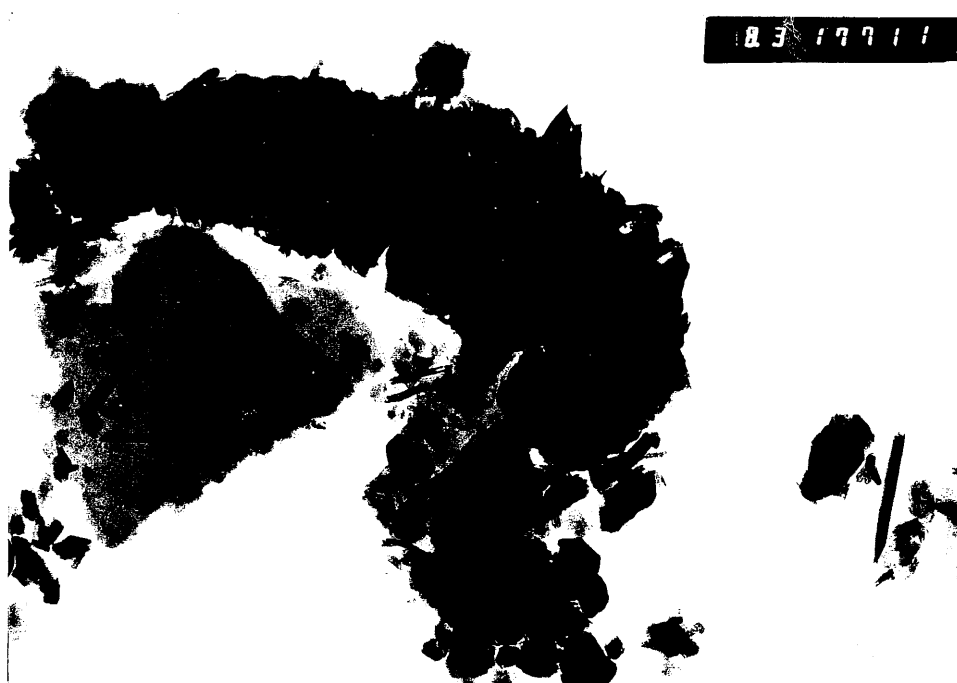


Figure 20. Transmission electron micrograph showing a large stack of kaolinite crystals from Bolivia. Note also the presence of some halloysite 'tubes' (X 12000).

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Figure 21. Transmission electron micrograph of tubular halloysite from Kenya (X 20000).

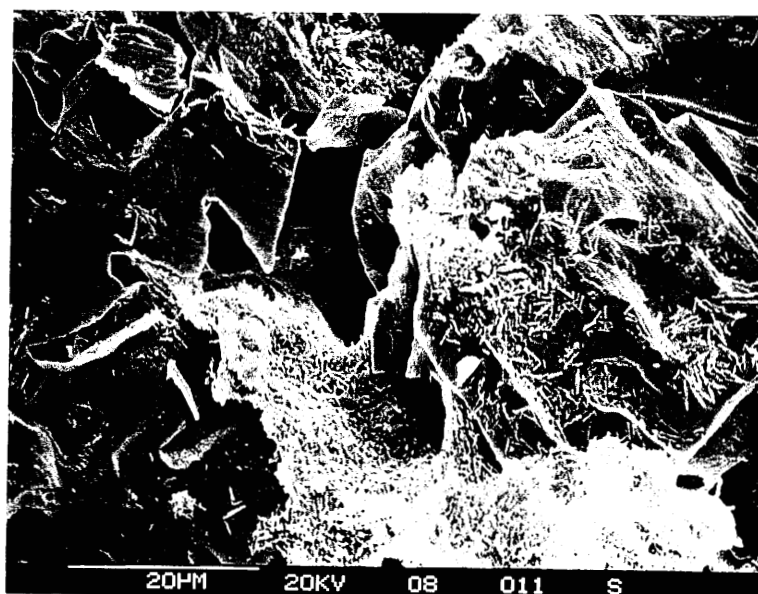


Figure 22. Scanning electron micrograph of tubular halloysite forming from corroded feldspar, Bolivia (scale bar = 20 μm).

Kaolin

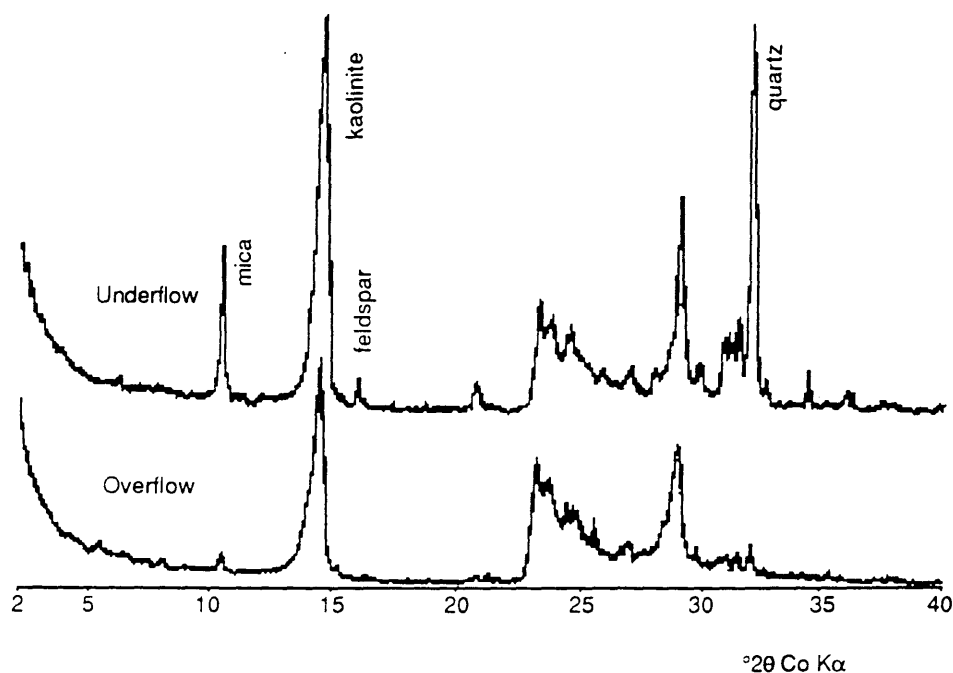


Figure 23. XRD traces showing contrasting mineralogy of under- and overflow fractions separated from a Bolivian kaolinite-bearing rock.

5.3.2 Chemistry

Major element chemical analysis is generally carried out on kaolin products which have potential applications in the ceramics industry. As discussed in Section 4.3, iron content is particularly critical when assessing kaolin for this application. Concentrations of alkalis and elements such as titanium also influence fired properties such as shrinkage and fired colour. A variety of analysis methods may be used, depending on facilities and equipment. The preferred method for major element analysis of kaolins in the BGS laboratories is X-ray fluorescence (XRF) spectrometry.

5.3.3 Particle-size distribution

Particle-size distribution data on the raw sample and the various products of beneficiation trials are critical in assessing economic

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potential. Along with colour, fine particle size is the property which makes kaolin commercially valuable.

'Whole-rock' particle size is determined from weight distribution in screen residues, combined with sub-sieve analysis carried out using a sedimentation method such as Andreasen pipette or X-ray sedigraph. Hydrocyclone products are also analysed using sub-sieve sedimentation techniques. Appendix 3 details procedures for these techniques.

Particle-size data are generally plotted on log-normal paper. Related products may be plotted on the same chart to assess the efficiency of the process (Figure 13). In the assessment of economic potential, critical point values include percentage $<2\ \mu\text{m}$, % $<10\ \mu\text{m}$ and % $>53\ \mu\text{m}$ (see Section 4). It is theoretically possible to calculate the recovery of $<2\ \mu\text{m}$ material to the various separation products. This can be calculated in a similar way to kaolinite recovery from size data and weight percentage distribution between the products. However, this proves difficult to carry out in practice because the high-shear conditions encountered by the kaolin suspensions within the hydrocyclones tend to increase the proportion of $<2\ \mu\text{m}$ material as aggregates are broken up (Bain & Morgan, 1979). This effect invalidates the relationship between the amount of $<2\ \mu\text{m}$ material in the products and the amount in the $<63\ \mu\text{m}$ suspension from which they were derived.

