Mechanisms of Fat, Oil and Grease (FOG) deposit formation in sewer lines

CrossMark

Xia He [a], Francis L. de los Reyes III [a], Michael L. Leming [a], Lisa O. Dean [b], Simon E. Lappi [c], Joel J. Ducoste [a,*]

[a] Department of Civil, Construction and Environmental Engineering, North Carolina State University, Raleigh, NC 27695, USA
[b] Department of Food Science, North Carolina State University, Raleigh, NC 27695, USA
[c] Department of Chemistry, North Carolina State University, Raleigh, NC 27695, USA

ARTICLE INFO

ABSTRACT

FOG deposits in sewer systems have recently been shown to be metallic salts of fatty acids. However, the fate and transport of FOG deposit reactant constituents and the complex interactions during the FOG deposit formation process are still largely unknown. In this study, batch tests were performed to elucidate the mechanisms of FOG deposit formation that lead to sanitary sewer overflows (SSOs). We report the first formation of FOG deposits on a concrete surface under laboratory conditions that mimic the formation of deposits in sewer systems. Results showed that calcium, the dominant metal in FOG deposits, can be released from concrete surfaces under low pH conditions and contribute to the formation process. Small amounts of additional oil to grease interceptor effluent substantially facilitated the air/water or pipe surface/water interfacial reaction between free fatty acids and calcium to produce surface FOG deposits. Tests of different fatty acids revealed that more viscous FOG deposit solids were formed on concrete surfaces, and concrete corrosion was accelerated, in the presence of unsaturated FFAs versus saturated FFAs. Based on all the data, a comprehensive model was proposed for the mechanisms of FOG deposit formation in sewer systems.

1. Introduction

Fat, Oil and Grease (FOG) in wastewater discharged from Food Service Establishments (FSEs) and high density dwellings may lead to FOG blockages in sanitary sewer pipes, and consequently sanitary sewer overflows (SSOs) in many wastewater collection systems. SSOs can potentially release high concentrations of pathogens, nutrients, and solids that impose a risk to public health and the environment. A 2004 U.S. EPA report indicated that approximately 3–10 billion gallon of untreated wastewater is discharged annually as a result of SSOs (EPA, 2004). Fifty percent of SSOs are due to line blockages, of which half are attributed to FOG deposits that accumulate in sewer lines (EPA, 2004). In previous research, high concentrations of fatty acids and calcium were found in FOG deposits, collected from 23 cities around the United States (Keener et al., 2008).

By mixing the two major components (free fatty acids and calcium), our research group was able to reproduce FOG deposits under laboratory conditions (He et al., 2011). Fourier Transform Infrared (FTIR) spectrometer analysis provided evidence that both laboratory-produced and sewer based FOG deposits are calcium salts of fatty acids, and formed as a result of saponification (He et al., 2011). Since sewer related FOG

deposits adhere to interior pipe walls above the water line (Keener et al., 2008), the reaction between free fatty acids and calcium likely occurs via an interface reaction. Free fatty acids (FFAs), which were generated from the cooking process or microbial activity (Canakci, 2007; Brooksbank et al., 2007), trigger the saponification interface reaction leading to the formation of FOG deposits in sewer lines.

A recent study indicated that biodegradation of oil content associated with a transformation of fatty acid profiles from unsaturated to saturated forms occurred in sewer systems (Williams et al., 2012). However, the role of different types of FFAs in this interface reaction is unknown. Investigation on the effect of palmitic-, oleic-, and linoleic acid on the interface reaction would provide insight into understanding the mechanisms FOG deposits formation in sewer systems. All three FFAs have been identified in grease interceptor FOG (Monterfrio et al., 2010) and were the three major fatty acids present in FOG deposits (Keener et al., 2008; Williams et al., 2012).

Although calcium ions are naturally present in domestic and industrial wastewater, Keener et al. (2008) observed no correlation between calcium concentrations in FOG deposit samples and water hardness. However, in a later study, Williams et al. (2012) observed an increasing content of calcium and physical property changes (i.e., melting point increasing and moisture content decreasing) with increasing water hardness from FOG deposits collected in the UK sewer system. Williams et al. (2012) further argued that the excess calcium found in deposits may be due to biofilms that may enrich calcium and encourage FOG deposit formation. However, no microbial work was performed to confirm this mode of calcium accumulation. Another possible source of calcium in the sewer system is concrete. Both Keener et al. (2008) and Williams et al. (2012) observed high values of iron and aluminum, and Keener et al. further reported the presence of silicon, that together with iron and aluminum, are readily found as calcium complexes in cement (i.e., calcium silicates, calcium aluminates, and calcium aluminoferrites) (Kosmatka et al., 2002). The corrosion of concrete in sewers has been documented for many decades. Hammerton (1944) described corrosion of concrete sewers as early as 1944. The mechanisms are now reasonably well established and include the dissolution of calcium compounds from concrete by attack by acids formed from H_2S released by anaerobic bacterial action, typically in a biofilm. Additional studies of the precise effects of conditions and roles of various microbial species continue, however. Calcium along with other metals may be released due to microbially induced concrete corrosion (MICC) (Gutierrez-Padilla et al., 2010; O'Connell et al., 2010; Bielefeldt et al., 2010). In MICC, the production of sulfuric acid is a key step (Gutierrez-Padilla et al., 2010). Thus, pH variations could be an important factor determining the amount of calcium released from corroded concrete in sewer systems.

The objectives of this study were to examine the calcium leaching from concrete under different pH conditions and to investigate the saponification interface reaction to further understand the mechanisms of FOG deposit formation in sewer lines. Identifying the mechanisms of FOG deposit formation could ultimately lead to an improvement in sewer management and maintenance strategies that will reduce blockages caused by FOG deposits.

