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Fast agglomeration of ultrafine hydrophobic particles using a high internal phase emulsion binder comprising permeable hydrophobic films

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ABSTRACT: A novel hydrophobic binder consisting of tightly-packed drops of aqueous salt solution, stabilized by thin films of oil, in the form of a high internal phase water-in-oil emulsion was used to agglomerate ultrafine hydrophobic particles in seconds to a size sufficient for their capture on a 150 micron screen. Almost complete recovery of the particles, extending from sizes of more than 100 microns to below 500 nanometers, was achieved. Examination of the process revealed that the agglomeration appears to be governed primarily by the length scale of the thin oil films, of order 30 nm, and their ability to efficiently deliver organic liquid to the particles quickly. Moreover, it appears that the hydrodynamic resistance that develops when a particle is

driven towards an interface is reduced due to the permeability of the films. Water permeation driven by osmosis also appears to assist the transport of the particles towards the interface.

1. Introduction

The significance of froth flotation over the past 100 years is almost beyond parallel, selectively recovering fine hydrophobic particles to produce many of the valuable metals required by the modern world^{1,2,3}. However, the challenges have been escalating due to falling ore grades and increased demand for metals, while advances in separation performance have plateaued. Economy of scale has driven increases in the volume of the aerated and agitated flotation cells by an order of magnitude every 20 years⁴, reaching a massive 600 m³ in 2015 as shown in Figure 1. At this rate multiple flotation cells, each 10,000 m³ in volume (equivalent to four Olympic swimming pools) will be needed by 2045! While new ways of thinking are indeed emerging, including strategies aimed at minimizing the quantity of finely ground particles to be floated, an ultrafast separation technology is needed that is also capable of recovering particles well below the hydrodynamic limits of flotation.

Figure 1. Economy of scale in froth flotation⁴

Nearly fifty years ago another remarkable method for recovering and concentrating fine hydrophobic particles from water attracted significant attention worldwide. The method, known as oil agglomeration, utilized an oil binder, dispersed under shear, to selectively agglomerate fine hydrophobic particles^{5,6,7}. The aggregates that formed were then of sufficient size and strength for separation from the water and any hydrophilic particles using a mechanical screen. However, oil agglomeration was never adopted by industry due to the significant consumption and hence cost of the oil.

In this paper we examine what may prove to be the next step in this evolution, a discovery that offers a new way forward to recover hydrophobic particles from water. Motivated by the oil agglomeration technology, and the need to reduce the oil consumption, we introduced a concentrated water in oil emulsion as a substitute for the conventional oil binder⁸. This type of emulsion, also known as a high internal phase (HIP) emulsion, is characterised by a high internal phase volume fraction, achieved by tightly packing droplets of the internal phase within a thin film of the external phase. Figure 2 presents a series of light microscope images that illustrate the development of this structure as the aqueous internal phase volume is increased from 60 vol% to 95 vol%. The continuous phase consists of kerosene and an emulsifier, sorbitan mono-oleate.

Figure 2. Light microscope images of a water in oil emulsion with increasing internal dispersed phase volume fractions.

Figure 2 shows that as the internal phase volume fraction is increased the aqueous droplets become finer and more tightly-packed, while the continuous organic phase spreads into increasingly thinner films around the droplets. In oil agglomeration, the oil consumption can be reduced significantly by replacing the pure oil binder with an emulsion consisting of such a structure, formed almost entirely of water, stabilised by the continuous organic phase.

Initial results using the emulsion binder demonstrated some promise, revealing at first a 2 to 3 and, later, a 7 fold reduction in the quantity of oil required compared to conventional oil agglomeration⁸. More recently this performance was improved using a similar binder consisting of a 95% aqueous phase and 5% oil phase, as shown in the final image of Figure 2⁹. A 3 wt% NaCl aqueous phase was used to resist so-called Ostwald Ripening¹⁰ of the drops, while a hydrocarbon

solution consisting of equal portions of the emulsifier, sorbitan monooleate, and kerosene formed the continuous phase. The use of this binder led to a nominal ten-fold reduction in the oil consumption, while achieving equivalent selectivity and agglomeration⁹. This reduction was significant, making the process of selective agglomeration economic for the first time. However, it should be noted the organic liquid dosage required in the new process, while economic, exceeds that required in froth flotation¹¹.