5.3.4 Surface area

Surface area of kaolins is closely linked to particle size. This relationship is clearly shown in Figure 24 where surface area data from a series of kaolin products derived from the same raw material are plotted against percentage material falling below $2\ \mu\text{m}$. Surface area values increase as the particle size of the kaolin decreases. Table 7 gives typical surface area values for a range of kaolins. These values were obtained using the single-point N_2 BET method. Surface area values are often quoted for higher-value commercial kaolins, such as those used in paper manufacture.

Table 7 shows that the surface area values of fine-grained paper coating grade clays exceed those of coarser filler grade. Hydrocyclone products derived from halloysitic clays generally show a much higher surface area than most of their kaolinitic equivalents. This contrast is probably due to fundamental differences in particle shape. Appendix 4 gives information on preparation of kaolin samples for surface area analysis using the N_2 BET method.

Kaolin

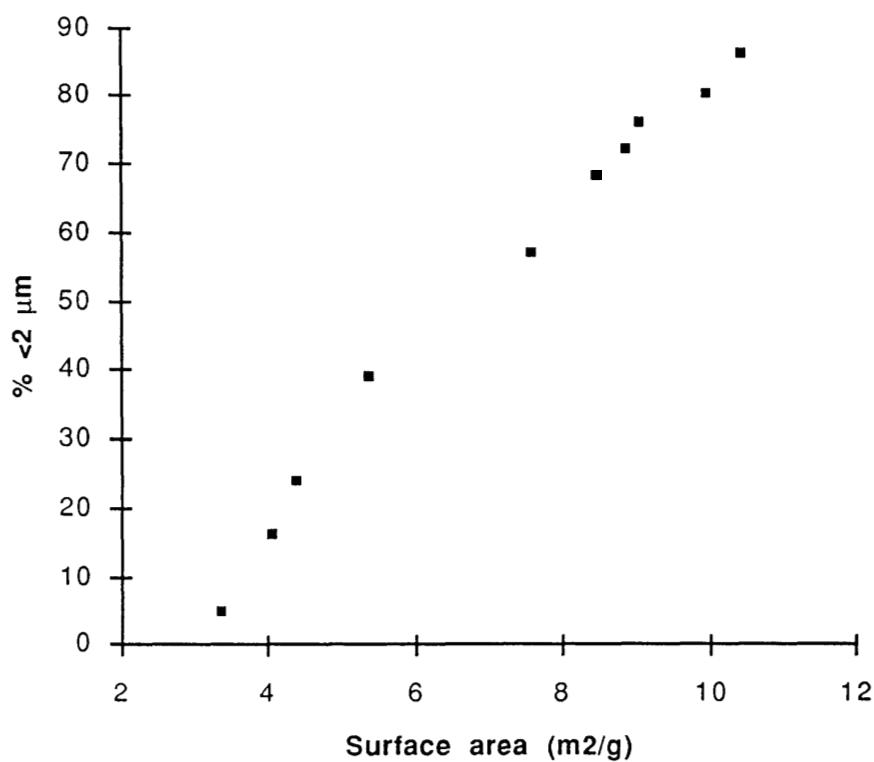


Figure 24. Plot showing relationship between particle size and surface area in a series of products from a Tanzanian kaolin.

Table 7. Typical N₂ BET surface area values for kaolins and halloysites.

	Surface area (m ² /g)
SPS (paper coating clay)*	13
Superclay F (paper coating clay)*	10
Filler M (paper filler clay)*	8
Pugu 'soft': (kaolin): Tanzania	10
Pugu 'hard' (kaolin): Tanzania	22
MUR 9 (halloysite): Kenya	17
ELD 2 (halloysite): Kenya	28

* Kaolins produced by ECC International Ltd.

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5.3.5 Colour measurement

Quantitative measurement of colour, or 'brightness' (or 'whiteness'), is of critical importance in the economic evaluation of kaolin products. As discussed in Section 4, natural brightness is crucial in assessment of kaolin for the paper and filler markets, whereas fired colour is important in kaolins for use in ceramics.

Measurement of colour of white mineral powders (including kaolin) is generally carried out by determining the percentage reflectance from the powder compared to a perfectly reflecting standard (BaSO_4). The reflectance spectrophotometer measures the amount of light reflected from the surface of a powdered sample. The light is filtered so that only that within a chosen narrow band of the spectrum (wavelength) is measured. Depending on the colour of the sample, the amount of light reflected varies with different filters.

There are various methods of measuring colour using the reflectance spectrophotometer, but perhaps the simplest involves the determination of a spectrophotometric curve for the sample (Figure 25). Here, the colour of the sample is expressed as wavelength against reflected intensity. A pure white sample shows no change in overall reflectivity with different wavelengths. A grey sample show the same but with lower overall reflectivity. A red sample shows higher reflectivity at the long wavelength end of the spectrum.

Kaolin

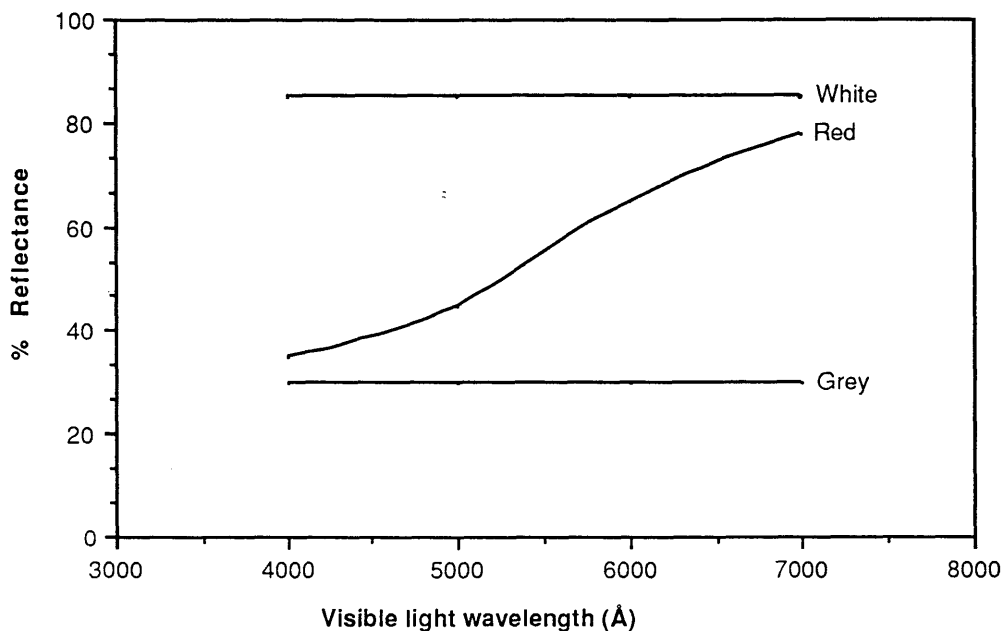


Figure 25. Spectrophotometric curves of white, grey and red mineral powders as measured by a reflectance spectrophotometer.

As discussed in Section 4.2, industry brightness measurement is becoming increasingly standardised. Brightness is generally measured against a white ISO-approved standard using a Carl Zeiss Photoelectric Reflection Photometer ('Elrepho'). The EEL Reflectance Spectrophotometer provides a low-cost alternative to this sophisticated and expensive equipment. Although not directly comparable to the 'Elrepho', quantitative data from this apparatus are of sufficient quality for reconnaissance studies of kaolin products. A procedure for the measurement of kaolin brightness is given in Appendix 5.

Some typical spectrophotometric curves from kaolin products are shown in Figure 26. Natural kaolins generally show higher reflectance at longer wavelengths of light. This yellow or red coloration may or may not be detectable by the human eye. Colour specifications by manufacturers and consumers are generally given as the ISO brightness at 4570 Å (or 457 Nm). This figure can be read from the spectrophotometric curve. Although the value derived from the EEL instrument is not strictly equivalent to the ISO standard, it does provide a useful method for comparing the colour of 'unknown' samples with proven commercial products which have been analysed using the same equipment.

