

EFFECT OF PARTICLE CHARACTERISTICS ON THE SOLIDS DENSITY
OF BAYER MUD SLURRIES

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The solids density that is achieved in residue areas, washer underflows or on filters varies considerably with bauxite type. In particular Jamaican mud settles to a much lower g/l solids than those derived from most other bauxites. A fundamental study of the physical properties that affect solids density was undertaken to determine if the differences could be explained. This included particulate modelling based on particle interactions. Various characteristics of muds were measured including particle size, porosity, surface area, mineralogy and absorptivity. Sizing of muds was complicated by the effect of pH on sizing. Those data, together with the particulate modelling, enabled predictions of differences in solids densities that compared well with those obtained in practice. Comparisons between muds must be on a volume/volume basis.

Introduction

The solids density that can be achieved in thickeners, washers and in mud stacking operations is a critical parameter affecting refinery efficiency. A high % solids is required to improve the efficiency of washer operations, reduce the capital requirement and minimise residue volume. The slurry at such high solids must still be pumpable, ie have relevant rheological properties.

The solids density attainable and that which is still pumpable is well known to vary with bauxite type. Most bauxite residues can be settled to g/l solids in excess of 500g/l with appropriate flocculent and equipment and still be pumpable. However, under similar conditions muds from certain bauxites achieve densities of around only 350g/l and can be quite unpumpable at 500g/l.

Differences in the rheological properties of various Bayer muds are well demonstrated in the work of Pashias (1) who measured the change in compressive yield stress with % solids for Bayer residues from several locations. Jamaican mud was significantly different to the other muds with a much lower % solids attainable and also high yield stresses at low % solids. Some typical rheological data from a more recent study comparing mud derived from a variety of bauxites is shown in Figure 1. The poor rheological properties of Jamaican bauxite- and mud-slurries are well known in the Industry. There is also variation within the Jamaican bauxites with the notorious yellow bauxite producing residues that are especially difficult to handle compared with those from the red bauxite.

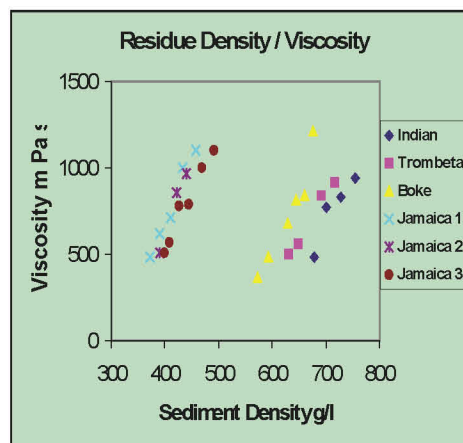


Figure 1. Comparison of rheological data for various bauxite residues.

There have been many studies at trying to improve the handling characteristics of the Jamaican residues to levels similar to those for other residues, generally with little success. Most success has come from physically altering the mud through high temperature digestion in which the goethite is converted to hematite (2). Indeed the goethite:hematite ratio is often cited as being the major factor (3). However the fine mud fraction of the Darling Range (Western Australia) and many other muds have similar goethite:hematite ratios to the Jamaican muds yet have good rheological properties. Generally it has not been possible to predict the solids density that will be achieved based on either chemical or mineralogical analysis. Consequently empirical testing is required to ascertain the % solids that would be obtained for muds from different bauxite.

There are physical differences between the muds, the goethitic bauxites generally having significantly higher surface area than their hematic counterparts. The size distribution of the muds can vary significantly. However, even with that information it is still difficult to predict differences between muds or the % solids that can be achieved.

An attempt was made to try and determine the reasons for the observed differences. The following approaches were taken.

- 1) A fundamental approach related to the factors that determine the settled density of muds
- 2) Modelling of the system based on fundamental considerations and measured properties to calculate slurry densities
- 3) Full characterisation of the red muds, in particular those physical properties that are relevant to the final solids density
- 4) A critical look at the validity of the measurement process such as particle size, surface area and in particular to check the validity as well as the accuracy of the measurement
- 5) Measurement of the settled solids densities and relevant rheological properties of various red muds to provide information on the effects.

If the fundamental properties can be isolated and measured then there is the potential for predictions of solids density to be made for new muds based solely on appropriate characterisation.

