



OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

TOGETHER

for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact <u>publications@unido.org</u> for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

17457

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION Distr. LIMITED PPD/ 17 August 1988 ENGLISH

EXPERT GROUP MEETING ON THE PROCESSING OF RAW MATERIALS Vienna, 22-26 August 1988

.

.

.

.

THE TECHNOLOGY OF KAOLIN MINING, BENEFICIATION AND INDUSTRIAL APPLICATION*

by

Henry E. Cohen UNIDO Consultant

11

* The views expressed in this report are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

2 3 AUG 1090

SSA User

1

1 1

HEC/JAM/UN/EGM/KC UC/INT/88/02 The Technology of Kaolin Mining, Beneficiation and Industrial Application

٠

.

..

Т

Table of Contents

	page	no.
Introduction	1	
Mining of Kaolin Clays	2	
Dry Processing	6	
Wet Processing	8	
Disaggregation and Dispersion	9	
Classification	11	
Cleaning Processes	13	
Froth Flotation	14	
High Intensity Magnetic Separation	15	
Bleaching	17	
Delamination	19	
Thickening	21	-
Filtration	22	
Finishing Treatment	23	
By-Product Minerals	24	
Trends in User Requirements for Kaolin Clays	26	

. 1 I 1 I I I I I I

1

1

11

1

П

т п

The Technology of Kaolin Mining, Beneficiation and Industrial Application A paper for the EGM, Vienna, August 1988 Henry E. Cohen

Introduction

The industrial and commercial background of kaolin clays, as well as the pertinent geological, mineralogical and processing aspects are surveyed in the attached paper, "Utilisation of Kaolin in Developing Countries". That paper provides an overall appraisal and strategies for developing countries to increase their participation in the production of kaolin clays. It also directs attention to potential added value benefits from combining clay production with kaolin-based manufactures.

The follow-up in this paper presents technological and process details of current techniques of kaolin production, fields of application and user requirements. It underlines the care and the complexities of treatment needed for preparing a seemingly simple mineral raw material to meet modern industrial specifications. Kaolin clay resources are widely distributed and capable of better utilisation. The main attribute needed in developing countries to gain market acceptance is reliable operator performance rather than special operator skills.

1

.

Mining of Kaolin Clays

The majority of economically workable deposits of kaolin clays occur close to the earth's present surface, under sufficiently shallow overburdens to permit extraction in open pit workings. Open pit workings of kaolin clays can reach depths up to about 150 metres (e.g. at St. Austell, Cornwall), but are generaly more shallow.

Underground mining is used only where extraction of good quality material is not feasible by opencast methods, or where the amount of overburden would make an open pit uneconomic. Typical examples include some ball clays in England and Germany and volcanically derived clays in China. Underground mining is always more expensive than opencast working, sometimes by as much as a factor of 10.

Open pits are frequently worked dry, in benches, variously using scrapers, mechanical excavators, drag lines or bucket wheel excavators and power shovels or front end loaders. Overburden is normally stripped with scrapers, in advance of mining. Dry mining is evidently appropriate for kaolin clays intended for subsequent dry processing routes. Depending on their hardness, the raw clays may have to be either crushed or shredded before being stored in several separate stock piles. These act as buffer stocks with a turnover in the region of two to four weeks. Separate stockpiles also facilitate selective mining and subsequent blending for greater flexibility in quality control. Conveyor belts, dumper trucks or bottom dump trailers are used to haul the raw kaolin to the processing plant which may be nearby or up to 25 miles distant from the pits.

If a dry mined clay deposit requires wet processing, the material is crushed or shredded, if necessary, and stockpiled. Blended raw clays from the stock piles are passed to large stirred tanks for dispersion in water

and are then degritted (a first removal of coarse waste) by classification. Comminution, dispersion and degritting are commonly carried out at or near the pit before pumping the raw clay slurry to the processing plant. For example, at the Felipe deposit of Caulim da Amazonia, the degritted raw kaolin slurry is pumped 5km to further processing.

As an alternative to dry mining a deposit, hydraulic mining employs a jet of water under high pressure to break down the pit face. Finer materials, mainly clay and sand, are washed to a collecting sump on the pit floor. Coarse waste is bulldozed aside and dumped. Subsidiary blasting is needed sometimes to remove hard bodies of rock. The water jet is normally trained along the base of the pit face, undercutting it and thus causing a slice of the whole height of the face to collapse. Several jets ("monitors") may be remotely controlled to work on different pit faces simultaneously, thus blending the raw clay. Treatment beyond the collecting sump is dealt with below, under the heading of wet processing.

