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Oil-Mineral Flocculation and Settling Velocity in Saline Water

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11 Abstract

10

Cohesive particles in aquatic systems can play an important role in deter-12 mining the eventual fate of spilled oil via the generation of Oil-Mineral Ag-13 gregates (OMAs). Series of laboratory experiments have been conducted 14 aiming at filling the knowledge gap regarding how cohesive clay particles in-15 fluence the accumulation of petroleum through forming different aggregate 16 structures and their resulting settling velocity. OMAs have been successfully 17 created in a stirring jar with artificial sea-water, crude oil and two types 18 of most common natural cohesive minerals, Kaolinite and Bentonite clay. 19 With the magnetic stirrer adjusted to 490 rpm to provide a high level ho-20 mogeneous flow turbulence (Turbulence dissipation ϵ estimated to be about 21 $0.02 \text{ m}^2 \cdot \text{s}^{-3}$), droplet OMAs and flake/solid OMAs have been obtained in 22 oil-Kaolinite sample and oil-Bentonite sample, respectively. Kaolinite clay 23 with relatively low flocculation rate $(R_f = 0.13 \text{ min}^{-1})$ tends to physically 24

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attach around the surface of oil droplets. With the lower density of oil, these 25 oil-Kaolinite droplet OMAs generally show lower settling velocity compar-26 ing to pure mineral Kaolinite flocs. Differently, Bentonite clay with higher 27 flocculation rate $(R_f = 0.66 \text{ min}^{-1})$ produces high porous flocs that can ab-28 sorb or be absorbed by the oil and form compact flake/solid OMAs with 29 higher density and settling velocity than pure Bentonite flocs. Some of the 30 large oil-Bentonite OMAs are measured to have settling velocities up to 10 31 $mm \cdot s^{-1}$. In the mixture condition (Kaolinite:Bentonite = 1:1 in weight), oil 32 can be considered to preferably interacting with Bentonite. The microflocs 33 $(< 160 \ \mu m)$ are dominated by Kaolinite with lower oil participation and 34 lower settling velocity, but the Macroflocs (> 160 μ m) which dominates the 35 entire sample's average properties are more influenced by the oil-Bentonite 36 characteristics. 37

³⁸ Keywords: Oil-Mineral Aggregates (OMAs), settling velocity, microfloc,

³⁹ Macrofloc.

40 **1. Introduction**

Since the petroleum exploration and transportation became one of the most critical industrial activities for the global economic growth, extremely large oil spill disasters, such as the 1989 Exxon Valdez spill (0.26 million barrels of oil released to Alaska's Prince William Sound) (Peterson et al., 2003) and the 2010 Deepwater Horizon (DWH) disaster (4.9 million barrels of oil were released into the Gulf of Mexico) (Crone and Tolstoy, 2010; At-

las and Hazen, 2011), and increasingly smaller size spills occurred in the 47 coastal zones (Hayakawa et al., 2006; Doshi et al., 2018; Liu and Callies, 48 2019). These oil spill accidents pose detrimental impacts on sea-based hu-40 man activities (Peterson et al., 2003), ecosystem contamination of aquatic 50 bio-communities (Ainsworth et al., 2018) such as fishes (Murawski et al., 51 2014), birds (Henkel et al., 2012), coral (White et al., 2012) or plankton 52 (Almeda et al., 2013, 2016). Although most mitigation methods focus on 53 spilt oil floating onto the water surface (Reddy et al., 2002, 2012; Liu et al., 54 2012), there can be a considerable portion of spilt oil settles to the sea-floor 55 after flocculating with natural cohesive materials, including sediments and 56 organic particles (Chanton et al., 2014; Yan et al., 2016; Jones and Bridge-57 man, 2016; Romero et al., 2017; O'Laughlin et al., 2017). 58

Flocculation with cohesive mineral sediments can be especially common 59 in more energetic coastal environments where resuspension of sediment is 60 more likely or near river mouths where new supplies of sediments are abun-61 dant (Strom and Keyvani, 2016; Shen et al., 2018). When crude oil is released 62 into aquatic systems in nature, oil droplets can be open to flocculate with 63 suspended particles (Sterling Jr et al., 2005). Through settling and depo-64 sition, the oil mineral aggregates may eventually preserving in the sea-floor 65 depositions over geological time (Romero et al., 2017). Therefore, the in-66 teractions of oil and aquatic mineral particles, or biological materials can 67 play an important role in the fate of spilt oil (Khelifa et al., 2002, 2005a; 68 Passow and Hetland, 2016; O'Laughlin et al., 2017). This study focuses on 69

the influence of mineral sediments on oil droplets through flocculation. Some insights into the flocculation of oil droplets with biological materials, namely the marine snows, can be found in, for instance, Passow et al. (2012) and a comprehensive review article of Daly et al. (2016).

Oil droplets tend to aggregate with, and finally be stabilized by, cohesive 74 particles or suspended particle materials (SPM) in the water column and 75 form oil-mineral aggregates (OMAs) (Khelifa et al., 2002), oil-SPM aggre-76 gates (OSAs) (Khelifa et al., 2005a) or oil-particle aggregates (OPAs) (e.g., 77 Zhao et al. 2014, 2016, 2017). In the present study, the term "OMAs" has 78 been used because only mineral clay has been utilized to flocculate with oil 79 droplets in the cases. Several earlier studies focus on the structure of OMAs 80 using microscopy imagery and "droplet OMAs", "flake OMAs" or "solid 81 OMAs" are most commonly observed OMA structures (Lee and Stoffyn-82 Egli, 2001; Stoffyn-Egli and Lee, 2002). Droplet OMAs are combination or 83 enclosure of one or several oil droplet(s) and mineral particles/flocs via sur-84 face attachments. On the contrary, flake OMAs have a similar shape as 85 solid OMAs which have membrane-like sheets with an orderly arranged oil 86 and mineral particle configuration (Stoffyn-Egli and Lee, 2002). With higher 87 shear strength, structures of flake OMAs could be altered to become solid 88 OMAs because the crumpling or breaking of flake type OMAs may form more 89 compact and denser floc structures (Stoffyn-Egli and Lee, 2002; Loh et al., 90 2014). They can be highly compact with oil and mineral absorbed together 91 and organized in dendritic or foldable feather-shape structures. 92

Later, several important OMAs studies have been focused on the for-93 mation mechanisms and influence factors. Omotoso et al. (2002) presented 94 a flocculation index based on the sedimentation behavior of a sheared oil-95 mineral-water mixture. It was used to quantify the degree of interaction of 96 oil and minerals in water which was found to be dependent on the viscosity 97 of the crude oil and the type of mineral present. On the other hand, Khelifa 98 et al. (2002) suggested that droplet shape and size were not correlated to 99 oil viscosity, but the concentration of oil droplets decreased rapidly with oil 100 viscosity, temperature and asphaltenes-resins content (ARC). Le Floch et al. 101 (2002) quantified the amount of oil incorporated into OMA with the salinity 102 ranging from $0 \sim 35$ ppt. They demonstrated that the OMA formation was 103 significantly enhanced by salinity when comparing to distilled water condi-104 tion. However, the amount of oil contained in OMAs saturated at low salinity 105 of only 2 ppt and further enhancing salinity showed almost no effect OMA 106 formation. This salinity threshold depends on other parameters including oil 107 type and the nature of the mineral present. Below this salinity threshold, 108 there is a linear decrease in the amount of oil incorporated in OMA, to prac-109 tically zero in distilled water. Hill et al. (2002) presented an equation that 110 defines the time required to coat and stabilize oil droplets with mineral par-111 ticles suspended in a turbulent medium. The finding that OMA form rapidly 112 given adequate sediment concentration should play a key role in oil spill re-113 sponse decision. With the high demand of quantitative understanding in the 114 formation of OMAs processes, some further laboratory experimental studies 115