Packing Density – Fundamental Considerations

Packing metrics

The packing of particles has been a subject of research for many years (4). Concepts such as porosity (void volume fraction) and its related parameters, packing density (=1-porosity) and specific volume (1/packing density), are widely used in the macroscopic characterisation of particle packing. In the Industry solids are normally expressed as either % solids or as g/l as those are the direct measurement units. For control purposes any of these metrics are adequate and for design purposes for sizing equipment and mass balances, they are ideal. However, for comparing and assessing different muds, the comparison is better made on a volume/volume basis.

Effect of particle size

It has been established for coarse (>100µm) mono-sized spheres that porosity is constant, equal to about 0.4. However, if the particle size is smaller than a certain value, weak forces such as

van der Waals and electronic forces become significant in addition to gravity. These forces often restrict the relative movement between particles and may result in the formation of agglomerates. Consequently, as shown in Figure 2, decreasing particle size increases porosity (5).

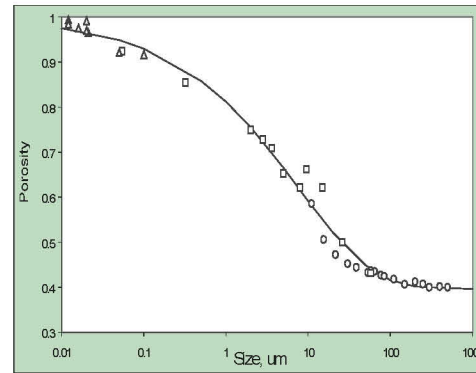


Figure 2. The effect of absolute particle size on packing of mono-sized particles.

Effect of particle shape.

The shape of particles affects the friction and relative motion between particles, which in turn affects porosity significantly. This effect is used to advantage in materials such as filter aids where, for optimum permeability irregular and varying shaped particles perform best. Consequently materials such as perlite and diatomaceous earth (which contain skeletons of diatoms and other such creatures) provide a myriad of shapes. Among the parameters devised to describe particle shape, sphericity is probably most common (6). For mono-sized particles, the relationship between porosity and sphericity has experimentally been established, as shown in Figure 3 (7).

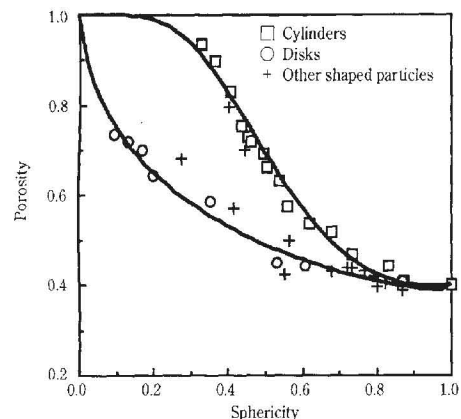


Figure 3. The effect of particle shape on packing of mono-sized particles.

Effect of particle size distribution

When particles of different sizes are mixed and packed together, a denser packing can result compared to that of mono-sized spheres. This is obvious for the binary packing of coarse spheres, as shown in Figure 4a. The decrease in porosity is due to the filling of the void space among the large particles by the small particles and/or the filling of space by large particles which is otherwise occupied by a combination of small particles and voids. However, as shown in Figure 4b, such porosity reduction is not always there, particularly when there is a significant difference in porosity of mono-sized particles. Nonetheless, Figure 2 clearly demonstrates that particle size distribution (rather than the absolute size) is also a critical factor for predicting or making comparisons. Understanding and modelling the dependence of porosity on particle size and shape distributions is a key issue in the study of particle packing (4,8).