Kaolin

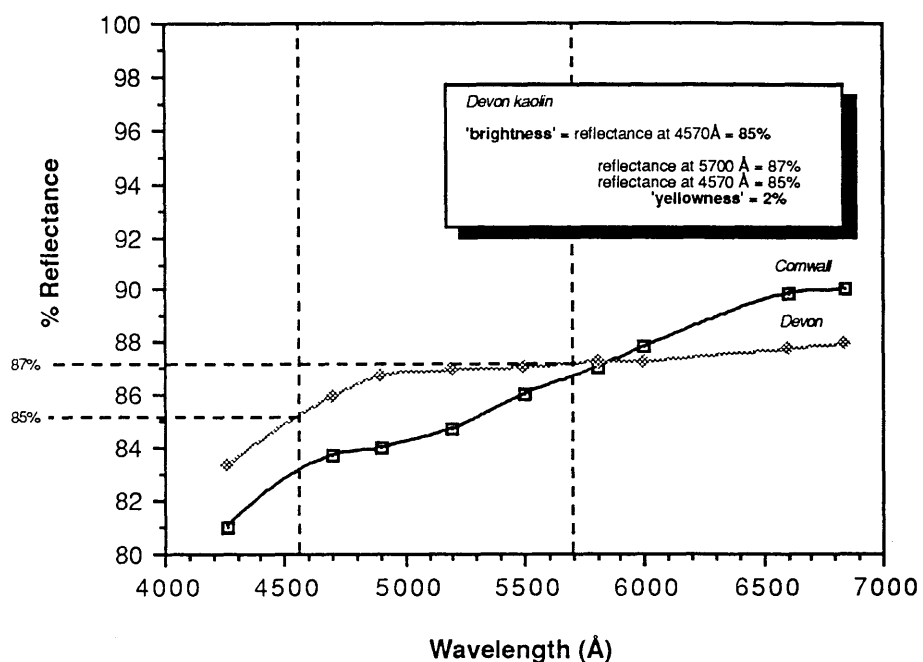


Figure 26. Spectrophotometric curves and brightness data for two kaolins from south west England.

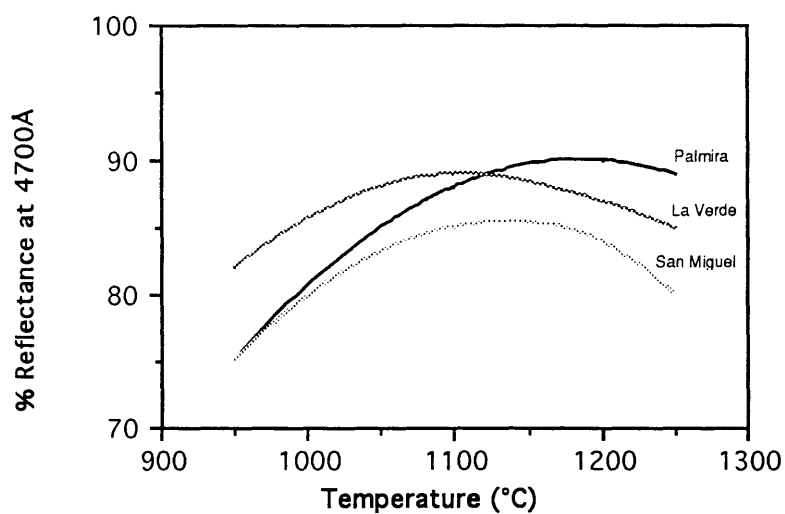


Figure 27. Change in 4700 Å reflectance values with firing temperature shown by kaolins from Bolivia.

Kaolin

The degree of slope on the curve is sometimes expressed as 'yellowness'. This value is derived by subtracting the brightness value at 4570 Å from that at 5700 Å (see Figure 26). Again this is not strictly comparable to yellowness values given in commercial specifications.

In assessing the potential of ceramic-grade kaolins, fired brightness is of crucial importance. Samples are prepared by dry (dust) pressing discs of raw kaolin (usually in a powder press used for preparing discs for X-ray fluorescence analysis). These discs are then fired to a set temperature or range of temperatures prior to colour measurement. The procedure for colour measurement of fired material is identical to that used in the analysis of natural kaolins. Fired colour is generally expressed as brightness at 4570 Å at a specific temperature (Table 4) or plotted as a curve to show the change in brightness over a range of firing temperatures (Figure 26). Determination of other fired properties is discussed in Section 5.2.7.

5.3.6 Rheology

Viscosity measurements of kaolin slurries are essential in evaluation of potential for high-value applications such as paper making and cast ceramic bodies. The most widely-used instrument for the measurement of low-shear viscosity in kaolin slurries is the Brookfield Viscometer. Viscosity is a measure of the resistance of a liquid to flow, and the amount of shear required to induce flow is used as a measure of the apparent viscosity. Most clay slurries behave as a non-Newtonian fluid where shear stress is not proportional to shear rate.

Kaolin slurry viscosity is influenced by a number of factors including viscosity of the fluid medium, solids concentration, particle geometry, particle interaction, particle-size distribution, non-kaolinite mineralogy (especially smectite), soluble salt content, pH, and temperature.

Viscosity measurement procedures used in the BGS laboratories are based on those developed by ECC International Ltd for testing kaolin products for the paper industry. Mitchell (1991) gives a more detailed review of viscosity measurement of kaolin slurries. Detailed procedures for the various viscosity tests are given in Appendix 6. These comprise:

- *Flowability* - the solids content at which the clay slurry just begins to flow.
- *Deflocculant demand* - the minimum amount of deflocculant required to obtain a minimum-viscosity slurry.
- *Viscosity concentration* - the solids concentration of a fully deflocculated clay which has a viscosity of 5 poise at 22°C.

Kaolin

These tests are sequentially related. The flowability value is required in order to determine deflocculant demand, which in turn is needed to determine viscosity concentration. Figure 28 shows a typical deflocculant demand curve for a coating grade kaolin. A curve used to calculate the viscosity concentration for the same clay is shown in Figure 29.

The above test procedures are specific to the paper industry, although those used in testing for ceramic applications are similar. In the procedure for ceramic applications a slurry is prepared by adding deflocculant in small amounts until flowability is reached. The slurry is then left to stand, after which further additions of deflocculant are made until viscosity no longer falls. At this point water is added until the viscosity is 5 poise. The solids content of this final slurry is known as the *casting concentration*. This test is equivalent to the viscosity concentration used for testing kaolins for paper.

Table 8 details the rheological properties of some commercial kaolins, together with kaolin products from laboratory beneficiation trials. These data show that some of the laboratory-processed African kaolins have similar viscosity concentrations to commercial coating and ceramic grade clays.

The influence of particle shape on viscosity is illustrated by comparison of the viscosity concentration values of the Muranga halloysitic clays with those from 'normal' kaolins (Table 8). Shape influences the effective or swept volume which a particle occupies during movement of the slurry (Millman, 1964). The swept volume of non-spherical particles, such as plates (kaolinite) and rods (halloysite), is controlled by the largest diameter, and volume increases disproportionately with increase in size. The presence of halloysite increases viscosity because the rod-shaped particles have a higher swept volume than plates and also have a tendency to tangle with each other.

Kaolin

Table 8. Rheological properties of selected commercial kaolins and products of beneficiation trials on a series of kaolinite-bearing rocks from Africa.

Sample	Kaolinite content (%)	Particle size		Flowability (wt %)	Deflocculant demand*	Viscosity concentration (wt%)
		<10 μ m	<2 μ m			
<i>Commercial kaolins: coating grade</i>						
SPS	82	97	79	67.5	1.4	66.3
Supreme	95	98	92	66.6	1.5	66.4
Dinkie A	88	97	70	70.5	1.3	71.1
<i>Commercial kaolins: ceramic grade</i>						
Standard						
porcelain	85	97	65	64.6	1.3	64.7
Treviscoe	83	89	37	66.3	1.7	62.1
<i>African kaolins</i>						
Eburru	97	96	63	64.6	1.4	61.7
Muranga A†	97	92	51	64.9	1.9	57.0
Muranga B†	94	95	49	48.6	2.5	52.9
Pugu H	98	90	79	45.7	1.1	62.0
Pugu S	85	97	47	47.9	1.1	71.2

* Deflocculant demand values represent volume (ml) of sodium hexametaphosphate (Calgon) solution required per 100 g of sample to attain minimum viscosity.

