

## The Effect of Colloidal Forces on the Sedimentation and Reslurrying Characteristics of Silica Slurries

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### Abstract

Preliminary work has been completed to investigate the effect of particle-particle interaction forces on the flow properties of silica slurries. Classically Hydrotransport studies have focused on the flow of coarse granular material in Newtonian fluids. However, with current economical and environmental pressures, the need to increase solid loadings in pipe flow has led to studies that examine non-Newtonian fluid dynamics. The flow characteristics of non-Newtonian slurries can be greatly influenced through controlling the solution chemistry. Here we present data on an “ideal” slurry where the particle size and shape is controlled together with the solution chemistry.

We have investigated the effect of adsorbed cations on the stability of a suspension, the packing nature of a sediment and the frictional forces to be overcome during reslurrying. A significant change in the criteria assessed was observed as the electrolyte concentration was increased from 0.1mM to 1M. In relation to industrial processes, such delicate control of the slurry chemistry can greatly influence the optimum operating conditions of non-Newtonian pipe flows.

Keywords: Interaction forces and Reslurrying

### 1. Introduction

Pipeline transport of highly concentrated tailings is now standard practice in the mineral and mining industries [1]. Research into such tailings which contain a high percentage of surface-active sub-micron particles has led to the optimization of mixing and pumping processes. The use of rheological modifiers to avoid plug formation in pipeline transport [2, 3], to improve hydraulic pumping gradients [4, 5] and to avoid sediment compaction during process shutdown [6, 7] has become an area of academic and industrial interest over the last 20 years. The information collected whilst studying mineral operations has now become applicable to the nuclear industry, where many waste management projects are encountering issues with dense sediment conveying.

Over the last decade, operators of nuclear facilities in the United Kingdom have become increasingly focused on solving issues associated with legacy waste and waste clean-up. Many of the existing storage facilities would not provide a suitable solution for long term storage. As a result, modern facilities utilising current technologies are being constructed to house the waste before it goes to deep-geological disposal facilities. The material transferred from the ageing to the new facilities can be categorised into three groups; i) fluid (very few particulates entrained), ii) slurry (low to intermediate particle concentrations, exhibiting Newtonian/non-Newtonian behaviour), iii) paste (high solids concentrations exhibiting non-Newtonian behaviour). Categories ii and iii contain enough fine particles that the slurry/paste chemistry can influence the conveying nature of the material.

The rheological behaviour of a slurry containing fines can be influenced through controlling particle-particle interaction forces. These forces dominate in systems where the particles are small enough that Brownian motion is not dominated by gravitational effects. Such forces are best described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [8, 9]. The theory describes the total interparticle interaction energy as the sum of the electrostatic repulsion force and van der Waals attractive force. Depending upon the system requirements, particles can be aggregated either by salt-induced coagulation or polymer-induced flocculation. Through controlling such interactions: i) the shear yield stress of a slurry/sediment [10, 11], ii) the sedimentation rate of the particles [12], and iii) the packing structure of particles in a bed can all be controlled [6].

Nuclear waste consists of a complex mixture of particles (different size, shape, density, roughness) surrounded by a complex mixture of ions in solution. In order to understand how best to handle such material, the modelled waste needs to be simplified, so that variables can be assessed individually against set criteria. Here we present work that examines the packing and reslurrying nature of mono-dispersed colloidal silica spheres (Fig. 1) in electrolyte solutions of  $\text{KNO}_3$  and  $\text{KCl}$ .

## **EXPERIMENTAL DETAILS**

A mono-dispersed sample of  $1\mu\text{m}$  silica spheres (Fig. 1) was obtained from FUSO Chemicals (Japan), with a particle density of  $2.26\text{ g/cm}^3$ . All suspensions were prepared 24 hours in advance of measurement with the particles dispersed by ultrasonication. The electrolyte concentrations ( $0.1\text{mM}$  and  $1\text{M}$ ) were controlled with analytical grade  $\text{KNO}_3$  and  $\text{KCl}$ , and adjustments to the suspension pH were undertaken using analytical grade  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{KOH}$ .