Both dry and hydraulic mining systems are linked closely to first steps of processing in order to keep down the costs of removing coarse waste. This is very important with kaolin formations in granites where waste can amount to 85% of the mined material (e.g. at ECC, Cornwall). The selection of dry or wet opencast mining methods depends on the character and shape of the deposit, the hardness of the clay, the topography, availability of water and climatic conditions. Land restoration has become a significant additional f..ctor. The choice of dry transport of raw clay and disposal of separated coarse waste from the pit by means of conveyors or trucks depends on comparative costs which are influenced mainly by local factors. These include gradients, distances and the scale of the operation, as well as comparative costs of electric power, diesel fuel, tyres and other spares.

Trucking is more flexible, but also more labour intensive than conveyors. Pipeline transport of raw clay is carried out at solids concentrations in a range of 40-50% (by weight). Proper allowances need to be made for supplies and costs of transporting 50-60% of water.

Great importance is attached to grade control for best utilisation of the deposit and both dry and wet opencast mining are best regarded as the first steps in controlling product quality. Grade control starts with extensive drilling and analysis of core samples, followed by selective mining and separate stockpiling according to clay quality. Blending raw clays for feeding the processing plant and blending of semi-processed clays can now be computer-based. This eases feed quality adjustments for meeting specific product requirements and improves the utilisation of low quality sections of a deposit.

Underground mining of seams of ball clay must be selective to produce qualities of clay which can justify the mining cost. It is caried out in adits, or drifts, driven in stable ground at gradients up to 1 in 3 or 1 in 2 until the clay seams are intersected. Main roadways are developed in the seams with gradients from 1 in 10 to 1 in 4. Good ventilation, using upcast shafts to complete the ventilation circuits, is essential when there is a possible presence of methane derived from organic debris. Working is by room and pillar method, with levels and sublevels connecting the spams. Areas of good clay are blocked out for total extraction. Some backfilling may be used, but controlled subsidence is normally practiced.

The clay may be won by hand with compressed-air spades or, where space permits, by boom-type cutter loaders. Hand tramming of tubs is still common, followed by winched haulage of trains of tubs to the surface, for discharge from an overhead gantry into different storage bins for

subsequent blending. Hydraulic tipping gear may be remotely operated from the winding control cabin. However, unlike opencast mining, underground mining may yield only one quality of raw clay and the possible range of products then depends on processing.

Underground mining of in situ clay formations of volcanic origin broadly follows similar conventional practices, with modifications adapted to the more irregular shapes and inclinations of such formations.

They cannot be expected to adopt the kinds of mechanisation and automation which have almost swept away traditional mining methods in larger metal or coal mines. Mechanical and electrical engineering are taking over in such operations, with sophisticated controls, communications and instrumentation systems. Small clay mines, needing high selectivity and with an annual turn-out of perhaps less than 100.000 tonnes of clay, cannot justify the costs of such developments. It is likely that they will have to retain conventional mining methods, although they can benefit from improved machinery and instrumentation. This appears to imply that new underground clay mines in developing countries would not be in a strong competitive position for widely marketing their raw materials. Their best prospects for development would appear to rest with local uses for their clays, e.g. in ceramics or other manufactures which can accrue added value benefits.

Dry Processing

Dry processing routes are inexpensive and relatively simple compared with wet routes, but cannot yield high quality coating clays.

In its simplest form, dry processing comprises no more than mining, crushing and blending to provide a lump material of even quality. For example, SOKA at Meudon, Brittany, supply a rough lump grade of china clay for the production of ceramic tiles, with a high content of silica and low alumina (SiO_2 66.1%; Al_2O_3 22.8%). Such simple practice would be attractive for initiating operations in developing countries where cash and skills may have to be built up, possibly with an associated manufacture of tiles.

Ball clays for use in the manufacture of ceramics, refractories, fertilisers, etc., are often supplied simply in shredded form. A simple type of shredder consists of a revolving plate with sharp knives, fed from a hopper. Shredding provides an opportunity for blending and facilitates subsequent handling. The cut pieces of clay fall on to a high speed conveyor which throws them into a storage area. Some shredded ball clays are dried on fluid bed dryers and are known as "granulated" clays. with moisture contents reduced from about 20% to below 10%. For use as anticaking agents in fertilisers, such clays can receive an amine coating by means of a simple vapourising treatment.

On the whole, dry processing tends to be employed for meeting less demanding product specifications. It is used preferably for treating raw clays that are relatively close to the desired product grade, but require corrections of purity and/or particle size. Sometimes referred to as "air floating", dry processing uses diverse methods of milling and air classification to separate coarser and heavier material from clay particles which are mostly below 0.002mm in size.