† Halloysitic clays

Kaolin

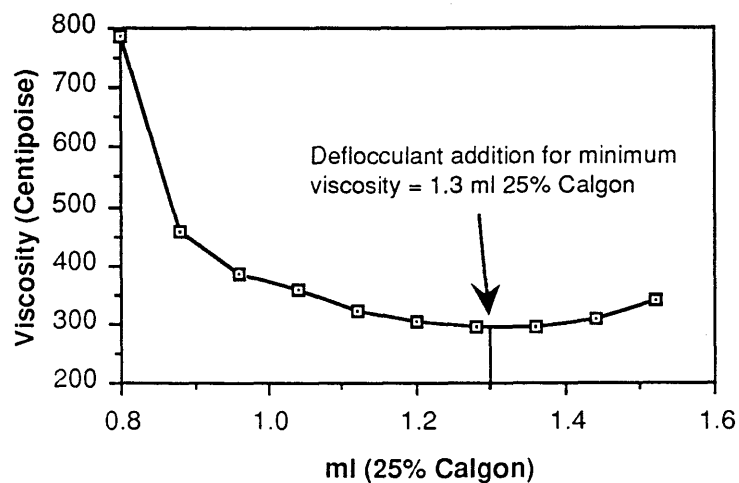


Figure 28. Deflocculant demand curve for a coating grade kaolin from south-west England.

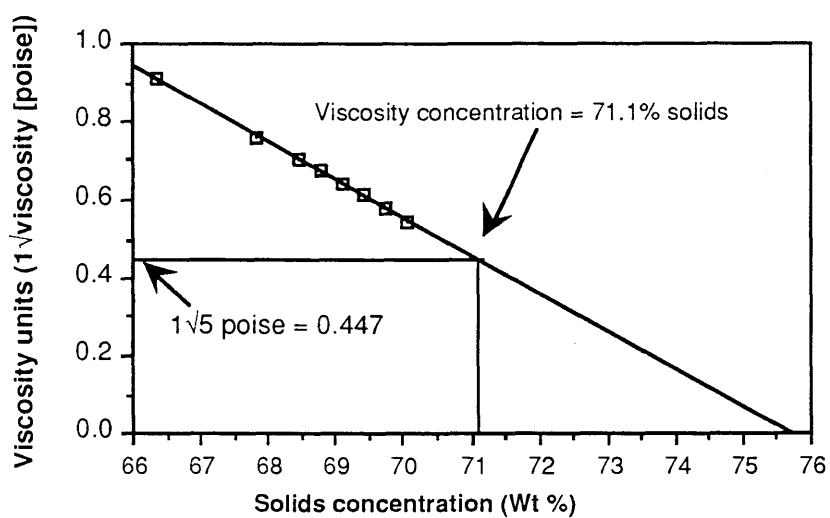


Figure 29. Viscosity concentration curve for a coating grade kaolin from south-west England.

Kaolin

5.3.7 Modulus of rupture

Knowledge of the modulus of rupture (MoR) of a kaolin being considered as a raw material for fine ceramics is necessary because of its contribution to strength. Semi-dry and dry unfired ceramic articles must have sufficient strength to enable them to be handled, finished and placed for firing. The strength of a dried clay rapidly decreases as moisture is adsorbed; however, at 80% relative humidity the equilibrium moisture level of a clay is such that small moisture changes do not significantly alter the strength. This is near the average condition in which clay strength is significant in industry, and a detailed appraisal of the strength of a clay would therefore include MoR determination of the clay conditioned at approximately 80% RH as well as of the dried clay. As will be seen below, MoR results are very dependent on the preparation and preconditioning of the clay test pieces and on the exact conditions of measurement. Relationships between MoR measurement and experimental conditions are discussed by West (1969) and Williamson (1971).

The MoR of a kaolin is determined on a three-point-load test rig (Figure 30), most conveniently on a rod-shaped test piece.

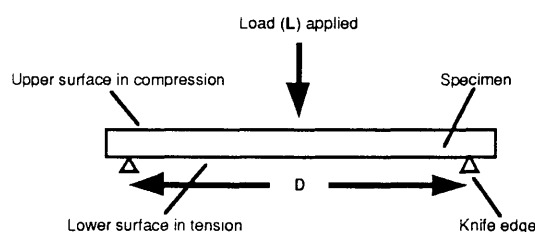


Figure 30. Three-point loading for MoR test.

The centre load point is gradually moved against the test piece until it fractures, and the MoR is calculated using the following formula:

$$\text{MoR} = \frac{8LD}{\pi d^3} \quad (\text{kg/cm}^2)$$

where: L = breaking load in kgf
 D = distance between supports in cm
 d = diameter of test piece in cm.

Kaolin

The ratio of D to d should be as near to 6:1 as possible and the MoR is taken as the average of 10 measurements. Because flaws and air bubbles in the test pieces can seriously affect MoR results, test pieces should be inspected visually before testing and unsatisfactory ones rejected. A standard deviation of <5% should be aimed for on the MoR measurements: results on any test pieces significantly below the provisional mean should be disregarded and the mean recalculated on the reduced number of test pieces. If more than three samples deviate significantly from the provisional mean then a new batch of test pieces should be prepared.

The most important variable when measuring MoR is the rate of loading. In general, as the rate of loading is increased so the MoR increases. Modern MoR testing machines are electronically controlled so a constant rate can be guaranteed - a rate of 20 mm per minute is a satisfactory average for comparative testing purposes. Measurement of unfired modulus of rupture of kaolins (which are relatively low-strength compared to other clays) requires a high-sensitivity machine. Table 9 gives some typical MoR values for kaolins.

Table 9. Typical modulus of rupture values for kaolins from south-west England

	Modulus of rupture (Kgf/cm ²)	
	at 80% relative humidity	dried at 110°C
ECC 'Super Standard Porcelain'	27.0	55.0
ECC 'Grolleg'	10.0	25.7
ECC 'Remblend'	5.0	11.0

Preparation of test pieces for MoR measurement For routine measurements on a reconnaissance basis, determination of MoR on extruded test pieces dried at 105°C is recommended. The procedure follows that described in Appendix 8, except that the test pieces are cut into 6 cm lengths, allowed to air dry for two hours and then dried at 105°C overnight. Before testing they are allowed to cool in a desiccator. Any further testing for suitability of kaolin for fine ceramics would involve a much more careful and reproducible preparation procedure (Appendix 7).

Kaolin

5.3.7 Fired properties

The properties of a fired kaolin product provides additional information on the potential of the clay for use in ceramics. Changes in physical properties such as shrinkage, porosity and colour are monitored over the temperature range generally used to produce clay body ceramics (900-1250°C). Variation in firing behaviour mainly results from differences in chemistry and particle-size distribution. Kaolins which are relatively high in alkalis and/or iron will develop high shrinkage and low porosity at lower firing temperatures; kaolins which are relatively low in these 'fluxing' elements will tend to be more refractory. Similarly, kaolins with a fine particle-size distribution tend to form a low porosity body at lower temperatures than a coarser-grained clay of equivalent temperature.

The fired properties of a laboratory-processed kaolin from Bolivia are shown in Figure 30 as a series of 'vitrification curves'. Porosity shows little alteration up to 1100°C, from which point it falls rapidly. Values change little up to this point, though the refractory kaolinite undergoes sintering and solid-state reaction. Mullite and cristobalite will form from the kaolinite through the latter process. This is indicated by an increase in specific gravity up to 1100°C.

As temperature increases, grains begin to melt and the liquid produced fills the space between particles. This action decreases pore volume and specific gravity (disordered liquid has a lower SG than crystalline material). As porosity decreases, shrinkage and bulk density increase. This occurs slowly at first, but then becomes more rapid as melting takes over from sintering and solid-state reaction as the dominant process within the ceramic body. The alkali and/or iron content will influence the rate at which melting will occur through their fluxing action on silica and alumina. Fine particle size will tend to increase the rate at which these reactions occur.

A procedure for measurement of fired properties is described in Appendix 8. Determinations are carried out on test pieces extruded from the kaolin product. In BGS laboratories, test pieces are fired in a temperature-gradient furnace which allows simultaneous firing to eight points over a temperature range 900-1250°C. The process can be carried out equally well with separate stage firings of test pieces to different temperatures in a laboratory muffle furnace. Porosity, volume shrinkage, specific gravity and bulk density are determined by comparison of weight in air and under mercury (before firing) and weight in air, under mercury and following water absorption (after firing).

As with some other test methods described in this manual, assessment of fired properties using this technique is best carried out by comparison of 'unknown' material with the behaviour of test pieces prepared from

Kaolin

commercial ceramic grade kaolins which have been subjected to the same tests. The refractoriness of different clays can then be assessed by comparing volume shrinkage and porosity at particular firing temperatures.