2. Materials and methods

Experiments were designed to recreate the formation of FOG deposits under different wastewater quality conditions, amount and quality of FOG, the role of FOG as not only in the formation of hydrolysis products (i.e. FFA) but also an interfacial partitioner, and water flow conditions. Tests were performed in the presence and absence of a concrete surface to help elucidate the role of concrete corrosion that leads to the release of calcium and surface roughness on the accumulation of FOG deposits on sewer pipe surfaces.

2.1. Leaching of calcium from concrete

A concrete sample (19% Type II Portland cement, 31% sand, 42% coarse aggregate and 8% water) was produced in the NCSU Department of Civil, Construction, and Environmental Engineering Concrete Lab. The sample was cut into rectangular blocks ($5 \times 2 \times 2$ cm). Calcium leaching tests on concrete blocks were performed using a jar-test apparatus (Phipps & Bird Jar Tester), at a mixing speed of 20 rpm and temperature of 20 °C for 24 days. Since the production of sulfuric acid is the cause of concrete corrosion in the MICC process (Gutierrez-Padilla et al., 2010), the pH on concrete surface would decrease from basic to as low as 3, relatively large amounts of calcium hydroxide would be released to neutralize the concrete surface. Thus, in these tests, a single concrete block was suspended vertically in each beaker, and half of the concrete block was submerged in 1 L de-ionized water or grease interceptor (GI) effluent (COD of 1136 ± 368 mg/L, pH of 6.9 ± 0.25, average calcium of 9.1 mg/L) collected from a steakhouse in Cary, NC. Six beakers with de-ionized water and GI effluent were tested at different pH levels of 3, 4, 5, 6, 7, and 8. The pH in each beaker was maintained over the entire test period by daily additions of sodium hydroxide or sulfuric acid. Liquid samples from tests with de-ionized water were collected from each beaker every three days for calcium analysis using a Perkin—Elmer 2000 inductively coupled plasma optical emission spectrometer (ICP-OES) (He et al., 2011). For calcium analysis of GI effluent, liquid samples were collected at day 1 and day 24.

2.2. Formation of FOG deposits on concrete surface

Batch tests were performed in beakers with solutions mixed at 20 rpm and temperature of 20 °C for 14 days to simulate attached FOG deposit formation in sewer lines. As in the leaching tests, a single rectangular concrete block ($5 \times 2 \times 2$ cm) was suspended vertically in a beaker with half of the block submerged in 1 L GI effluent to which calcium chloride (400 mg/L Ca^{2+}) was added. After mixing for 14 days, 1 g soybean oil was added to the system. Solid samples, formed in the presence of soybean oil, were scraped off the concrete block for Fourier Transform Infrared (FTIR) spectrometer analysis (He et al., 2011).

2.3. Role of oil in the saponification interface reaction

Experiments to assess the role of oil in the saponification interface reaction were conducted using a jar-test apparatus

(mixing speed at 20 rpm and temperature at 20 °C) for 32 days. In each beaker, 1 g soybean oil was added to 1 L calcium chloride solution (400 mg/L as Ca). Three pH conditions were tested in duplicate: pH 8, pH 9, and no pH adjustment (initial pH of 7). The pH levels were maintained using sodium hydroxide and sulfuric acid to mimic the sewer environment in the presence of concrete. Solid samples were collected on day 32 in each beaker for FTIR analysis. Another three conditions were studied where concrete blocks (5 × 2 × 2 cm) were placed in 300 mL beakers that contained: 1) 100 mL soybean oil; 2) a mixture of 25 mL soybean oil and 75 mL de-ionized water; 3) 100 mL soybean oil to which 1 g palmitic acid (C16:0) was added. In each beaker, half of the concrete block was submerged. The solutions were mixed using a multi-position magnetic stirrer (Fisher Scientific Thermix Stirrer Model 120S) at 20 °C for 24 days under mild mixing intensity conditions (speed level = 2).

2.4. Effect of different types of fatty acids on saponification interface reaction

Palmitic (C16:0), oleic (C18:1), and linoleic (C18:2) acids (Fisher Scientific; Sigma—Aldrich) were used to examine the effect of different types of fatty acids on the saponification interface reaction. For these experiments, 0.25 g palmitic acid (Palmitic_1), 1 g palmitic acid (Palmitic_2), 0.25 g oleic acid, and 0.25 g linoleic acid were added, individually, to 25 mL soybean oil and 75 mL de-ionized water in a 300 mL beaker. All tests were performed at 20 °C for 32 days in triplicate. The beakers were placed on a multi-position magnetic stirrer (Fisher Scientific Thermix Stirrer Model 120S) under mild mixing intensity conditions. After mixing overnight to dissolve all the FFAs, a concrete block (5 × 2 × 2 cm) was suspended vertically into the solution. The pH was measured every 2 days. After 32 days, the solids that accumulated on the concrete surface were scraped off. Solids in solution were collected by filtering the solution through a wet-strengthened qualitative filter paper (>25 μm). All collected solids were dried at 105 °C overnight and then weighed. After weight measurement, the dry samples were analyzed by FTIR. Since there was small amount of oil existing in the liquid after filtration, triplicates of the liquid samples after filtration were collected from each test for calcium analysis.