have been reported. Khelifa et al. (2005b) presented the laboratory results 116 showing a positive correlation of OMA sizes and the concentration of mineral-117 stabilized droplets with salinity positively from zero to a critical aggregation 118 salinity in the range of $1.2 \sim 3.5$ ppt. And it is believed that the effect if 119 salinity on droplet size distribution is strongly influenced by clay type. More 120 recently, Sun et al. (2010, 2013) presented the experimental results showing 121 that the formation of oil suspended particle matters aggregates increased 122 exponentially with the mixing time and reached an equilibrium within $4 \sim 5$ 123 hours at a provided turbulence dissipation rate of 2.6 $m^2 \cdot s^{-3}$. They believed 124 the shaking rate (turbulence) largely influences the maximum oil trapping 125 efficiency in OMAs. And it is found that most of the formed aggregates were 126 solid aggregates and single droplet aggregates with low mixing energies, and 127 multi-droplet oil suspended particles aggregates with high mixing energies. 128

Among all the previous OMA literature, very limited studies have been 129 reported to systematically investigate OMAs settling dynamics. Khelifa et al. 130 2008 reported a series of detailed laboratory experimental jar tests on chem-131 ical dispersed oil and natural mixture sediment aggregation. Their data, 132 probably for the first time, showed a direct relationships between the mea-133 sured settling velocity and OMA size. They suggested that those flocs with 134 low oil concentration may barely change the oil-sediment aggregates behav-135 iors, but with high oil concentration within the oil-sediment aggregates, their 136 density can be much smaller than pure sediment flocs having similar floc sizes. 137 For most sediment types they tested, the effective density of the oil-sediment 138

aggregates can be about $2\sim3$ times less than those of pure sediment flocs. 139 Importantly, in their samples, it is suggested that the presence of chemical 140 dispersed oil may enhance the stickiness of sediment grains which helps build-141 ing up the large flocs with oil participation. More recently, O'Laughlin et al. 142 (2017) reported measured results of dilbit-derived OMAs settling velocity 143 from series of laboratory and wave tank experiments in response to the pres-144 ence or absence chemical dispersants. They suggested that settling velocities 145 of artificially formed OMAs on the order of $0.1 \sim 0.4 \text{ mm} \cdot \text{s}^{-1}$. Moreover, the 146 OMA size, settling velocity and effective particle density were increased in 147 response to the higher concentration of suspended sediment. Their data also 148 show evidences that dispersant may inhibits flocculation. These two stud-149 ies clearly indicated the importance of cohesion(stickiness) in determining 150 the resulting oil-floc and their settling velocity. As mentioned above, earlier 151 studies also provided very comprehensive understanding on the structures 152 of OMAs. Here, we further hypothesize that a main factor controlling the 153 structures of OMA is the properties of the mineral sediments, for example, 154 their stickiness. Hence, a reasonable next step is to further relate different 155 type of OMA structures with their settling characteristics. 156

The present study is motivated to investigate the effect of mineral types, which provide different stickiness, in determining the OMA structures and the resulting settling velocities. Data obtained from the controlled laboratory experiments are analyzed with three main objectives: 1) To understand the OMAs structures formed with different types of common clay minerals

by high-resolution digital microscopy, 2) to measure physical characteristics 162 of OMAs, such as their sizes and settling velocities using LabSFLOC-2 cam-163 era, and the most importantly 3) synthesize measured data to gain insights 164 into OMA structure and settling dynamics due to different clay types. The 165 remaining of this paper is organized as follow. Section 2 focuses on the labo-166 ratory methods, including the OMA generation, turbulence characterization, 167 microscopy and LabSFLOC-2 system for studying settling characteristics. 168 Results are presented in terms of OMA structures and characteristics in Sec-169 tion 3, discussions are in Section 4 and important concluding remarks are in 170 Section 5. 171

172 2. Materials and methods

173 2.1. Laboratory experiment setup

An experimental stand set (Figure 1a) has been designed and a series 174 of magnetic stirring jar experiments have been conducted at the Center 175 for Applied Coastal Research, University of Delaware. White Kaolin clay 176 (92.3±2.5 % Kaolinite), Wyoming sodium Bentonite clay (85.2±2.3 % Mont-177 morillonite) (two most common clay types with large difference in cohesion 178 in saline water) and raw Texas crude oil (Dynamic viscosity: $7.27 \times 10^{-3} \ \mathrm{Pa}{\cdot}\mathrm{s}$ 179 at 20 °C) with various proportions are used to generate OMAs. As summa-180 rized in Table 1, we specify oil-to-sediment ratio close to 2 with clay mineral 181 concentration of 0.5 g per litre of saline water, which provide a condition 182 for maximum OMA formation efficiency condition according to the previ-183

ous studies (Guyomarch et al., 2002; Khelifa et al., 2008; Ajijolaiya et al., 184 2006). Artificial seawater (Salinity ≈ 35 ppt) has been made from mixing 185 clean water and pure salt. The jar has a diameter of 11 cm and the flow 186 depth is 13 cm (1 liter salt water). Magnetic stirring speed is set to 490 rpm 187 (Device range: $0 \sim 1000 \text{ rpm}$) for providing the constant turbulence intensity 188 for OMAs generation. Three-component flow velocities are measured by a 189 Vectrino Profiler (Nortek), which was mounted on the shelf above the mag-190 netic stirrer with the sensor probes located 5 cm below the water surface in 191 the jar (in Figure 1a). Flow velocity data was collected without crude oil and 192 sediment but in otherwise the same flow conditions (artificial seawater in the 193 jar with same flow depth). The time series of turbulent velocity fluctuations 194 are transformed into Fourier space to obtain turbulent kinetic energy spec-195 trum. Turbulence dissipation rate is then estimated to be $\epsilon \approx 0.02~{\rm m^2 \cdot s^{-3}}$ 196 via matching the Kolmogorov spectrum with Taylor frozen turbulence ap-197 proximation (e.g., Voulgaris and Trowbridge 1998; Huang et al. 2018). The 198 corresponding shear parameter is of seawater (Salinity ≈ 35 ppt) at 20 °C 199 (Viscosity $\approx 1.08 \times 10^{-3}$ Pa·s). 200

Different types of mineral flocs and Oil-Mineral Aggregates (OMAs) samples are generated, including 1) Kaolinite flocs, 2) Bentonite flocs, 3) Mixed Kaolinite-Bentonite flocs, 4) Oil-Kaolinite aggregates, 5) Oil-Bentonite aggregates and 6) Oil-Kaolin-Bentonite aggregates. Each experimental run last up to 2 hours and OMAs are allowed to settle down overnight (~ 8 hours) which should be long enough for all the particles aggregation and settling.



