MATERIAŁY CERAMICZNE /CERAMIC MATERIALS/, 63, 2, (2011), 233-238

www.ptcer.pl/mccm

Advances in Test Methods for Designing Optimised Ceramic Blends from a Raw Material Supply Perspective

PETER SHEPPARDSON

Sibelco Europe Marketing and Sales Team, England
e-mail: peter.sheppardson@sibelco.com

Abstract

Traditionally, clay blend development for ceramic applications has been done empirically from background knowledge of how the individual components are likely to behave in a given ceramic system. At Sibelco, modern advances in testing methodologies allows the rapid design and development of new clay blends tailored to customer needs. Three topics of key importance in the development of optimised ceramic clay blends are presented and discussed; namely, particle size, rheology and mineralogy. The paper concludes with two examples of how these methods can be brought together to develop high performance clay blends that meet the customers' needs.

Keywords: Yield, Optimised, Particle Size, Rheology, Mineralogy

POSTĘP W METODACH BADAWCZYCH DO PROJEKTOWANIA ZOPTYMALIZOWANYCH MIESZANEK CERAMICZNYCH Z PERSPEKTYWĄ ZAOPATRZENIA SUROWCOWEGO

Tradycyjnie, przygotowanie mieszanek surowców ilastych do zastosowań ceramicznych przeprowadzano empirycznie na podstawie wiedzy o tym jak poszczególne składniki mogą zachować się w danym układzie ceramicznym. W Sibelco, nowoczesny postęp w metodologiach badawczych umożliwia szybkie zaprojektowanie i przygotowanie nowych mieszanek surowców ilastych zgodnie z potrzebami klienta. Zaprezentowano i przedyskutowano trzy tematy mające kluczowe znaczenie dla przygotowania zoptymalizowanych mieszanek surowców ceramicznych, a mianowicie rozmiar cząstek, reologię i mineralogię. Artykuł kończą dwa przykłady ilustrujące połączenie takiej wiedzy w celu przygotowania mieszanek ceramicznych o wysokiej jakości, które spełniają wymagania klienckie.

Słowa kluczowe: wydajność, zoptymalizowany, rozmiar cząstki, reologia, mineralogia

1. Introduction

Founded in 1872, Sibelco has grown into a truly multinational business, today operating more than 280 sites in 38 countries (Fig. 1). Our-multi mineral portfolio is used in an extensive range of applications including glass, ceramics, construction, metal and energy. We work closely with our customers to create real value, drawing on the Group's global resources and expertise to deliver local solutions.

Fig. 1. World map indicating key Sibelco production sites.

Research and development forms the core driver behind many innovative customer products, for ceramics this technical effort is focused on two key 'mega trends', namely local solutions and energy. The first of which is all about ensuring that Sibelco provides customers in all locations with multi-mineral solutions that are economically sustainable and meet end-user requirements with the minimum of freight costs. The second, energy, is about adding value to minerals by reducing the energy needed in their manufacture or end-user application.

'Energy reduction' is not just about lowering firing temperatures to save on fuel bills. Although Sibelco have developed a range of fluxing systems that do achieve this, the primary focus is in improving efficiency and yields within the factory; one case study which can be used to demonstrate some of the work currently being done is the "Advances in test methods for designing optimised ceramic blends".

In most manufacturing industries focus is given to reducing costs as a way to improving profits; however, in the ceramics industry, most factories have the opportunity to improve the yield as well which is quite often overlooked (Eq. 1).

$$Profit = f\left[\frac{Yield}{Costs}\right] \quad (1)$$

Fig. 2. Example of financial savings achieved by improving yield.

Fig. 2 shows an example of how, although raw material costs have increased in achieving an improved yield in a sanitaryware factory, significant savings can still be achieved. Highlighting the fact that it is not always correct to just think of cost savings and the whole production should be considered.