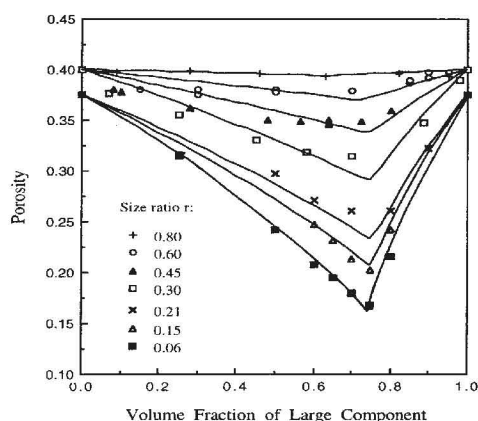


Figure 4a

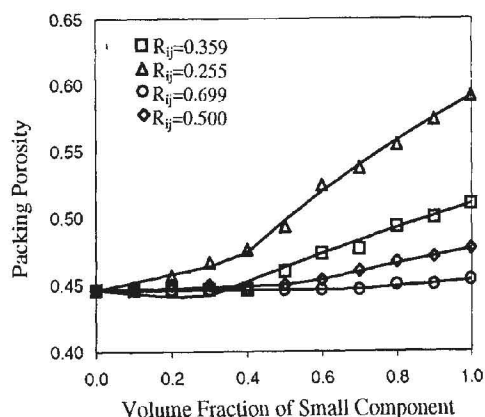


Figure 4 b

Figure 4. Typical results of binary packing of different sizes: (a), coarse spheres; (b), fine spheres.

Effect of liquid phase

The presence of liquid phase will affect particle packing (9). As the liquid content increases, dry-based porosity increases to a maximum, then becomes independent of liquid content. However if the liquid content is greater than the maximum amount of liquid that can be held by particles, it increases with liquid addition. Further increase in liquid content will move to the packing regime in which liquid is the carrier and particles are packed in the liquid rather than gas medium. This behaviour is considered to be directly related to the capillary force acting on individual particles and the resulting formation of agglomerates or aggregates. Understandably, particle characteristics and material properties are all important factors.

Another factor that should also be considered is the formation of a fine layer of liquor on the surface of a particle separating adjoining particles. The layer is similar to the classic double layer on surfaces from a surface charge perspective. It is difficult to put physical dimensions on double layers as the interaction energy depends on the liquor concentration and varies considerably with distance. Calculations of this DLVO layer by Pashias (1) suggested the layer would be in the 1 – 5nm range. Consequently fine particles will occupy a proportionally larger volume than coarse particles, as their effective size is larger. This will lead to a lower volume fraction of solids. The effect will only be significant for particles of less than 100nm in size.

Obviously, fines particles are associated with cohesive forces, such as van der Waals and capillary forces, and liquor layer, all of which lead to high porosity. Applying pressure to such a packing can either partially or completely overcome this effect and result in denser packing. Consequently, fine particles have a greater potential for improvement than coarse particles.

Particle density

Particle density has little effect on particle packing but is required information for converting a volume/volume basis to an appropriate g/l or % solids basis. The density of the solids as measured with a pycnometer includes closed pores but not open pores. For particles, internal voids (closed or open) will effectively contribute as part of the solids volume; the porosity will also have the effect of reducing the density of the particle. Consequently, the porosity of the particles is also required.

A good example of this effect is comparison of the packing density for hydrate and alumina. The particle size is the same as one is simply the calcined product of the other. There is a small amount of shrinkage (10), but that is a minor secondary effect. For the alumina approximately one third of the weight has been removed through removal of the water. Hence comparing the packing density of hydrate and alumina, the hydrate has a much greater packing density when expressed as g/l or wt%. The difference is that the density of the alumina particles is lower than the hydrate.

Computer modelling of particle packing.

System considered

The system considered is assumed to be composed of n components, with each characterized by its initial porosity ϵ_i and

nominal diameter d_i ($i=1, 2, \dots, n$; $d_1 \geq d_2 \geq \dots \geq d_n$). The so-called nominal size here can be any measurable particle size, eg equivalent volume diameter. The porosity of this system ϵ should be a function of ϵ_i , d_i , and the fractional solid volume of the i th component X_i . d_i and X_i represent a particle size distribution. Particle shape can also be considered in the modelling (11).