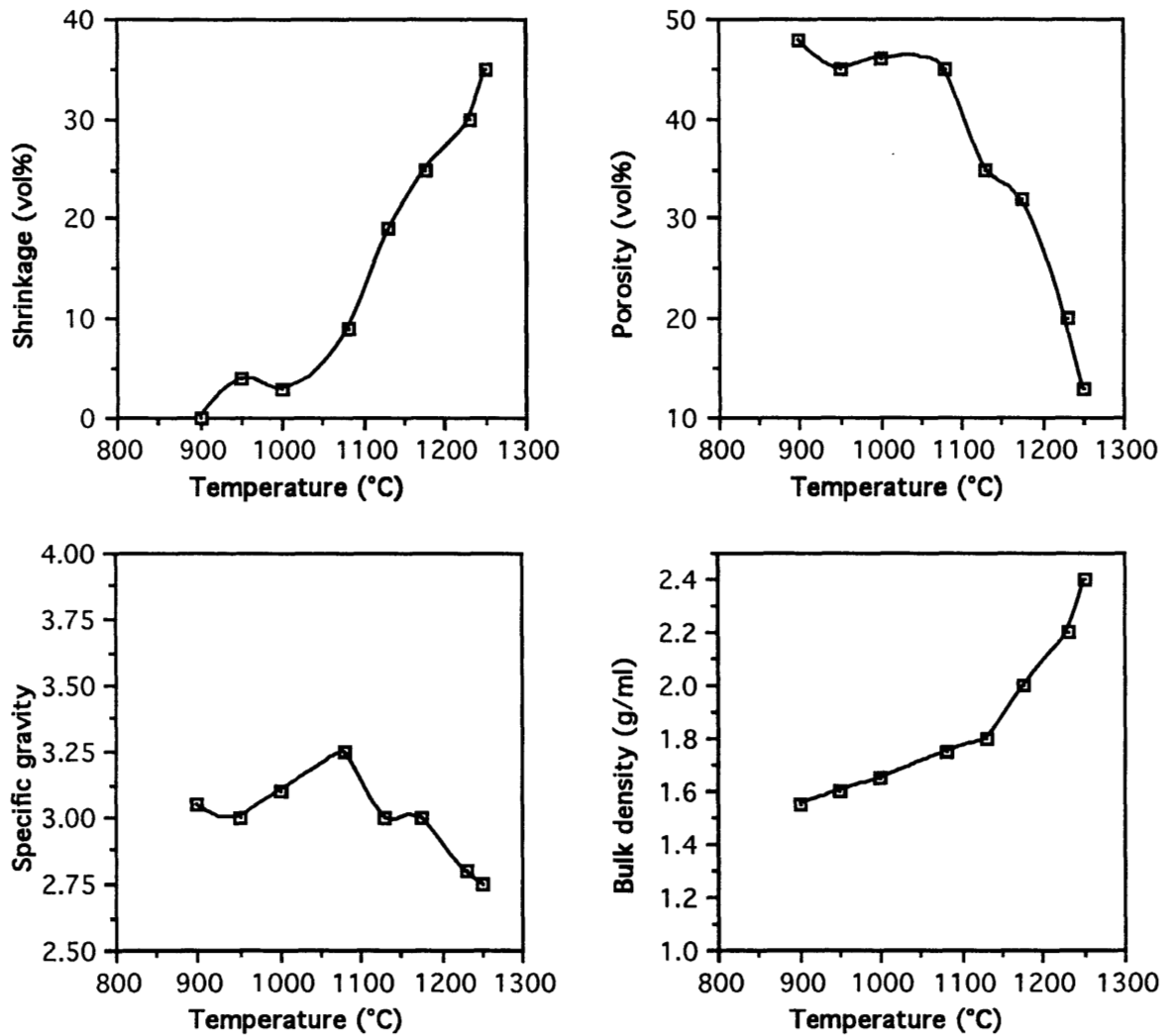


Figure 30. Fired properties of a kaolin from Bolivia.

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Kaolin

Appendix 1: Dispersion and wet screening of kaolinite-bearing rock.

This procedure is used in the preparation of a <63 μm suspension suitable for hydrocyclone treatment. Wet screening also allows the particle-size distribution of the >63 μm portion of the rock to be calculated.

The amount of starting material ('head' sample) required depends on the kaolinite grade and on the type of hydrocyclone/pump to be used in the beneficiation trials. High-grade head samples will require less starting material than low-grade to produce a <63 μm suspension containing a similar amount of kaolinite. A pilot-scale hydrocyclone test rig will require about 20 l of suspension in order to function, whereas a reasonable separation can be achieved using a small glass cyclone with about 1 l of suspension. While the solids concentration in a hydrocyclone feed should not exceed 10%, a 5% suspension is probably optimum. The solids concentration is easily measured by subsampling a small known volume and weighing the residue after oven-drying.

The attrition scrub dispersion and wet screening procedure used in BGS laboratories for kaolinite-bearing rocks is as follows:

Apparatus

Bucket
Electric stirrer
Screens: 4 mm
2 mm
1 mm
500 μm
250 μm
125 μm
63 μm
Automatic wet sieve shaker
Evaporating dishes
Drying oven set at 60°C
Top-loading balance

Method

1. Oven-dry head sample overnight at 60°C, weigh and place in a large plastic bucket. Cover with enough distilled water to make up a suspension approximately 10% by weight.
2. Place a large paddle stirrer in the bucket and set at 250 rpm for two hours.

Kaolin

Appendix 1 (continued)

3. Set up a nest of sieves (4 mm, 2 mm, 1 mm, 500 μm , 250 μm , 125 μm and 63 μm) on the automatic wet sieve shaker. Set up a bucket to receive the <63 μm suspension.
4. Carefully pour the contents of the bucket on to the topmost sieve and set the sieve vibrator and water spray. This may have to be done in stages to avoid clogging the finer sieves.
5. The combined action of the vibrator and water spray will fractionate the different size ranges on the sieves. Monitor each screen carefully to avoid clogging. The end point is reached when the water passing through each sieve becomes clear of particulate matter.
6. Disassemble the sieve stack and wash each residue into an evaporating dish and dry overnight at 60°C. Weigh and retain for binocular microscope examination.
7. Sub-sample the <63 μm suspension for particle size analysis and to calculate solids concentration. When sampling ensure that all solids are in suspension.
8. Calculate amount retained on each sieve as a percentage of the weight of the head sample. Calculate percentage <63 μm by difference.

Note: If an automatic wet sieve shaker is unavailable, then wash material through each screen individually into a bucket, starting with the coarsest screen. Take care not to use an excessive amount of water.

Kaolin

Appendix 2: Kaolinite grade and recovery calculation

A 'worked example' of a kaolinite grade and recovery calculation is given below:

Kaolin-bearing rock, Eburru, Kenya

Head grade (by thermogravimetry) = 94% kaolinite

Head sample weight = 551.5 g

therefore **weight kaolinite in head** = $(551.5/100) \times 94 = 518.4$ g

Weight material retained on sieves = 15.4 g

Hydrocyclone underflow grade = 91% kaolinite

Hydrocyclone underflow weight = 99.4 g

therefore **weight kaolinite in underflow** = $(99.4/100) \times 91 = 90.45$ g

therefore **kaolinite recovered from head to underflow** = $(90.45/518.4) \times 100 = 17\%$

Hydrocyclone overflow grade = 95% kaolinite

Hydrocyclone overflow weight = 436.7 g

therefore **weight kaolinite in overflow** = $(436.7/100) \times 95 = 414.86$ g

therefore **kaolinite recovered from head to overflow** = $(414.86/518.4) \times 100 = 80\%$

Results may be summarised as follows:

Size fraction	Weight (g)	Weight (%)	Kaolinite grade (%)	Kaolinite recovered from head (%)
<i>Sieve residues</i>				
>500 μm	5.7	1.0		}
500-250 μm	6.0	1.0		3*
250-125 μm	2.1	0.5		}
125-63 μm	1.6	0.3		}
<i>Hydrocyclone products</i>				
underflow	99.4	18	91	17
overflow	436.7	79	95	80
Total	551.5	100		100

* composite value calculated by difference

Kaolin

Appendix 3: Sub-sieve particle-size analysis

This appendix gives a detailed procedure for particle-size analysis of <63 μm kaolin suspensions and hydrocyclone under- and overflows by Andreasen pipette. A procedure for analysis by X-ray sedigraph is not given since this is specific to the particular instrument.