For a long time, blending of controlled plastic clay seams from different areas of a quarry or even different quarries has been standard procedure at Sibelco's operations in the production of high quality plastic clay blends. Traditionally, the blend development is done empirically from a background knowledge of how the individual components are likely to behave in a given ceramic system. Now, new plastic clay blends are designed and engineered based on the results of advanced scientific measurements on the individual bulk plastic clay quarry selections. Advanced rheological, mineralogical and particle sizing methods are used alongside more traditional tests to fully characterise the individual components available and the information then used to optimise the final clay blend for the properties required.

2. Particle size

If we consider all of the particles in a ceramic slip or paste as spheres then it can be 'visualised' as in Fig. 3, with the red spheres representing the hard minerals (flux and filler), blue representing kaolin and yellow representing the plastic clay.

It can be clearly seen that if any part is changed slightly the gaps between the particles will change, affecting most of the important properties, including; the rheology, casting rate, drying shrinkage, and strength. The affect on these properties is further enhanced when the increase in surface activity is also considered; for the same volume, there is a ten fold increase in surface area for a corresponding drop in particle size, this is before any consideration is given to the fact that such a change in particle size of the clay, kaolin or overall body is likely to be associated with a change in mineralogy which will further influence the properties.

Thus, the particle size distribution of the overall system, and control thereof, is of the utmost importance, influencing most of the characteristics that are paramount to efficient sanitaryware production.

Particle size measurement plays a major part in process and product control and design in many industries. The ceramic industry traditionally utilises sedimentation techniques for measuring particle size. All, from the most basic Andreasen pipette methods to the more sophisticated instruments based on X-Ray attenuation, such as Sedigraph™, measure the settling rate and obtain the equivalent spherical diameter (e.s.d.) from Stokes' law for settling spherical particles.

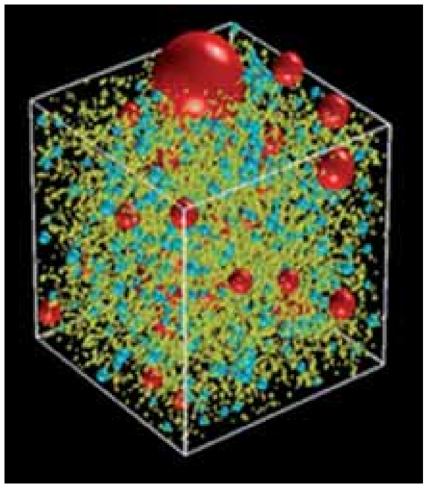

Fig. 3. Schematic diagram showing packing of traditional ceramic raw materials.
Note: The volume of material within the cube has to remain constant to keep the same bulk or slurry density. Thus, for example, if there were more fines then the effect would be compounded by the same volume reduction in coarser material, i.e., what appear small changes to a system can have a large affect on the properties.

Referring to Fig. 4, Stokes' Law is the mathematical description of the force required to move a sphere through a quiescent, viscous fluid at a specific velocity:

$$F_{drag} = 6\pi\eta a v \tag{2}$$

The buoyancy force is simply the weight of the displaced fluid:

$$F_{buoyancy} = m_{fluid} g = V\rho_2 g \tag{3}$$

Balancing Forces:

$$F_{drag} + F_{buoyancy} = F_{weight}$$

$$(6\pi\eta a v) + (V\rho_2 g) = mg \tag{4}$$

Rearranging Eq. (4) gives the Stokes settling equation:

$$v = \frac{2a^2(\rho_1 - \rho_2)g}{9\eta} \tag{5}$$

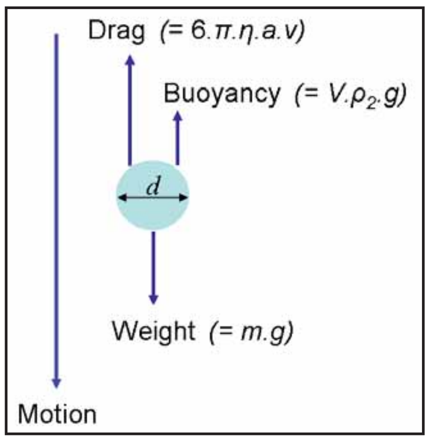

Fig. 4. Schematic diagram showing forces acting on a sphere in a fluid.