Preparation for air classification involves at least two stages of comminution, usually integrated with drying by means of sweeping the mills with pre-heated air. These milled and air-classified products may have moisture contents as low as 2%. Some ball clays of good plasticity are first extruded through vacuum auger presses to form "noodles" which are then dried, pulverised and classified. For ceramics and refractories, ball clays can be pelletised, fired in rotary kilns at about 1350°C and sold either as pelletised or powdered chamctte.

The acceptable complexity of dry treatment depends on the product specification and is reflected in the price. This can range from US\$ 30 for shredded bulk clay to more than US\$150 per tonne for pulverised, air floated and bagged clay. However, raw clays differ greatly in their characteristics and hence in their suitability for different forms of processing, even within one deposit. Detailed tests are therefore essential for determining the most profitable deployment of each clay. When a new clay project is initiated it is easier to succeed with a relatively simple dry processing route which also provides an opportunity for attaining better practical familiarity with the properties of the clay.

Wet Processing

1.111

1[']011 0

Only wet processing routes are capable of yielding the very highest quality kaolin clays where both purity and finest particle sizes are of dominant importance. All the wet processing routes, starting with dry or wet mining, follow similar patterns of process stages in a well-established sequence: Thorough disaggregation of the mined material - thorough dispersion of the clay - removal of coarse waste - removal of progressively finer-sized impurities - size classification of the clay minerals - cleaning of the clay minerals - dewatering and conditioning of the clay products. Blending of different qualities of raw clay may be carried out before or after dispersion, as well as during subsequent stages of treatment. The main purpose of early blending is to achieve uniform operating conditions which benefit the quality uniformity of products. The main purpose of later blending is to adjust products so as to meet specifications to best advantage.

•. *

The number of unit processes and the types of equipment used in any one stage of a flowsheet can vary considerably, even for apparently similar clays. Details depend on local circumstances such as nature of the material, the scale of the operation, latitude in product specifications and overall optimisation of profitability.

8

Disaggregation and Dispersion

The processes of disaggregation and dispersion are jointly responsible for achieving good liberation of clay from associated waste minerals. This is important for avoiding losses of clay with discarded waste and for obtaining the highest possible extraction of clay per tonne of rock min.ed. As mined, the raw clay-bearing material usually has an acid pH, in the region of 4.5 - 5.0, hence the clay tends to be coagulated in addition to adhering intimately to associated gangue minerals.

Vigorous disaggregation and dispersion assist with delamination of coarse "books" of clay, the larger stack-like crystals of clay, into thin platelets. Thus, high shear in crushing and shredding, or in hydraulic mining, may contribute to increasing the valuable finest clay fractions. Dispersion in high-speed stirred tanks, at high solids concentrations (40-50% by weight), achieves better clay liberation than older more quiescent methods of treatment and may contribute to delamination.

Undispersed or poorly dispersed slurries of kaolin clays have very high viscosities, hence good dispersion incidentally lowers energy consumption in stirring and assists in working at high solids concentration. Good dispersion is achieved by means of pH control and by the addition of dispersing agents. With dispersion and degritting at the mine, the substantial increase in fluidity lowers the power consumption for transfer pumping of the clay slurry to the processing plant.

Most kaolin clays become well dispersed at a pH in the range of 6.0 - 8.5. The optimum practical pH value depends on the specific mixture of mineral phases and may be influenced by characteristics of the process water. For adjusting the pH it is common practice to use sodium carbonate or sodium hydroxide, in combination with sodium polyphosphates and sodium silicate as

deflocculants. Optimum combinations and quantities of these additives need to be ascertained experimentally for each new deposit and with due attention to the quality of the available water. For example, sodium carbonate and sodium polyphosphate additions per tonne of clay can range over 1-10kg and 2-6kg respectively. Blending of different grades of raw clays may have a significant influence on the type and quantity of reagents needed, as wells as on the time needed to achieve good dispersion.

After dispersion, the first stages of degritting previously relied on simple gravitational settling in open tanks. These were not very efficient and the prolonged residence times increased the hazards of contamination. Mechanical classifiers are now the norm for first-stage, in pit degritting. Either simple sand drags are used, or bowl classifiers which have rakes or spirals for removing the waste sediment. Fed with slurry from the dispersion tanks at 40-50% solids, via protective screens, their agitation and residence times are adjusted to achieve sedimentation of waste coarser than 0.050mm. Sand drags are cheaper in capital and operating costs, but are somewhat less efficient than bowl classifiers in separating +0.050mm waste from the clay.

Dewatered wastes are dumped and the very dilute overflow slurry from these classifiers may be pumped to large stirred thickeners and pH adjusted for removal of some water. The thickeners also act as storage/buffer tanks for subsequent processing. The water overflowing from the thickeners is recycled to the storage pool which feeds the monitors. The thickener underflow feeds the raw clay slurry to the main stages of classification and thence to cleaning, possible further blending, dewatering and finishing plants.