It was also found that a selective separation was possible in a few seconds using the novel binder, some two orders of magnitude faster than oil agglomeration and froth flotation^{12, 13}. Figure 3 presents this rapid separation as a series of images showing pre-mixing of the white binder in water ($t=0s$), the pouring in of the black suspension ($t=0.5-1s$), and the continued mixing ($t=2s$). A buoyant separation is apparent after turning off the mixer ($t=3-4s$), while the final separation of the black hydrophobic agglomerates from the brown hydrophilic particles is achieved by pouring the entire contents over a screen.

Agglomeration of Black Hydrophobic Particles

Recovery of Agglomerates

Figure 3. Agglomeration of black hydrophobic particles in 2 s using the novel hydrophobic binder followed by separation of the product over a screen

Our purpose here is to establish an understanding of the underlying mechanisms responsible for these observations. We know that the hydrophobic force is likely to play a significant role in the action of the novel binder. Through direct measurement of surface forces¹⁴ and fundamental studies of flotation^{15, 16}, it has been demonstrated that hydrophobic particles experience long-range attractive forces over distances as great as 30 nm or even up to 300 nm¹⁷. The consequence of this interaction is that hydrophobic surfaces experience strong, long-range, mutual attraction and tendency towards adhesion, resulting in coalescence, or agglomeration, thus delivering the observed selectivity.

We believe, however, that other short range and long-range phenomena are needed to explain our observations as the novel binder delivers almost complete recovery of the hydrophobic

particles, extending from sizes of more than 100 microns to below 500 nanometres, all within the ultrafast time-frame. This result, presented for the first time here, is significant because in froth flotation, which also utilises the hydrophobic force, recovery varies significantly with particle size, declining strongly below about 20 microns¹⁸ due to the diminishing inertial forces. Interestingly, however, ultrafine recovery has been reported in oil agglomeration¹⁹, but over much longer mixing times. This, again, suggests that the ultrafast kinetics of the new process must involve additional mechanisms.

In our previous work the emulsion binder was used to selectively separate naturally hydrophobic coal particles from hydrophilic mineral matter through selective agglomeration. These particles are heterogeneous in nature, exhibiting a broad range of hydrophobicity, while also exhibiting varying degrees of surface porosity and hence a tendency to absorb oil. In order to develop a clearer understanding of the underlying mechanisms we chose to conduct new experiments using a model system more readily defined and replicated. Therefore, silica was selected as the material to be agglomerated. Silica is naturally hydrophilic but can be made hydrophobic via different methods including surfactant adsorption, reaction with silanes, and plasma polymerisation^{20, 21, 22}. In this work we have opted for the surfactant adsorption route in the interest of simplicity, using the surfactant cetyltrimethylammonium bromide (CTAB).

Agglomeration experiments were carried out on a number of silica feeds with different size distributions. In a given experiment, the silica was suspended in water, conditioned using CTAB at an optimum concentration, and then agglomerated using (i) the novel emulsion binder or (ii) a conventional oil binder. It should be noted that selectivity, which arises naturally from the hydrophobicity of the binder, was not investigated here. All of the particles in the system were conditioned to be hydrophobic and hence all were available for recovery by the binder.

Through this study we aim to provide a new explanation for the speed and importantly why consistently high recoveries are achieved within the ultrafast time across the size range studied which extends to below 500 nm. More generally, we also seek to challenge the conventional paradigm of using air bubbles in froth flotation to selectively recover hydrophobic particles, proposing the use of novel hydrophobic materials instead. Economic and environmentally sustainable solutions that can achieve complete extraction of hydrophobic particles from water in little more than a second could find applications in mining industries and in the treatment of water to remove sub-micron contaminants. While we have used a concentrated water in oil emulsion, we are convinced that other options can either be conceived or derived from nature to achieve a similar performance.