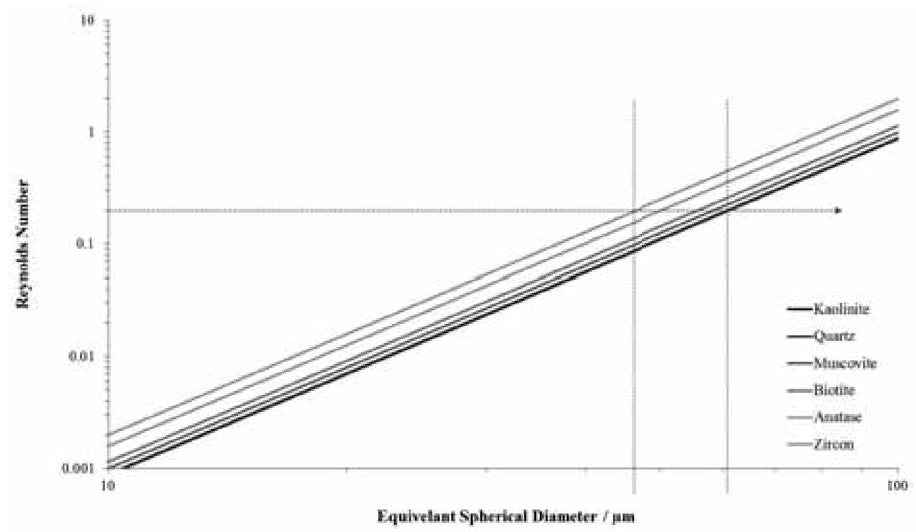

Fig. 5. Plot of estimated spherical diameter (e.s.d) versus Reynold's number.

where v is the rate of settling of a particle of volume V, density ρ_1 and an equivalent spherical radius of a in a fluid of density ρ_2 and viscosity η.

While Stokes' Law is straight forward, it is subject to some limitations. Specifically, the relationship is only valid for Laminar flow; engineers distinguish between this and turbulent flow by the utilisation of a parameter known as the Reynold's number. The Buckingham Pi Theorem relates the Reynold's number (N_{RE}) to the viscous forces within a fluid according to the following equation:

$$N_{RE} = \frac{2\rho_2 v a}{\eta} \quad (6)$$

Using the Stokes' and Reynold's equations (5) and (6), Reynold's number can be plotted against equivalent spherical diameter. Fig. 5 shows such a plot for a selection of common minerals in water at 20 °C. A Reynold's number greater than 1 denotes full turbulent flow and less than ~0.2 full laminar flow. Using a Reynold's number of 0.2 as an absolute upper limit, it can be seen that typical 'heavy' minerals such as zircon or anatase can not be reliably measured above ~46 µm e.s.d; this upper measurable limit is increased slightly to ~61 µm for lighter minerals such as feldspars and clay minerals. Note that if a sample contains particles greater than these sizes the turbulent flow created will affect the result for the finer particles. Brownian motion plays a major part in settling experiments at small particle sizes; particles of 2 µm e.s.d will almost certainly be effected and particles less than 1 µm significantly so, and possibly to the point that they do not settle at all, giving an apparently finer result.

Two further factors that can influence the result of a settling experiment are worth noting:

(i) Hindered settling: in general this has an effect at solids levels greater than ~1 % by mass and, hence, settling experiments should be conducted at concentrations less than this.

(ii) Mixed materials with differing densities; such as zircon and feldspar in a glaze slurry: the density used for the calculations is an average for the system, thus, giving an 'averaged' combined result for the e.s.d.

The main alternative to sedimentation techniques, Low Angle Light Scattering (LALS), until recently also had serious limitations; for example, among others, i) the wavelength of the helium neon red laser (633 nm) used as a light source limited the minimum particle size measurable and ii) absorption or refraction of light by the particles under evaluation is greater at smaller diameters and was not accounted for in the Fraunhofer model originally used to calculate the equivalent spherical diameter.