Preparation of a stable suspension prior to Andreasen pipette analysis

Apparatus/materials

Oven set at 60°C
Pestle and mortar
125 μm screen
Balance (1 or 2 figure)
500 ml plastic bottle
250 ml measuring cylinder
10 ml pipette
Andreasen pipette and cylinder
20 wt% solution sodium hexametaphosphate ('calgon')

Method

1. Dry suspension sub-sample overnight at 60°C.
2. Hand-crush dry sample to pass 125 μm using a pestle and mortar.
3. Sub-sample approximately 12 g and place in 500 ml plastic bottle.
4. Add 100 ml distilled water, shake for 1-2 hours and leave overnight.
5. Transfer clay suspension to pipette cylinder and add 20 ml 2% Na-hexametaphosphate deflocculant ('Calgon'). Make up to 10 cm mark.
6. If suspension stable after 1 hour, then make up to 20 cm mark (accounting for volume occupied by pipette stem). Total volume is about 590 ml.

Kaolin

Appendix 3 (continued)

7. If suspension is not stable, then try adding more deflocculant in small increments (say 2 ml). Keep a careful record of amount of deflocculant added. Once stable, make up to 20 cm mark with distilled water.
8. Accurately add a further 20 ml distilled water to make up to 600 ml.
9. Calculate 'deflocculant correction' i.e. weight contribution of deflocculant to weight of sediment taken in each 10 ml sample.

Example calculation as follows:

20 ml 2% solution deflocculant added to suspension = 0.4 g deflocculant

0.4 g in 600 ml (total suspension vol) = 0.0667% deflocculant

therefore weight of deflocculant in 10 ml sample = 0.0667 / 10

'deflocculant correction' = 0.0067 g

Determination of particle-size distribution using the Andreasen pipette

Apparatus

-10 + 110°C mercury thermometer
Andreasen pipette and cylinder (short pipette optional)
Stopwatch
Balance (4-figure)
Weighing bottles with lids
Oven set to 105-110°C

Method

1. Following preparation of a stable suspension, the cylinder should be allowed to stand for 1 hour to allow for temperature equilibration.
2. Note temperature of suspension and calculate appropriate sampling times using the nomogram given below. Record these and all subsequent data on the worksheet given below.
3. Turn the cylinder horizontal with the pipette in place and the stopcock closed and shake from side to side.

Kaolin

Appendix 3 (continued)

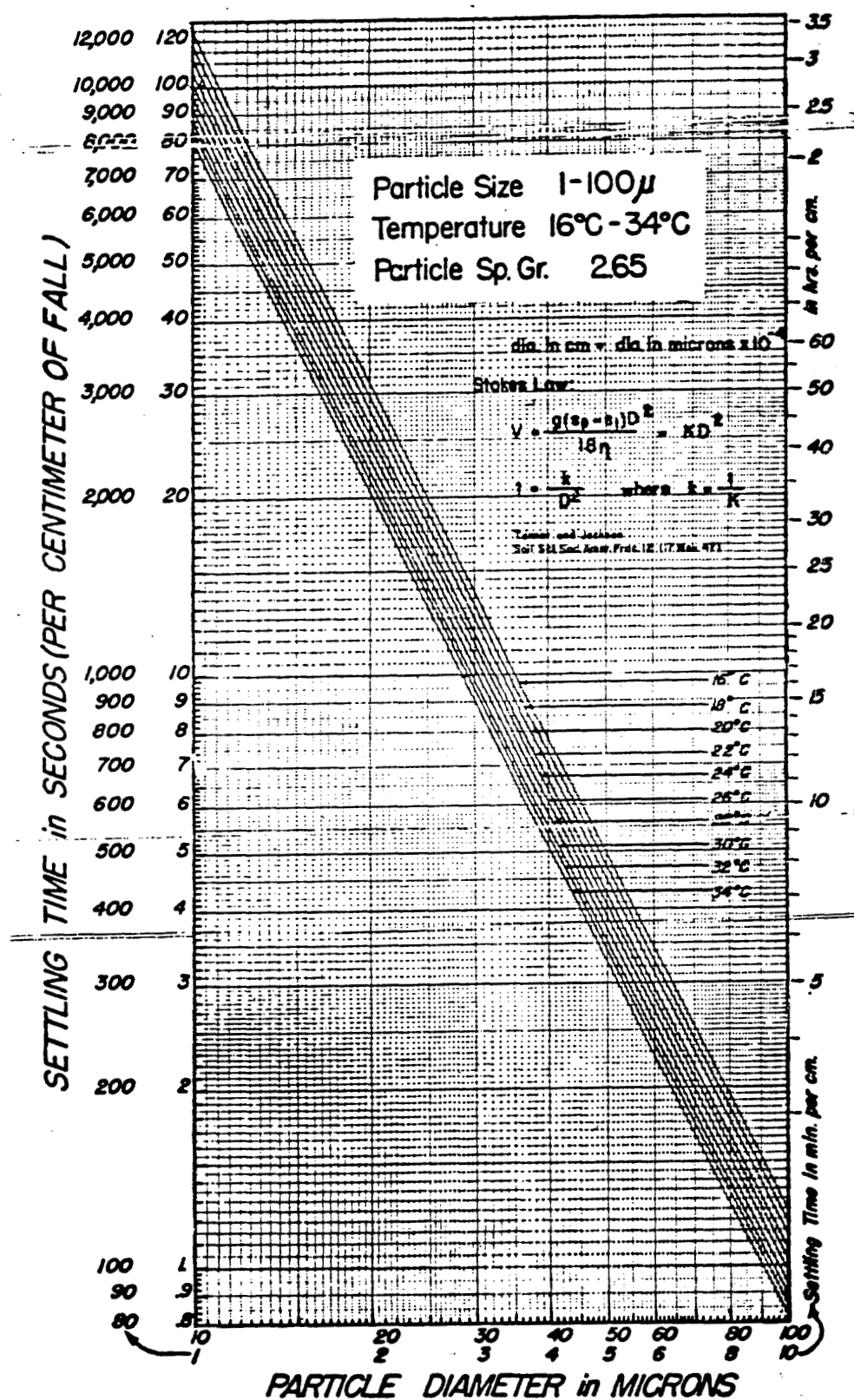
4. A sample is immediately pipetted from the suspension into the 10 ml reservoir.
5. Discharge the 10 ml sample into an accurately weighed weighing bottle. Care should be taken to wash all traces of material from the pipette reservoir and discharge tube into the weighing bottle.
6. The weighing bottle + sample are placed in an oven set at 110°C and evaporated to dryness overnight.
7. Repeat steps 3 - 6. The two samples taken at this stage will be used to calculate the original concentration (C_o).
8. Shake the cylinder with pipette in place and stopcock closed. Place on bench and start stopwatch.
9. Remove 10 ml samples by pipette at calculated times, discharge into weighing bottles and dry overnight at 110°C. These samples give the concentration C_t . Note that these samples are taken without shaking the cylinder and that settling times are cumulative from the beginning of rest.
10. Remove bottles from oven and ensure lids are in place. Weigh accurately and calculate weight of residue. Subtract deflocculant correction. Two initial corrected values represent overall concentration (C_o), subsequent corrected values reflect concentration less than a given particle diameter (C_t).
11. Calculate % less than each size fraction (d_t) represented by sampling times.
$$\% \text{ less than diameter } d_t = C_t / C_o * 100$$
12. Plot values on log/normal paper to obtain cumulative percent less than size distribution curve. If these data are derived from a <63 μm suspension and are required for an overall particle size distribution of the rock, they should be normalised to the percentage total material passing the 63 μm screen (see Appendix 1).

Note: Timing of sample removal from suspension may present some difficulties in terms of incorporation into one or two working days. If this proves to be the case, then a short pipette may be substituted for the standard pipette at step 8. Calculate the sampling time for 2 μm (the short pipette is at a depth of 2 cm) and remove sample after this time. Remove short pipette and replace with standard, repeat step 8 and

Kaolin

continue. If a short pipette is not available, the long pipette can be modified by attaching to a stand and inserting to a depth of 2 cm. Remember to recalculate 50 - 5 μm sampling times to account for change in pipette depth due to prior removal of 2 μm sample.

Kaolin



Nomogram for calculating particle settling times (from Tanner & Jackson, 1948).