Linear packing model

There are quite a few mathematical models for predicting porosity ϵ , or its related parameters such as packing density ρ ($=1-\epsilon$) or specific volume V ($=1/\rho$) (8). Among these models, to date the so-called linear packing model is probably the best because of its simplicity and flexibility. In fact, this model is the only one that has been applied to non-spherical and/or fine particles (5,11), in addition to coarse spherical particles. According to this model, the specific volume of a packing can be determined by the following equation:

$$V = \text{Max.}\{V_1^T, V_2^T, \dots, V_n^T\} \quad (1)$$

where

$$V_i^T = \sum_{j=1}^{i-1} [V_j - (V_j - 1)g(d_i, d_j)]X_j + V_i X_i + \quad (2)$$

$$\sum_{j=i+1}^n [1 - f(d_i, d_j)]V_j X_j$$

and V_i are the initial specific volumes, equal to $1/(1-\epsilon_i)$ by definition and ϵ_i can be empirically quantified as shown in Figure 2. Eq (1) means that V equals the maximum of V_i^T ($i=1, 2, \dots, n$). $f(d_i, d_j)$ and $g(d_i, d_j)$ are referred to as the interaction functions between components i and j . The two functions can be quantified based on the results of binary packing, and it has been found:

- 1) For coarse particles, they can be determined by the following equations (11)

$$f(r_{ij}) = (1 - r_{ij})^{3.3} + 2.8r_{ij}(1 - r_{ij})^{2.7} \quad (3)$$

and

$$g(r_{ij}) = (1 - r_{ij})^{2.0} + 0.4r_{ij}(1 - r_{ij})^{3.7} \quad (4)$$

where r_{ij} is the small-to-large size ratio, equal to d_j/d_i ; $i < j$. The packing size d_i depends on particle size (equivalent volume diameter d_v) and particle shape.

- 2) For fine spheres, r_{ij} can be related to R_{ij} , i.e. the size ratio between components i and j in terms of d_v , by the following equation (5):

$$r_{ij} = R_{ij}^p \quad (5)$$

where parameter p depends on both absolute and relative particle sizes, although it appears to be constant under certain conditions (5,8).

- 3) For wet particles, the interaction functions will also depend on liquid content. For the packing of fine or wet particles, material properties and packing method are also important. To date, general equations for their quantification are not available yet, although some progress has recently been made on the packing of coarse particles with water addition (12).

With the presence of cohesive forces, particles may form agglomerates or aggregates and do not behave as individuals in a

packing process. Such behaviour is macroscopically taken into account by varying the interaction functions as described above. An alternative method is to measure the size distribution of agglomerates and then use it in the model calculation, giving the so-called inter-porosity. In this case, the so-called particles are agglomerates which have properties, such as internal structure, intra-porosity and "particle density", different to those of primary particles. This approach was attempted for coal (13) and is probably worth being explored further in future research.

Application to Bayer Residue

An example of the modelling predictions is shown in Figure 5 for red muds derived from Jamaican and Boke bauxite. The predictions were for dry mud, not slurries. The Boke mud had a much higher packing density than the Jamaican mud, 0.27 compared to 0.20. Calculations on the packing density for mixtures of the two muds gave a virtual linear relationship. The modelling work clearly indicates that much lower solids densities would be expected with Jamaican mud.

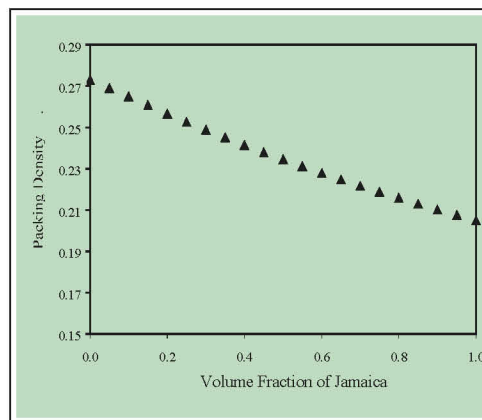


Figure 5, Application of model to mixing of Jamaican and Boke residues whose particle size distributions were determined by Laser sizing.

Particle Characterisation

From the above, the study of particle packing must include critical parameters such as particle size, particle shape, the density of particles and their porosity. Some of those properties can be measured directly whereas many, such as particle size for fine materials, are measured indirectly (often inferred from some signal such as a laser diffractogram and application of various algorithms).

Particle size

The particles of Bayer muds are fine and most are less than 20µm in size. The measurement needs to be made on the slurry as drying results in agglomeration and consequent incorrect particle size. (Extended washing does not totally prevent this and it also results in decomposition of some of the mud products such as DSP.) Two mud slurries were added to the laser machine and measured as normal. Ultrasonics were then applied and further measurements obtained (Table 1). The muds respond differently to the ultrasonics because of breakdown in the floc structure.