With the introduction of blue lasers (with shorter wavelengths) and improved detector electronics in instruments such as those produced by Malvern™, particles down to 0.02 µm can now be detected. In addition, increased computing power allows the highly complex, but more accurate Mie theory of light scattering to be more readily solved. This theory incorporates the Fraunhofer model but also takes into account other factors such as the refractive index and absorption of the particle (Fig. 6). The choice of refractive indices and absorption factors for LALS experiments is critical, and also, for analogous reasons to the importance of density in settling methods of particle size analysis, refractive index and absorption differences in mixed material systems can cause problems.

Thus, both methods have their inherent differences and limitations, but in general a settling experiment result normally appears finer than the equivalent light scattering one.

The particle Size distribution of the material is also partly responsible for many of the parameters, such as fluidity, shrinkage or strength, used to select a plastic clay (or a kaolin) for silicate ceramic manufacture; however, limiting focus to only one or two figures, e.g. % passing 2 µm and % greater than 125 µm (residue) is insufficient to fully characterise a clay. In reality it is the particle packing of the whole body formulation that is most important in controlling these properties, but obviously it is the contributions from the particle size distributions of the individual components that build-up to produce the overall distribution

3. Rheology

Various methods of measuring this important variable have been, and are used, in the ceramic industry, from visual assessment and operator experience though ford cups and Technio Torsion Viscometers (TTV, gallenkamp) to fairly so-

