Characterising highly active nuclear waste simulants

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**Abstract**

Reprocessing of spent nuclear fuel produces a highly active liquor (HAL) waste stream, which is typically stored over extended periods in waste tanks equipped with extensive heat exchange capability. Over time, particulates are known to precipitate from the HAL within these tanks. Particle simulants provide a route for understanding the physical behaviour of these HAL solids under different agitation and transfer conditions. Particle and dispersion characterisation techniques are used here to understand the behaviour of two types of simulant HAL solids, viz. caesium phosphomolybdate (CPM) and zirconium molybdate (ZM), in dispersion. Distinct properties are established for CPM and ZM and compared to a common oxide particle material titanium dioxide (TiO2). The results of this study highlight the influence of key aspects of the HAL particulates, such as size and shape, on relevant solid-liquid properties such as sedimentation and rheology. The influence of bulk liquid properties such as electrolyte concentration and pH is also investigated. The results indicate various possible behaviours within the tanks which may impact the storage, remobilisation and pipeline transport of this class of nuclear waste.

1. Introduction

Nuclear power is a non-carbon emitting energy supply which provides around 30% of electricity in the EU (Gonzalez-Romero 2011). A key advantage of using nuclear energy for electricity generation is the reduction in carbon dioxide emissions to the climate (van der Zwaan 2002). Issues regarding the nuclear industry have been discussed at length by many authors and include political issues, environmental impacts, economic evaluation and public opinion (Comission 2008; Van der Zwaan 2008). Amongst the most significant issues are the wastes produced and the strategy to manage and dispose of them. Therefore, it is of interest to further improve nuclear waste treatment strategies which ultimately contributes to an improvement in nuclear and environmental safety aspects.

Reprocessing of nuclear fuel is part of a spent fuel management strategy that is used heavily in some countries such as the UK and France. In such cases, it is the penultimate stage of the nuclear fuel cycle where separation of waste products takes place from the residual usable uranium and plutonium, which can then be recycled into new fuel material. The spent fuel obtained from a nuclear reactor typically contains approximately 3% waste. The waste consists of fission products and minor actinides dissolved in nitric acid. After it is concentrated, this is known as highly active liquor (HAL). In the UK, this process takes place at the highly active evaporation and storage (HALES) plant at Sellafield, UK. The HAL is stored in a number of highly active storage tanks (HASTs). Within the HASTs, solid materials are known to have precipitated from the HAL over time and it is simulants of these solid-liquid systems that are of interest in this study.

An understanding of the solid-liquid properties of this HAL waste is required for its safe transport, storage and eventual disposal if the HASTs are to be safely emptied and decommissioned. However, characterising such waste has proven to be challenging due to its hazardous radioactive nature. Realistic simulants have been produced as an alternative to direct materials sampling, to represent the solid particles contained in HASTs. Currently, a key priority is to reduce the quantity of stored HAL and it is therefore important to determine the behaviour of the HAL solids for emptying and post operational clean out (POCO) of the HASTs.

Key rheological parameters link directly to the engineering design of any waste treatment process involving solid-liquid dispersions. A current issue with the HASTs is that despite the fact there are jet ballasts and air-lifts to maintain the dispersion, some of the dense particulate materials are expected to settle rapidly out at the bottom of the tank and on other pipework. Studies of settled beds of the particulates can provide insight into the permeability and compressibility of any sediment that forms. Rheological flow curves are also used here to study the hydrodynamic properties of the suspensions as a function of particle volume fraction. The sedimentation rate is another important parameter relevant to transfer of the suspension from the tank; any sedimentation within the pipes during transfer may cause blockages and this must be avoided.