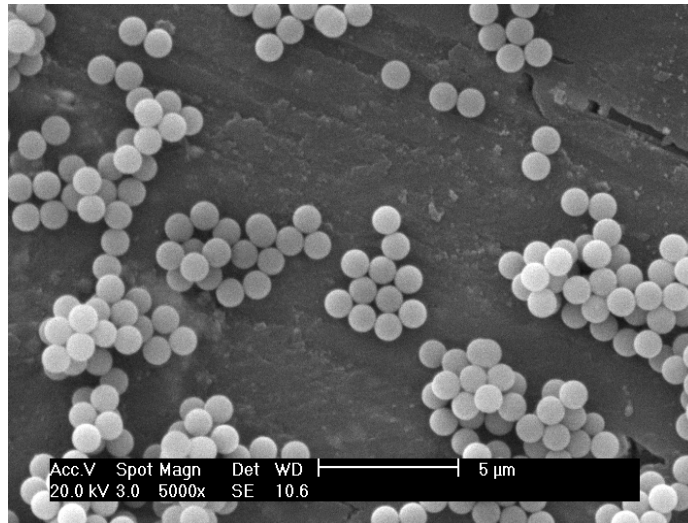


Figure 1. Mono-dispersed silica spheres imaged using ESEM.

A) **Zeta-potentials:** the zeta potentials of the particles were determined using a Malvern Instruments Zetasizer Nano (Malvern, United Kingdom), using a technique which is described elsewhere in detail [13]. Suspensions were prepared to 10000ppm and the pH adjusted to 9, before titrating down using the appropriate acid.

B) **Sedimentation rate and sediment structure:** the rate of sedimentation was determined using a LUMiFuge® stability analyser (L.U.M. GmbH, Germany). Parallel near infrared light illuminates the entire sample cell and the transmitted light through the sample is then detected. Regions of high particle concentration exhibit a low transmission value and regions of low particle concentration exhibit a high transmission value. A trigger value is then set by the user to intersect the transmission profiles, thus, determining a transmission value as a function of time at a given cell position. The sedimentation rates of the particles in suspension were investigated at pH 6 as a function of the strength and type of electrolyte. Suspensions were prepared to 10000ppm and the centrifuge was set to 300rpm with transmission profiles recorded at 10 second intervals.

The packing structures of the fully consolidated sediments were investigated through determining the suspension gel point in 0.1mM and 1M  $\text{KNO}_3$  and KCl electrolyte solutions at pH 6. Suspensions were prepared to 12%vol with suspension heights varying from 55mm to 200mm.

C) **Yield stress:** The bulk rheological properties of fully consolidated sediment beds were determined by measuring the yield stress using a Brookfield HB DVII+ Viscometer (Brookfield Engineering, United States). Suspensions were prepared to 12%vol in 0.1mM and 1M  $\text{KNO}_3$  and KCl electrolytes at pH 6. Once fully consolidated, the vane tool (V72) was lowered gently into the sediment until it touched the container bottom. It was then raised 5mm to ensure that the vane tool

was in the same geometrical position for all experiments. The rotational speed of the viscometer was increased from 0 to 3rpm in increments of 0.01rpm/sec. The data were interpreted by using the maximum viscosity value to determine the torque at the point of yielding. The torque is then simply related to the shear yield stress as detailed elsewhere [14, 15]

D) **Lateral force:** During reslurrying of a sediment bed, the erosion characteristics of the bed are related to the lateral force of interaction between the particles. A BioscopeII Atomic Force Microscope (Veeco Instruments) was used to measure the lateral force between a silica particle and a silica flat. The experiments were performed in pH adjusted electrolyte solutions. The RMS roughness of the silica surface was measured to be about 1.2nm over  $10\mu\text{m}^2$ . A  $28\mu\text{m}$  silica particle was mounted onto a V-shaped tipless cantilever (nominal normal spring constant  $0.2 \pm 0.03$  N/m) using a very small amount of Araldite. Prior to the measurement the silica flat was washed in 2% Decon, exposed to UV-ozone and then rinsed thoroughly in de-ionised water to ensure that the surface was hydrophilic. The force measurements were completed in a liquid cell following a method which is described in more detail elsewhere [16].

E) **Bed erosion characteristics:** The flow properties of the slurries and the reslurrying behaviour of fully consolidated sediment beds were investigated in a 25mm horizontal pipe flow loop. A 15Hz dual pulsed Nd-Yag Particle Imaging Velocimetry (PIV) unit was utilised to monitor the erosion of the sediment-fluid interface as a function of time. The reslurrying behaviour is to be studied in the laminar, turbulent and transitional flow regimes. Turbulent resuspension and transportation of coarse granular material has been studied in great detail over the last 60 years [17-19]. With improved technologies many current multiphase process lines contain a high percentage of fines and colloidal material. Such material during transportation does not require the same energy to maintain a homogenous flow, and can therefore be pumped in the laminar or transitional regime. Transitional flows exhibit pressure fluctuations greater than those observed in turbulent flow conditions. These fluctuations introduce large shear forces in the flow which can be utilised to keep particles in suspension as well as aiding reslurrying [20, 21]. Such phenomenon is to be investigated in the near future.