2. Experimental

2.1 Emulsion Binder Preparation

The emulsion was prepared in 300 g batches in a relatively standard way^{23, 24, 25}. Firstly equal mass portions of kerosene (Recochem Inc) and the emulsifier were combined using a Russell Hobbs Hand-Held Mixer (RHMx1) in a stainless steel mixing bowl. The emulsifier, sourced from Vic Chem, consisted of 60 wt% sorbitan monooleate and 40 wt% glycerol monooleate. Then, under continued mixing using the hand-held mixer set at maximum speed, a 3 wt% aqueous NaCl (Cerebos Ltd) solution was added to the organic solution, such that the volume of the salt water added at a given time was much less than the volume of the emulsion at that time. This addition was continued until the aqueous phase reached 95% by volume. The emulsion was opaque and hence white in colour, and highly viscous at the completion of the salt water addition.

2.2 Internal Emulsion Droplet Size Distribution Measurements

The size distribution of the internal aqueous droplets within the binder was measured via laser diffraction in a Mastersizer S. Approximately 0.5 ml of emulsion was dispersed in approximately 20 ml of the continuous phase (kerosene), effectively diluting the emulsion and mobilising the internal droplets. The impeller within the Mastersizer S measurement cell was set at the lowest speed, maintaining the suspension of water drops. The Mastersizer S measured the volume distribution of the drops and the final result was the average of three measurements.

2.3 Hydrophobic Agglomeration

The agglomeration was achieved using a Waring high speed blender (model number LB20EG) operated at 22,000 rpm. Silica feed, supplied in a number of size distributions according to the classifications, 60G, 100G, 200G, 350G, and 400G, was sourced from Sibelco, while a much finer material, Imsil A8, consisting of microcrystalline silica, was sourced from Unimin. The size distributions of each of the feeds are shown in Figure 4 together with the Sauter mean diameters, d_{32} , which can be related directly to the specific surface area of the particles.

Figure 4. The size distributions of the silica feeds

In all experiments, the silica flour suspensions were prepared using tap water and had a volume of 500 ml and a solids concentration of 12 wt%. Initially, the concentration of CTAB within the

silica suspensions was varied in order to identify the ideal level required to produce hydrophobic particles. The yield of agglomerated material provided a convenient measure of hydrophobicity, as shown in Figure S1. The optimum CTAB concentration, in the range 2×10^{-4} to 4×10^{-4} mol/L, is consistent with the finding of Bi *et al.*²⁰.

The efficacy of the novel hydrophobic binder was then studied using a Waring blender operated at 22,000 rpm, applying a standard mixing time of 7 s. Conventional agglomeration experiments were also carried out using a kerosene-only binder to serve as a comparison. A much longer mixing time of 120 s was required in this case. Images prior to and following the agglomeration using the novel hydrophobic emulsion binder are shown in Figure 5. It should be noted that the buoyancy of the product in the latter picture is believed to be due to entrained air, as the agglomerates rise almost immediately to the surface of the liquid upon ceasing the mixing. The combined density of the particles and emulsion within the agglomerate alone would not be sufficient to provide the observed buoyancy.

Figure 5. A) Suspension of silica flour in water and B) Silica agglomerated using the novel binder at the optimum CTAB concentration and 7 s of mixing.

The agglomerated product is defined as the material retained on a screen with the aperture selected to be larger than the maximum primary particle size. The material that passes through is not deemed to be agglomerated and is classified as the reject. During screening, a light wash water

was applied to the agglomerated material to ensure all non-agglomerated particles were removed from the product, and sent to the reject. The recovery value of a given experiment was the dry mass% of material from the feed retained on the screen in the form of agglomerates. The binder dosage for a given experiment was calculated based on the mass of organic liquid in the binder relative to the dry mass of solid material in the feed.

2.4 Particle Size Distribution Measurements

After drying, each sample was analysed via laser diffraction using a Mastersizer 3000 in order to obtain the size distribution. Each sample was dispersed in 800 mL of reverse osmosis water with an obscuration level between 10-20%. The obscuration level, provided by the Mastersizer, relates to the extent to which the laser light is scattered by the particles within the suspension and provides a guide for achieving an appropriate sample concentration. The wet sample dispersion unit which accompanies the Mastersizer was used to disperse the particles along with the inline sonication device. The impeller was operated at 3000 rpm and the sonication device was set at 40 W and a frequency of 40 kHz. The addition of a non-foaming detergent (Dri-Decon) was also used to assist particle dispersion. The Mastersizer 3000 measured the volume distribution of the particles. The final result was the average of three measurements.