Table 1: Sizing of residues from Jamaican and Boke bauxite on sonification.

Sonification Time	Jamaican mud			Boke mud		
	% <1um	% +5um	% +20um	% <1um	% +5um	% +20um
0	14	25	7	25	38	20
15 secs	22	20	5	30	38	21
30 secs	28	17	4	32	38	22
1 min	35	14	2	34	38	22
2 min	44	13	2	35	39	22
4 min	53	12	2	37	38	21
6 min	59	11	2	39	38	21

When slurries are measured they are diluted which reduces the pH of the liquor. The effect on size over the pH range that can be encountered during sizing measurement for two different muds is shown in Table 2. The sizing can change dramatically depending on the measurement pH. Direct observation of the mud particles confirmed the sizing data reflect a large degree of natural agglomeration (these particular muds had not been treated with any form of flocculent). The pH's in Bayer liquor (both the concentrated liquor and that of the final washed residue) are such that the particles are negatively charged; this will lead to a large degree of natural flocculation. Such flocculation effectively produces a larger particle, but one with a significantly lower density because of its open structure.

To investigate the extent of natural flocculation, samples of residues were observed optically at different pH. Figure 6 reveals that natural flocculation varies greatly with pH and the extent may not be captured by laser sizing techniques. It is also noted that Jamaican mud had a stronger propensity to self flocculate than other residues.

The mud was also sized using sedimentation to determine if the density of such natural flocs varied with pH. There was relatively little difference at the different pH's suggesting that, even at the lowest pH tested, the particles consisted of agglomerates of finer particles.

The base unit particle size of mud components can be determined by techniques such as TEM and XRD.

The DSP in muds tends to occur as micron sized particles (14), although the size and degree of agglomeration can vary depending on type and amount of reactive silica and the digest conditions used – eg with or without predesilication digestion.

The iron oxides in most muds consist of very fine crystallites of goethite and hematite with crystallite sizes of the order of 20 – 30nm. They can occur as loose agglomerates and as more compact particles.

From the above, measuring, or even defining the particle size is difficult. The size required for predicting the packing density and rheological properties is that of the effective agglomerate size under the relevant liquor conditions rather than the absolute size of the particles. The sizing is probably best obtained on slurries that have been treated by using ultrasonics or physical means to break up any flocculation caused by flocculent addition. A combination of techniques such as sedimentation, direct sizing by observation of the particles as they settle and laser sizing, needs

to be used to obtain the required information, rather than a single technique.

Particle shape.

The shape of the particles for fine particles is difficult to measure and with such a myriad of particle shapes, from the wool balls of the DSP to the plates of hematite and goethite, and the variety in between, assuming a uniform shape is a reasonable first approximation. Also, the shape is really that of the natural agglomerates formed rather than the individual particles. That information could be obtained by direct observation of the particles settling such as with the floc density analyser (15).

Table 2: Laser size analysis of Jamaican and Kwinana mud slurries at a range of pH.

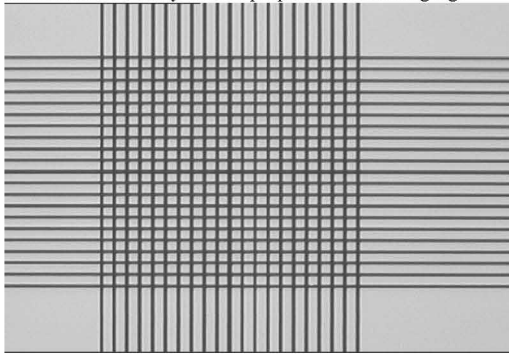
Mud sample	pH	Percentile size (µm)		
		10 th	50 th	90 th
Jamaican	7	1.1	2.1	12.8
	9	2.8	6.4	13.6
	11	2.8	8.8	25.9
Kwinana	7	1.5	11.5	129.1
	9	2.5	6.0	40.3
	11	2.4	7.4	27.4

Particle density

Measurement of the porosity of very fine particles is difficult as the pore space between particles needs to be differentiated from that within the particles, for example as with a mercury porosimeter. The surface area of Bayer muds generally range between 20 and 40m²/g. That is equivalent to individual particles of around 20nm in size. That number fits well with the crystallite size of the iron oxides but is significantly finer than the apparent particle size of 0.1 – 10µm. This suggests that many particles consist of agglomerated crystallites with many pores.