Here, we focus on the characterisation of relevant particulates and their associated liquid dispersions for two HAL simulants, caesium phosphomolybdate (CPM) and zirconium molybdate (ZM). Standard particle characterisation techniques are used to provide information about the simulants in terms of particle shape, size and density. The effect of these properties on solid-liquid behaviours such as sedimentation and rheology is then used to broaden the understanding of how these features can affect the process plant operations. Additionally, the similarity in behaviour between the synthesised simulants and a titanium dioxide (TiO2) powder is investigated. TiO2 is a readily available species in large quantities, therefore it would be an attractive and cheap alternative to the use of the caesium and zirconium simulants. TiO2 has been previously used as a nuclear waste simulant (Omokanya 2009), while generally a great deal of literature exits on its rheological properties (Turian, Ma et al. 1997; Yang, Li et al. 2001; Chadwick, Goodwin et al. 2002; Tseng and Lin 2003). Chadwick et al. and Tseng et al demonstrate rheological behaviour as a function of volume fraction whereby non-Newtonian behaviour is exhibited. However, Yang et al. suggests at very low volume fraction TiO2 suspensions Newtonian behaviour is exhibited.

1. Materials and methods

*2.1 Materials*

Nuclear relevant analogues for radioactive slurry materials can be costly to manufacture and difficult to handle. As a result, initial research in this project concentrated on slurries prepared from TiO2. TiO2 has three naturally occurring forms known as rutile, anatase and brookite. Research reported here is for anatase particles obtained from Degussa (Germany).

The data collected using this TiO2 sample provides baseline information for comparison with nuclear waste analogue slurry materials. Initial samples of CPM and ZM were supplied by the National Nuclear Laboratory as relevant analogue materials for the solids found in the HASTs.

Synthesis of CPM involves preparing phosphomolybdic acid (PMA) solution and caesium nitrate solution. The solutions are individually prepared by dissolving the solids in 2M nitric acid. PMA is added to caesium nitrate over time with continuous stirring, the reaction is kept at 50°C. Synthesis of ZM requires conditioning of zirconyl nitrate solution in 6M nitric acid at 100°C. The zirconyl nitrate solution is added to CPM over time with continuous stirring, the reaction is kept at 90oC. The experimental set-up of ZM synthesis is similar to that of (Doucet, Goddard et al. 2002). The conversion of ZM is time consuming and the raw materials required for both synthesis routes are costly.

Initial stages of this research focus on characterising two types of ZM samples: (a) normal ZM and (b) sol-gel ZM. The difference between these particles is the preparation method, normal ZM is produced from the conversion of CPM with the addition of zirconyl nitrate. ZM sol-gel is prepared from is produced from a chemical synthesis known as the sol-gel method (Hench and West 1990). ZM sol-gel in this research has been prepared in a similar method to that described by (Clearfield and Blessing 1972). This method involves mixing zirconium oxide dichloride octahydrate (ZrOCl2·8H2O) and sodium molybdate dihydrate (Na2Mo4·2H2O) solutions with water, a white ZM gel is formed. A point of interest in the nuclear industry is to modify the morphology of ZM particles at some point in the process. This research studies two types of ZM particles to understand the changes to particle characteristics with synthesis method, and which type may best be suited for morphological modification.

*2.2 Particle characterisation*

Particle density was measured using the Micrometrics AccuPyc 1330 helium pycnometer (Micromeritics Instrument Corporation, US). The input weight of the solids were measured, the density is determined by the pressure change of the helium in a calibrated volume.

Dry particle shape and size was characterised using a LEO/Zeisss 1530 scanning electron microscopy (SEM) (LEO Elektronmikroskope GmbH, Germany). Each sample was thoroughly dried and then coated with platinum before being imaged.

A Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK) was used to obtain particle size distribution information for liquid dispersions of the TiO2 and nuclear waste simulant samples. For each sample tested here, the particulate solids were suspended in water and a few drops of this stock suspension were added to a water-filled, stirred measuring cell until the correct obscuration value needed for accurate data was obtained. Each sample was analysed over 10 seconds and 10 repeat measurements were carried; the average of these 10 measurements are presented in the paper.

*2.2 Sedimentation techniques*

The sedimentation rate as a function of volume fraction was determined using a Turbiscan® (Formulaction, Ramonville, France). In this device, the dispersion is placed in a cylindrical glass measurement cell. Backscattered light intensity measurements are taken through its entire length, as a function of time, to establish sedimentation profile of the particles under gravity. In a typical experiment, ~20 mL of a given dispersion placed into the Turbiscan®. For each volume fraction the sample was left to run for 3 hrs 30 mins and data was collected every 2 minutes.