ANDREASEN PIPETTE PARTICLE SIZE ANALYSIS

Sample Operator
 Remarks Date

Particle diameter (µm)	Depth (cm)	Settling time (h:m:s)	Bottle No.	(a) Bottle weight	(b) Bottle + sample weight	(c) Sample weight (b-a)	(Co) Sample-deflocc. (c-de)	(dt) Cum. % < 63 µm (Cl/Co*100)
Co								
Co								
							(Cl) Sample-deflocc. (c-de)	
50								
40								
30								
20								
10								
5								
2								

Water temperature: °C
 Deflocculant correction (de): g.

Worksheet for Andreasen pipette particle size calculations.

Kaolin

Appendix 4: Iron oxide/oxyhydroxide removal by sodium dithionite bleach

Apparatus/reagents

Water bath
Centrifuge
Sample shaker

Sodium dithionite
0.3M sodium citrate solution
1M sodium hydrogen carbonate solution
Saturated sodium chloride solution

Method

1. Place 10 g of powdered sample in a beaker.
2. Add 100 ml sodium citrate solution and 12.5 ml sodium hydrogen carbonate solution. Heat to 75°C in water bath.
3. Add 2.5 g sodium dithionite. Stir continuously for 5 minutes then occasionally over a further 15 minutes.
4. Add 25 ml sodium chloride solution to flocculate clay.
5. Stir the suspension and centrifuge for about 5 minutes (or until the supernatant becomes clear). Decant the clear supernatant.
6. Repeat steps 2 to 5 once or twice as necessary depending on the degree of brightness improvement with successive treatment.
7. Add 25 ml sodium citrate solution and agitate for 2 hours on a sample shaker.
8. Repeat step 5.
9. Add 200 ml distilled water and agitate for a further 10 minutes on a sample shaker. Stir and centrifuge for 5 minutes and decant supernatant if clear.
10. Repeat step 9 until the supernatant remains cloudy after centrifugation for 5 minutes.
11. Pour suspension into an evaporating dish and dry overnight at 60°C.

Kaolin

Appendix 5: Brightness determination

The procedure given here covers the measurement of brightness of white mineral powders (including kaolin) using the EEL reflectance spectrophotometer. The method includes the preparation of a test surface from a mineral powder.

Apparatus

EEL reflectance spectrophotometer
ECC design cylinder, piston and press
ECC design brass rings and holders
Unglazed ceramic tile
100 ml measuring cylinder
Pestle and mortar
125 μm sieve

Method

1. Clean the surface of the tile and place on the sole plate of the press.
2. Grind about 20 g dry clay to pass 125 μm . Fill the measuring cylinder with the ground clay up to the 20 ml mark.
3. Place a brass ring on the tile, place the cylinder on the ring and fill with the 20 ml of clay. Level the clay off.
4. Lower the piston into the cylinder until it rests on the clay. Adjust the position until the lever spigot of the press engages the centre dimple of the piston. This will exert a pressure of 1.2 kg/cm^2 at the piston head. Maintain this pressure for 20 seconds.
5. Raise the lever and remove the piston and cylinder.
6. Place the holder over the ring and, keeping the tile in place, invert. Carefully remove the tile from the test surface.
7. Switch on the spectrophotometer and leave to stabilise (preferably overnight).
8. Set the filter wheel in the spectrophotometer head to 601 (4260Å) and place on the test surface of the BaSO_4 standard (prepared using steps 3 to 6) within the light proof box. Shut the lid.
9. Adjust the spectrophotometer to read 100%.

Kaolin

Appendix 5 (continued)

10. Replace the standard with the test surface of the kaolin and note the % reflectance reading.
11. Turn the filter wheel to the next filter and repeat steps 8 to 10 until reflectance against the BaSO₄ standard has been measured over the entire range of wavelengths (filters 601 to 609; 4260Å to 6840Å).
12. Plot the % reflectance against wavelength the kaolin. Read off % 'brightness' (reflectance at 4570Å) and 'yellowness' (% difference between reflectance at 4570Å and 5700Å).

Note: Fired brightness is determined on dry pressed discs prepared in an XRF powder press or similar. Discs should be inspected before following steps 7 to 11 to ensure that the surface to be measured is completely flat (thin discs sometimes distort on firing).

Kaolin

Appendix 6: Viscosity measurement

Step-by step procedures are given for the flowability, deflocculant demand, and viscosity concentration tests. These tests are interdependent and must be performed in sequence.

Apparatus/reagents

Pestle and mortar
500 μm sieve
oven set at 60°C
beakers and glass rods
high-torque mixer fitted with a rev. counter
Brookfield RVF 100 viscometer
10% (wt) sodium hexametaphosphate ('Calgon') solution
10% (wt) NaOH solution

Preparation and moisture content determination

1. Gently grind the equivalent of 200 g dry weight of clay in a pestle and mortar to pass a 500 μm sieve.
2. Determine the moisture content of the clay by drying 20 g at 60°C overnight in a moisture extraction oven.

Flowability test

3. To a 100 ml beaker add 4 ml of distilled water (including any water present in the sample), 0.75 ml of 10% sodium hexametaphosphate solution and 0.2 ml of 10% NaOH solution.
4. Add the equivalent of 20 g dry weight of clay and mix with a glass rod.
5. Add 0.2 ml of distilled water and stir. Continue to add water until the slurry just flows from the glass rod. The solids content at this point is the flowability.

Note: Ensure that the slurry is thoroughly mixed between additions of water and that a reasonably thick glass rod is used, about 6 mm diameter.)

Kaolin

Appendix 6 (continued)

Deflocculant demand

6. To a tall 125 ml beaker add 2 ml of 10% sodium hexametaphosphate solution and 1.0 ml of 10% NaOH solution.
7. Add enough distilled water such that when the dry equivalent of 100 g of clay is added the solids content is the flowability plus 3% (i.e. if the flowability is 60% then start at 63% solids content). Volume of slurry required is that which will cover the shaft of the viscometer spindle past the indentation, with at least 5 mm gap between the spindle and the bottom of the beaker. 125 ml of slurry is usually enough. The slurry volume is roughly equivalent to the dry volume of the kaolinite.
8. Add 70 g of clay to the beaker, mix thoroughly using a low-speed, high-torque mixer and then gradually mix in the remainder of the clay. At this point the solids content will exceed the flowability, making the slurry a thick paste and difficult to stir. Fluidity of the slurry is maintained by 1 ml additions of distilled water until the slurry is fluid. Note the total addition of water.
9. The slurry should be mixed for a total of 25,000 revolutions from the start of stage 8 onwards or 25 minutes using a speed of 1000 rpm.
10. Cool the slurry to $22 \pm 1^\circ\text{C}$; after mixing, the temperature of the slurry commonly exceeds 30°C . Partially immerse the beaker in cold water to lower the temperature of the slurry. Tap the beaker down on a work surface repeatedly in order to remove any bubbles entrained during mixing.
11. Measure the viscosity of the slurry using a Brookfield viscometer RVF 100 at 100 rpm and 22°C . The choice of spindle depends on the viscosity of the slurry; the lower the viscosity the lower the spindle number (see table below for the viscosity ranges of spindle/speed combinations). The spindle should be carefully screwed into place by holding the spindle coupling (the spindle has a left-hand thread to prevent it loosening during measurement). Do not use the spindle guard. The spindle is immersed up to the middle of the spindle shaft, in the indentation, above the disc. Position the spindle centrally, away from the sides and bottom of the beaker.

Kaolin

Appendix 6 (continued)

12. After starting the motor allow the slurry to reach equilibrium - two minutes is sufficient - and take a reading. Depress the clutch lever and flick the on/off switch a few times until the dial needle is visible in the window. If the reading is over 100 use a higher spindle number and vice versa if the reading is under zero.
13. Take three consecutive readings; if they coincide to within $\pm 1\%$, average the values and multiply by the appropriate factor to convert to viscosity in centipoise. Viscosity measurements are accurate to within $\pm 1\%$ of the range maximum of the spindle /speed combination used, therefore readings from the Brookfield are more accurate the closer they are to 100 on the dial.
14. Add 0.08 ml 25% sodium hexametaphosphate from a burette, stir with a glass rod until homogeneous and measure viscosity. Continue adding calgon and measuring viscosity until the viscosity stops falling and starts to rise again.
15. Plot the weight of deflocculant added per 100 g of clay against viscosity. The amount of deflocculant required to produce the minimum viscosity is the deflocculant demand. During the test the viscosity may fall below the viscosity range of the spindle being used, measurements below 10 on the dial are unreliable. Record the viscosity using both the old and new spindles. It is preferable to use one spindle throughout the test.