3. Results and discussion

3.1. Calcium leaching from concrete

Concrete is a potential source of calcium participating in the formation of FOG deposits in sewer systems. Numerous research studies have demonstrated the release of calcium and other calcium based complexes from concrete corrosion (Mori et al., 1996; Gutierrez-Padilla et al., 2010). When concrete blocks were placed in de-ionized water under different pH conditions, the calcium concentration in solution increased at higher rates with decreasing pH (Fig. 1) indicating that the concrete block experienced greater corrosion rates with decreasing pH. When the concrete sample was hydrated in this study, calcium hydroxide was likely released and reacted
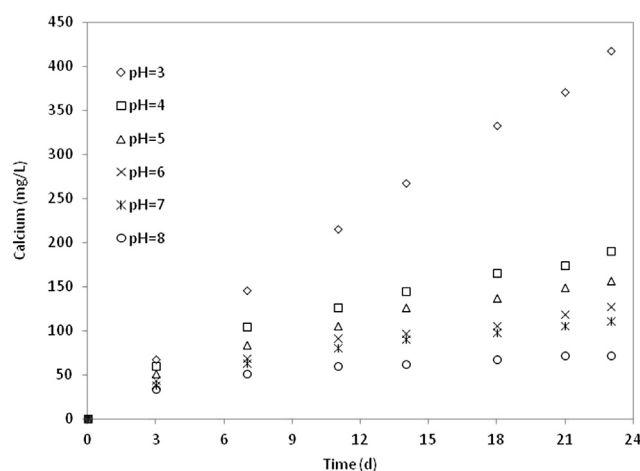

Fig. 1 — Calcium concentration released from concrete over time in de-ionized water at different pH.

with sulfuric acid to form calcium sulfate, which can further react with calcium aluminate present in the cement mixture to produce ettringite $((CaO)_3 \cdot Al_2O_3 \cdot (CaSO_4)_3 \cdot 32H_2O)$ (Gutierrez-Padilla et al., 2010). Ettringite is an expansive product and can result in small cracks in concrete (Gutierrez-Padilla et al., 2010) and changes into gypsum $((CaSO_4) \cdot 2H_2O)$ when the pH is decreasing (Negishi and Maeda, 1999). In sewer lines, gypsum and ettringite may be removed by the flow thereby accelerating the corrosion process (Mori et al., 1996).

At pH = 3, the calcium concentration in solution displayed a linear profile and reached 418 mg/L on day 24. At higher pH levels (≥4), the calcium leaching trends were similar but not linear. The large difference between pH = 3 and pH = 4 may be due to lime buffering. At pH = 3, the highly acidic environment led to a significant release of calcium hydroxide from the concrete sample but an inability to buffer the solution. In addition to calcium hydroxide, calcium from calcium silicate may be released under these aggressive conditions. For pH 6, 7, and 8, the released calcium concentrations were 127, 111, and 72 mg/L, respectively, on day 24. These results suggest that considerable amounts of calcium can be released from the concrete sample, even near neutral pH conditions. It should be noted that in grease interceptors, pH values have been observed to be as low as 3.8 to 4.3 (Aziz et al., 2012; He et al., 2012).

When concrete blocks were placed into the GI effluent solution, the released calcium concentrations from concrete on day 24 were 381, 130, 89, 90, 53, and 45 mg/L under pH 3, 4, 5, 6, 7, and 8, respectively. A lower concentration of calcium leaching from concrete was observed at all six pH conditions when compared to the corrosion conditions in DI water. This lower rate of calcium leaching may be due to a reduced calcium concentration gradient present in the GI solution as the GI effluent contained around 10 mg/L calcium. Calcium would begin to precipitate in an open system when pH is increased from neutral to basic condition. However, under pH = 8, in both DI water and GI effluent beakers, no solid particles precipitated in the solution. A considerable amount of dissolved calcium was released from concrete near neutral pH in both DI water and GI solution, which demonstrated that the

role of concrete as a source of calcium in the sewer system is not negligible. In sewer systems, we anticipate that calcium release from precast concrete grease interceptors is similar to the experiments in the beakers with concrete block immersed in the liquid from the GI effluent. However, in sewer pipe lines, the scenario is more complicated. Many factors can affect the calcium released from concrete and the subsequent diffusion into the surrounding wastewater, such as the formation of a biofilm on the concrete surface, shape of the concrete surface, the composition of wastewater, the flow pattern in sewer lines, and the varying composition of the cement/concrete material during the manufacture of the sewer pipe. These additional complications are difficult to replicate under laboratory conditions.

3.2. Formation of FOG deposits on concrete surface

Photographic evidence has revealed that a large fraction of FOG deposits form along the pipe cross-section above the low-flow water line (Keener et al., 2008). This location along the upper portion of the pipe perimeter suggests the preferential accumulation of FOG deposit precursors at the water surface. The hydrophobicity of compounds and the minimization of surface area in contact with water may also act as driving forces in FOG accumulation at an interface. Such accumulation may occur with the addition of non-polar material such as oil, which is also a potential FOG deposit precursor. Samples subjected to 1 g oil addition that had half of the concrete block submerged in GI effluent displayed white solid formation within 2 days at the concrete and water interface (Fig. 2). Most of the white solids adhered to the concrete surface above the water line and significantly less was found on glass walls and at the bottom of the beaker. The formation of solids at this concrete block location may be due to the surface roughness and the availability of free fatty acids as oil accumulated around the concrete block because of the rotational mixing pattern. In addition to white solids, brown particles were observed in solution. FTIR analysis of the white solids collected on the concrete and at the bottom of the beaker revealed that they were soaps according to the four characteristic absorption bands associated with calcium soap
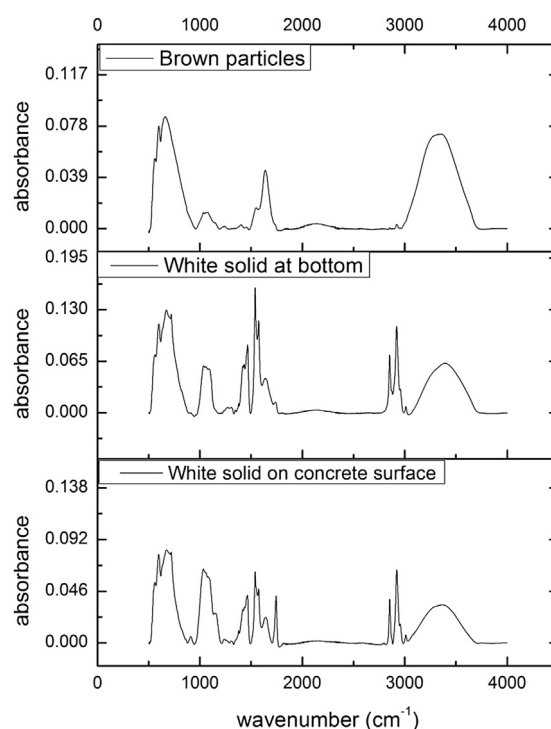