A Lumisizer® (L.U.M. GmbH, Berlin, Germany) was also employed here as an alternative route to determine the sedimentation rate and to allow further information about the sediment bed to be obtained. This device also determines sedimentation information using transmitted light through a measuring cell as a function of height in the cell and time. A key difference between the two techniques is that the Turbiscan® measures the settling rate under gravitational force whereas the LumiSizer® employs a centrifugal force. The main advantages for employing the LumiSizer® are that more than one sample can be measured simultaneously (12 samples), the temperature at which the sample is measured can be easily adjusted, the maximum speed of the centrifuge can be controlled up to 4000 rpm, and the quantity of material is relatively low (400 µL).

In a typical measurement here, an aliquot of 400 µL was extracted using a syringe from a 10 mL stock suspension and transferred into a polyamide (PA) cell. The cell was then loaded into the Lumisizer® for analysis and 250 profiles were collected at intervals of 300 s for suspensions of 6 vol%, at 500 rpm.

(a)(b)

Fig. 1: Dimensions of the sample holders for each sedimentation technique (a) Turbiscan sample cell with an internal diameter of 30 mm and an initial sample height of 42 mm (b) Lumisizer sample cell with an internal diameter of 8 mm and initial sample height of 22 mm

*2.3 Rheological techniques*

The Bohlin C-VOR Rheometer was employed to obtain rheological flow curves with respect to particle volume fraction.

**Fig. 2**: A schematic diagram of the different geometries employed (a) the cup & bob (b) the vane tool (c) a cross-section of the vane tool

In a cup and bob measurement system, either the bob (inner cylinder) or the cup (outer cylinder) can rotate whilst the other surface remains stationary. In the case of the C-VOR, it is the bob which rotates and the outer cup remains stationary. The main advantages for this geometry are that it provides good repeatability, has good temperature control, a low quantity of material is required, and its large surface area enables measurements for low viscosity fluids. The key issue of concern is the possible presence of wall slip in the data. Wall slip is commonly described as a depletion layer formed by the dispersed phase away from the solids boundary layer (Barnes 1995). This behaviour significantly reduces the viscosity of the material due to lubrication effects. Wall slip effects are enhanced by increased particle content and the rheological geometry employed (Chen, Duan et al. 2009). A vane tool when immersed into the sample results in minimal damage to any material structure for a solid-liquid system and is therefore the measurement tool of choice for yield stress data. The effects of wall slip are also minimised with this geometry (Dzuy and Boger 1983).

The geometry used to obtain rheological data here was selected based on the volume fraction of solids. A cup and bob system is suitable for low viscosity suspensions, i.e. low volume fraction suspensions; the vane tool is suitable for high viscosity suspensions, i.e. high volume fraction suspensions (Chong, Christiansen et al. 1971). Hence, suspensions of between 6-12 vol% were analysed using a cup & bob geometry whilst a cup & vane tool was used for suspensions of between 15-21 vol%.

The cup & bob system used here was a 2 ml Mooney cell. Samples were prepared in 20 ml vials, a 3ml pipette was utilised to extract 2ml of the suspension which was then immediately transferred to the cup. A V25 vane tool was used here with a C35 cup which requires ~40ml of material. In all cases, the bob/vane is immersed into the particulate fluid which is contained in the cup.

The C-VOR rheometer transforms the raw torque into an applied stress on the sample. When carrying out experiments a range of stress is chosen and this is applied to the sample, the resultant shear rate is then recorded. The temperature was maintained at 20 °C for all experiments.

1. Results and discussion

*3.1 Particle characterisation*

The effect of particle size, shape and density on the sedimentation and rheology of relevant nuclear waste simulants is investigated here. As noted previously, establishing the effect of particle properties on sedimentation and rheological behaviour is essential for designing a successful waste treatment process.