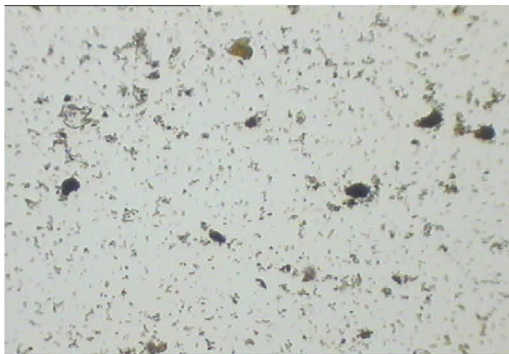
An alternative method is to measure the porosity by water absorption. Data for Jamaican, Boke and Kwinana mud are shown in Table 3. The Jamaican mud adsorbed significantly more water. When allowed to equilibrate in air after drying, the Jamaican mud was still slowly increasing in weight after 6 weeks. Jamaican bauxite is well known for its high moisture content and can dust at very high moisture content. Also, when dry, it can act as a very efficient spill control soaking up liquor.

Figure 6. Calibration image, and optical microscope images of Kwinana and Jamaican muds at various pH's, shaken immediately before preparation for imaging.

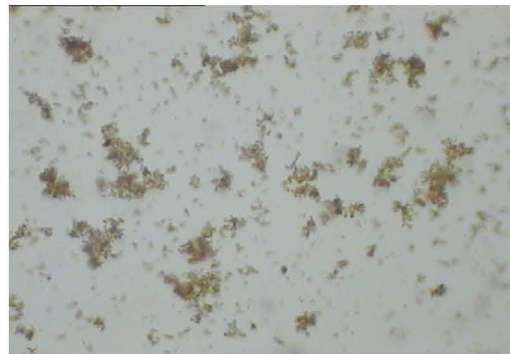


10µm per division

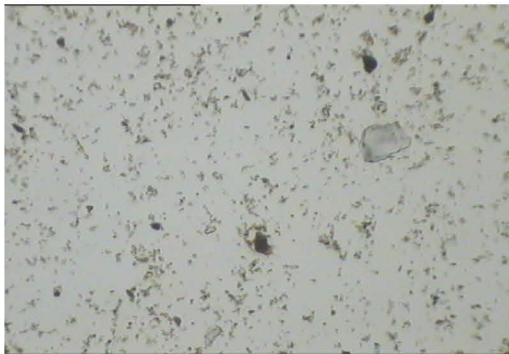
The three numbers at the lower right of the mud images are the 10th, 50th, and 90th percentiles for sizing by Malvern (no delay after adjusting pH).