.....

Classification

Waste removal at progressively finer sizes is carried out in a sequence of classification units which may variously include hydrosizers, hydrocyclones and centrifuges. Large diameter hydrosizers used to predominate, but preference is now moving towards a sequence of hydrocyclones followed by centrifuges. The advantages are sharper classification cuts, short residence times and total enclosure. In a typical example, slurry at 5.5% solids may pass to 350mm diameter hydrocyclones, with the fine product from these passing to 125mm diameter hydrocyclones. Again, the fine product may be fed to 50mm diameter hydrocyclones. This sequence of three stages of classification would reduce a content of around 60% of +0.010mm material in the feed to about 30% in the final fine product. The latter would contain around 38% of -0.002mm clay, with a recovery of about 85% of that fraction from the feed. The coarse underflow products from the hydrocyclones are discharged to waste, at solids densities around 45-50%.

Further classification of the fine product for removal of +0.002mm material is carried out by means of continuous horizontal bowl centrifuges or, in latest practice, with 10mm hydrocyclones before centrifuging. A closecoupled three-stage array of 10mm hydrocyclones, operating as an integral unit, is capable of delivering a fine product of the order of 80% -0.002mm. The object of further size classification by centrifuging is a separation of the clay into products with different size qualities rather than any further discard of impurities.

Good classification is a pre-condition for attaining high quality end products. This requires a high degree of control of process variables such as pump performance, pulp density and flow rate/residence time. Modern electronic instrumentation and computer control are essential aids in this

respect, but they need to be supported by good equipment maintenance. It should be noted t⁺at classification at decreasing particle and cut sizes entails an increasing pulp dilution, sometimes down to about 5% solids (by weight). This implies handling, conditioning and controlling up to 20 tonnes of water per tonne of clay.

The chosen complexity of classification stages and equipment should relate mainly to the natural feed characteristics and the desired characteristics of the products. Classification should be as simple as possible and as efficient as possible, but should not be regarded as a substitute or standby for blending or storage. The process design stage for a new operation offers an opportunity for selecting the most appropriate modern equipment for the chosen scheme of classification. Changing equipment later on is usually difficult, because capital costs and plant lay-out tend to become frozen. It is therefore desirable that classification should be thoroughly pilot tested on a realistically large scale of throughput. This is relatively easy with hydrocyclones which are available and fully representative as single unit test rigs. Testing individual centrifuge units is not more difficult, although much more expensive. However, pilot testing of large hydrosizers is virtually impossible due to the sheer quantity of material that would have to be prepared and handled.

It may be concluded that the design and performance of hydrocyclone classification can be specified with some confidence on the basis of tests. For centrifuges and especially for hydrosizers, it is necessary to accept performance projections from manufacturers, based on experience elsewhere. This would necessitate allowances of considerable latitude in performance. It would also have to be accepted in the plant design that the rate of throughput may have to be traded against product quality.

пт п

Cleaning Processes

Additional cleaning may have to be used for further improvement of finer clays for coating grades and coarser clays for ceramics or fillers after centrifuging or other classification stages. The brightness, or whiteness, the gloss and the covering power of kaolin products are of prime importance in defining their commercial value for use in paper, but also for paints, plastics. ceramics and other applications. These user-specified characteristics are affected by the particle size distribution and by the purity of the clay product. Interfacial light scattering and the total surface reflectance (for white light) by clay platelets increase with decreasing particle size. Finer size fractions reflect more light and thus have higher brightness and gloss characteristics, as well as greater covering power than coarser size fractions of identical purity. This confirms the value of fine fractionation of the clay by centrifuging, but classification alone is usually not capable of removing very fine impurities, or discolouring contaminants and stains adsorbed on clay particles. Such discolourants necessitate the use of one or more additional cleaning processes to meet product specifications:

Froth flotation and/or high intensity magnetic separation can be used for removing fine free waste particles. Bleaching is commonly used for removing iron oxides. Processes of delamination are included here under cleaning, because they also expose discolc. ants for more efficient removal by bleaching. However, delamination improves clays mainly by breaking up larger crystals of kaolin, not by removing impurities. Delamination shears +0.005mm crystals into thin platelets, thus increasing the yield of higher value -0.002mm products.

Froth Flotation

Separation of hydrophobic from hydrophyllic minerals by froth flotation, using natural or induced selective surface conditioning, is an important industrial process for many ores and mineral products. After appropriate surface conditioning, streams of air bubbles passing through a particle suspension collect the hydrophobic material, for removal as a froth from the surface of the slurry. Fluid dynamic conditions in the slurry/bubbles system limit efficient particle collection to a size range with upper and lower limits. Particle shape and density also have an influence, but the size range is broadly from 0.2mm to 0.02mm. Flotation efficiency declines sharply above and below these limits. Hence, flotation requires special adaptation to be usable for the removal of impurities from kaolin clays, in a particle size range below 0.005mm.

