

Oil-Mineral Flocculation and Settling Dynamics

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Abstract

In recent decades, oil spill contamination has tended to occur more commonly in deltaic and estuarial systems. The management of oil spillages has been a major challenge in the surrounding deltas due to the highly sensitivity nature of deltaic ecosystems. Many deltas have an abundance of clay minerals that can flocculate, and these play an important role in determining the transport of spilled oil contamination and its eventual fate, particularly given that suspended sediment and microbial activities are often prevalent and diverse in natural environments. The primary work presented here focuses on laboratory experimental studies that help develop improved parameterizations of flocculation processes for oil-sediment-bio-geochemical modeling. Oil-mineral flocs (OMA) have been successfully created from a series of laboratory flocculation experiments. A floc video instrument LabSFLOC-2 has been adopted for the first time to study the settling dynamics of OMAs. Experimental results reveal OMAs can easily form in any oil, cohesive sediment, and seawater mixtures. However, Kaolin and Bentonite forms dramatically different OMA structures, which leads to their variable characteristics. In the Bentonite clay cases, the oil flocs tend to be much larger and with higher densities than those in Kaolin clay cases, resulting in significant variability of flocs settling velocities.

Keywords: cohesive sediments, flocculation, settling velocity, floc measurement, oil-mineral floc, sediment dynamics, oil contamination

1. Introduction

1.1 Scope of the problem

The rise in anthropogenic activities and industrialized related development in coastal and marine environments, and their ensuing recovery, from contamination by oil spillages, have been a considerable challenge [1]; especially in coastal deltaic regions where they have high vulnerability to aquatic ecosystem and associated public health issues [2]. During the past decades, contamination from oil spill incidents has gravitated to occur more frequently in vulnerable deltaic waters [3, 4]. To illustrate the global scale of the problem, a few examples of delta regions from around the world are presented.

In Africa, oil spill sites are a common phenomenon in the Niger Delta region. Between 1976 and 1996, a total of 4647 incidents resulted in the spilling of approximately 2,369,470 barrels of oil into the environment [5]. Of this quantity, an estimated 1,820,410.5 barrels (77%) were not recovered [5]. They tend to originate from a variety of sources including: leaks during processing, corrosion of oil pipes, poor maintenance of infrastructure, and deliberate acts of vandalism or theft of crude oil from pipes.

The Nigerian coastline is about 853 kilometers in length from the border with the Republic of Benin in the west to the Republic of Cameroon in the east. Encompassing an area of approximately 70,000 km², the Niger Delta is one of the largest wetlands in the entire world. The region comprises: sandy and muddy morphological features, swamp forests (both seasonal and permanent), low-land rain forests, and mangroves—both saline and brackish [6]. The region is topographically characterized by numerous rivulets, creeks, canals, and rivers of various sizes. The coastal line borders the Atlantic Ocean and is subjected to direct tidal interaction. In contrast, the mainland experiences episodes of flooding from the riverine networks, dominated by the River Niger. The soils underlying the Niger delta are generally characterized as soft, highly compressible, organic, and inorganic silty clays overlying fine sands at great depths [7].

Historically, the largest oil spill in Nigeria occurred during January 1980, when an offshore well blew out and oil spread throughout Nigeria's Atlantic coastline. This spill caused extensive damage to nearly 340 hectares of mangrove [5] and was equivalent to approximately 200,000 barrels of crude oil (this is equivalent to 8.4million US gallons). Although not fully verified, over the past half century, it is estimated that oil spill incidents account for nearly 546 million gallons of oil [8] into the Niger Delta environment. This is comparable to approximately 11 million gallons per year [9]. UNEP [10] reported that many communities in the Niger Delta, in particular Ogoniland region, are continuing to live with a persistent state of pollution from oil spills.

Oil spills have blighted a myriad of the Nigeria Delta environment including: the ambient air, ground and surface waters, and crops (via bioaccumulation). Ordinioha and Brisibe [8] disclose that associated contaminants can include (but not limited to): trace metals; hydrocarbons, such as carcinogens, namely polycyclic aromatic hydrocarbon and benzo (a) pyrene; and naturally occurring radioactive substances.

For example, the Bodo oil spill in the Niger Delta region in 2008, which was caused by operational problems, recorded approximately 4000 barrels of oil spill a day for a 10-week period. The scale of the spill is likened to the Exxon Valdez 1989 disaster in Alaska, where 10 million gallons of oil destroyed the remote coastline [5].

The Niger Delta has ecologically sensitive wetlands, which makes the impact of oil spills to be widely felt by the people in the region. The people depend on the environment for traditional livelihood (farming and fishing) and subsistence; thus the contamination of water, land and air quality continuously erode their capacity to support the lifestyle and economy survival [9, 11]. When spills occur, whether on lands or waters caused by operational error, sabotage and theft, equipment failure, and aging pipeline, it contaminates water use for domestic purpose, fishing and farming activities with severe impact on the local people who are left with no alternative.