## RESULTS AND DISCUSSION

Figure 2a, shows the zeta potential versus pH in 0.1mM and 1M potassium salts ( $\text{KNO}_3$  and  $\text{KCl}$ ). Two mono-valent salts were chosen for the study; to investigate the ion-specific strength on particle stability. In the high electrolyte solutions there is no discernible difference between the  $\text{KNO}_3$  electrolyte and the  $\text{KCl}$  electrolyte. However, in the 0.1mM (weak electrolyte) solutions it is clearly observed that the  $\text{KCl}$  salt reduces the magnitude of the zeta potential compared with the  $\text{KNO}_3$  salt. The diffuse layer potential for the high electrolyte salts is equally screened and is virtually independent of pH due to the high ion concentration in solution. In these suspensions the attractive forces dominate, and during particle collision through

Brownian motion, the particles strongly adhere to each other forming large, open porous aggregates. For the low electrolyte salts, the reduction in the magnitude of the zeta potential for the KCl salt is a result of ion-specific strength [22]. The strong electrolyte suspensions can be classified as un-stable, independent of pH. While, the weak electrolyte suspensions can be classified as stable, with a dependency on pH. A general ‘rule of thumb’ says that a transition from stability to coagulation with a change in either pH or salt concentration occurs at around  $\pm 30\text{mV}$ . The repulsive energy barrier that prevents particles forming aggregates is known as the diffuse double layer. The thickness of the diffuse double layer is commonly referred to as  $1/\text{Debye}$  length. In an aqueous solution of a symmetrical electrolyte at  $25^\circ\text{C}$  the Debye length can be calculated using the following equation:

$$\kappa = 0.329 \times 10^{10} \left( \frac{cz^2}{\text{mol dm}^{-3}} \right)^{1/2} \text{ m}^{-1} \quad (1)$$

Clearly, as the strength of the electrolyte increases the surface charge density increases, resulting in a collapsing of the double layer thickness. This is shown in Fig 2b.

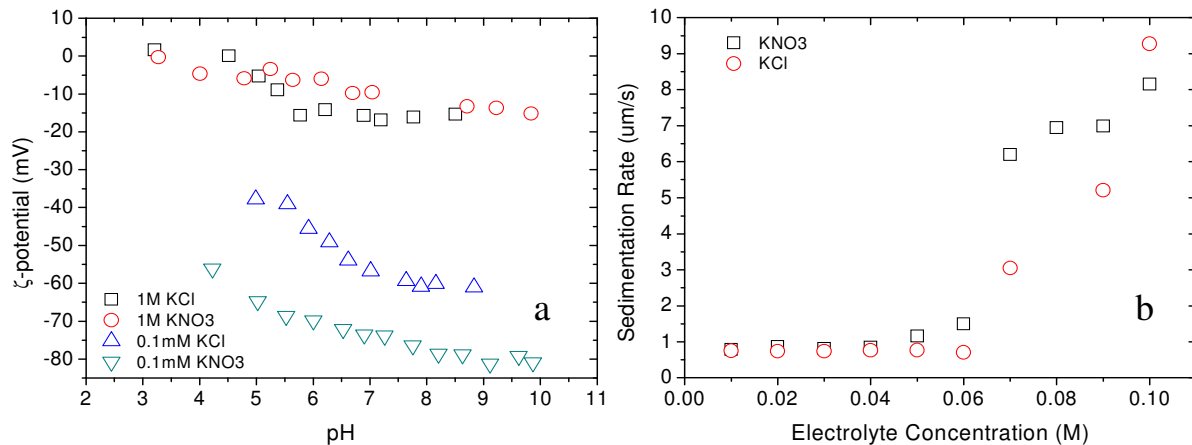


Figure 2 a) Zeta potential versus pH for silica suspensions prepared in 0.1mM and 1M  $\text{KNO}_3$  and  $\text{KCl}$  electrolytes and b) Suspension critical coagulation concentrations determined from settling experiments.

The critical coagulation concentration (c.c.c.) is the electrolyte concentration where a transition from stability to coagulation occurs. For the two salts investigated, Fig 2b. shows the c.c.c. for the silica suspensions investigated in both potassium salts at pH 6 to be approximately 0.06M. This figure shows how the apparent sedimentation velocities of the particles in suspension dramatically increase as the c.c.c. is surpassed. The sedimentation rates for the 0.1mM  $\text{KNO}_3$  and  $\text{KCl}$  suspensions are  $0.8\mu\text{m/s}$  and  $0.7\mu\text{m/s}$ . In 1M the rates increase to  $12.7\mu\text{m/s}$  and  $12.9\mu\text{m/s}$  respectively.