Figure 1: Schematic of the laboratory experimental setup. a) shows the self-designed Vectrino stand set and b) show the LabSFLOC-2 system

Table 1: Various proportions of mineral cla	y and oil in each experimental run.
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Sample	Saline water(L)	Kaolinite clay(g)	Bentonite $clay(g)$	Texas crude oil(g)
S01	1.00	0.50	/	/
S02	1.00	0.50	/	1.00
S03	1.00	/	0.50	/
S04	1.00	/	0.50	1.00
S05	1.00	0.25	0.25	/
S06	1.00	0.25	0.25	1.00

The mass settling velocity of OMAs were observed using the low intrusive 207 LabSFLOC-2 system (the 2nd version of Laboratory Spectral Flocculation 208 Characteristics instrument) (Figure 1b). This instrument was originally de-209 veloped by Manning and Dyer (2007) and first used by Gratiot and Man-210 ning (2004). It measures the entire floc population for each sample being 211 assessed and has been successfully applied in many cohesive sediment trans-212 port studies (Manning et al., 2010; Manning and Schoellhamer, 2013; Uncles 213 and Mitchell, 2017). LabSFLOC-2 utilizes a low-intrusive 2.0 MP Grasshop-214 per monochrome digital video camera to optically observe individual flocs 215 (e.g. Manning and Dyer (2002)) as they settle in a 350 mm high by 100 mm 216 square Perspex settling column. The video camera, positioned nominally 75 217 mm above the base of the column, views all particles in the center of the 218 column that pass within a 1 mm depth of field, 45 mm from the Sill TZM 219 1560 high-magnification (5 μ m pixel resolution) Telecentric (maximum pixel 220 distortion of 0.6 %), 0.66 (1:1.5) magnification, F4, macro lens fitted behind 221 a 5 mm thick glass faceplate. The LabSFLOC-2 settling column sampling 222 was conducted at the end of each OMA sample's experiment and these OMA 223 samples are believed in an equilibrium stage. 224

A high-resolution digital microscope system has been used to observe detailed floc structures and to carry out statistical analysis on floc numbers in order to evaluate flocculation rate. All the floc samples were directly collected from the running experiment in real-time using wide mouth (> 2 mm) plastic pipettes to minimize floc disturbance and to transfer the samples from the mixing jar to the microscope slides without using coverslip to prevent the samples being squeezed. Floc samples are observed with a $4\sim10$ times zoomin screen on a DELL laptop by the camera software provided by AmScope Inc.

234 2.2. Data processing

235 2.2.1. LabSFLOC-2 camera floc data

As one of the most commonly used floc video camera instruments in es-236 tuarine and coastal suspended sediment transport study, the LabSFLOC-2 237 produces not only visible floc individual images but also other essential quan-238 titative floc properties including floc size, floc shape and floc settling velocity 239 (Manning et al., 2010). Through additional theories, other floc quantities can 240 be derived, such as floc density, fractal dimension and so on. The recorded 241 videos of floc settling videos can be analyzed with Matlab software routines 242 based on the HR Wallingford Ltd DigiFloc software (Benson and Manning, 243 2013) and Java Script to semi-automatically process the digital recording 244 image stack to obtain floc size and settling velocity spectra (Manning et al., 245 2010; Uncles and Mitchell, 2017). Using the measured floc diameter D (floc 246 sphere-equivalent diameter), settling velocity W_s , and floc shape, a modified 247 Stokes Law (Stokes, 1851) is used to estimate individual floc effective density 248 (Manning and Schoellhamer, 2013): 249

$$\rho_e = \frac{18W_s\beta}{\alpha} \cdot \frac{\rho\nu}{g} \cdot \frac{1 + 0.15Re^{0.687}}{D^2} \tag{1}$$

in which ρ the is the saltwater density, ν is the kinematic viscosity, g is gravitational acceleration, α and β are shape-related coefficients and they equal to 1 for perfect spheres. Re in the equation is the particle Reynolds number, defined as

$$Re = W_s D / \nu \tag{2}$$

This modified Stokes' Law is used for encountering flocs which have particle Reynolds numbers greater than its original unity. By assuming floc has a fractal structure, the fractal dimension of floc (n_f) can be calculated via the following relationship (Winterwerp and Van Kesteren, 2004):

$$\left(\frac{D}{d}\right)^{n_f - 3} = \frac{\rho_e}{\rho_s - \rho} \tag{3}$$

²⁵⁸ in which d is the minimum primary particle size which is assumed as ??? ²⁵⁹ (Manning and Schoellhamer (2013)), ρ is the seawater density.

260 2.2.2. Microscope images analysis

The floc images (e.g., Figure 2a) collected from the digital microscope of each floc sample allow a detailed investigation of floc and OMA structures and the red contours point out the individual flocs which can be manually selected under the screen by real-time observation. Microscope images also provide independent and high-resolution data of floc population, which are number counted manually according to the contours, and shape analyzed for further statistical analysis and flocculation rate evaluation. For each sample,



Figure 2: Examples of digital microscope images. a) shows floc number manually counted from a microscope screenshot. The red parts indicate the individual floc can be recognized manually for further statistical analysis. b) shows oil droplets can be manually counted to give the averaged droplet size. The oil droplets are formed and measured after 20 minutes stirring under given turbulence.

six different microscopy images have been analyzed which cover hundreds to
 thousands individual flocs.

We also use microscope images to calculate averaged oil droplets size under the given turbulence level (e.g., see Figure 2b). The statistical analysis of the pure oil droplets samples images shows the maximum oil droplets size can be up to 120 microns and the mean droplets size is approximately fractional droplets size distribution under the constant given turbulence and salinity has been provided in Figure 2b.

276 2.2.3. Mineral stickiness quantification (Flocculation rate (R_f))

In this study, we quantify the effect of different mineral clays on OMA flocculation by their stickiness. In the study of flocculation with significant organic content, such as due to the presence of transparent exopolymer par-

ticles (TEP) (e.g., Passow (2002)), the stickiness can be quantified by per-280 forming experiments to estimate flocculation (efficiency) rate Engel (2000). 281 We perform flocculation rate experiment for three types of mineral particles 282 without the presence of oil, namely cases S01 (Kaolinite), S03 (Bentonite) 283 and S05 (half-half mixture of Kaolinite and Bentonite) (see Table 1), respec-284 tively. Temporal microscopy images (six images for each sample at a time) 285 have been collected during mineral flocs development in a magnetic stirrer 286 jar from beginning (0 minute) to the end (2 hours) for each mineral sample. 287 By counting all the floc numbers and normalizing by maximum floc number 288 of each mineral sample which covers hundreds to thousands individual flocs, 289 flocculation evolution time series has been obtained for each type of min-290 eral clay (Figure 3). The manually counted floc numbers cover hundreds to 291 thousands individual flocs which are statistically significant to represent the 292 entire floc distribution and characteristics of each tested sample. 293

Due to flocculation, the number of particles in each case decays in time. In 294 the semi-logarithmic plot shown in Figure 3, we observed a nearly exponen-295 tial decay of particle number in the first couple of minutes of the flocculation 296 before the particle number becomes more or less constant in time. By fitting 297 the first three data points in each run, we obtain the representative floccu-298 lation rate: R_f . The three trend lines in Figure 3 indicate that Kaolinite 299 clay has the lowest flocculation rate of $R_{f_{-Kaolinite}} = 0.13 \ (min^{-1})$ while the 300 Bentonite clay shows a high flocculation rate of $R_{f_Bentonite} = 0.66 \text{ (min}^{-1})$ 301 nearly 5 time larger. The mixture of equal amount of Kaolinite and Bentonite 302

has an intermediate flocculation rate of $R_{f_mixed} = 0.32 \text{ (min}^{-1}\text{)}$. Following 303 Engel (2000), we will consider Kaolinite having the lowest cohesion, followed 304 by the mixture of Kaolinite-Bentonite and Bentonite is among the most co-305 hesive sediments investigated in this study. Noticeably, in the Bentonite (red 306 dots) and mixture (yellow dots) samples, floc numbers increase slightly after 307 reaching the maximum flocculation (lowest normalized floc number) at $5 \sim 6$ 308 minutes and reach to equiburium stage after 30 minutes, which may imply 309 the break-up of part of the larger fragile flocs. This indicates that the partici-310 pant of kaolinite not only reduces the cohesion of pure bentonite, meanwhile, 311 the existence of bentonite weakens the stability of pure kaolinite flocs. 312