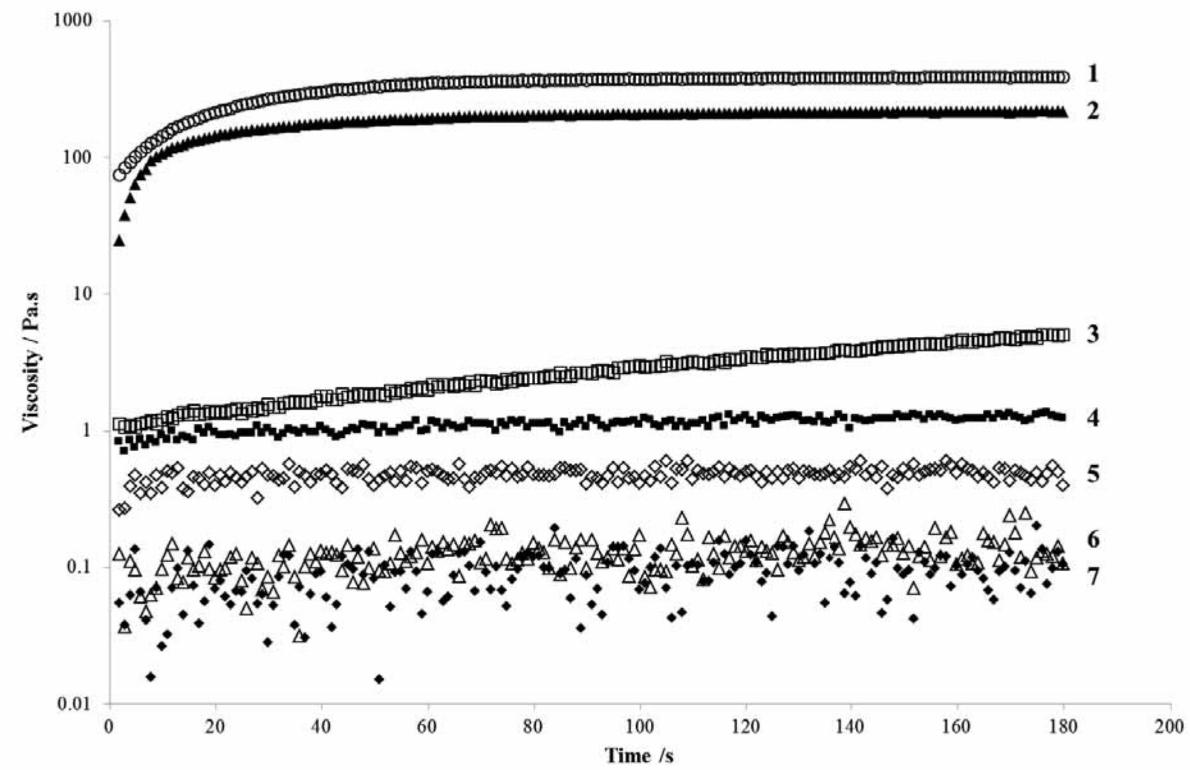

Fig. 6. Thixotropy build-up curves for slips at different levels of deflocculation for clay from 3 sources at 55% solids using a TA Instruments AR2000, with parallel plates at constant low shear rate. Key: 1. UA, 0.35% deflocculant added (280/150), 2. UK, 0.20% deflocculant added (293/112), 3. DE, 0.20% deflocculant added (312/97), 4. UA, 0.50% deflocculant added (340/1), 5. UA, 0.65% deflocculant added (342/0), 6. UK, 0.35% deflocculant added (355/0), 7. DE, 0.35% deflocculant added (358/0), (/*) indicates the fluidity/thixotropy measured using a TTV with 11/16" cylinder and 30 swg wire.*

phisticated viscosity measuring devices such Brookfield™, depending on sector and geography etc. However, most give a single or a few values that describe the nature of the slurry and are best used for quality control.

Modern rheometry enables us to evaluate the visco-elastic behaviour of any raw material in slurry or paste form.

There are many different rheological tests that can be performed to evaluate a material. For example, a method is shown here whereby three samples (UK, UA and DE) have been evaluated at different levels of deflocculation, using a method that measures the viscosity build–up with respect to time (thixotropy) after a high shear pre-treatment, large difference can be seen (Fig. 6).

It can be immediately noticed that partially deflocculated UA and UK plastic clay samples (traces 1 and 2, Fig. 6) have similar responses when subjected to this test method. The difference being that the UA clay requires more deflocculant to produce the slip with this response. The curve shows that when the applied shear is relaxed, the viscosity rapidly builds with respect to time and then stabilises. This is the desired effect when casting silicate ceramics; a structure is formed in the slip and then held for the duration of the casting time allowing a controlled thickness to build on the mould face; at the end of the casting process, the slip has a controlled viscosity which allows efficient clean drainage of the hollow sections. When a further small deflocculant addition is made, the UK material fully deflocculates and gives a flat response (trace 6, Fig. 6), whereas the same deflocculant addition to the UA slip gives a lower viscosity than previously but it still shows a small amount of thixotropy build-up and is not fully deflocculated (trace 4, Fig. 6). Only at a further deflocculant addition is full deflocculation achieved (trace 5, Fig. 6). The base level viscosity of the fully deflocculated UA slip is approximately 3 times higher than that of the UK clay slip. The DE clay slip has a completely different response compared with that of the UK and UA materials when partially deflocculated (trace 3, Fig. 6). Here the viscosity starts much lower than that of the UK and UA clay slips and then continues to build at a steady rate; the slip appears to take much longer to respond to the removal of the applied shear which could lead to less predictable casting rates and, if the viscosity builds too much, sluggish drainage of hollow sections after the casting process is complete. As with the UK material, the DE clay sample completely deflocculates with a further small addition of deflocculant to a base level similar to that of the UK clay (trace 7, Fig. 6).

4. Mineralogy

Traditionally, ceramists use prior knowledge and chemistry (or other indirect methods) for quantifying the mineralogy of raw materials by rational analysis, sometimes assisted by qualitative X-Ray diffraction. Although a mature technique, quantitative XRD has, until recently, been reserved for research and geological exploration samples due to the skills and time required for accurate result interpretation.

With the advent of the modern computer, the time taken for interpretation has decreased significantly making this a viable technique for blend development

Again using three plastic clays from different geographical areas as an example, and analysing them by X-Ray Powder Diffraction (XRPD) (Fig. 7), at first the 3 plastic clays could