3. Results and Discussion

3.1 Organic Liquid Requirements

The recovery of 200G silica as a function of the weight % organic liquid is shown in Figure 6A for the emulsion binder and Figure 6B for the kerosene binder. Simple curve fits have been added to illustrate the trends in each data set.

Figure 6. Recovery as a function of organic liquid dosage for the 200G silica for A) the emulsion binder and B) kerosene. Trend lines have been added to guide the eye.

It can be seen that the overall trend is consistent between the two binders, but with an order of magnitude difference in the organic liquid dosage required to achieve a given recovery. This 10-fold reduction in the organic liquid requirements when using the emulsion binder, as compared to the oil binder, is consistent with the findings in our previous work⁹.

Data similar to that presented in Figure 6 were generated for each silica feed and analyzed to determine the influence of feed particle size, and subsequently the specific surface area, on the organic liquid requirements of the process. In order to correlate these values, a standardized method for comparing the organic liquid dosage requirements of each binder for each feed had to first be established. The method that was developed was based on fitting the organic liquid dosages and values of $(100 - \% \text{recovery})$ to a simple exponential decay function. The dosage at 90% recovery was then calculated using the fitted function for each data set and this single parameter was used to represent the level of binder required to achieve saturated agglomerates for each silica feed. The complete set of fitted curves for the emulsion binder and the kerosene binder are presented in Figure S2 and Figure S3, respectively. The standardized method developed for

determining the organic liquid dosage requirements is also described in further detail in the Supporting Information.

Figure 7 shows the volumetric dosage of organic liquid per unit volume of silica, as established via the method described above, as a function of the silica surface area per unit volume of silica. The silica specific surface area is related directly to the inverse of the Sauter mean diameter of the particles forming the product ($6/d_{3,2}$).

Figure 7. The volumetric organic liquid dosage as a function of specific surface area of solid particles for the emulsion binder and the kerosene binder

By selecting the units of volumetric dosage and specific surface area to be $\text{m}^3_{\text{organic liquid}}/\text{m}^3_{\text{silica}}$ and $\text{m}^2_{\text{silica}}/\text{m}^3_{\text{silica}}$, respectively, the slopes of the straight lines fitted to the data presented in Figure 7 can be used to describe a notional thickness of organic liquid across the surface of the agglomerated particles. This value was calculated to be 66 nm for the emulsion binder, while for conventional oil agglomeration the film thickness was 1044 nm. Therefore, the asymptotic advantage of the novel binder is $1044/66 \sim 16$. It is also noted that Galvin and van Netten²⁶ applied this approach to fine coal, which is highly porous, obtaining a thicker layer of 178 nm using the emulsion binder.

The superior performance of the emulsion binder, compared to kerosene, for this notional measure can be explained by considering the properties and structure of the high internal phase emulsion binder. The emulsion binder is highly viscous, meaning it behaves differently to a low viscosity oil in the high shear aqueous environment. In conventional oil agglomeration the oil disperses into droplets greater than 5000 nm in diameter, after which collisions must occur between the droplets and particles, and then between the wetted particles²⁷. Due to the large size of the oil droplets initially, this mechanism produces relatively thick layers of organic liquid across the surface of the particles. This mechanism contrasts with the emulsion binder that appears to fragment into larger, gel-like pieces, each consisting of numerous water droplets and a network of thin oil films. Figure 8 presents an image of these gel-like fragments, created by subjecting the binder to shear in the absence of particles. It should be noted that the smaller, primary, fragments coalesced upon cessation of the mixing, and thus the visible binder portions in the image were considerably larger than the original fragments.

Figure 8. Binder fragments in water

It is believed that during the agglomeration process, these fragments act as a scaffolding, onto which particles can deposit. Figure 9 presents a schematic representation of the proposed agglomerate structure formed from a binder fragment and solid particles. It can be seen that the particles adhere to the binder via

the thin oil films and the water drops provide a ‘space-filling’ function between the particles within the agglomerate. It should be noted that the image is for illustrative purposes only and is not drawn to scale. Moreover, it is assumed that in reality the entire 3D surface of the binder fragments would be covered in solid particles, and it is expected that particles would also migrate and become embedded within the binder fragments as a result of subsequent collisions.