Fig. 3 — Baseline corrected infrared spectra of white solids that formed on concrete, white solids at the bottom of the beaker, and brown particles in solution.

(He et al., 2011) (Fig.3). With the addition of oil, we were able to conclusively reproduce the formation of FOG deposits on concrete surfaces under laboratory conditions.

While the Ca—O bond was identified in the FTIR spectral analysis of the brown particles, the signals of the bands representing the carboxylate group (1350—1800 cm^{-1}) and bands representing the aliphatic chains (1180—1350 cm^{-1}) of the calcium soap were very weak, and the bands representing the frequencies of the aliphatic chains of the calcium soap did not appear in the region between 2800 and 3000 cm^{-1}. The lack of the characteristic regions for organics showed that there were
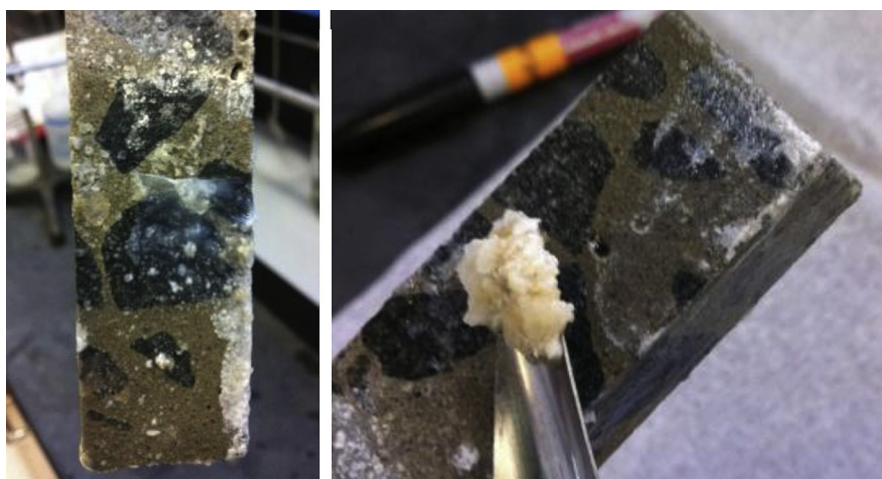

Fig. 2 — Solids formed on concrete surface with the addition of oil in GI effluent.

less free fatty acids available to react with calcium. Solids were formed without the addition of oil, as free fatty acids from the GI effluent reacted with calcium leaching from the concrete sample. However, none of these solids accumulated on the concrete surface above the water line. Unlike the natural FOG deposits that display an adhesive character and can become securely bound to interior pipe walls, these submerged solids were easily detached once the mixing speed was increased to 50 rpm. These results suggest that the presence of oil may be required in the formation of FOG deposits at the air/water and water/concrete interfaces. However, more research is needed to quantify the occurrence FOG hydrolysis in the sewer collection system downstream from the grease interceptor effluent.

3.3. The role of oil in the saponification interface reaction

There are two possible roles for oil in the interface reaction to form FOG deposits on sewer pipe walls: (i) when oil is exposed to a basic (i.e., alkaline) concrete surface, it undergoes alkali hydrolysis from the release of calcium hydroxide to form free fatty acids and then reacts with calcium to form soap; (ii) oil acts as a non-polar partitioner that aids in transporting any pre-hydrolyzed free fatty acids to the air–water interface that then react with the calcium available on the concrete surface. In the second scenario, oil may or may not play a role in any further release of free fatty acids from surface hydrolysis reactions.