When designing and operating pipelines that contain a lot of fines, an important piece of information is the solids concentration at which a three-dimensional space filling network forms in the slurry (gel-point) [6]. This network will induce a yield stress in the material and the slurry will exhibit non-Newtonian characteristics. For the 0.1mM KNO<sub>3</sub> and KCl the gel points are 46.9 and 40.2 %vol respectively, compared with 27.4 and 27.2 %vol for the 1M electrolyte suspensions. The gel points indicate that for the slurries of interest, when the particles are dispersed in 0.1mM electrolytes, a higher concentration of solids can be slurried without introducing a yield stress.

Bed formation can occur in a pipeline due to a variety of reasons; i) process shut-down, ii) pump station failure, iii) operating below the deposition velocity and iv) unexpected sedimentation of fines in shear flow.

In order to reslurry a sediment bed, information on the stress chains penetrating through a bed structure and the forces acting between individual particles is required. The on-set of resuspension is brought about when individual particles roll and lift detaching themselves from neighbouring particles. The adhesion force holding the particles in position depends on the particle-particle interaction energy and the packing network of the sediment bed (yield stress). The fluid-particle interaction creates a shear force which dissipates through the particle network. Depending on the scale of the shear force applied (velocity dependent) and the packing network, the particle may be lifted from the surface or jammed into neighbouring clusters.

The yield stress values for the fully consolidated silica sediments in varying potassium salts were; 69Pa (1M KNO<sub>3</sub>), 57Pa (1M KCl), 455Pa (0.1mM KNO<sub>3</sub>) and 341Pa (0.1mM KCl). The data show that the shear yield stress of the sediment bed considerably increases as the electrolyte concentration is reduced. This feature is a result of the particles packing more efficiently in the weak electrolyte solutions, increasing the solids concentration of the sediment bed. When the attraction between the particles is relatively weak, they can come into close proximity with each other several times without forming a bond. This enables the particle to diffuse deeper into the aggregate before sticking, thus, producing small compact aggregates. However, when attraction forces are strong the particles will adhere immediately upon coming into contact forming large open porous aggregates [6]. The resulting aggregate structure then affects the overall solids concentration of the consolidated sediment bed, and therefore the yield stress.

As stated previously, the reslurrying behaviour of a sediment bed depends upon both the bulk sediment properties and the individual interaction forces between neighbouring particles. Figure 3 illustrates how the frictional force ( $\Delta V$ ) acting between a particle and a flat, changes with applied loading in the electrolytes considered.  $\Delta V$  is half the difference between the friction signal in retrace and that in trace, and can be converted into a frictional value using a method described elsewhere in detail [23]. Many of the theoretical methods include assumptions that can introduce large errors when interpreting the data quantitatively. The actual friction force produced during scanning is dependent on a variety of factors such as; scan

speed, surface roughness and the compressibility of the glue holding the particle on the cantilever. Therefore, for the purpose of this study we are only interested in the trends and not the quantitative analysis of such a system.

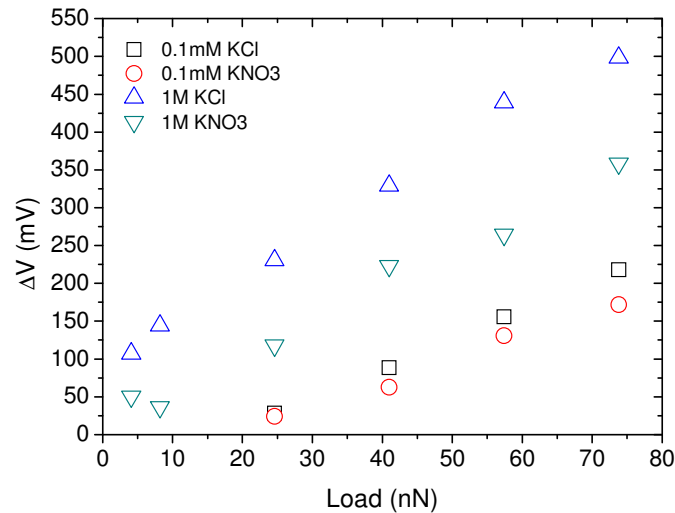


Figure 3. Lateral force interactions between a silica sphere and silica flat. Scan size 500nm and scan speed 0.1 $\mu$ m/s.