Figure 9. Simplified schematic representation of the binder fragment/solid particle agglomerate structure.

If the proposed structure in Figure 9 is correct, then the instant the binder is added to the suspension of particles, the subsequent adhesion involves a common organic film length scale, irrespective of the size of the particle and binder fragment involved in the collision. This length scale is dictated by the thickness of the pre-existing network of thin oil films.

Analysis of the emulsion binder revealed that the water droplets within binder fragments have a Sauter mean diameter of $3.28\ \mu\text{m}$. Thus if it is assumed that the oil is spread evenly over the entire surface area provided by these droplets, the average thickness of this oil film is $29\ \text{nm}$. Of course,

as the droplets interface with each other within the emulsion the average thickness of the oil film between them is 58 nm, with both droplets contributing a film of 29 nm.

Interestingly, the 29 nm film thickness associated with the surface area of the water droplets is equal to approximately half of the notional film thickness of 66 nm associated with the surface area of the silica particles. These values suggest that the surface area of the particles is half the surface area of the droplets comprising the saturated agglomerates. Hence the oil comprising the emulsion binder must extend its coverage by 50% in order to include the silica particles within the saturated agglomerates. Thus the average film thickness covering the combined water droplets and particles within the agglomerates is $2/3$ the value for the water drops within the emulsion binder, approximately 20 nm, corresponding to a spatial distance between opposing interfaces of 40 nm.

The results in Figure 7 indicate that the pre-established films around the water drops provide an efficient way for the hydrophobic particles to acquire organic liquid very quickly, directly forming agglomerates through collisions with the binder fragments. Moreover, the results appear to indicate that ultrafine particles can be captured by the emulsion binder with the same efficiency as coarser particles in the short time scale studied, given the strong linearity in the data extending out to ultrafine particle sizes. Therefore, subsequent experiments were carried out to further examine the influence of particle size on recovery using the emulsion binder.

3.2 Influence of Particle Size

The ability of the binder to recover particles over the wide size range examined in this study, within a few seconds, is significant. Additional experiments involving lower mixing intensities, but a fixed mixing time of 7 s and organic liquid dosage of 2.5 wt%, were therefore conducted in order to promote conditions assumed to be less favourable to the recovery of the finest particles.

Figure 10A presents the overall recovery of 400G silica as a function of mixing intensity and Figure 10B presents each data point from Figure 10A in terms of the recovery of each particle size for each mixing intensity. The data used to produce Figure 10B were based on the particle size distributions of the primary particles of the feed, agglomerates, and reject samples; a sample calculation is presented in the Supporting Information.

Figure 10. The influence of mixing intensity during agglomeration on a) overall recovery and b) recovery as a function of particle size.

As can be seen in Figure 10A, the overall recovery of silica decreases as the mixing intensity is reduced, with the mixing time held constant at 7 s. This result was expected, as reducing the mixing intensity results in a reduced number of collisions per unit time. Contrary to expectations, however, recovery as a function of particle size remained relatively constant as the mixing intensity was decreased, as shown in Figure 10B. It was anticipated that as the mixing intensity decreased, a substantial reduction in the recovery of the ultrafine particles below 1 μm would become apparent. While the recovery of the particles clearly decreases, the reduction is evident across the full size range, with the ultrafine particle recovery marginally higher. This lack of particle size selectivity over the very short (7 s) time period studied was surprising, given that in froth flotation recovery varies significantly with particle size, declining strongly below about 20 microns¹⁸. And in oil

agglomeration, recovery of the ultrafine particles is kinetically much slower than for the coarse particles¹⁹.

3.3 Water Permeation into the Binder

A particle driven through a viscous fluid towards a planar surface experiences a strong hydrodynamic resistance. By introducing a permeable interface, the same particle experiences a significantly lower hydrodynamic resistance²⁸. This reduced hydrodynamic resistance occurs because the local pressure drives the permeation, allowing the particle to adhere to the binder. If the novel binder exhibits strong permeability, then the agglomeration should be kinetically fast, and the recovery should not decline with a decreasing particle size as observed for froth flotation.