**Fig. 3**: Particle size distribution of highly active nuclear waste simulants in comparison to titanium dioxide

Size distribution data in figure 2 shows clearly that the CPM, TiO2 and ZM exhibit essentially mono-modal size distributions with, respectively, increasing peak mean values of size. The ZM sol-gel sample is distinguished by a major peak at a much larger size with an extended tail of smaller material. Key size data for each sample is provided in the table below.

**Table 1**: Percentile distribution data of particle size analysis

These data further highlight the relatively narrow distributions for the CPM, TiO2 and ZM samples. The ZM (sol-gel) sample clearly has a wider distribution with the ratio of d (0.9) / d (0.1) being considerably greater than for the other samples. SEM images provide supporting information on particle size as well as allowing an analysis of shape. Images of the simulant materials are presented in figure 3. A close examination of figure 3(a) suggests that the micron-sized TiO2 particles measured by light scattering consist of fused submicron primary particles. The size of the aggregates seen here is just larger than 1µm, this complements the particle size data obtained from the Mastersizer®. The apparent shape of the primary particles from the image suggests that they are almost plate-like, with an approximately spheroidal shape for the aggregates.

**(c)**

**(b)**

**(a)**

**Fig. 4**: SEM images. a) TiO2; b) CPM; c) ZM; d) ZM sol-gel

From figure 3(b) we see that there are similarities, in terms of both mean size and shape, between the TiO2 and CPM, with the CPM also consisting of spherical aggregates of smaller primary particles. The images show a size for the agglomerates that is consistent with the Mastersizer® data.

In contrast, SEM images show that the basic particle shape for the ZM samples is cuboidal. Images of the samples from the normal ZM preparation and the sol-gel sample show a higher degree of agglomeration in the sol-gel case. From the images it can be seen that, in general, ZM crystals are much larger in size than CPM crystals. Individual particle sizes range from 3-4µm and the agglomeration of particles is low in the standard ZM example. Figure 3(d) suggests that the primary particle size in the ZM (sol-gel) agglomerates are around 3-4 µm, consistent with the largely unagglomerated ZM sample prepared from the normal synthesis route.

The densities of the simulant samples are given in Table 2.

**Table 2**: The density of highly active nuclear waste simulants and TiO2

The increased density for the ZM and CPM samples when compared to the TiO2 is attributed to the incorporation of dense elements such as molybdenum within the simulants and is as expected for these materials.

Comparing the solid properties of the nuclear waste simulants to TiO2 highlights similarities between TiO2 and CPM in terms of particle shape; both solids consist of spheroidal aggregate particles that are produced from submicron primary crystallites or particulates. In addition, the mean sizes for these two materials differ only by a factor of 2, although the density analysis (Table 2) highlights that not all particle properties correlate well. In contrast to the general similarities between CPM and TiO2, the ZM sample has no particle characteristics that correlate with the TiO2 in terms of particle size, shape or density, and therefore TiO2 is not an appropriate comparison material for ZM. Additionally, whilst differing in size by a factor of 3, the densities for the CPM and ZM samples are comparable. Information about the effects of particle size may be available therefore through a comparison of these two samples.

*3.2 Sedimentation*

The combination of particle size, shape and density will obviously lead to different settling properties for the different systems. Figure 5 illustrates settling curves.

Figure 5: Settling curves of (a) titanium dioxide (TiO2), (b) caesium phosphomolybdate (CPM) and zirconium molybdate (ZM). The data presented were collected using the Turbiscan over a period of 3.5 hours. The data indicate the sedimentation rate as a function of volume fraction.

The settling curves for both TiO2 and ZM suspensions are similar in terms of the number of stages during sedimentation. There are two distinct behaviours for both the suspensions, ZM (below 10vol%) and TiO2 (below 6vol%). The initial stage indicates gravitational settling of the particle network whereby the rate at which the fluid is being expelled increases. This then leads to the consolidation of the particles, this is where the system gradually approaches an equilibrium height where the gravitational and drag forces decrease to zero. The second stage, which is apparent in the TiO2 and CPM settling curves, is where no sedimentation of the particle network occurs.