The primary goal of this mineral flocculation rate quantification present 313 here is to compare the difference of stickiness (not floc number) of bentonite 314 and kaolinite because floc numbers between bentonite and kaolin cases have 315 huge difference (bentonite aggregates much larger but less numbers of flocs 316 because of the much higher stickiness) although bentonite sample and kaolin 317 sample have equivalent mineral concentration under same turbulence condi-318 tion. This information will be shown later to be very useful for the interpre-319 tation of the OMA structure and LabSFLOC-2 settling column experimental 320 results. 321



Figure 3: Statistical results of temporal (120 minutes) floc evolutions of normalized floc number for Kaolinite run (blue, S01), Bentonite run (red, S03) and mixed Kaolinite-Bentonite run (yellow, S05). The initial particle number of each run is used for normalization. Each data point comes from manually counted floc number from six different images of each pipette sample which covering hundreds to thousands individual flocs and normalized by the maximum floc number (Kaolinite:1260, Bentonite:782 and Mixture:1323) of each sample.

322 3. Results

323 3.1. Floc structures

Samples from each case presented in Table 1 were collected after the flocculation reached equilibrium and have been analyzed by microscopy. Highresolution images provided the details of each mixture floc structure with a magnification factor of 10. Three basic floc types have been observed depending on mineral type: pure mineral flocs/aggregates (no oil) (Figure 4a₁,b₁ & c₁), oil droplets attaching/combining Kaolinite aggregates (Figure 4a₂₋₄), and large flake shaped oil-Bentonite aggregates (Figure 4b₂₋₄).

Figure 4a₁ shows a representative microscope image of settled pure Kaoli-331 nite clay flocs (500 mg·l⁻¹, S01 in Table 1). With the addition of 1 g Texas 332 crude oil (S02 in Table 1), the oil droplets can be observed being attached or 333 embraced within the Kaolinite clay structures (such as Figure $4a_{2-4}$). The at-334 tachment is limited to the surface of oil droplets while the droplets structure 335 remains intact. The oil-Kaolinite aggregates observed are consistent with the 336 droplet OMA type reported in the previous studies (such as Stoffyn-Egli and 337 Lee 2002; Khelifa et al. 2002), in which oil droplets are coated by sediment 338 aggregates through surface attachment. The quantity of mineral attached to 339 a droplet is highly variable. 340

The OMA obtained from the Bentonite clay run (S03 in Table 1), generated with same turbulent dissipation rate, are shown in Figure $4b_{1-4}$. The Bentonite flocs are generally larger than Kaolinite flocs and their size can be up to $100\sim200$ m in width and several hundred micrometers in length (Figure

 $4b_1$). These features are distinct from the pure Kaolinite run (S01) shown in 345 Figure $4a_1$. As demonstrated in section 2.2.3 (or Figure 3), pure Bentonite 346 clay particles are much cohesive and attachable than Kaolinite particles. 347 More importantly, the more cohesive characteristic of Bentonite floc leads 348 to an entirely re-shaped oil-mineral structure (see Figure $4b_2$, S04 in Table 349 1). Compared with oil-Kaolinite flocs, the sphere-shaped oil droplets disap-350 peared, and the oil-Bentonite flocs show much larger size of oil soaked mineral 351 having a flake-shaped aggregates up to hundreds of microns in size (see Fig-352 ure $4b_{2-4}$). Compared with the previous studies (Stoffyn-Egli and Lee, 2002; 353 Khelifa et al., 2002; Zhao et al., 2016), the dominant oil-Bentonite aggre-354 gates observed here belong to a dense type of oil-aggregate called flake/solid 355 OMA. Flake aggregates have the appearance of membrane structures, usu-356 ally floating or neutrally buoyant, which can attain hundreds of microns in 357 length. Their microstructure is highly organized as dendritic or feather-like. 358 Experimental results suggest that high shear strength (i.e. extended or faster 359 agitation) tends to break or crumple flake aggregates. The crumpled flakes 360 (Figure $4b_{2-4}$) may be distinguished from mineral-embraced droplet OMA 361 (Figure $4a_{2-4}$) by their folds or preferential orientation of the minerals. 362

After mixing equal amount of Kaolinite and Bentonite clay for Case S05, the mixture flocs contain both Kaolinite floc and Bentonite floc structures (see Figure 4c₁), and importantly, although the general size of the mixed flocs (Figure 4c₁) are smaller than pure Bentonite case (Figure 4b₁). The Bentonite floc structure appears to be dominant in the mixture mineral sample. With the addition of oil in the mixture sample S06, large flake shaped OMA can be observed in Figure 4f which has similar floc size with those in the oil-Bentonite case (S04, see Figure $4b_{2-4}$). However, both droplet OMAs and flake OMAs can be observed (Figure $4c_{3-4}$).

Due to different cohesion between Kaolinite and Bentonite clays, the resulting OMA structures are also distinctly different which is expected to lead to different settling velocities. In the next sections, we will investigate different mineral flocs and OMAs settling velocity and discuss their relationship to floc structures.

377 3.2. Floc physical properties

The previous section provided insights on the floc structures for differ-378 ent types of OMAs by microscopy images. This section is devoted to more 379 quantitative study of floc physical properties, particularly their settling ve-380 locities. The scatterplots in Figure 5a, 6a & 7a illustrate individual spherical-381 equivalent dry mass weighted floc sizes (x-axis) plotted against their corre-382 sponding settling velocities (y-axis) of each sample (see Table 1) collected 383 and analyzed by LabSFLOC-2 camera system. The scatterplots allow sub-384 sequent statistical analysis for floc properties using 12 different size classes 385 (Size Band details are shown in the bottom of Figure 5-7). The physical 386 properties of particular interest here are, the counted floc numbers of each 387 size band (Figure 5c, 6c & 7c), the settling velocity (Figure 5d, 6d & 7d, floc 388 density (Figure 5e, 6e & 7e) and fractal dimension (Figure 5f, 6f & 7f). 380



Figure 4: Floc images from the high-resolution digital microscope camera. a1-a4) Kaolinite (S01) and oil-Kaolinite (S02) samples; b1-4) Bentonite (S03) and oil-Bentonite (S04) samples; c1-4) mixed Kaolinite and Bentonite (S05) and oil-Kaolinite-Bentonite (S06) samples.