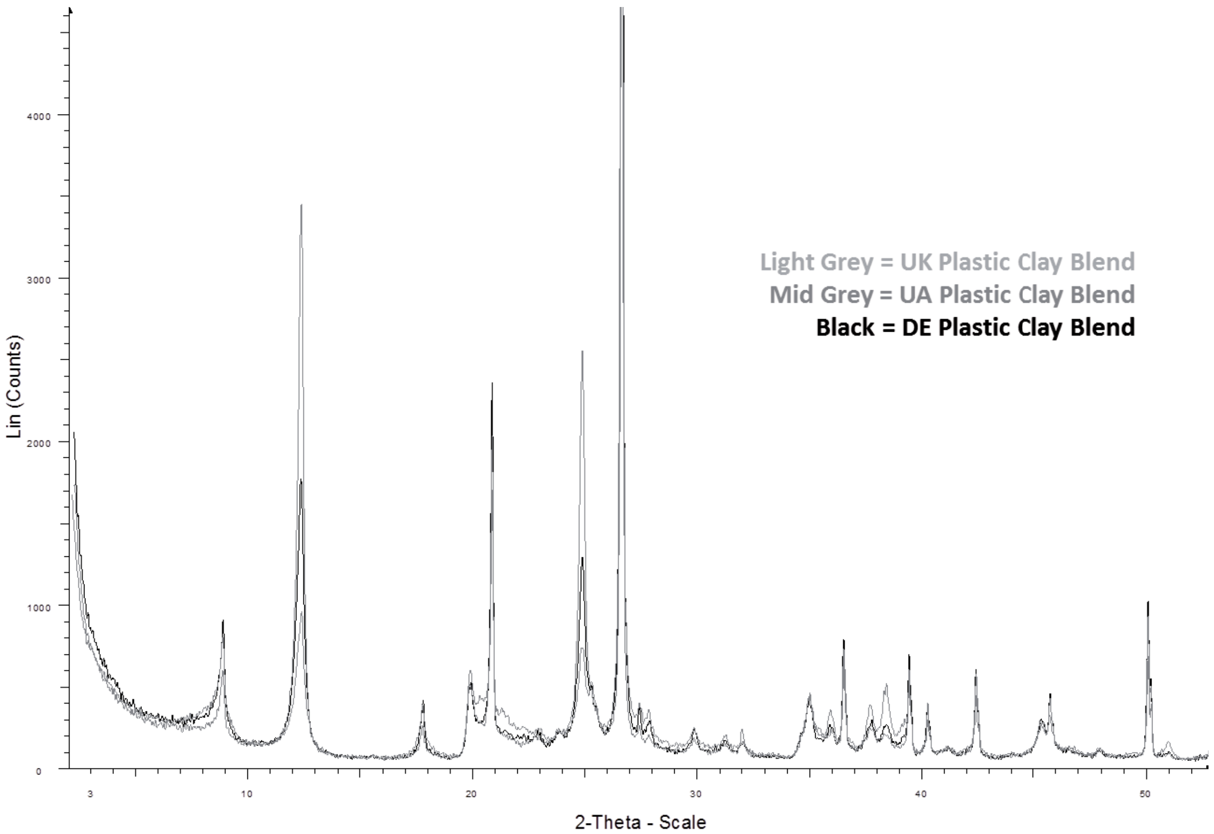

Fig. 7. XRPD patterns for plastic clay from 3 sources.

appear to have similar compositions. On closer inspection, although there is some overlap of other peaks, it can be seen that there are slight differences in the quartz content between the clays with the UK clay containing slightly less than the other 2 clays (Fig. 3, peaks at 20.8 and 26.6 °2θ). The UA clay contains less kaolinite than the DE sample which in turn contains less kaolinite than the UK clay, the kaolinite in the UK clay is also more ordered, indicated by more detail in the kaolinite peaks between 19 and 22 °2θ. The UK clay sample also contains less Illitic/Micaceous mineral than the other two materials. From the ratio of the mica peaks at 8.9 and 17.7 °2θ an idea of how illitic the clay is can also be gained, in this case the UK is the most micaceous and the DE clay the most illitic.

However, it is only on a very detailed evaluation, along with other tests being conducted, that the real differences in mineralogy can be established. The further experimentation and evaluation reveals the differences in clay mineralogy between the clays from the 3 sources (Fig. 8).