To test the first hypothesis, 1 g oil was added to 1 L calcium chloride solution at three pH conditions (pH 8, pH 9, no pH adjustment [initial pH $\sim$ 7]). When the pH was maintained at 9, white solids were observed on day 28. When the pH was kept at 8, white solids were formed on day 32. Finally, with no pH adjustment, no solids were formed. The FTIR spectra of the three samples (collected on day 32) along with the pure oil sample are shown in Fig. 4. The FTIR results confirmed that in the sample with no pH adjustment (pH $\sim$ 7), the spectrum was identical to that of pure oil. The FTIR spectrum of the pH 8 sample was the same as that of the pH 9 sample. Compared with pure oil, three significant differences were noted in these two samples. First, a significant peak was displayed at 665 cm^{-1}, which was one of three characteristic calcium soap bands representing the Ca–O bond (Negishi and Maeda, 1999). Another difference was the appearance of a significant peak at 3400 cm^{-1}, representing the bound water associated with calcium soap. The third difference was the appearance of the band at 970 cm^{-1}, which is in the region where absorption bands describe the appearance of glycerol (Poulenat et al., 2003), a product of oil hydrolysis. Although the bands for the other two characteristic regions were not observed for samples collected at pH = 8 and 9 conditions, the appearance of these other three bands indicate that the saponification process was ongoing. These samples were likely intermediates during the soap formation process. At pH below 10, the soap formation process due to possible oil hydrolysis was so slow that it cannot be the explanation for the soap formation on the concrete surface in two days under the GI conditions above. Therefore, when a significant amount of free fatty acids were present in wastewater, the major role of any oil was to act as a carrier of free fatty acids and facilitate the surface reaction during soap formation in the pH = 8 and 9 conditions.
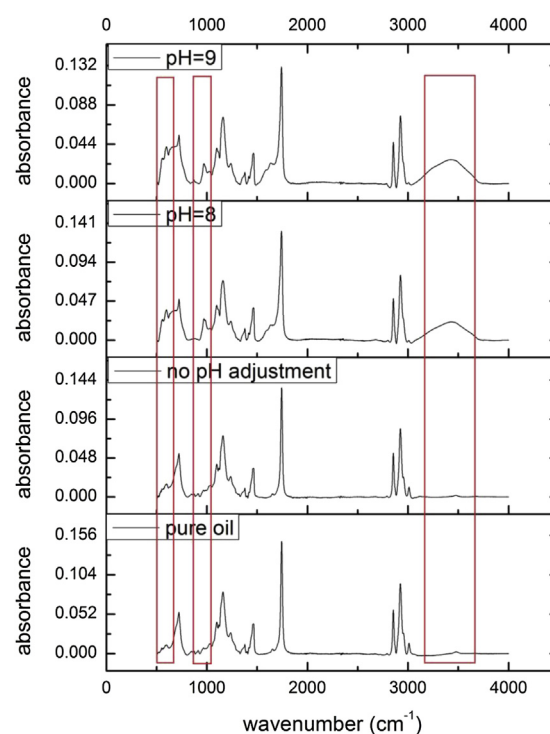

Fig. 4 – Baseline corrected infrared spectra of soybean oil, sample under no pH adjustment, white solid sample at pH = 8, and white solid sample at pH = 9.

To obtain a clear understanding of the role of oil in sewer pipe walls, the concrete blocks were placed in pure oil (only soybean oil), soybean oil and water mixture, and a mixture of palmitic acid and soybean oil. After mixing for 24 days, no solids were observed on the concrete surface in all three conditions. Soap was not formed even though palmitic acid was dissolved in oil and was available to react with calcium. In the presence of water, only a small amount of calcium hydroxide may have been released from concrete since the pH increased from 7 to 8 on day 12 and then remained at 8. The fact that no solid was formed in 24 days was further evidence that the saponification interface reaction occurs slowly if there is no free fatty acid present.

3.4. Effect of different types of fatty acids on the saponification interface reaction

Three major fatty acids (palmitic, oleic, and linoleic acid) present in FOG deposits (Keener et al., 2008; He et al., 2011; Williams et al., 2012) were studied. When the concrete block was exposed to a mixture of oil, water, and palmitic acid, solids started to accumulate on the concrete surface within 2 days and continued to accumulate throughout the testing period. After 32 days of mixing, a soft and sticky solid surrounding the concrete surface was observed (Fig. 5). The solids that formed on the concrete surface and in solution were weighed. An average of 9.4 g of solids was scraped off the concrete surface for Palmitic_2 but only 1.2 g was weighed for Palmitic_1. No solid was found in the bulk solution of
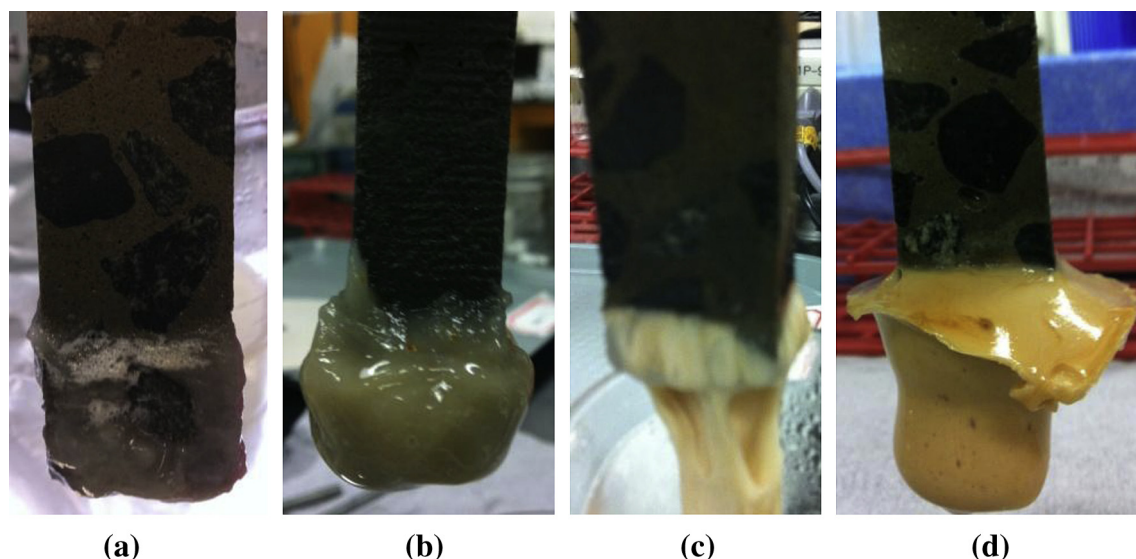
Fig. 5 − Solids formed using different FFAs. (a) Palmitic_1: addition of 0.25 g palmitic acid; (b) Palmitic_2: addition of 1 g palmitic acid; (c) Oleic: addition of 0.25 g oleic acid; (d) Linoleic: addition of 0.25 g linoleic acid.