390 3.2.1. Kaolinite and Oil-Kaolinite flocs

The scatterplot presented in Figure 5a indicates that the Kaolinite clay 391 flocs (S01) cover a size range from 20 to 400 microns while their settling 392 velocities vary from 0.04 to 10 $\rm mm \cdot s^{-1}$. Although with some notable scatters, 393 the floc settling velocities are more or less proportional to floc sizes. Adding 394 oil into Kaolinite mineral (S02) shows negligible change in the floc size range 395 (see Figure 5b). However, when floc size is greater than about 80 micron, 396 the peak settling velocities (about 4 $\text{mm}\cdot\text{s}^{-1}$) show almost no change with 397 respect to floc size. Also, there exist some low-density flocs in the rather large 398 size range of $200 \sim 400$ microns with settling velocities ranging from $0.2 \sim 0.6$ 399 $\text{mm}\cdot\text{s}^{-1}$ (around the red constant density line of 16 kg·m⁻³ in Figure 5b). 400 This is due to the large Oil-Kaolinite flocs having much lower density than 401 those of pure Kaolinite flocs. A more quantitative understanding on these 402 interesting features can be obtained by examining the statistics of 12 size 403 bands. 404

The number of Kaolinite flocs increases dramatically from Size Band 405 (SB)-1 (20~40 microns) to SB-3 (80~120 microns) and then drops quickly 406 from SB-3 to SB-8 ($320 \sim 400$ microns) (Figure 5c, blue bands). Adding oil 407 to Kaolinite significantly increases floc number for small size flocs $(20 \sim 80)$ 408 microns) at SB-1 and SB-2 while floc numbers at larger size class are gener-409 ally lower than or similar to those of pure Kaolinite flocs (Figure 5c, orange 410 bars). The settling velocities of Kaolinite samples (S01 and S02 in Table 1) 411 averaged for each size class are shown in Figure 5d. Evidently, pure mineral 412

flocs (S01) show a rapid increase of settling velocities with respect to the 413 increase of floc sizes for the entire size class spectrum (SB-1 to SB-8). On 414 the contrary, oil-Kaolinite flocs show milder increase of settling velocity with 415 respect to floc size from SB-1 to SB-6 until a completely different trend is 416 observed for larger size class (SB-6 to SB-8), namely, a significant decrease 417 of settling velocity with respect to increase of floc size. Overall, adding oil to 418 Kaolinite decreases flocs settling velocity, particularly for larger size classes 419 (by nearly factor 3 in the SB-6 and nearly a factor 7 in the SB-8). Consider-420 able reduction of settling velocity at SB-6 to SB-8 is clearly associated with 421 the significant decrease of floc effective density due to the addition of oil to 422 Kaolinite at this size range (see Figure 5e). Generally, adding oil reduces floc 423 effective density in all size ranges of flocs but the reduction is much more 424 pronounced at large size class. In SB-2 and SB-3, effective density decreases 425 by approximate 1/3 to 1/4 by adding oil while settling velocity also decreases 426 by 1/3 to 1/4. In SB-4 to SB-8, the effective density decreased by half or 427 much more especially in the largest sized flocs, and their settling velocity 428 shows a remarkable reduction in large size flocs such as SB-6 to 8. Since av-429 eraged droplet size is about 57 microns as measured in the laboratory tests, 430 it is very likely that there is less oil contained in smaller flocs size classes. 431 Overall, the results presented here is consistent with the presence of oil as 432 droplets (see Figure $4a_2$ - a_4) having lower density than saltwater or mineral. 433 The low density oil droplets contribute to the reduced settling velocity (or 434 floc density) particularly at the large floc size range. 435

The fractal dimension for Kaolinite flocs or Kaolinite-oil flocs is in the range of 2.4~2.6 except for a small number of large flocs in SB-7/8. In general, adding oil slightly reduces fractal dimension to 2.4. A notable exception is that when oil is added to Kaolinite, the largest flocs in SB-8 show a much lower fractal dimension of 2.05 due to containing low density oil droplets in the large structure.

442 3.2.2. Bentonite and Oil-Bentonite flocs

In the pure Bentonite sample (S03, Figure 6a), we observe some very 443 large size flocs up to $400 \sim 700$ microns that do not exist in the pure Kaolinite 444 sample (S01). The resulting settling velocity range is also wider $(0.01 \sim 20)$ 445 $mm \cdot s^{-1}$) than that in Kaolinite samples. A more careful examination further 446 suggests that many large size flocs (in SB-9 SB-12 in Figure 6c, $400 \sim 700$ 447 microns) in pure Bentonite sample (S03) are of very low density (within 50 448 kg·m⁻³) and their settling velocities are limited to range of 1 \sim 5 mm·s⁻¹, 449 despite very large floc size. Importantly, adding oil further increased the 450 floc size up to 800 microns (Figure 6b), and it also shows an upper limit of 451 settling velocity but at much higher value of about 10 $\mathrm{mm} \cdot \mathrm{s}^{-1}$ compared to 452 that of oil-Kaolinite (see Figure 5b). 453

Quantitatively, floc number increases from SB-1 to SB-5 and then reduces afterwards to SB-12 (floc number < 5 in SB-12) (Figure 6c). Comparing to Kaolinite samples (S01 and S02), the most notable difference is that the floc numbers for Bentonite samples are significantly lower than those in Kaoli-



Figure 5: Floc characteristics from the LabSFLOC-2 analysis. a) & b) show the plots of floc sizes vs. settling velocities of Kaolinite (S01) and Oil-Kaolinite (S02), respectively. The three diagonal lines present contours of Stokes settling velocity calculated with a constant effective density (i.e. floc bulk density minus water density) of 1,600 kg·m⁻³ (pink line, equivalent to a quartz particle), 160 kg·m⁻³ (green) and 16 kg·m⁻³ (red line). c)-f) show the 12 Size Bands trends of floc number, settling velocity, floc density and fractal dimensions respectively for both Kaolinite (blue) and Oil-Kaolinite (orange) samples.

nite sample. Larger floc sizes and lower floc number in Bentonite samples 458 are consistent with the high flocculation rate (high stickiness) of Bentonite 459 discussed in Section 2.2.3. When oil is added to Bentonite (S04) we observe 460 an increase of settling velocities with the floc size (Figure 6d), except at the 461 largest size class (SB-12). This trend is more or less consistent with pure 462 Kaolinite sample (S01, Figure 5d) and Bentonite sample (S03, Figure 6d), 463 but different from the oil-Kaolinite sample (S02, Figure 5d). This suggests 464 that oil interact differently with Kaolinite and Bentonite samples and it is 465 consistent with their distinct droplet OMA and flake OMA structures pre-466 sented in Figure 4. More importantly, when oil is added to Bentonite, we 467 observe a more rapid increase of settling velocity when floc size increases from 468 SB-9 to SB-12. Furthermore, comparing to the pure Bentonite condition, we 469 obtain an increase of settling velocity by more than a fact of 2 in SB-11, while 470 recall that for Kaolinite samples, adding oil to Kaolinite (S02) significantly 471 reduces the floc settling velocity. These observations are supported by the 472 data from floc effective density. From Figure 6e, we can see that adding oil 473 to Bentonite clay generally increases floc effective density with the most sig-474 nificant increases occur at SB-1 and SB-9 to SB-12 (contrast with Figure 5e. 475 adding oil reduces floc effective density in Kaolinite samples). In this case, 476 the oil droplets no longer exists and become absorbed into mineral flocs. It 477 is likely that at such micro-scale, oil changes the adhesion characteristic and 478 make the small flocs more compact, dense with lower porosity. 470

480

The fractal dimension for Bentonite floc or Bentonite-oil flocs are in the

range of $2.2 \sim 2.4$ which is slightly lower than those of Kaolinite samples. 481 However, adding oil to Bentonite generally increases fractal dimension with 482 the largest increase occurs at SB-1 with a fractal dimension near 2.5. It 483 is interesting to the point out that, a notable fractal dimension changes 484 after adding oil is in larger size class floc of SB-8 ($320 \sim 400$ microns) for 485 Kaolinite sample and in the smallest size class of SB-1 $(20 \sim 40 \text{ microns})$ for 486 Bentonite sample. This drastic difference is again consistent with different 487 OMA structure of Kaolinite and Bentonite clays. 488