However for CPM suspensions there are three distinct sedimentation behaviours as a function of volume fraction. Volume fractions below 6vol% show clear sedimentation in the hindered settling regime. Volume fractions above 6vol% indicate little/no sedimentation, this suggests a stable particle network. However, at 6vol% three distinct sedimentation behaviours are apparent from figure n(b). The initial stage suggests a space-filling network is being formed, the particle network it restructuring it self. This is defined as the lag time, within this period the particles continuously re-structuring themselves as well as settling. As time progresses, beyond the lag time, the systems yields and a sudden collapse of the particle network takes place. This is due to the fact the colloidal network progressively builds up an internal stress as a result of localised rearrangements, which in turn ultimately leads to the collapse of the sediment front (Bartlett, Teece et al.)The final stage is where compaction of the particle network takes place and is consolidated to an equilibrium height. It can be suggested from the figure that for CPM suspensions 6 vol% is a transition volume fraction whereby a build up of internal stress causes the ultimate sedimentation of the particle network.

From the data given in figure 2, we can see that in general, for CPM and TiO2 suspensions, as the volume fraction of the particles in water increases, the sedimentation rate decreases, as expected. Increased contributions from hindered settling drives this effect. Hindered settling functions are based on collective particle interactions and sedimenting particles are influenced and slowed by neighbouring particles (Kumar, Pirog et al. 2000; Vesaratchanon, Nikolov et al. 2008).

**Figure 7**: Sedimentation rate as a function of volume fraction. The data represents nuclear waste simulant (caesium phosphomolybdate & zirconium molybdate) and titanium dioxide suspensions

At a given volume fraction, the differences in settling behaviour can be ascribed to the distinct properties of the particle samples. Figure 4 indicates at any volume fraction, CPM and TiO2 particles have a higher settling rate than both ZM. In relation to Stokes law (Stokes 1851), a consideration of its small particle size and almost spherical shape we might expect this sample to be the slowest settling solid. However, in the case of CPM the higher density appears to dominate the settling when compared to ZM.

The differences between the ZM and CPM samples are less easy to explain. As the ZM crystals are significantly larger (and have a similar density to CPM) one would expect correspondingly a faster settling rate. However, although the settling rate at high volume fractions (above 6 vol%) appear to be slightly above the CPM, at low to moderate volume fractions it is significantly lower. Further discussion of these observations will be provided below with additional settling and size data.

Particle shape is, of course, a potential influence on this behaviour, as non-spherical particles change their orientation during sedimentation and therefore affect the overall velocity of the particles. A study by (Ilic and Vincent 1994) suggests cubic shaped particles have a slower settling velocity than spherical and cone shaped particles. It can be assumed that particles with a larger aspect ratio will change orientation during sedimentation, in order to achieve its most stable position which minimises the drag force. However, further studies have been carried out by Fan et al. and Lau et al. they suggest this not the case. Elongated particles tend to oscillate during sedimentation with varying orientation. Orientation is defined as the angle between length of the prominent axis of the particle to the direction of flow (Lau, Hassan et al.). The most stable form is when the particle is horizontal, i.e. perpendicular to the direction of flow (Lau, Hassan et al. ; Fan, Mao et al. 2004).

Furthermore, Liu et al have looked at the change in orientation as function of particle concentration (Liu and Joseph 1993)**.** At lower volume fractions the angle of tilt is at its minimum where the cylindrical particle will settle with the major axis of the particle perpendicular to the direction of flow. At higher volume fractions the cylindrical particle orients itself where the major axis of the particle is parallel to the flow. This suggests that the drag on the particle at high volume fractions is reduced. Comparing CPM and ZM at higher volume fractions the settling rate of ZM is faster than CPM (which is not the case >6 vol%). This could be due to the orientation of the particle during sedimentation. Although we are not able to make such a definitive conclusion from the data provided here.

Due to the mean size of ZM particles accelerated settling rates are expected. Figure 5 provides images for the ZM and CPM suspensions after a 3hr 30min settling period.