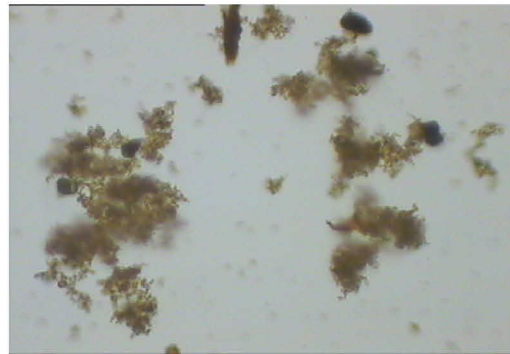
Kwinana Mud @ pH = 7 1.3 5.0 130



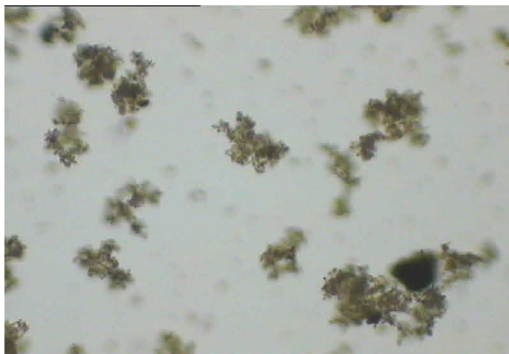
Jamaica Mud @ pH = 7 1.3 3.0 17



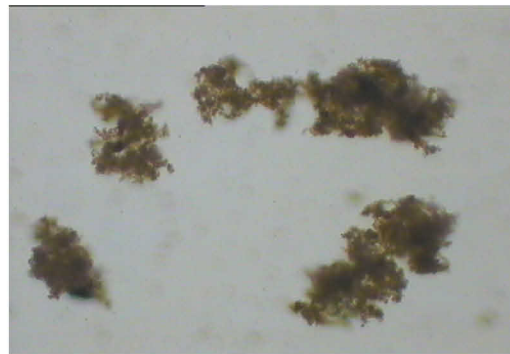
Kwinana Mud @ pH = 9 1.4 4.8 123



Jamaica Mud @ pH = 9 1.8 7.3 16



Kwinana Mud @ pH = 11 4.5 24 56



Jamaica Mud @ pH = 11 4.2 25 52

Table 3: Wt % increase over time for bauxites and residues from Jamaica, San Ciprian, and Kwinana, exposed to ambient and elevated humidity conditions.

Sample ID	Ambient Conditions (Kwinana, Western Australia)			Elevated Humidity (approximately 70% R.H.)			Ambient Conditions (Kwinana, Western Australia)		
	1 hr	2 hr	20 hr	1 hr	2 hr	5 hr	1 wk	2 wk	6 wk
Jamaican Bx	0.7%	1.0%	1.0%	2.0%	2.4%	3.6%	0.8%	1.0%	1.3%
Jamaican Mud	1.6%	3.2%	4.7%	7.6%	9.4%	13.7%	5.8%	6.1%	6.7%
Boke Bauxite	0.3%	0.4%	0.4%	0.7%	0.8%	1.2%	0.2%	0.3%	0.3%
Boke mud	0.5%	0.8%	1.0%	1.9%	2.4%	3.8%	1.0%	1.2%	1.2%
Kw -45um Bx	0.3%	0.4%	0.4%	0.8%	1.1%	1.4%	0.4%	0.5%	0.6%
Kw -45um Mud	0.7%	1.0%	1.2%	2.1%	2.5%	3.8%	1.0%	1.2%	1.0%
Kw -8µm Mud	0.8%	1.4%	1.7%	3.4%	4.4%	6.0%	1.8%	2.0%	2.3%

Table 4. Effective particle density and g/l solids density of the various muds.

	Particle Size	Particle Size	Particle Size	Surface Area	He Density	Porosity	Particle Density*	Solids Equivalent**
	D10 µm	D50 µm	D90 µm	M ² /g	g/cc	%	g/cc	g/l
Jamaican mud	1.1	2.1	13	35.5	3.4	13.7	2.27	340
Boke mud	1.3	3.7	140	18.5	3.3	3.8	2.96	500
Kwinana mud	1.5	12	130	15	3.2	3.8	2.96	500
Kw mud (<8um)	2.4	7.5	32	N/D	N/D	6	2.78	420

Comparison of Jamaican and other muds

Some typical rheology data for Jamaican mud and others were shown in Figure 1. There is a very large difference in the g/l solids at an equivalent viscosity, approximately 380g/l compared to 650g/l at a viscosity of 500mP.

The particle sizing of some muds (from laser sizing) are shown in Table 4 (conditions used were to get as close as possible to the free particle size). The Jamaican bauxite is significantly finer. The surface areas were 35.5 and 18.5 m²/g and the porosity as measured by moisture absorption was 13.7 and 3.8 % for Jamaican and Boke mud respectively.

Using these data then the difference in packing density between the two scenarios based on packing density was calculated. If 650g/l is considered the base case then Jamaican mud would be expected to settle to 505g/l solids simply from particle size effects. The 14% pore volume changes the effective density of

the particle from 2.98 to 2.27. This in turn reduces the 505g/l down to 385g/l which is not too dissimilar to that measured.

Conclusions

Comparison of the % solids or g/l solids for different muds should be made on a volume/volume basis. The known inferior rheological properties and lower % solids of Jamaican mud is primarily a result of the physical characteristics of the particles – their fine size and that the individual particles have a high porosity.

Modelling of fine particle systems together with correct measurement of the relevant parameters can enable predictions of the relative properties of the muds such as final settled volume etc to be obtained.

Measurement of the particle size and density of mud relevant to rheological properties is compromised by the natural agglomeration of particles in Bayer liquor.

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