In the United Kingdom, since 1924, the Firth of Forth has received effluent from Scotland's major petrochemical industry and refinery in addition to hydrocarbon inputs from many other sources [12]. This has created a large residue of hydrocarbon contaminants within its sediments. The major inputs have produced localized lethal effects, in that productive estuarine intertidal habitat has been lost or its

functioning altered. The changes are primarily due to organic enrichment with only very near-field toxic effects. Some of the effects result from historical contamination, but existing discharges continue to have a deleterious effect. New petrochemical discharges in both firth and estuary appear to have a minimal impact, although the historical contamination makes this partly inconclusive [12].

Of particular note, the largest oil spill event in human history (at the time of publication) occurred in 2010 and was the Deepwater Horizon (DWH) disaster. This occurred in the vicinity of numerous coastal delta zones, and a significant net influence on: human activities, ecosystem contaminations, and environmental changes. Of the habitats recurrently oiled throughout the DWH spill event, Martin [13] reported that salt marshes were among the most frequently affected (45%), with remedial activities occurring on less than 9% of the affected territories [14]. The resilience of these salt marsh habitats is vital to the persistence of the native fish species that populate these marsh regions, together with the vivacity that is redirected to pelagic food webs [15]. The vulnerability of estuarine ecosystems and their fauna to oil released from DWH has been illustrated by numerous studies (e.g. [16–19]).

DWH released approximately 4.9 million barrels (or 779 million L) of crude oil into the Gulf of Mexico [20, 21]. Michel et al. [14] estimated that the DWH spill directly affected approximately 1773 km of the shoreline habitat (much of this deltaic). In addition to the bleak ecological impacts the spill site imposed on neighboring shoreline, there was an unanticipated sedimentation of oil-associated marine snow (often referred to as Marine Oil Snows - MOS) throughout the water column, extending down to the seafloor; this gave rise to a supplementary prolonged impact on benthic zones [22–24].

Once oil is spilled into an aquatic environment, it tends to float as it is less dense (i.e., more buoyant) than the surrounding water, and this connection with the overlying atmosphere can facilitate the natural weathering processes on the oil contaminants. Having said that, a number of studies [23, 25] observed that a significant amount of the floating oil droplets readily aggregated with suspended matter already present in the water column, including (but not limited to): fecal pellets, detritus, sediments, and phytoplankton. In addition, both Passow and Alldredge [26] and Malpezzi et al. [27] found that this aggregation process was markedly enhanced by the presence of biologically secreted substances specifically Transparent Exopolymer Particles (TEP) or the more generic Extracellular Polymeric Substance (EPS; e.g. [28–30]). These MOS would eventually settle and deposit on the seafloor as they were transported through the water column [22, 31].

Following an oil spill, chemical dispersants are frequently chosen to remedy visible surface contaminants [32–34]. However, in the wake of dispersing an oil slick into smaller constituent oil droplets, there is a likelihood that these diminutive oil droplets agglomerate with other cohesive suspended materials present in the water column to further augment MOS flocculation and settling [35, 36]. Many deltaic regions, including estuarine and coastal water systems with energetic flows [37–39], are often dominated by muddy sediments comprising clay-based minerals and EPS (such as those exuded by phytoplankton). When oil is introduced into the sedimentary matrix, Zhao et al. [40] report that they can freely flocculate into oil-particle aggregates (OPAs). Ye et al. [41] concluded that this interchange between cohesive minerals, oil contaminants, and biological EPS collectively perform a pronounced role in the fate of oil spills in a natural ecosystem. Thus, an improved understanding of the formation, physical characteristics, and settling dynamics of OPAs is extremely advantageous when assessing how they will affect a subaquatic ecosystem [42–44].

Apart from the large amount of spilt oil floating at the water surface, there is still a considerable portion of oil being transported within the water column and settling to the seafloor after/during flocculating with natural sediment (especially clay mineral in deltaic regions) and biological materials (including EPS). And the interactions of oil and aquatic particles (sediment and biological materials) can be one of the keys for the spilt oil bio-degradation, oil-weathering or geological deposition, and resuspension processes. However, the flocculation processes of the different types of natural clay minerals when combined with oil are still poorly understood; especially their resultant settling dynamics.

From the 2010 Deepwater Horizon event, for example, round 3–5% spilt oil settling into the seafloor and still 11–25% spilt oil still uncaptured for transporting or settling in the ocean water column (e.g., [20, 21]). The aggregation and settling processes can potentially lead to oil eventually residing in a quasi-preserved status within the seafloor sedimentary deposits, and these oil-contaminated sediments having an extended residence time. As such, this problem triggered this study, which not only addresses the improvement of our poor understanding of the multiple oil-mineral structures but also the oil-mineral flocculation processes and its resultant settling dynamics under certain turbulent flow conditions.

Through a series of well-controlled laboratory experiments, our goal is to improve our understanding of the settling velocity and floc properties associated with the flocculation of oil-contaminated clay minerals. This laboratory research is part of the Consortium for Simulation of Oil-Microbial Interaction in the Ocean (CSOMIO) with an overarching goal to advance the numerical model predictions for the future oil spill mitigation.