Thus a separate series of experiments was conducted to firstly examine the question of water permeation and then to investigate the effect of this permeation on the agglomeration process. To examine the question of water permeation, 30 g of binder was added to 120 g of tap water and subjected to intense mixing at 22,000 rpm for 3 s to form a suspension of binder fragments. The suspension was then allowed to rest for set periods of time. The suspensions were then passed over a 38 μm screen to recover the emulsion fragments. The underflow, which consisted of clear water, was weighed to determine the mass of external water and, by difference, the mass of water taken up by the binder through permeation. Clearly, the binder fragments on the screen were wet, and hence it was also necessary to quantify this residual water. The initial experiments involved conditions that produced increasing levels of permeation over time, while another set of experiments was designed to produce no evidence of water permeation. These latter experiments provided a measure of the residual water content external to the binder retained on the screen, hence the necessary correction required for all the data.

Figure 11 presents the normalised water uptake into the structure of the binder as a function of time for three cases: a positive osmotic driving force into the binder, a neutral osmotic environment, and a negative osmotic driving force into the binder. The results were normalised relative to the original mass of water within the binder.

Figure 11. Normalised water uptake into the binder as a function of time for three cases: a positive osmotic driving force into the binder, a neutral osmotic environment, and a negative osmotic driving force into the binder. The accompanying schematic indicates the osmotic conditions on either side of the thin oil films in each case.

When the internal NaCl concentration of the binder was 3wt% and the concentration of salt in the water external to the binder was 0wt%, producing a positive osmotic driving force, the water content of the binder was observed to increase by 11% during the 3 s of mixing, by 30% in just 60 s of resting time, and to asymptote to nearly double the original level after 1800 s. However, when the concentration of the salt in the water external to the binder was raised to 3wt%, producing a neutral osmotic environment, there was no measureable water permeation into the binder. Finally, when the internal salt concentration of the binder was 3 wt% and the concentration of salt in the water external to the binder was 10 wt%, producing a negative osmotic driving force, the water

content of the binder was observed to decrease by 18% during the 3 s of mixing and by 50% in just 120 s of resting time. By 1800 s the majority of the internal water had moved out of the emulsion as the curve can be seen to asymptote to -0.6 at this time. These results suggest that the oil films within the binder are permeable to water and that the permeation of water can be controlled by the osmotic conditions on either side of the thin oil film. Moreover, the findings presented in Figure 11 indicate that water permeation into the binder occurs during the agglomeration process as a positive osmotic driving force is established through the use of a 3 wt% NaCl solution as the internal aqueous phase of the binder.

It should be noted that this work is not the first to demonstrate water permeation across oil films in double emulsions, which is effectively what is created when the emulsion binder is dispersed in water. Previous studies concerning liquid membrane processes have reported water permeation driven by a difference in water activities and have attributed the transport to diffusion of hydrated surfactants^{29, 30, 31}. However, in this previous work, the oil films were considerably thicker than those in the present work. Future work is therefore planned to examine the structure of the thin oil films within the emulsion with the aim of determining the mechanisms by which water transport across these films occurs.

It should also be noted that in the previous work water permeation was not induced with the aim of achieving rapid adhesion between fine particles and the oil film. Indeed, in many cases, the water transport was considered to be undesirable and to be minimized. Therefore in the following set of experiments we examined the effect of water permeation driven by osmosis on the agglomeration process. To vary the osmotic driving force across the thin films within the binder, the salt concentration of the silica suspensions used in the agglomeration experiments was varied, according to the experiments described above. Figure 12A shows the recovery of the 200G silica

as a function of the agglomeration time for the three different cases: a positive osmotic driving force into the binder, a neutral environment, and a negative osmotic driving force into the binder. In all cases the binder was formed using 3 wt% NaCl solution while the NaCl concentrations in the external silica suspensions were 0%, 3% and, 10% for the positive, neutral, and negative cases, respectively. Figure 12B then presents the influence of the osmotic driving force on the recovery as a function of particle size. Each set of data in Figure 10B are from samples taken at the optimum mixing time, *i.e.* 7s.