Palmitic_1 but 6.3 g solid were obtained in the bulk solution of Palmitic_2, indicating that the amount of solids formed increases with the amount of palmitic acid added. Low concentrations of calcium were released in solution in Palmitic_1 (17.1 mg/L Ca^{2+}) and in Palmitic_2 (14.3 mg/L Ca^{2+}) (Fig. 6), likely due to the neutral pH (pH = 7) and the formation of solids which prevented calcium hydroxide in concrete from being released to the surrounding solution.

The infrared spectra of the solid samples were different from that of pure oil as they both displayed two additional bands as shown in Fig. 7a: one at 970 cm^{-1} representing the existence of glycerol; and another near 1577 cm^{-1} representing the carboxylate ion asymmetric stretching vibration, a characteristic band of calcium soap (Poulenat et al., 2003). The appearance of these two bands indicated the ongoing saponification process that was incomplete on day 32.

When oleic acid was added, solids were not formed on the concrete surface as quickly as in the palmitic acid samples.
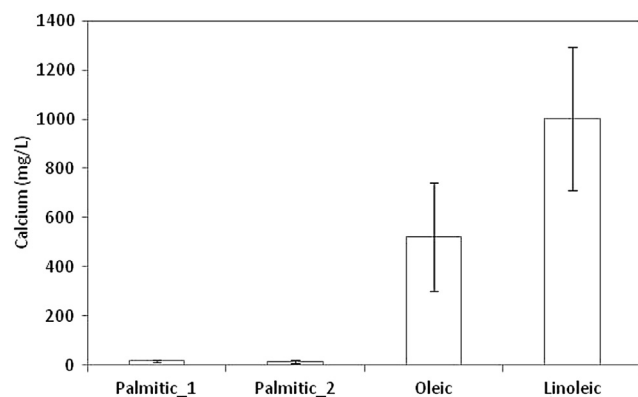

Fig. 6 − Calcium released from concrete block using different types of fatty acids.

However, the oleic samples were more viscous and the total amount of solids in the oleic sample was significantly higher than in the palmitic samples. In the oleic samples, the pH experienced a sudden drop to 5 on day 23 and then remained at 5 which likely accelerated the calcium hydroxide leaching from the concrete sample to buffer the solution. This explanation is supported by the average calcium concentration, which was 521.3 mg/L (on day 32), a concentration significantly higher than the amount in Palmitic_1 and Palmitic_2 (Fig. 6).

The infrared spectrum of the solid in the oleic sample (Fig. 7b) was also different from that of the palmitic samples. Two characteristic bands of calcium soap appeared at 665 cm^{-1}, representing the calcium oxygen bond, and at 3400 cm^{-1}, representing O−H stretching vibration of hydrated water in soap. These bands were not present in the solids of Palmitic_1 and Palmitic_2. Glycerol was also found in the oleic sample given the presence of the absorption band at 970 cm^{-1}. Although the characteristic band at 1577 cm^{-1} was not found, an absorption band at 1588 cm^{-1} appeared in that region, which may shift to 1577 cm^{-1} if more time were allowed for the reaction. The saponification process was also incomplete in the oleic samples as the bands were likely in the process of shifting that resulted in carboxylate bands representing soap intermediates or free fatty acid turning into calcium soap if a longer reaction period is allowed.

For the linoleic acid samples, all solids were affixed to the concrete block (Fig. 5d). The pH dropped from 8 to 5 at day 15. One possible explanation for the pH drop in both the oleic and linoleic samples is the oxidative rancidity of unsaturated fatty acids. The oxidative rancidity reaction occurs in three stages. The initiation reactions produce small numbers of free radicals (Coultate, 1989). In this case, the free radical may have been generated by the reaction between oxygen and elemental ferrous since small amounts of (up to 0.4%) ferrous oxide is present in Portland cement (Lea et al., 1971; Barry and
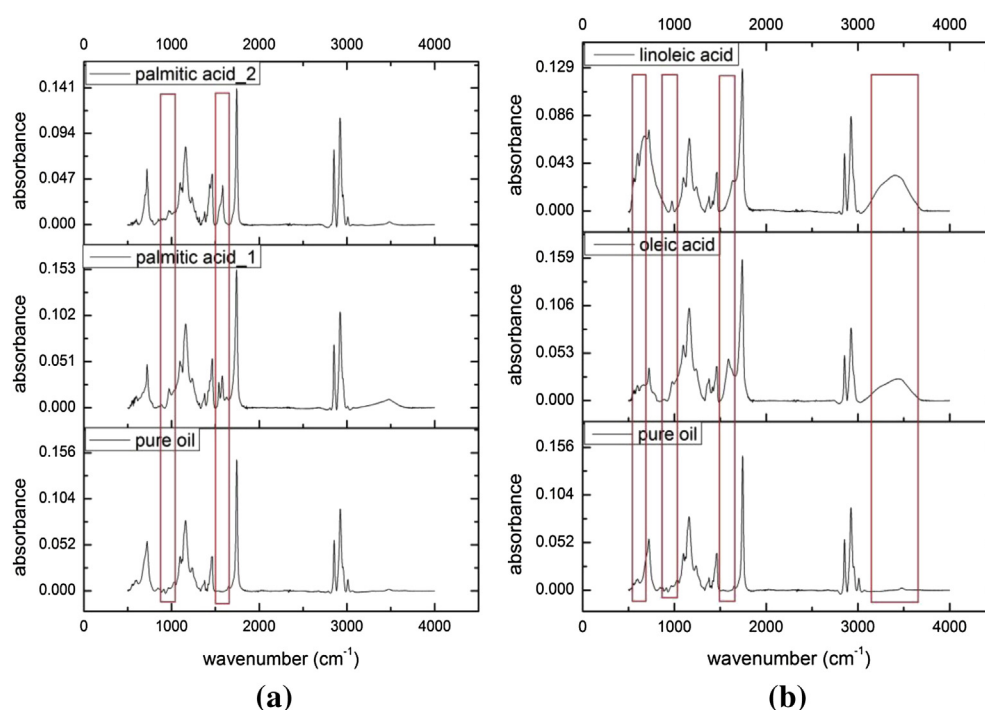
Fig. 7 – Baseline corrected infrared spectra of solid samples formed on concrete surface with addition of different types of fatty acids.