An adaptation known as "ultraflotation" was developed specifically for the removal of anatase (TiO_2) from kaolin clays in Georgia, USA. This should be adaptable elsewhere for the removal of other impurity minerals.

In ultraflotation, coarser particles of an easily floated "carrier" mineral are added to a clay slurry to collect particles of anatase which are too finegrained for direct flotation. The carrier mineral is marble (crystalline calcite, $CaCO_3$), chosen for its effectiveness and low cost. It is ground to -0.05mm and is added to the clay slurry in a proportion within the range of 150 to 300kg per tonne of dry clay. The pulp is conditioned with fatty acid (mixtures of tall oil and petroleum sulphonate) and ammonia is used to adjust the pH to 9.0. With one rougher and three or four cleaner stages more than 85% of the anatase can be removed, with kaolin recoveries above 90%. The brightness of the kaolin is raised from around 82 to 88 or better and there is no contamination by residual calcite.

High Intensity Magnetic Separation

Various impurity minerals have magnetic susceptibilities significantly above those of pure kaolin clays and are sufficiently paramagnetic for magnetic separation. These include certain forms of mica (e.g. biotite, phlogopite, zinnwaldite, etc.), iron oxides, tourmaline and other oxides and silicates. Other types of impurities suitable for magnetic removal include coatings of iron oxides on clay particles and clay crystals with magnetic inclusions. However, the effective magnetic susceptibilities of all these forms of impurities are feeble and necessitate the use of magnetic forces close to the maximum available with present technology. Magnetic force is the product of field strength and field gradient, hence it is advantageous to use separator designs which combine highest field strengths with highest field gradients.

Matrix separators come closest to meeting these criteria. They employ a matrix of secondary poles in a high intensity field along the axis of a solenoid. If the solenoid is a conventional copper coil, the peak field strength in the core is about 2.0-2.5 tesla. With superconducting solenoids, the usable peak field strength can be raised to about 3.5 tesla, although the maximum peak field on the superconducting coil (inaccessible within a cryostat vessel) may be 6 tesla or more.

The matrix filling the solenoid core (with about 95% voidage), consists usually of stainless steel wire wool. The concentration of magnetic field lines passing into each steel fibre creates local field gradients up to 1 tesla per millimetre, thus combining extremely high gradients and field strengths.

The mode of operation is to run the clay slurry through the matrix. Magnetically susceptible particles are captured and retained around the

wires, whereas the non-magnetic water/clay dispersion passes through. After a period of collection, the matrix is removed from the magnetic field and the magnetics are washed out. This cyclic process is repeated either by means of switching the magnetic field, or by arranging the matrix in blocks in a large ring structure (known as a "carousel"). The ring has a step-wise rotary motion, moving each matrix block alternately past collecting and washing positions.

Two problems with this cyclic process are blockages due to unexpected floods of magnetics in the feed and potentially high clay losses due to entrapment in the magnetic product. Both capital and operating costs of this process are relatively high, hence its inclusion in a new project would need severe technical and economic evaluation. Capital costs of high intensity, high gradient, magnetic matrix separators are disproportionately large for smaller units, hence their suitablility for small throughputs is in doubt, except for making very high quality products.

1 1 1 1 1

Bleaching

The name of this process, well established in kaolin production world wide, is somewhat incorrect and the term "leaching" would be more appropriate. The process is used for cleaning clay particles which are coated or stained by more or less hydrated ferric iron oxides. The colours of these coatings can vary from dark brown, almost black, to reddish brown, red, beige, yellow and even green. Resultant colours of clays can vary from off-white or grey, to reddish or creamy yellow. The discolouring effects in clay products are disproportionately strongly visible, considering the small proportion of iron oxide present, often well below 1%.

Before treatment, it is important to select the correct size range for bleaching so as to minimise the consumption of reagents. Many clays have significantly higher contents of iron oxides in coarser sizes, say above about 0.050mm. Grinding of coarse iron-contaminated fractions should be avoided if this were to add substantial proportions of iron oxides to the finer fractions and thus increase the costs of bleaching.

The ferric oxides are usually quite hard and cannot be removed from clay by scrubbing. They are also insoluble in water and to render them soluble they are treated with a strong reducing agent such as sodium or zinc hydrosulphite (dithionite). A raised temperature (about 60° C) can increase the speed and efficiency of this treatment.