Figure 12. The influence of the osmotic driving force across the thin oil films of the binder on recovery as a function of a) time and b) particle size. The latter is for the optimum mixing time of 7 s.

Figure 12A shows that the recovery is nearly 100% for the positive driving force case after 7s of mixing. For the neutral driving force, where there is no salt concentration difference, hence little or no water permeation into the binder, the recovery peaks at only 67% before declining. For the negative driving force in which water permeation out of the binder occurs, the recovery peaks at only 48% before declining. Clearly, for the positive driving force case, the overall recovery increases more rapidly, consistent with a strong water permeation. These results support the proposition that water permeation driven by osmosis into the binder increases the speed of the agglomeration, while water permeation out of the binder has the opposite effect.

Again, it was assumed that by promoting less favourable conditions for agglomeration a disproportionate decline in the recovery of the finest particles would be observed. This was expected especially for the case in which a negative osmotic driving force was applied. However, as shown in Figure 12B, the recovery remained constant across the entire size range for each of the cases studied.

To explain the results presented in Figure 12B, we considered that, despite the absence of water permeation into the binder, the thin oil films should retain their property of strong permeability. Hence when a particle is driven towards the oil film, any pressure that develops between the particle and the film simply produces local permeation through the film, minimizing the hydrodynamic resistance^{28, 32}. This mechanism is especially significant for ultrafine particles that have a lower inertial force. Conventional oil agglomeration should also be supported by the property of permeability, albeit at a much lower level due to the finite solubility of water within the oil.

4. Conclusions

In this paper model aqueous suspensions of silica particles ranging in size from less than 500 nm to greater than 100 μm were agglomerated using a novel hydrophobic binder consisting of a concentrated water in oil emulsion. Previous work using the novel binder and an aqueous system consisting of naturally hydrophobic coal and naturally hydrophilic mineral matter indicated that the agglomeration process was ultrafast, exhibited excellent selectivity, and required significantly less oil to achieve agglomeration than the conventional process that uses a pure oil binder^{8, 9, 26}. However, the mechanisms responsible for these observations remained unclear. This study was motivated by the need to investigate the underlying physical mechanisms responsible for these observations, utilising a model system of hydrophobised silica.

An investigation into the influence of the particle size distribution of the feed material on the organic liquid requirements revealed that the nominal thickness of the organic liquid across the surface of the particles within the agglomerates was approximately 66 nm, about double the average film thickness of 29 nm responsible for stabilising the water drops within the binder. In effect, the pre-existing thin films of oil around the water droplets within the emulsion provide an efficient system for delivering the oil to the surface of the hydrophobic particles. Moreover, the binder was found to achieve almost complete recovery of the hydrophobic particles, extending from sizes of more than 100 microns to below 500 nanometres, within the ultrafast time-frame applied in this work. These findings are not observed in other processes used to recover hydrophobic particles from water^{18, 19}.

To account for the latter findings, it was considered that the thin oil films within the binder must be permeable. Subsequent work quantified the strong water permeation across the thin films of oil, leading to the conclusion that thin film permeability supports the primary action of the long-range hydrophobic force, delivering rapid agglomeration of the particles across the size range studied.

We believe this is the first time the fields of liquid membranes^{29, 30} and hydrophobic particle recovery have been formally connected. Given the potential to rapidly recover submicron particles, this process may find applications in the recovery of valuable particles, such as submicron rare earths, that are not recoverable using current techniques¹⁸. It is also conceivable that the benefits from the novel hydrophobic binder could be extended to support solid-liquid separation. Our agglomerated product contains the original binder, which is mostly water, but once inverted through intense shear, remarkably low moistures are observed²⁶. We believe this is due to the organic liquid, which remains on the surface of the particles after the emulsion structure is

destroyed, thus providing a basis for residual agglomeration. Future work will be used to explore the application of the binder in these areas.

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website.

Optimization of the CTAB concentration; Organic liquid dosage/Yield data for each feed and each binder; calculation of the recovery as a function of size from size distribution data.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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