**Fig. 8**: This image illustrates the nuclear waste simulant suspensions of (a) ZM and (b) CPM after a settling period. The suspensions are shown to be in the Turbiscan sample holder, both suspensions have an initial concentration of 6 vol% and all experiments have been carried out at ambient temperature.

These dispersions indicate that the CPM particles settle out fully and form a definitive sediment bed. ZM suspensions, however, display a residual milky appearance which indicates incomplete settling. Further characterisation of ZM suspensions was undertaken by extracting an aliquot of both the supernatant and sediment to analyse using the Mastersizer®. The data are presented in figure 6.

(a)

(b)

**Fig. 9**: Size distribution data of ZM suspension (a) supernatant (b) supernatant and sedimentation bed

Figure 6 (a) suggests the supernatant contains fine particles of 0.18-0.48 µm. For the sediment bed, the size distribution is within the range of 0.18-2.73 µm. This suggests that ZM suspensions are more size polydisperse than was apparent from the initial sizing data given in Figure 2. It is clear, from figures 5 and 6, a significant fraction of slow settling fine particles are left in suspension. Figure 4 illustrates the influence of the fine particle properties on the apparent sedimentation behaviour when measured using the Turbiscan®.

Factors which influence the hindered settling functions are the extent of size polydispersity, particle concentration and self-induced hydrodynamic interactions (Hassen and Davis 1989). For size polydisperse ZM suspensions, the distinctive feature of this system is segregation and sedimentation, this results in areas of different particle concentration. It can be suggested that the Turbiscan is monitoring the sedimentation of the larger 3µm ZM particles and neglecting the finer sub-micron particles which are still left in suspension. This can be supported by the particle size data in figure 6(b). The figure indicates the particle size measurements after the 3.5 hr settling period where by a sample of the sediment bed was taken and shows the larger 3µm ZM particles have settled out over a period of time and formed a sediment bed. Furthermore, it may be presumed that the large scale segregation could potentially affect the orientation of the larger particle during sedimentation.

An alternative method to observe the settling rate, with an accelerated driving force, is the LumiSizer®. The sedimentation data represent suspensions of 6 vol% with a speed of 500 rpm, the sedimentation rate of each particulate system and the height of the sediment bed can be estimated.

**Fig. 10**: Sedimentation profiles for highly active nuclear waste simulants at 6 vol% solids. The data indicate (a) sedimentation rate and (b) the final height of the sediment bed

Figure 7(a) indicates ZM sol-gel to have the fastest settling rate and the ZM, once again, to have the slowest. The settling velocity for ZM sol-gel was calculated as approximately 52 µm s-1, CPM as 36 μm s-1 and ZM as 18 μm s-1. The extinction profiles were collected using STEPTM-technology (Space and Time resolved Extinction Profiles), this allows analysis of velocity profiles and particle size distribution. The transmission profiles were obtained during centrifugation at 500 rpm, this corresponds to a centrifugal acceleration of 32 x g). The radial position at the bottom of the sample cell is 114 mm.

ZM sol-gel suspensions contain particles as large agglomerates with a mean size of 40-50 µm (Figure 2); this is sufficiently large when compared to the other samples to dominate the settling rate. The CPM and ZM sedimentation data is broadly consistent with the data collected using the Turbiscan®, and indeed the applied centrifugal force in the Lumisizer may additionally accelerate the particulate segregation that is occurring within the ZM samples. It is noted that settling data is estimated in both the Lumisizer® and Turbiscan® by measuring the large transmission increase at the supernatant boarder with time. If high levels of segregation are occurring, larger particles may settle quickly within the dispersion zone, and not therefore be measured in the transmission increase of the supernatant boarder. Therefore, it is assumed the measured settling rates for ZM are slower, simply because such light scanning techniques that focus only quantifying the change in supernatant boarder are not suited to measuring polydisperse suspensions which do not settle in hindered modes.