1.2 Overviews of oil-mineral aggregates (OMAs) studies

Oil-mineral aggregates (OMAs) are oil droplets stabilized by fine mineral particles in water. Since the mineral particles and oil interactions in aquatic system were first mentioned by Poirier and Thiel in 1941, for the few past decades numerous studies have been examining how oil hydrocarbons absorb onto mineral particles at a molecular level, (e.g., [45–47]). More recently, most oil-mineral aggregates (OMAs) studies have been focused on the: formation mechanisms [48, 49], characterizations [50], and “influence factors” such as salinity [51], temperature [50], oil types [50], and temporal turbulence [52]. Most of these past OMAs studies were predominantly based on laboratory experiments in order to better quantify the flow conditions and particle/oil concentration. The complex nature of OMAs has resulted in several challenges to simulate/mimic their formation and fate in numerical models, especially when they interact with the cohesive particles present in natural deltaic aquatic systems.

The first laboratory experiment related to minerals and oil droplets was presented by Delvigne [53], which suggested that oil types, mineral types, turbulence energy, and water salinity were the main influence on the aggregation process. Subsequently, numerous OMAs laboratory studies have been conducted and most indicate that spilt oil bio-degradation can be enhanced by increasing oil-mineral flocculation in a natural water column [54–56]. Floch et al., [51] quantified the amount of oil incorporated into OMAs and suggested that the extent of OMA formation is not significantly different from that of seawater for salinity values as low as 1.5–0.15 (1/20 to 1/200 of pure seawater). Omotoso et al., [48] found that the degree of oil-mineral interactions should be dependent on the

viscosity of the crude oil and the type of mineral present, because the oil droplet surface changes with dynamic viscosity parameter.

A series of shaker jar tests by Khelifa et al., [50] indicated that although droplet size and shape were not correlated to oil viscosity, the concentration of oil droplets present during the flocculation process became extremely sensitive to the oil viscosity, temperature, and asphaltenes-resins content (ARC). Cloutier et al., [57] conducted an annular flume experiment to determine critical shear stress removing oil from a surface by resuspension and the effect of suspended sediment concentration (SSC) on the oil erosion processes. They found that SSC at 200–250 mg/l was observed to give maximum erosion efficiency and is therefore suggested as the optimal concentration for erosion and elimination of heavy crude oil at a water temperature of 13°C.

A more recent laboratory study was conducted by Sun et al., [58] to investigate the kinetics of oil-sediment aggregates formation under various mixing intensities using marine sediments (standard reference material 1941b) and Arabian heavy crude oil. Sun et al., [58] noticed that the formation of oil suspended particles aggregates increased exponentially throughout the mixing duration and peaked during a 5-hour period. Optimum trapping effectiveness of oil rose from 24 to 47%, and the necessary shaking (i.e. physical agitation) time lessened from 4.5 to 1.2 hours as both the mixing level and sediment concentration intensified. The maximum oil-to-sediment ratio reached 240–680 mg of oil per gram of sediment during the aforementioned 5-hour period. Observations of revealed that during more quiescent conditions, the oil-sediment aggregates formed were predominantly of a solid type and single droplet aggregates. While higher turbulent agitation resulted in more multidroplet type aggregates.

Moreover, many OMA studies have been focused on oil-mineral aggregates formation and their appearance using microscopic and imaging analysis in laboratory. Stoffyn-Egli and Lee [49] used laboratory protocols and microscopic methods to detect and classify the OMA types. They identified three types of OMAs: droplet, solid, and flake aggregates, and these are controlled by mineral types, oil surface properties, viscosity, and oil/mineral ratios. Moreover, they also report clear evidence that turbulence greatly enhances the OMA formation. Delvigne [59] used natural sediment in the laboratory experiment to study the physical appearance of oil contaminated sediment. Through his quantitative investigations, it was concluded that the division of oil in the different phase is affected by the oil-sediment interaction process, oil type, and oil concentrations.

Delvigne's [59] microscopic observations of oil-contaminated sediment samples lead to three possible phases of presence of oil: oil droplets, oil-coated sediment particles, and "oil patches." Therefore, both Stoffyn-Engli and Delvigne found the existence of consistent OMA types through their laboratory studies, including ① mineral particles attaching around the surface of big oil droplet, ② small oil droplets coated by sediments, and ③ flake-shaped oil-mineral aggregates. Khelifa et al., [50] reported more detailed OMAs study by using an epi-fluorescence microscopy to analyze the shape, size distribution, and oil concentration within OMAs. These results also show these types of OMAs with further quantification on more specific oil components. Furthermore, O'Laughlin et al. [60] used a high-resolution imagery method to record settling OMAs to analyze the particle size, density, and settling velocity. Their investigation revealed the settling velocities of artificially formed OMAs to be on the order of $0.1 \sim 0.4 \text{ mm}\cdot\text{s}^{-1}$. The OMA formation increases with suspended sediment concentration ($>50 \text{ mg}\cdot\text{l}^{-1}$).

Following the path led by all the abundant laboratory experiments of OMAs for the last decades (mentioned previously), numerical models have been adapted to