On gylcolation, the UK clay shows some evidence of expandable smectite, with a possible peak appearing at 17 angstroms, the DE clay shows less evidence of expandable

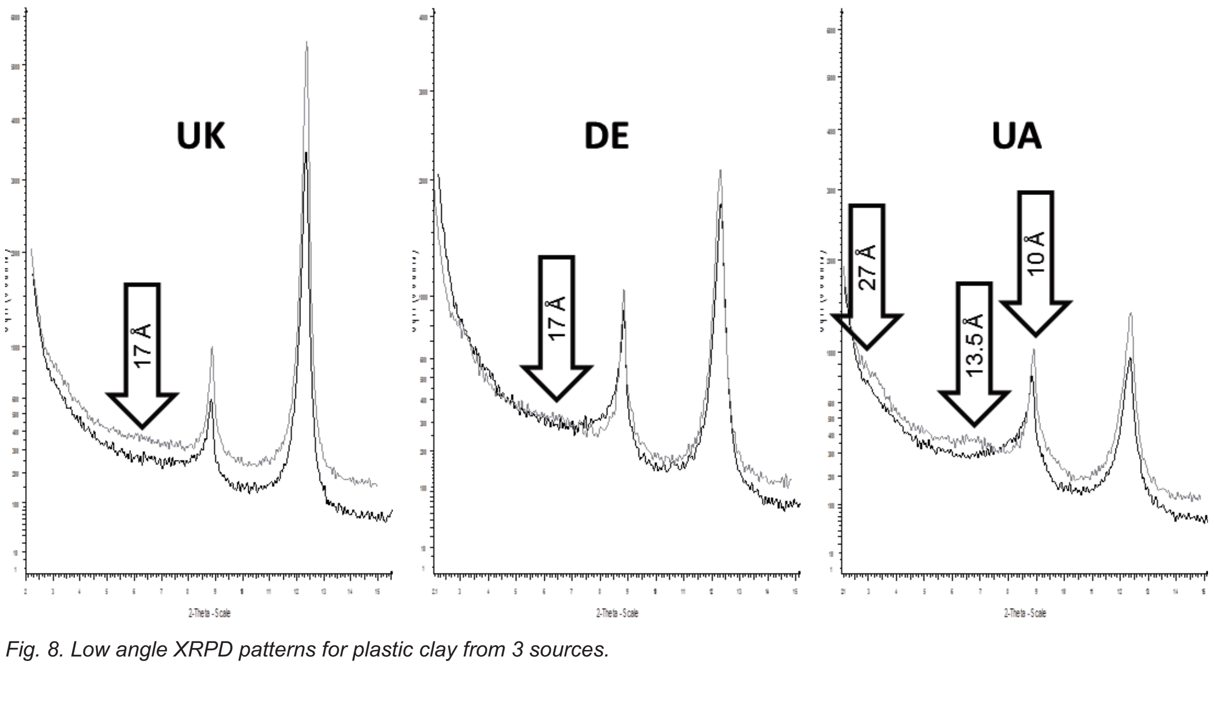

Fig. 8. Low angle XRPD patterns for plastic clay from 3 sources.