Viscosity concentration test

16. Follow stages 6 to 13, adding enough calgon to meet the deflocculant demand.
17. Add 2 ml of distilled water, stir with a glass rod until homogeneous and measure the viscosity. Keep adding water and measuring the viscosity until the viscosity has fallen below 5 poise. Plot the reciprocal of the square root of viscosity (in poise) against the solids concentration. The viscosity concentration is the solids content at 5 poise.

Kaolin

Appendix 6 (continued)

Factors to convert Brookfield readings to viscosity in centipoise.

Spindle Number	Factor	Speed of rotation (rpm)			
		100	50	20	10
1	100/N	1 (10-100)	2 (20-200)	5 (50-500)	10 (100-1000)
2	400/N	4 (40-400)	8 (80-800)	20 (200-2000)	40 (400-4000)
3	1000/N	10 (100-1000)	20 (200-2000)	50 (500-5000)	100 (1000-10,000)
4	2000/N	20 (200-2000)	40 (400-4000)	100 (1000-10,000)	200 (2000-20,000)
5	4000/N	40 (400-4000)	80 (800-8000)	200 (2000-20,000)	400 (4000-40,000)
6	10,000/N	100 (1000-10,000)	200 (2000-20,000)	500 (5000-50,000)	1000 (10,000-100,000)
7	40,000/N	400 (4000-40,000)	800 (8000-80,000)	2000 (20,000-200,000)	4000 (40,000-400,000)

The conversion factor for each spindle/speed combination is calculated by dividing a factor by the speed of rotation (N). To convert to viscosity, in centipoise, multiply the Brookfield reading by the appropriate spindle/speed conversion factor. The figures in brackets underneath the factors are the ranges of viscosity (in centipoise) that a specific spindle/speed combination covers. The conversion factor is also the accuracy, in centipoise.

Kaolin

Appendix 7: Preparation of test pieces for modulus of rupture determination

This appendix gives a procedure for preparation of 12.5 mm diameter test pieces for MoR determination. Test pieces of different dimensions could be prepared using a similar procedure, depending on the sensitivity of the instrument used to measure MoR. A procedure for MoR determination is not given since this is specific to a particular instrument.

Apparatus

Electric stirrer
2 litre vacuum filtration flask
Filter pump
Buchner funnel
125 μm sieve
Hand-operated extruder fitted with 12.5 mm die

Method

1. Disperse 200 g of clay in water at a solids concentration of 25-50% using the stirrer.
2. Pass the 'slip' through a 125 μm sieve and pour into a 2-litre vacuum filtration flask.
3. Evacuate the flask to remove air bubbles in the slip.
4. Poured the slip onto a filter paper in a Buchner funnel and dewater to a plastic condition.
5. Hand-wedge (knead) the plastic clay, taking care not to re-introduce air. During this wedging process, adjust the moisture content to a level appropriate to just below the plastic limit.
6. Pack the wedged clay into the hand extruder and extrude each test piece to length of 60-70 mm and air-dry for 24 hours. Oven-dry at 60°C for 6 hours and then at 105°C overnight
7. Store test pieces in a desiccator before testing, or conditioned in a particular relative humidity over an appropriate saturated salt solution.

Kaolin

Appendix 8: Determination of fired properties

In BGS laboratories, fired properties of kaolins and other clays are determined using small extruded test pieces. Where large numbers of clay samples are being processed - e.g. in a regional survey of clay resources - extruded test pieces provide a means of providing a uniform test pieces relatively rapidly. Other methods of forming test pieces include hand moulding of briquettes and slip casting into plaster moulds. Discs used for fired colour measurement are generally pressed dry using an XRF powder press or similar. A small hand-operated extruder will provide approximately 10 test pieces 50 mm long by 6.3 mm in diameter from about 100 g of dry clay. This number is sufficient for simultaneous temperature-gradient firing using a specially designed furnace.

Test piece extrusion

Apparatus

- Hand-operated extruder fitted with 6.3 mm die
- Glass plate
- Hand-operated plant sprayer filled with distilled water
- Large pallet knife
- Steel rod (or similar) about 300 mm long by 10 mm in diameter
- Mounted needle
- Oven set at 110°C
- Pestle and mortar
- 125 µm sieve

Method

1. Gently grind 100g dry clay to pass 125 µm screen.
2. Spread the dry clay on a glass plate and spray with water whilst mixing the clay with the pallet knife.
3. Continue adding water and mixing until the clay just begins to change colour, develops a 'crumbly' texture, and/or just smears when squeezed between finger and thumb.
4. Tip moistened clay into the barrel of the extruder and tamp down using steel rod to remove as much air as possible from the clay.
5. Assemble plunger mechanism and rotate handle until 30 or 40 mm of extruded clay appears through die. Cut this material off and discard.

Kaolin

Appendix 8 (continued)

6. Whilst attempting to maintain an even rotation of the extruder handle, cut about 10 test pieces from the clay extrusion as it appears. Discard any bent or cracked pieces.
7. Number each test piece using a mounted needle and carefully set down on a flat glass or ceramic tile or tray. Oven dry overnight at 110°C.

Test piece weighing and firing

Apparatus

Top-loading two-figure balance
Mercury displacement apparatus (rack and cradle assembly)
Beaker filled with sufficient mercury to allow test piece to be completely covered to a known depth
Temperature-gradient kiln or programmable muffle furnace (max. temp. 1250°C)
Vacuum desiccator
Vacuum pump

Method

1. Weigh eight of the oven-dry test pieces. Record these and other weighing data on the worksheet given below against individual test piece number.
2. Record weight under mercury of empty rack and cradle assembly.
3. Record weight of each oven dry test piece under mercury.
4. Place each test piece in one of the eight cells in the temperature-gradient kiln. The maximum temperature of each cell ranges from 900°C (cell 8) to 1250°C (cell 1). The heating rate is about 4°C/minute; this allows the firing cycle (including a 30 minute isotherm or 'soak' at maximum temperature) to take place within the working day. If a kiln of this type is unavailable, then a suitable laboratory muffle furnace can be programmed to heat individual test pieces to the same range of temperatures. This is more time consuming although different samples can be batched together to be fired simultaneously.
5. Allow the kiln to cool overnight. Repeat steps 1 to 3 with fired test pieces.

Kaolin

Appendix 8 (continued)

6. Submerge test pieces in a dish filled with distilled water. Place the dish in the vacuum desiccator and evacuate for 3 hours.
7. Remove individual test pieces from water, dry off any excess and immediately weigh.
8. Calculation of fired properties is carried out as follows (see also worksheets 1 and 2 below):

Before firing

c = weight of test piece

d = weight of test piece under mercury

h = weight of empty assembly under mercury

After firing

e = weight of test piece

f = weight of test piece under mercury

hf = weight of empty assembly under mercury

g = weight of test piece after water absorption

$$ab \text{ (water absorption)} = 100 \times (g-e)/e$$

$$vf = 100/c \times (f-hf)/13.557$$

$$v = 100/c \times (d-h)/13.557$$

$$\text{Porosity (vol. \%)} = 100 \times ab/vf$$

$$\text{Shrinkage (vol. \%)} = 100 \times (v-vf)/v$$

$$\text{Bulk density} = 100/vf$$

$$\text{Specific gravity} = 100/(vf-ab)$$

Note: Mercury weighings should be carried out in a suitable fume cupboard.

Kaolin

Results of ceramic tests

Sample code & firing temp	Before firing			e Wt testpiece after firing	After firing		g Wt testpiece after water adsorbtion
	c Wt of testpiece (dried 110°)	d Wt of Testpiece under mercury	h Wt empty assembly under mercury		f Wt of Testpiece under mercury	hf Wt empty assembly under mercury	

Fired properties worksheet 1.

Kaolin

Calculation of firing properties

Sample:

(Water adsorption)	ab	vf	v	Porosity	Shrinkage	Bulk density	Specific gravity
ab = 100 (g-e)	$vf = \frac{100}{c}$	$v = 100 \frac{(f-h)}{c}$	$v = 100 \frac{(d-h)}{c}$	$= 100 \frac{ab}{vf}$	$= 100 \frac{(v-vf)}{v}$	$= \frac{100}{vf}$	$= \frac{100}{(vf-ab)}$
e	c	c	c	vf	v	vf	(vf-ab)
	13.557		13.557				

Fired properties worksheet 2.

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