Figure 3 clearly shows the expected linear increase in the friction force as the normal loading force is increased. The friction forces increase in the following order 0.1mM KNO<sub>3</sub> – 0.1mM KCl – 1M KNO<sub>3</sub> – 1M KCl. An increase from a weak to a strong electrolyte results in an increase in the observed lateral force. This trend does not however compare to recently published data [24]. The recently published work studying the lateral force between a 6-8 $\mu$ m silica sphere and a silica wafer in pure water and LiCl salts, has shown a decrease in the friction force as the electrolyte concentration is increased. This is believed to be a result of a hydrated layer of adsorbed cations on the silica surface, structuring water to form a highly efficient lubrication layer. In comparison to the present study where K<sup>+</sup> will be adsorbed onto the silica surface, their ability to structure water is less than Li<sup>+</sup> ions; therefore, forming a very thin or no lubrication layer between the silica surfaces. For all of the loading conditions, stick-slip was observed which would again suggest that there was no lubrication layer present, or the applied forces were able to collapse and penetrate through the very thin layer. Reference [24] does not present any raw friction data and does not comment on the stick-slip phenomena, so it is difficult to comment on the validity of the lubrication layer as the loading forces used were considerably higher than those used in the present study.

## CONCLUSIONS

It has been recognized over the last 20 years that understanding slurry rheology is an important issue when operating pipelines that contain a large percentage of fines. Through treatment of the slurry chemistry a certain degree of control can be gained, making possible improvements to the process efficiency, reducing the cost and hazards of operation. One area that has still largely gone un-investigated is the

reslurrying of compact sediment beds. As mentioned, the two properties that would govern the reslurrying behaviour are the bulk properties of the sediment (yield stress) and the contact forces (lateral and normal) between the individual particles. We have observed that the yield stress for a fully consolidated bed (12 %vol slurry) increases in the following order 1M KCl, 1M KNO<sub>3</sub>, 0.1mM KCl, and 0.1mM KNO<sub>3</sub>. The strongest adhesion force is observed for the 1M KCl solution, and the weakest force for 0.1mM KNO<sub>3</sub>. Therefore, it could be expected that the reslurrying behaviour is characteristic of either the lateral forces, the bulk properties or a balance of the two mechanisms. To investigate this further we have constructed a 25mm horizontal pipe loop which will enable us to monitor the reslurrying behaviour of sediments in different flow regimes (Fig. 4). Further work in this area will be presented at the conference.

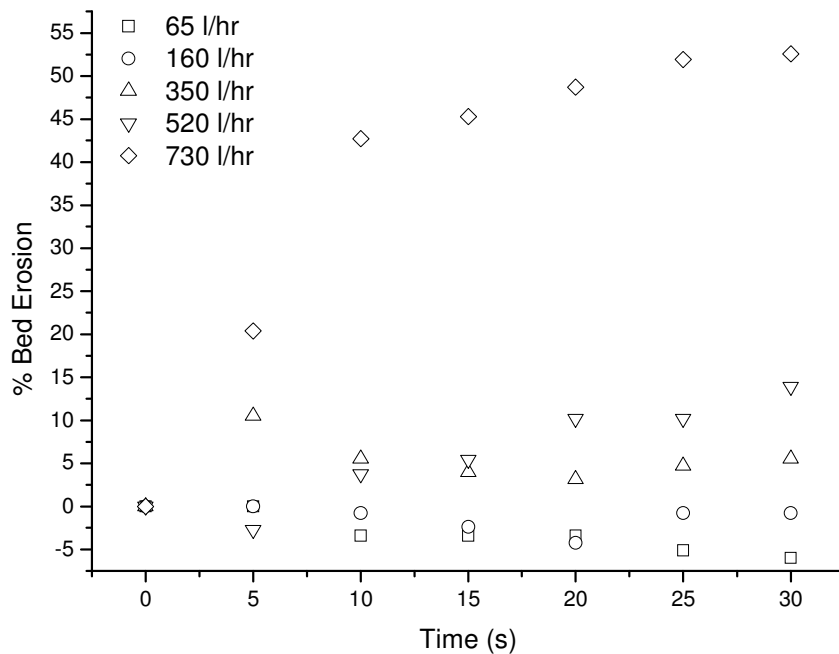


Figure 4. Sediment erosion characteristics as a function of the slurry flow rate.  
Suspension properties: 10-4M KNO<sub>3</sub>, pH 6, 5wt%.

## ACKNOWLEDGMENTS

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