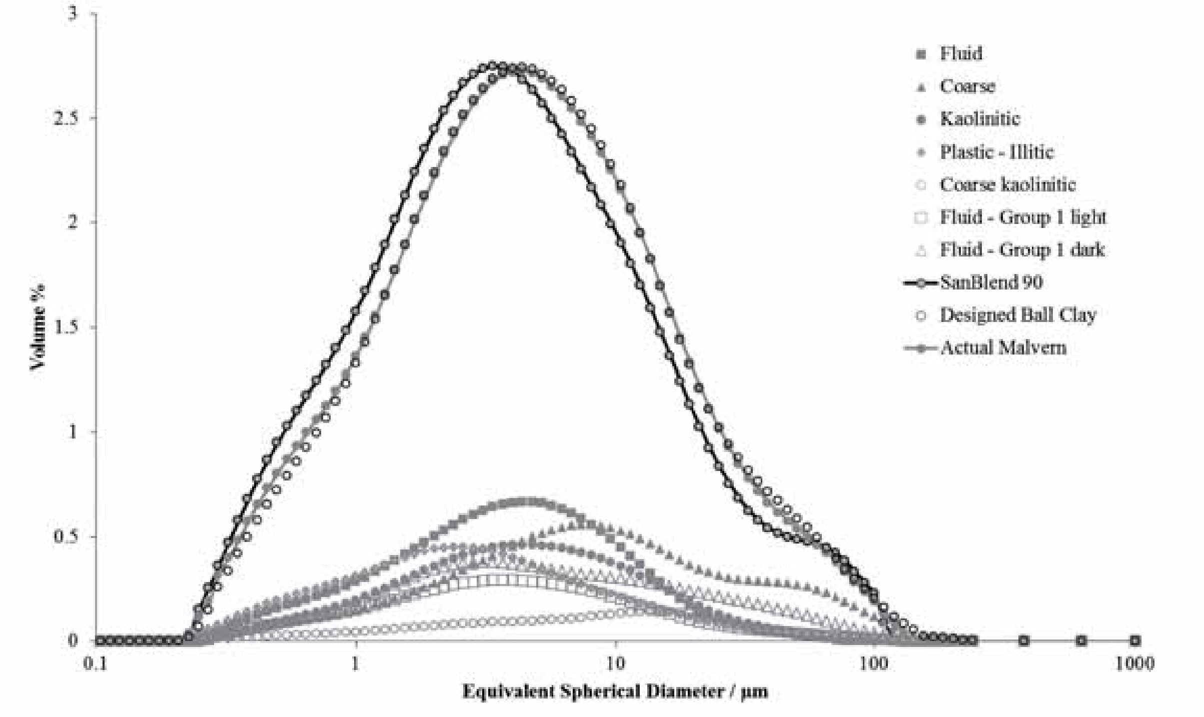

Fig. 9. The design of application specific ball clay blends.

smectite but instead there is evidence of the illite/mica peak at 8.9 angstroms sharpening and possibly a peak at 13.5 angstroms appearing, there is stronger evidence of this in the UA sample and is thought to be a disordered illite/smectite mixed layer mineral.

It is this disordered illite/smectite mixed layer mineral and the illite content that is largely responsible for the rheological properties seen above and also, quite often without knowing, for the traditional selection of certain types of plastic clay for an application. For example, the disordered illite/smectite mixed layer mineral is responsible for giving plasticity and green strength to the Ukrainian clays which are usually selected for large format tile manufacture.

5. Conclusion

By using these and other advanced techniques, together with the in-depth knowledge of our plastic clay deposits, clay blends can be engineered to fulfil and exceed the requirements of the application they are designed for. Inter–quarry blends are developed in order to maximise the key parameters needed for the application, such as rheological performance for sanitaryware production or strength and plasticity for tile manufacture. By utilising this methodology to engineer clay blends, the maximum amount of 'local' components may be included leading to the added benefit of considering the environment in terms of reduced logistics.

6. Appendix

6.1. Example 1

A customer of Sibelco requested a ball clay blend optimised for inclusion in a pressure casting body along with their preferred, single, kaolin. Fig. 9 shows the results of the design process. Naturally, the fitting routine is constrained to take into account, for example, the required chemistry and rheology. Although only the result for the ball clay is shown, it is vital to consider the overall body packing in order to maximise the casting performance and strength; failure to consider all the body components is likely to lead to serious rheological problems! The requirement for high fluidity effectively means that the number of fine particles needs to be controlled. The performance of the designed ball clay met all the customers' requirements.

6.2. Example 2

In Russia and the Ukraine, typically 50 % plastic Ukrainian clay is supplemented with fluid German or English clay to produced a sanitaryware casting slip suitable for use in faster traditional or pressure casting processes, by engineering the plastic clay blends, up to 80 % Ukrainian clay can now be used to produce these high performance slips.

A further benefit of these advanced plastic clay 'design' techniques is that a plastic clay or even a full body formulation can be tailored to suit a specific customers needs, even if they intend to part use a 'local' plastic clay from another source for ecological/economical reasons.

♦

Received 30 September 2010; accepted 13 October 2010