Thickening (see below) may have to be carried out before bleaching in order to obtain a reasonable solids concentration for cost-effective treatment. At about 30% solids, the clay slurry is first flocculated by adding alum and sulphuric acid, lowering the pH to about 3.5-4.0. The ferric oxides are reduced to the ferrous state, become water-soluble and are later removed with the process water. Acid consumption for pH control is of the order of

0.2-0.3kg and dithionite consumption is in the range of 2-3kg, per tonne of dry clay. The presence of other impurities may influence the optimal dithionite rate. Higher additions do not necessarily improve iron removal, but may instead lead to the formation of sodium or aluminium sulphates. This requires detailed testing for each new clay product.

Substantial discolourations of clays may be due to the presence of organic material in addition to iron oxides. In this case it is preferable to use hydrochloric acid and sodium dithionite, after rendering the organics soluble by oxidising them with chlorine gas.

Removal of organics is not necessary with clays destined subsequently for calcining or other heat treatment, for example in the production of ceramics. Such firing burns out any organic contents and the associated reducing conditions assist in producing very white fired products.

1

THE DIE T. T. T. T.

Delamination

The main purpose of delamination is to break up coarse crystals of kaolin minerals into thin cleavage platelets which have a significantly higher value. This raises the total clay extraction and improves the convertible grade of a deposit by increasing the ratio between contained and recoverable values, as well as yielding higher price products. As an additional benefit, discolouring coatings and stains of iron oxides are rendered more accessible for bleaching. The disadvantages include extra costs and added risks of contemination from grinding media. Improvements in optical and coating qualities (plus increased yield of fine clay fractions) need to be evaluated against the significant costs, including the necessary further classification after delamination grinding.

Three types of delamination processes are available: Wet grinding with abrasive media; dry fluid energy milling; and chemical delamination.

The safest and most dependable method of delamination is wet grinding under conditions of high shear. Fluid energy milling achieves dry delamination through particle collisions. This may enhance plasticity and calcining characteristics, but there is a risk of deformation of the kaolin flakes which is deleterious for brightness and gloss. Chemical delamination, employing organic chemicals to assist with particle disruption, tends to be most expensive, has flammability risks and a high energy consumption.

Wet delamination grinding uses small sand particles or plastic beads, approximately 2.5mm in diameter, as grinding media. These are employed either in high speed stirred tanks, or in revolving cylindrical grinding mills. Coarse particles are sheared out and also have miscellaneous projections broken off. Clay particles smaller than 0.002mm are virtually unaffected and their proportion can be increased by up to 20%.

Delamination in fluid energy or jet mills of different designs employs variously shaped mill chambers. Jets of either compressed air or superheated steam (to avoid condensation) are used for generating high speed particle collisions. The combination of energy of the particles plus volumetric concentration (mean free path) should result in adequate impact. Thus, the rate of throughput depends on adequate numbers of collisions plus adequate impact force. This force requirement (proportional to particle mass) limits the lower particle size attainable to about 0.001mm. Smaller particles have too little mass to produce sufficient impact forces.

Chemical delamination relies on chemical activation under conditions of high shear. Small additions of organic liquids can be used to provide polar molecules which are adsorbed on the surfaces of kaolin crystals. There, hydrogen bonds can be broken by substances of low molecular weight such as formamid, acetamid, hydrazine, or urea, which form intercalation compounds in water or alcohol. Hydrazine is a particularly good "wedge" to form intercalation compounds. These are formed with lithium or sodium acetate. alkali salts of amino acids, benzidine, or octylamine, starting with solutions in hydrazine and water, or hydrazine and alcohol. Mechanical energy is needed to achieve delamination, hence use is made of high speed agitators, pearl mills, 3-roll mills, or similar devices capable of producing high shear. The need for high shear necessitates prolonged working at high pulp densities (in the region of 60-70% solids by weight) and this results in high energy consumptions per tonne of clay treated. The use of specially designed equipment is essential because of the flammability hazard associated with the organics.

20

шт

Thickening

Following completion of the cleaning processes, the kaolin clay products are ready for dewatering. If the preceding treatment has left the clay in a state of dispersion (e.g. in classification), it is necessary to flocculate the product by lowering the pH to about 3.5-4.0. Other products (e.g. from bleaching) are already in a flocculated condition. The solids density at this stage may be anything in the range of 7-20% solids by weight, too low for efficient filtration. This necessitates some preliminary thickening with high speed nozzle centrifuges. No solids are lost with the water and the density is raised to 30-35% solids, suitable for filtration.