Interestingly, the sediment bed height for the CPM is considerably larger than for the ZM sample (Fig. 7(b)). Given the constant starting volume fraction of solids, this suggests a more open voluminous sediment, a feature that is possibly indicative of some aggregate formation. The ZM (sol-gel) also has a consolidated bed height that is larger than the ZM, which is consistent with its larger size creating more interstitial gaps, but it is still markedly denser than the much smaller CPM. The height of the sediment may also be related to the shape of the particle, the cuboidal shape of ZM may allow these particles to settle into a more compact sediment. The Lumisizer® has the ability to provide some insight on the difference in the settled bed structure which different particle samples form. Relating this to the HASTs the ZM particles are likely to settle and form compact bed which suggests that the energy required to re-suspend these solids will be much higher than that of the CPM solids. It can be assumed that the particles in the ZM settled bed have more contact points with other particles and will therefore create stronger interparticle forces and thus more energy will be required to break the structure of the bed. In the case of CPM the bed structure suggests from figure 7B that the particles are further apart from each other, this results in few interparticle forces and therefore lower energy is required to re-suspend these solids.

One of the main challenges of this research is the quantity of material available for experimental analysis. Sedimentation tests on a larger scale potentially involve manual extraction of sedimentation data by measuring the change in height between the supernatant and the particle interface as a function of time. Despite this technique reducing wall effects, it is not a feasible option for the material of study due to the large quantity of material required. As the Turbiscan is specific one type of sample holder (dimensions mentioned previously) further studies on the effect of the variation of sample holder diameter on sedimentation behaviour is not possible for this technique. As these particles have broadly similar particle size and the same volume fractions are studied it can be suggested that the wall and end effects are similar for each particulate system. Hence, the data are internally self-consistent.

*3.3 Rheology*

Further insight into the behaviour of the simulant materials was obtained from rheological measurements. Standard flow curve data for the TiO2 sample is given, as a function of volume fraction, in Figure 8. These baseline data were used to provide information on the preferred type of measurement geometry to be used here.

**Fig. 9**: Flow behaviour of TiO2 as a function of volume fraction; (a) shear stress as a function of shear rate, (b) Viscosity as a function of shear rate

We can see immediately from the data that TiO2 suspensions are strongly shear-thinning fluids (Turian, Ma et al. 1997; Q.D. Nguyen 2006), with a large reduction in viscosity as a function of shear rate. In general, we also see that as the volume fraction is increased the low shear viscosity increases, as expected.

Initially, the vane tool was employed for all rheology measurements. However, this tool is known to produce unreliable results for suspensions with low viscosities (Nguyen and Boger 1992). As an alternative, a cup and bob system was used for flow curve data for suspensions of 6 – 12 vol%. The larger surface area of this tool provides greater sensitivity at low viscosity and, as a result produces more reliable data (Darby 1985). The vane tool was employed for suspensions of 15 – 18 vol%. Generally, to obtain reliable data when using the Bohlin Rheometer it is important to select the geometry on the basis of its sensitivity to the viscosity of the suspension of interest.

The low shear region of the data in Figure 8 suggests the presence of wall slip; this is seen as a region of high noise in the data. (Magnin and Piau 1990) have suggested that roughened surfaces on the measurement tool is one method to reduce the effects of wall slip. Further research will be undertaken in the future to assess the benefits of using roughened cup surfaces for these systems. It is also known that the ratio of the vane diameter to that of the cup is an important factor to avoid slip, a cup that is twice the diameter of the vane tool gives the best possible rheological data (Dzuy and Boger 1985; Nguyen and Boger 1992). The vane tool used for these experiments was the V25 (vane tool diameter of 25 mm) and the cup was C37 (cup diameter of 37 mm), therefore in future work either the V25 and C50 or the V14 and C37 will be employed.

Initial rheological data for the CPM sample at a range of volume fractions and in two different mediums, water and nitric acid, are given in Figure 9. Nitric acid was used here to replicate conditions in the HASTs, where HAL solids are suspended in nitric acid during storage. During POCO, water will be employed to wash the tanks, therefore it is important to understand the behaviour of the solids in both mediums.