Glasser, 2000; Ko and Batchelor, 2010). The reaction proceeds as follows: $O_2 + 2H^+ + 3Fe^{2+} \rightarrow OH + OH^- + 3Fe^{3+}$ (Angelo, 1992). A small number of free radicals can trigger the propagation to produce lipid peroxide (Young and McEneny, 2001). In the final stage, the ferric, released from cement, would react with lipid peroxide (RCOOH) as $Fe^{3+} + RCOOH \rightarrow Fe^{2+} + H^+ + RCOO$. The production of H^+ would accelerate the release of calcium hydroxide from concrete and cause the pH to drop in the solution. Since there are two double bonds in linoleic acid and one double bond in oleic acid, twice the RCOOH should be produced leading to twice H^+ produced and twice calcium released in linoleic than in oleic. This difference in unsaturation would explain why the pH dropped several days earlier in linoleic samples compared to the oleic samples. The calcium analysis revealed that 1001 mg/L calcium was released in the linoleic solution, almost twice the calcium released in the oleic solution and further supporting the pH drop mechanism described above.

The FTIR spectral analysis also revealed similar profiles for both oleic and linoleic (Fig. 7). The only difference in absorption bands was in the region between 1550 cm^{-1} to 1650 cm^{-1}. The absorption band at 1630 cm^{-1}, instead of 1588 cm^{-1}, was observed in linoleic, which may be additional evidence supporting the hypothesis of band shifting from 1630 cm^{-1} to 1580 cm^{-1} and then to 1577 cm^{-1} as the formation of the carboxyl group of soap occurs. The similarities and differences among oleic, linoleic, and palmitic tests, as revealed by FTIR analysis, show that the steps of saponification are different between saturated fatty acids and unsaturated fatty acids.

In general, when saturated fatty acids, such as palmitic acid, react with calcium, less adhesive solids may be formed

and with less corrosion on the concrete surface. However, for unsaturated fatty acids, such as oleic and linoleic acids, with increasing number of double bonds, stickier solids may be formed and more corrosion can occur that results in significant amounts of calcium released from the concrete sample. The adhesive differences among solids formed by reactions between calcium and saturated or unsaturated fatty acids were supported by a recent observation that a FOG deposit sample with the highest oleic to palmitic ratio was harder than the one with the lowest ratio (Williams et al., 2012).

3.5. Proposed mechanisms of FOG deposit formation in sewer lines

The results of this study suggest that there are four major components contributing to FOG deposit formation on sewer pipe walls: calcium, free fatty acids (FFAs), FOG (or oil), and water. Here, the oil acts primarily as a transporter and a minor source of FFAs in sewer pipelines. FOG deposits will likely not form on concrete in the absence of any of the four components. The general understanding of FOG deposit formation in sewer lines is shown in Fig. 8. When FFAs produced from the cooking process (Canakci, 2007) or generated by microbial activities in the grease interceptor (Monterfrio et al., 2010) are discharged into sewer pipelines, they would partition into oil and flow on the wastewater surface. Calcium is either naturally present in the wastewater or released upstream from highly corrosive environments such as in precast concrete grease interceptors (He et al., 2012; Aziz et al., 2012) or regions where there has been evidence of biogenically induced concrete corrosion (Gutierrez-Padilla et al., 2010). In the presence
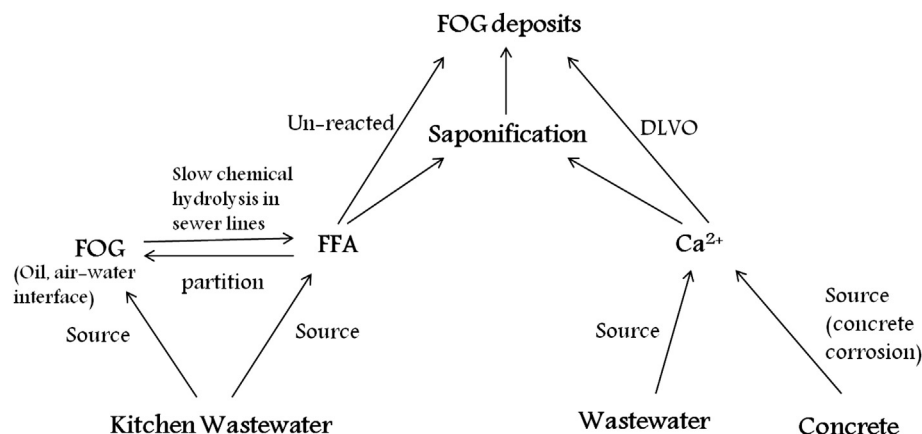
Fig. 8 − **Proposed mechanisms of FOG deposit formation in sewer lines.**

of calcium and FFAs at the oil/water or oil/concrete interface, saponification occurs at a fast rate. The type of free fatty acids may influence the adhesive quality of the soap produced. However, it is not known how much unsaturated fatty acid is needed to significantly change this adhesive characteristic. The buildup of FOG deposits in sewer lines is not only caused by saponification, but also due to the aggregation of excess calcium (He et al., 2011; Williams et al., 2012), un-reacted free fatty acids, and debris in wastewater (He et al., 2011). The saponified solid acts as a core affixed to the sewer pipe walls. The un-reacted FFAs move toward and are accumulated around the core. These un-reacted free fatty acids likely draw calcium and other cations toward the solid core matrix based on the effects of van der Waals attraction and electrostatic repulsion (DLVO theory) (He et al., 2011). Saponification occurs between un-reacted FFAs and calcium on the solid core matrix to form more saponified solids that result in FOG deposit accumulation on sewer pipe walls. Because of the adhesive character, surface charge, and flow restrictions in sewer lines, debris in wastewater would also accumulate and result in the formation of debris layers interspersed with hardened FOG. These layers have been identified in previous research (Keener et al., 2008).