Alternatively, or additionally, preliminary thickening can take place in large gravity settling tanks which also serve as surge tanks, for storage, or to provide a final opportunity for blending. Even coarse clay products have slow settling rates and require settling areas of about 10 square metres our tonne per 24 hours to yield an overflow of clear water. The thickened sediment (of 20-25% solids) is raked to a central underflow discharge feeding sludge pumps. Conventional thickener diameters are of the order of 50 to 60 metres.

Centrifugal thickening achieves higher solids densities (30-35% solids) and is always more efficient for the finest clay fractions which are very dilute and have very slow settling rates. Disc-bowl centrifuges are used and the thickened solids are discharged through small-diameter nozzles at the bowl periphery. The internal stack of discs serves as an efficient clarifier, providing a large number of surfaces, a short distance apart, on which the solids can settle and consolidate. Output capacities range up to 10 tonnes of solids per hour, proportional to centrifuge sizes and inversely proportional to the fineness of the product.

Filtration

After thickening, dewatering usually continues by means of filtration. Several characteristics of the clay slurry have important effects upon filtration. The relatively fine particle sizes of all kaolin clays create a low cake permeability. This necessitates using slurry densities of not less than 25-35% solids in order to reduce the volume of liquid to be removed from the filter cake. Higher feed solids concentrations cannot be used, because excessive viscosities above 35% solids inhibit dewatering and cake discharge also fails. All these factors grow worse with increasing fineness of the clay particles, hence finest clay products (coating clays and fine ball clays) are most difficult and slow to filter. Solids contents of filter cakes should be 60-65%.

The most widely-used filtration equipment for kaolin clays are recessed plate and frame filter presses, or large rotary-drum vacuum filters. Filter presses are slower, more labour intensive and more expensive to operate, but are better able to deal with ball clays and other very finegrained products. Micro-porous ceramic filter plates represent a very promising recent development, but industrial performance is as yet unknown. Disc or candle-type vacuum filters are favoured by some producers.

With drum filters, water rinsing is used to remove soluble bleach residues. Roll discharge is more suitable than string discharge, because a layer of clay on the take-off roll ensures good adhesion to the cake layer on the drum and safe discharge of the whole cake. A "doctor blade" cuts excess clay from the roll. Drum filters with string discharge must run at lower speeds to form an adequate cake thickness for blanketing the strings. Clay cakes are too thin for scraper knife discharge which would also compact the layer of filter cake remaining on the drum and thus impair permeability.

Finishing Treatment

When filter cakes are discharged, they are in a plastic state, have an acid pH of 3.5-4.0 and are known as acid clays. Apron and rotary driers are commonly used for drying acid clays down to a final moisture content of about 5%. With apron driers, the filter cake is mechanically extruded (like noodles) on to the drier belt or apron. After drying, a roller-type mill is used for fine grinding. With rotary driers, the acid clay cake is usually mixed with some dry re-cycled material to produce a non-balling and friable product. A pugging mixer is used to achieve the proper consistency. The dried product is in lumps up to about 15mm size and has a moisture content of about 5%. A pulverizer with a flash drying system may be used next to lower the moisture content to less than 1%.

Alternatively, the acid filter cakes may be re-pulped with an addition of a dispersing agent (deflocculant) and become quite fluid, even at 65% solids. These are known as dispersed, or pre-dispersed clays and may be sold dried, or liquid in bulk. Spray driers are in common use for dispersed clay slurries at solids concentrations in the range of 58-65%. The slurry is pumped into a spray wheel spinning at high speed (up to 15.000 rpm) and is atomised co-currently in a stream of hot air. The air is introduced tangentially above or below the spray head to form a cyclonic flow. The large surface area created by atomization causes rapid drying, with a maximum temperature drop within a short distance from the spray head. The short contact time (30 seconds or less) is important. It permits drying the somewhat heat-sensitive kaolin to a moisture content of less than 1% in a single stage, without harming the characteristics of the product. The kaolin is discharged as small beads with a bulk density of about 0.8 g/cm³, with free-flowing handling characteristics and is easily re-slurried.

By-Product Minerals

Depending on the genetic origins of kaolin clay deposits, opportunities may exist for the extraction of by-product minerals such as quartz, mica, or feldspar. Especially in clays of granitic origin, these minerals may constitute a dominant majority of the deposit. For example, at St. Austell, Cornwall, they represent 80% of the mined material. It may be templing, therefore to regard them as potential earners of revenue, but it must be stressed that their usefulness depends entirely on three factors:

1. They must be capable of being processed within given cost constraints to meet commercial or industrial specifications;

2. They must be located sufficiently close to markets so that they do not incur excessive transport charges;

3. The markets must be large enough to justify the investment needed for the additional process requirements.

Reverting again to the example of St. Austell, a distance of some 300 miles from London changes some 20 million tonnes of readily convertible mineral by-products of kaolin from potentially valuable aggregate material into dumped waste. Only a very small tonnage finds local usage for aggregate, "reconstructed granite" blocks, etc.