489 3.2.3. Mixed Kaolinite-Bentonite and Oil-Kaolinite-Bentonite flocs

In the mixed Kaolinite-Bentonite sample (Figure 7a), a large number 490 of small sized flocs (<80 microns) are observed which are lacking in pure 491 Kaolinite (Figure 5a) or pure Bentonite (Figure 6a) samples. The significant 492 portion of small flocs in SB-12 may due to in the mixture, the kaolinite 493 particles decrease the stickiness of the mixed floc comparing to pure bentonite 494 condition, which may also lead to more small bentonite flocs. Meanwhile, it is 495 likely that the bentonite flocs, when flocculate with kaolinite flocs, make the 496 whole mixed flocs more fragile and with the high turbulence level provided, 497 part of the mixture flocs tends to break-up into smaller flocs, even smaller 498 than those in pure bentonite or kaolinite cases. The observed large amount of 499 microflocs in Figure 7 at the equilibrium stage is consistent with the temporal 500 evolution of normalized floc number shown in Figure 3 that at the later stage, 501 normalized floc number increases. Therefore, when mixing low stickiness 502



Figure 6: Floc characteristics from the LabSFLOC-2 analysis. a) & b) show the plots of floc sizes vs. settling velocities of Bentonite (S03) and Oil-Bentonite (S04), respectively. The three diagonal lines present contours of Stokes settling velocity calculated with a constant effective density (i.e. floc bulk density minus water density) of 1,600 kg·m⁻³ (pink line, equivalent to a quartz particle), 160 kg·m⁻³ (green) and 16 kg·m⁻³ (red line). c)-f) show the 12 Size Bands trends of floc number, settling velocity, floc density and fractal dimensions respectively for both Bentonite (blue) and Oil-Bentonite (orange) samples.

kaolinite and high stickiness bentonite, the flocculation process is much more
complex and it takes longer time to reach equilibrium. This is because when
more porous/fragile bentonite floc structure initially combined with denser
kaolinite floc, the entire mixture flocs become fragile to high turbulence and
breaks into more small flocs.

The settling velocity for pure Kaolinite-Bentonite flocs peaks at about 508 $10 \text{ mm} \cdot \text{s}^{-1}$ for floc size greater than about 100 microns. When oil is further 509 added to the mixed Kaolinite-Bentonite sample (Figure 7b), we observe even 510 higher settling velocity flocs exceeding 10 $\mathrm{mm}\cdot\mathrm{s}^{-1}$, which is clearly due to 511 higher floc effective density in SB-3 to SB-9 shown in Figure 7e. We also 512 obtain more small flocs but their density is widely spread from nearly close 513 to water (below the red line of 16 kg \cdot m⁻³) to those high-density flocs (between 514 the green line of 160 kg·m⁻³ and red line of 1600 kg·m⁻³). 515

Generally, both Kaolinite-Bentonite minerals flocs and Oil-Kaolinite-Bentonite 516 flocs show increasing settling velocity with the increasing floc sizes (Figure 517 7d) except at the largest size class. In other words, by adding oil to equally 518 mixed Kaolinite and Bentonite mixture, the overall settling velocity trend is 519 similar to that of pure Bentonite (Figure 6d). This observation can be further 520 confirmed by examining floc effective density shown in Figure 7e. Similar to 521 adding oil to pure Bentonite (see Figure 6e), adding oil to Kaolinite-Bentonite 522 mixture generally increase floc effective density and hence the settling veloc-523 ity also increases in most Size Bands. A minor difference is that the rise 524 of settling velocity in SB-9 to SB-12 by adding oil is less dramatic in SB-9 525

to SB-12 in the Kaolinite-Bentonite mixture case. Also, there is simply less number of those large flocs in Kaolinite-Bentonite mixture cases, suggesting that adding oil to Kaolinite-Bentonite mixture does not increase the cohesion as much when comparing to adding oil to pure Bentonite, possibly due to the presence of less cohesive Kaolinite. Therefore, oil can be considered to preferably interacting with Bentonite and the presence of Kaolinite is of secondary effect to slightly reduce cohesion.

For Kaolinite-Bentonite mixture, the fractal dimension of small sized flocs can be up to 2.8 while the large flocs are of lower value around 2.4 to 2.6. The range of fractal dimension is larger than pure Bentonite (S03) and it is similar to pure Kaolinite (S01) except for the smallest size class (SB-1). By adding oil, flocs fractal dimension in larger size class SB-6 to SB-9 increases and those in small size class SB-1 to SB-5 show negligible change.

539 3.3. Microflocs and Macroflocs

In the cohesive sediment literature, two distinguished floc components: 540 microflocs and Macroflocs, have been utilized to quantitatively describe the 541 floc spectra (Manning et al., 2010; Manning and Dyer, 2007; Manning and 542 Schoellhamer, 2013), and a floc diameter of 160 m has been often used to 543 distinguish between microflocs and Macroflocs groups (Manning and Dyer, 544 2002; Manning, 2004; Manning et al., 2010). In order to obtain more gen-545 eral understanding on the floc physical properties, a summary of mean floc 546 properties for the entire floc population and sub-population categorized into 547



Figure 7: Floc characteristics from the LabSFLOC-2 analysis. a) & b) show the plots of floc sizes vs. settling velocities of mixed Kaolinite-Bentonite (S05) and Oil-Kaolinite-Bentonite (S06), respectively. The three diagonal lines present contours of Stokes settling velocity calculated with a constant effective density (i.e. floc bulk density minus water density) of 1,600 kg·m⁻³ (pink line, equivalent to a quartz particle), 160 kg·m⁻³ (green) and 16 kg·m⁻³ (red line). c)-f) show the 12 Size Bands trends of floc number, settling velocity, floc density and fractal dimensions respectively for both mixed Kaolinite-Bentonite (blue) and Oil-Kaolinite-Bentonite (orange) samples.

Samples	Kaolinite			Bentonite		Kaolinite-Bentonite			
Demarcation	Total	micro	Macro	Total	micro	Macro	Total	micro	Macro
N	2631	2128	503	1705	681	1024	2998	2420	578
$-\bar{D}(\mu m)$	120	101	199	185	105	238	104	76	225
$\overline{\rho_e}(\mathrm{kg}\cdot\mathrm{m}^{-3})$	315	336	224	127	187	87	410	461	200
$\overline{W_s}$ (mm·s ⁻¹)	2.41	1.82	4.89	2.00	1.08	2.61	1.97	1.27	4.90
$\overline{f_n}$	2.54	2.54	2.55	2.30	2.30	2.30	2.57	2.59	2.53
Samples	Oil-Kaolinite		Oil-Bentonite		Oil-Kaolinite-Bentonite				
Demarcation	Total	micro	Macro	Total	micro	Macro	Total	micro	Macro
N	3102	2696	406	1592	580	1012	2610	1975	635
$\overline{D(\mu m)}$	102	86	204	198	115	246	120	87	222
$\overline{\rho_e}(\text{kg}\cdot\text{m}^{-3})$	249	269	113	127	167	104	408	446	290
$\overline{W_s}$ (mm·s ⁻¹)	1.21	1.03	2.41	2.53	1.07	3.36	3.33	1.94	7.63
								-	

Table 2: Summary of microfloc and Macrofloc mean quantities of each sample investigated in this study.

microflocs and Macroflocs for all cases are presented in Table 2. Similar to the previous section, the physical floc properties of interest here are floc number (N), mean floc size (\overline{D}) , mean effective density $(\overline{\rho_e})$, mean settling velocity $(\overline{W_s})$ and mean fractal dimensions $(\overline{f_n})$.