4.   Conclusions and implications

Based on all the data, a comprehensive model of the mechanisms of the FOG deposit formation in sewer systems is proposed. Our study suggests that concrete corrosion may be a contributor to the formation of FOG deposits. The use of alternate materials for the construction of grease interceptors, non-corroding coatings on precast concrete surfaces (i.e., manhole structures), as well as coatings for cement mortar linings used in ductile iron pipes, may reduce the release of calcium from corroded concrete and consequently lead to a significant reduction of FOG deposit formation in sewer lines. A major role that oil plays in the saponification surface reaction is to transport pre-hydrolyzed FFAs to interfaces. Thus, locations in sewer lines where there is a high residence time of oil, such as sections with low flow velocity or shear force, may

be places where FOG deposits are most likely formed. Attention should also be paid to studying the relationship between the type of FFAs and the adhesive quality of FOG deposits.

Acknowledgments

REFERENCES

Angelo, A. J. St, 1992. Lipid Oxidation in Food. American Chemical Society, Washington, D.C.

Aziz, T., Keener, K., Holt, L., Groninger, J., Ducoste, J., 2012. Field characterization of grease abatement devices. Water Environment Research 84, 237−246.

Barry, T.I., Glasser, F.P., 2000. Calculation of Portland cement clinking reactions. Advances in Cement Research 12, 19−28.

Bielefeldt, A., Gutierrez-Padilla, M.G.D., Ovtchinnikov, S., Silverstein, J., Hernandez, M., 2010. Bacterial Kinetics of Sulfer oxidizing bacteria and their biodeterioration rates of concrete sewer pipe samples. Journal of Environmental Engineering-ASCE 136 (7), 731−738.

Brooksbank, A.M., Latchford, J.W., Mudge, S.M., 2007. Degradation and modification of fats, oils and grease by commercial microbial supplements. World Journal of Microbiology & Biotechnology 23, 977−985.

Canakci, M., 2007. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresource Technology 98, 183−190.

Coultate, L.P., 1989. Food − the Chemistry of Its Components. The Royal Society of Chemistry, London, U.K.

Gutierrez-Padilla, M.G.D., Bielefeldt, A., Ovtchinnikov, S., Hernandez, M., Silverstein, J., 2010. Biogenic sulfuric acid attack on different types of commercially produced concrete sewer pipes. Cement Concrete Research 40, 293−301.

Hammerton, C., 1944. The corrosion of cement and concrete. The Surveyor, 587.

He, X., Iasmin, M., Dean, L.O., Lappi, S.E., Ducoste, J.J., de los Reyes, F.L., 2011. Evidence for fat, oil and grease (FOG) deposit formation. Environmental Science & Technology 45, 4385–4391.

He, X., Osborne, J., de los Reyes, F.L., 2012. Physico-chemical characterization of grease interceptor with and without biological product addition. Water Environment Research 84, 195–201.

Keener, K.M., Ducoste, J.J., Holt, L.M., 2008. Properties influencing fat, oil and grease deposit formation. Water Environment Research 80, 2241–2246.

Ko, S., Batchelor, B., 2010. Effect of cement type on performance of ferrous iron-based degradative solidification and stabilization. Environmental Engineering Science 27, 977–987.

Kosmatka, S.H., Kerkhoff, B., Panarese, W.C., 2002. Design and Control of Concrete Mixtures, fourteenth ed. Portland Cement Association, Skokie, IL.

Lea, F.M., K, T., C., B., C. B., E., D., S.C., F. R. I., C., 1971. The Chemistry of Cement and Concrete. Chemical Publishing Company Inc, New York, N. Y.

Monterfrio, M.J., Tai, X., Obbard, J.P., 2010. Recovery and pre-treatment of fats, oil and grease from grease interceptors for biodiesel production. Applied Energy 87, 3155–3161.

Mori, T., Nonaka, T., Tazaki, K., Koga, M., Hikosaka, Y., Noda, S., 1996. Interactions of nutrients, moisture, and pH on microbial corrosion of concrete sewer pipe. Water Resources Research 26, 29–37.

Negishi, A., Maeda, T., 1999. A Repair System of Concrete Corroded by Bacteria Using HDPE Sheets and Mortar Admixed with Inhibitor. Dresden, Germany.

O'Connell, M., McNally, C., Richardson, M.G., 2010. Biochemical attack on concrete in wastewater applications: a state of the art review. Cement & Concrete Composites 32, 479–488.

Poulenat, G., Sentenac, S., Mouloungui, Z., 2003. Fourier-transform infrared spectra of fatty acid salts-Kinetics of high-oleic sunflower oil saponification. Journal of Surfactants and Detergents 6, 305–310.

U.S. Environmental Protection Agency (EPA), 2004. Report to Congress: Impacts and Control of CSOs and SSOs.

Williams, J.B., Clarkson, C., Mant, C., Drinkwater, A., May, E., 2012. Fat, oil and grease deposits in sewers: characterization of deposits and formation mechanisms. Water Research 46, 6319–6328.

Young, I.S., McEneny, J., 2001. Lipoprotein oxidation and atherosclerosis. Biochemical Society Transactions 29, 358–362.