It would be prudent, therefore, to insist that any new clay project should be designed to be entirely viable on the basis of its clay products, without taking account of possible by-product values.

The by-projucts may be grouped as follows:

In the coarse size ranges of reject material, clean mixtures of quartz, feldspar and mica may not be fully liberated, but should be free-draining. They should be free from clay and other finegrained minerals, free from excessive iron oxides and free from soluble alkali phases to be usable for

aggregates and building blocks. Processing to meet local road-making and building specifications should be relatively simple, in continuation of the processes used for their removal from the clay products.

At the other end of the particle size range of material rejected from clay production are classified fine size fractions, between 1mm and 0.01mm, that may consist predominantly of mica. These could find uses for fillers and extenders in various local products ranging from paints, plastics and rubber to nail varnish, depending on the mineralogical nature of the mica. For example, coloured biotite would be less desirable than colourless muscovite mica and uses would depend on available quantities, in relation to projected clay production. Froth flotation and other appropriate processing technologies exist, but detailed tests would have to confirm whether the mica can be purified monomically to respective product specifications.

Various intermediate reject products (from clay classification stages) probably contain mixed mineral populations which may require liberation grinding as well as mineral separation techniques. These could yield quartz fractions suitable for low quality glass (mainly bottle glass), or quartz feldspar mixtures suitable for ceramic glazes. Again, detailed test work would be necessary to ascertain the technical feasibility and the economic justification for producing some specified material. The geological provenance would be a dominant factor, but it is unlikely that any clay deposits would yield, for example, quartz of sufficiently high purity to be competitive for electronics on international markets.

It would be most realistic to identify mineral by-products for local uses and especially as substitutes for more costly imports. For example, finely ground quartz products could be used for toothpaste and domestic cleaners.

Trends in User Requirements for Kaolin Clays

There is a continually growing world market for Kaolin clays and paper will remain the dominant tonnage production target. Although there is increasing replacement of kaolin by calcium carbonate for both filling and coating, paper will continue to account for some 70-80% of total kaolin usage. However, there will be substantial growth in other uses for kaolin, both alone and in mixtures with swelling clays to achieve combinations of properties. Clay products are used increasingly for removing trace metals, for de-colourising, or for emulsifying, in processing industrial and food products and to make waste products safe for disposal. Lower grades of kaolin clays also gain an increasing demand for replacing more expensive organic thickeners in paints where some 1-2 kg of kaolin can be added to 450 litres of paint. The clay colour is not important and kaolin of low brightness is acceptable.

In new plastics, clay fillers are not just cheap extenders, but are added to impart better properties and to improve performance. In the USA alone, use for plastic motor car body panels will account for a clay consumption of 600.000 tonnes per year by 1990. Combinations of clay and mica receive increasing attention.

In cosmetics, ranging from face powder to perfume, high quality kaolin (priced at around US\$ 500/tonne) is used increasingly to replace magnesium carbonate (priced at around US\$ 1200/tonne). Thus it becomes attractive to produce relatively small quantities of highly refined "speciality kaolins", provided markets are also developed for associated tonnages of coarser lower-grade products. Kaolins in a size range of 0.020-0.045mm have uses not only for rubber and plastics, but also for fibre glass, welding electrodes, animal feeds, or insecticides.

Traditionally, ceramics offer wide-ranging markets for kaolins, from low grades for tiles and sanitary ware, to high quality porcelain for electrical and table ware products. To these traditional markets are now added new demands for more and more highly purified kaolins. These are needed for electronic and other tough new ceramics (e.g. "sialons") which have growing demand in engineering, structural and surgical uses. Such kaolins can command very high premium prices, but face exceedingly demanding specifications.

The wide choice of potential markets facing new kaolin producers necessitates careful evaluation of production strategies and targets. The inherent quality and reserves of a kaolin deposit are dominant factors, but clay products should be tailored initially to satisfy the types and quantities needed by domestic users. Where there is an absence of local industry, it may be desirable to consider integrated developments for the manufacture of industrial or consumer goods to replace imports. A necessity for creating a reservoir of skilled labour would also suggest that initial production plans should focus on simpler manufactures such as tiles, table ware, or electric insulators.

Local manufacture of refractories may offer another good support line for clay production if a country has pyrometallurgical operations in the vicinity. The cost benefits of cheaper transport and of soft currency should enable a new domestic producer to compete successfully with imports, even if the latter show initial quality advantages. However, longer term success and entry into export markets are attainable only with a combination of product quality, reliability and cost effectiveness. There is no good reason why these should not be achieved in kaolin production in developing countries.