(a)

(b)

**Fig. 10**: Viscosity as a function of shear rate for (a) CPM in water and (b) CPM in nitric acid

From figure 9, we see immediately that a change in the medium strongly effects the rheological behaviour of the dispersions at equivalent volume fractions of solids. Figure 9(a) suggests at lower shear rates (approximately between 10 and 300 s-1) there is a Newtonian plateau, deviation from this plateau occurs at shear rates exceeding 300 s-1 due to secondary flow affects (Laun 1984). Secondary flows are dependent on the geometry employed, these flows occur with cup/bob and Mooney-Ewart geometries. Both these geometries contain an inner cylinder, at high shear rates inertial forces create an axisymmetric secondary flow, known as vortices. An increase in particle concentration enhances the vortex flow (Zirnsak and Boger 1998).

In general, the viscosities of the TiO2 samples are much higher than the CPM at the same volume fraction of solids in water (compare Fig 9(a) to 8(b)). If we look at the sedimentation data in Figure 4, we see that at low volume fractions the CPM sample settled much more rapidly than the TiO2; this is consistent with a much lower viscosity for the CPM samples. One explanation for these differences in viscosity could be the surface charges of the particles and the overall colloidal stability. In aqueous systems, the surface charge is known to be dependent on the pH and for TiO2 systems the isoelectric point (iep) is typically in the range pH 5 – 7 (Parks 1965). The samples here at a pH of 6, this is located within the range of the iep and therefore the TiO2 particles may well be aggregated. This would be consistent with a higher overall viscosity of the samples tested here. This also suggests that the CPM sample is not close to its iep the particles have a high charge and are therefore colloidally stable. Indeed, the CPM samples buffer the dispersion at pH 2, and in such high ionic conditions, it would perhaps not be surprising if the crystals were highly charged.

Comparing the two data sets for the CPM we see that the viscosity in water is considerably lower than in nitric acid. High acid levels will result in a pH reduction as well as an increase in the concentration of background electrolyte. The latter will definitely drive a decrease in stability and an increase in aggregation. This is consistent with the increased viscosity of the suspensions. Similar behaviours have been observed whereby the increase in background electrolyte of nuclear waste simulants causes particles to aggregate, hence shear thinning behaviour is exhibited (Chang and Smith 1996; Smith, Rector et al. 2000).

Further work will focus on the measurement of particle zeta potentials as a function of dispersion conditions. Accurate analysis of the sedimentation and rheology data is clearly not possible without an understanding of the stability of each particle suspension.

1. Conclusions

The influence of particle size, shape and density on sedimentation and rheology of nuclear waste simulants have been investigated. Representative HAL solids contained in the HASTs were compared to the baseline data of TiO2. Similarities have been established between TiO2 and CPM particles in terms of shape and size, useful comparative studies were conducted. Initial data provides an insight on the complex sedimentation and flow behaviours. Further investigation into hindered settling functions, stability of the particle suspensions and rheological parameters is recommended to gain a greater understanding on sedimentation and rheological behaviours.

Relating the data to process issues such as transportation and long-term storage of the waste, it is suggested that dense particles and a reduction in concentration of the particles enhances the sedimentation rate. However, polydisperse suspensions provide interesting sedimentation behaviours which indicate a reduction in sedimentation due to the presence of fine particles. Therefore, the agitation system implemented in the tanks must keep the solids in suspension with respect to the differing sedimentation profiles associated with the precipitated solid. The rheological data indicate a change in medium affects the flow behaviour of the particle suspension. Newtonian behaviour is exhibited when particles are dispersed in water and non-Newtonian behaviour is exhibited with particles are dispersed in nitric acid. Furthermore, rheological behaviour is affected by the agitation system employed and therefore during the transportation and emptying of the tanks the agitation system employed must be tailored to the behaviour of the solids. In terms of storage the HAL solids are kept in nitric acid where the jet ballasts will provide re-suspension and agitation, the particles will have endured stress, the rheological data suggests that the suspension will endure shear-thinning behaviour where agitation will reduce the viscosity of the waste within the storage tanks.

**Acknowledgements**

We would like to thank Sellafield Ltd. and National Nuclear Laboratory (NNL) for carrying out experiments in their laboratories and funding for this research.

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