⁵⁵² 3.3.1. Mineral types influence on flocculation

⁵⁵³ A comparison between Kaolinite (S01) and Bentonite flocs (S03) show ⁵⁵⁴ that the Kaolinite flocs in total have around 35 % higher N (2631 versus ⁵⁵⁵ 1705) and 35 % smaller \bar{D} (120 versus 185 μ m) (see Table 2). Moreover, the ⁵⁵⁶ larger N in Kaolinite is only due to microflocs and Kaolinite has only half of

that of Bentonite in terms of Macrofloc numbers. This matches with the pre-557 vious clay flocculation studies in saline water (e.g., Zhang et al. 2019). Due 558 to the water salinity, the attraction forces (London-van der Waals' forces) 559 between the clay plates can be dramatically enhanced over repulsion forces. 560 Particularly for Bentonite clay, the enhancement of flocculation can be sig-561 nificantly larger than Kaolinite does under the same salinity which results 562 in more Macroflocs forming in Bentonite case. The $\overline{\rho_e}$ for the entire floc 563 population of Kaolinite floc is around 2.5 times higher than that of Ben-564 tonite floc. This is particularly due to the Macroflocs with significantly low 565 $\overline{\rho_e}$ (only 87 kg·m⁻³) in Bentonite with a mean density of only 87 kg·m⁻³. 566 Despite somewhat smaller D of Kaolinite flocs, their significantly larger $\overline{\rho_e}$ 567 results in approximately 20 % larger $\overline{W_s}$ than that of Bentonite flocs. Finally, 568 $\overline{f_n}$ of Kaolinite flocs is about 2.54, which is higher than that of Bentonite 569 flocs of around 2.3. The differences of Kaolinite and Bentonite flocs revealed 570 here can be directly link to the different types of mineral particle stickiness 571 in saline water (see Figure 3) which shows Bentonite have almost five times 572 higher R_f than that of Kaolinite in the seawater of 35 ppt. Even with the 573 much lower salinity condition $(1.2 \sim 3.5 \text{ ppt}, \text{tested by Khelifa et al. } (2005b))$, 574 the clay types still can be a significant factor for influencing the flocculation. 575 The microfloc \overline{D} in the mixed sample is 15 % smaller than that of Kaoli-576 nite, and yet in terms of the Macrofloc \overline{D} , mixed sample is 13 % larger. 577

⁵⁷⁹ comparable (only 5 % smaller) to that of pure Bentonite. Although the

578

In fact, the Macrofloc D for mixed Kaolinite-Bentonite sample is nearly

resulting $\overline{W_s}$ of mixed Kaolinite-Bentonite sample for the whole floc popu-580 lation $(1.97 \text{ mm} \cdot \text{s}^{-1})$ is very similar to that of pure Bentonite sample (2.0) 581 mm·s⁻¹), the mixed sample reaches the similar $\overline{W_s}$ due to having the largest 582 $\overline{\rho_e}$ (410 kg·m⁻³) and the smallest \overline{D} (104 microns) comparing with those of 583 the two pure clay samples. Looking more into the difference, we can see 584 that Macrofloc \overline{D} and Macrofloc $\overline{\rho_e}$ of Kaolinite-Bentonite mixture is about 585 13~% larger and 12~% smaller than those of pure Kaolinite sample, respec-586 tively, which suggests a slight increase of cohesion in Kaolinite-Bentonite 587 flocs, possibly due to the presence of Bentonite. In terms of microflocs, 588 Kaolinite-Bentonite sample show the smallest and the densest flocs which is 589 also more similar to the microfloc of pure Kaolinite sample, but distinctly 590 different from those of pure Bentonite sample. Moreover, examining the D591 of mixed Kaolinite-Bentonite sample further reveals distinct behavior be-592 tween microflocs and Macroflocs. The mixture sample possesses a dual fea-593 ture, namely, the Kaolinite behavior in microflocs and Bentonite behavior 594 in Macroflocs. When mixing two types mineral, the Macroflocs development 595 is slightly enhanced by the more cohesive Bentonite component, but for the 596 entire mixed floc characteristics the effect of Bentonite appears to be benign 597 while the effect of Kaolinite appears to be dominant, especially in microfloc 598 population. This seemingly subtle point between Bentonite and Kaolinite 599 is raised here because it may play a more important role when interacting 600 with oil droplets. Particularly for the oil spilled occurring in natural mixture 601 sediment environment, each clay type influence should be fully understood 602

603 necessarily.

604 3.3.2. Oil participation in mineral flocculation

By adding oil component to the Kaolinite floc sample (S02 in Table 1), 605 oil-Kaolinite N for the entire population increases by around 18 % while the 606 corresponding \overline{D} decreases by around 18 %. However, instead of obtaining 607 a slight increase of $\overline{\rho_e}$ commonly occurs due to decreased cohesion, the $\overline{\rho_e}$ 608 for the entire population also decreases by 20 %. As a result of both re-609 duced \overline{D} and $\overline{\rho_e}$, we obtain a significant reduction of $\overline{W_s}$ by 50 % (decreases 610 from 2.41 $\text{mm}\cdot\text{s}^{-1}$ to 1.21 $\text{mm}\cdot\text{s}^{-1}$, see Table2). Looking further into the 611 microfloc and Macrofloc statistics, we observe different response of microfloc 612 and Macrofloc due to the addition of oil to Kaolinite in the saline water. The 613 microfloc population shows a 27 % increase in N and 15 % reduction of \overline{D} , 614 while the Macrofloc population show 20 % reduced in N and very slight 2.5 %615 increase (or nearly unchanged) \overline{D} . This indicates a small shift to microflocs 616 and reduction of cohesion (flocculation rate) due to the addition of oil. The 617 common and more significant trend for both microfloc and Macrofloc is their 618 reduction of $\overline{\rho_e}$: the microflocs show slight (20 %) decrease of $\overline{\rho_e}$ while the 619 Macroflocs show nearly a factor 2 decrease of $\overline{\rho_e}$. As a result, the microfloc 620 and Macrofloc $\overline{W_s}$ are decreased by 43 % and 51 %, respectively. Overall, 621 the participation of lower density oil droplets reduces the OMA density, con-622 sistent with the droplet OMA structure presented in Figure 4. The settling 623 velocity data in Table 2 confirms that pure Kaolinite flocs tend to attach 624

with the oil droplets (around the surface) forming OMAs with much lower
density than the original pure Kaolinite mineral flocs.

For Bentonite clay, adding oil component decreases total N by around 7 627 % while \overline{D} for the entire floc population increases by around 7 %. On the 628 other hand, although the $\overline{\rho_e}$ for the entire floc population is unchanged by 629 adding oil, we obtain 11 % decrease of microfloc $\overline{\rho_e}$ while the Macrofloc $\overline{\rho_e}$ 630 is increased more significantly by 20 %. As a result, microfloc $\overline{W_s}$ is nearly 631 unchanged while the Macrofloc $\overline{W_s}$ is increased by 29 %. Since the total flocs 632 are dominated by Macroflocs in the Bentonite cases, the $\overline{W_s}$ for the entire 633 population is increased by 25 % when adding oil mainly and this is caused 634 by the increase of $\overline{\rho_e}$ in Macroflocs. 635

By adding oil into mixed Kaolinite-Bentonite clay (S06), the total N636 shows a reduction of around 13 %, and total \overline{D} increases by around 15 %. 637 Adding oil decreases microfloc N by 18 % and increases microfloc \overline{D} by 14 638 %. Oil also causes the Macrofloc N to increase by 10 % but with negligible 639 decrease of \overline{D} . Consistent with adding oil to pure Bentonite, here we see a 640 45 % increase in $\overline{\rho_e}$ of Macrofloc by adding oil to mixed Kaolinite-Bentonite 641 sample. As a result, $\overline{W_s}$ increases almost 70 % due to the minor increase of 642 microfloc \overline{D} as well as more dramatic increase of $\overline{\rho_e}$ in Macroflocs. 643

644 4. Discussion

The results presented above indicate unique differences of floccualtion characteristics between Kaolinite and Bentonite OMAs which may be closely

influenced by the OMA structures. Previously, this hasn't been clearly re-647 vealed by studying the natural mixture sediment samples directly (e.g., Khe-648 lifa et al. 2005b, 2008; Sun et al. 2010, 2013; O'Laughlin et al. 2017). Kaoli-649 nite particles tend to show lower cohesion and the resulting oil-Kaolinite 650 aggregates can be categorized as droplet OMAs. The pickering emulsions 651 (Chevalier and Bolzinger, 2013) may apply to the oil-Kaolinite droplets flocs 652 in terms of the single droplet OMA structures (e.g., Figure $4a_2$). But the 653 Kaolinite OMA also can be a bit more complex when multiple mineral flocs 654 and oil droplets can also possibly attach together and combine to larger 655 aggregates. In this case, the mineral clay particles/flocs adhere on the oil 656 droplets surface, and the mineral particles act as a web-structures surround-657 ing the oil droplet preventing its attachment to other oil droplets or fur-658 ther re-bonding to oil slicks. Previous studies (e.g., Zhao et al. 2017) have 659 found that equilibrium droplet oil-sediment aggregates can be considered as 660 very stable structure and hardly breakup. Since the Kaolinite mineral parti-661 cles can be attached together as a much larger structure than individual oil 662 droplet, the oil can be observed being attached or even embraced within the 663 Kaolinite flocs (Figure $4a_{2-4}$). Because oil droplets structure remains intact, 664 the oil-Kaolinite OMAs show significantly lower effective density and settling 665 velocity than the pure Kaolinite flocs. This also apply to the natural clay 666 mineral formed mixture oil sediment aggregates according to Khelifa et al. 667 (2008) suggesting that oil-sediment aggregates have 2 to 3 times lower effec-668 tive density than pure sediment flocs because of the low density oil droplets 669

attaching within the flocs. On the other hand, Bentonite particles are of 670 very high cohesion and are observed to form large, fluffy (low density and 671 high porosity) and complex aggregate structure. The Bentonite aggregates 672 tend to re-shape and absorb or be absorbed by the oil droplets forming large 673 (as large as 900 microns floc has been observed) dense oil-Bentonite aggre-674 gates (Figure $4b_{2-4}$). Previous experimental work also indicates that the 675 oil-sediment aggregates formed using natural sediment can be as large as 676 900 microns (O'Laughlin et al., 2017) and their settling velocity can be vari-677 able depending on oil amount trapped in sediment mixture aggregates (Sun 678 et al., 2010). They also suggest that higher sediment concentration may 679 lead to larger flocs with higher settling velocity. In the results presented 680 here further specify the clay type influence to the oil-sediment aggregates' 681 characteristics. Particularly for the Bentonite clay, because the oil droplets 682 no longer exists by themselves and the oil is mainly absorbed at micro-scale 683 level onto the mineral structure, the Bentonite particles can actually become 684 more compact together than its pure mineral floc structure (high porosity) 685 and the resulting OMAs are dominated by denser and larger Macroflocs. The 686 overall settling velocities of oil-Bentonite OMAs are also slightly larger than 687 the pure Bentonite flocs. The response of Kaolinite and Bentonite to the 688 addition of oil are distinctly different due to the corresponding droplet OMA 689 and flake/solid OMA structures, respectively. Overall, in Kaolinite, oil sig-690 nificantly decreases effective density and hence the settling velocity decreases 691 significantly for the entire floc population. Meanwhile, oil slightly increases 692

settling velocity of oil-Bentonite flocs due to increasing floc size and effective 693 density in Macrofloc population. Therefore, adding oil into pure Kaolin-694 ite has negative influence to the cohesion and flocculation which agrees with 695 Khelifa et al. (2008). However, the cohesion of Bentonite can be increased by 696 oil participation because of its unique high porous structure. The stickiness 697 (cohesion) can be one of the most significant key factor for the OMA floc-698 culation. Since chemical dispersant may increase the oil droplets stickiness 699 to enhance the oil-sediment flocculation after oil spill occourance in natural 700 enviornment (Khelifa et al. 2008), the higher stickiness of bentonite clay also 701 may have the similar effect on OMA flocculation positively. The significant 702 of stickiness influence may also change the relationship between turbulence 703 level and floc size. Noticeably, both previous study (e.g., Sun et al. (2010, 704 2013)) and present study show that in very high turbulence level, turbulent 705 Kolmogorov length scale has limited effect to the oil-mineral floc size. 706

Furthermore, by adding oil to mixture sample, oil selectively interacts 707 more actively with Bentonite in Macroflocs rather than with Kaolinite under 708 a condition of same amount of clay, respectively. The increase of total floc 709 size and decrease in total floc number by adding oil in the mixed Kaolinite-710 Bentonite sample (Table 2) indicate a slight enhance of floc cohesion due to 711 the addition of oil. However, a more careful observation suggests that the 712 changes due to the addition of oil are completely different between microfloc 713 and Macrofloc populations especially in the more significant changes of floc 714 effective density which directly leads to the settling dynamics difference. 715

Overall, adding oil transforms the Macroflocs into higher density OMAs with 716 higher settling velocity due to high stickiness Bentonite component. More-717 over, oil also increases the density and settling velocity in microflocs domi-718 nant by Kaolinite component with less oil participation. Therefore, with the 719 multiple mixed mineral types exist in the natural environments commonly, 720 their own flocculation capability and settling behaviors may vastly different 721 especially when meeting with other contaminant materials such as spilled 722 oil because the third participation during the mineral flocculation processes 723 may totally change the structures of flocs which may directly influence the 724 flocs characteristics such as porosity, density and most importantly settling 725 velocities. 726

727 5. Conclusions

To conclude, the LabSFLOC-2 system has been utilized in OMAs stud-728 ies to understand flocculation characteristics and settling velocities. Droplet 729 OMAs and flake/solid OMAs have been observed in OMA generation which 730 matches with the previous studies. Furthermore, multiple OMAs structures 731 have been studied. For the mixed oil-Kaolin-Bentonite case which is closer 732 to the natural sediment mixture condition, both Kaolin and Bentonite com-733 ponent can be aggregated with oil droplets and develop OMAs to settling. 734 However, Bentonite becomes more dominate in OMA flocculation efficiency 735 compare with Kaolinite especially in Macrofloc group. From the size-class 736 results, specific size ranges of OMAs can be known when influenced by min-737

eral particles or oil component participating in their flocculation. Since the
Bentonite clay is one of the most common mineral particles in natural environments, its role in absorbing oil, forming OMAs and influencing the fate
of oil need to be incorporated in future modeling efforts.

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