

# Characteristics of Black Goo From Leachate Collection Systems at Two North American Landfills

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# ABSTRACT

Black, sticky, gel-like matter, *aka* black goo, has been accumulating in leachate collection systems (granular layers, pumps, pipes, tanks, etc.) in municipal solid waste landfills in the humid regions of North America. This issue emerged in the last decade and is becoming more commonplace and problematic. Black goo clogs pipes, drainage layers, sumps, and pumps, requiring costly maintenance and making leachate extraction inefficient. To understand this phenomenon, analysis was conducted on black goo samples from two landfills in North America. Fourier-transform infrared (FTIR) spectroscopy and solid-state nuclear magnetic resonance (ssNMR) analyses were conducted to examine the chemical structure of the black goos. Loss on ignition (LOI) tests were conducted to determine the organic matter content. Thermogravimetric analysis (TGA) analysis was conducted to evaluate thermal decomposition and polymeric content. Both goos have high organic matter content (> 50%), contain bond structures typical of hydrocarbons, and appear to be primarily synthetic hydrophilic polymers. Mechanisms contributing to formation of black goo are being explored.

Keywords: Landfills, leachate collection systems, clogging, sticky material, characterization, instrumental analysis

# 1 INTRODUCTION

Leachate collection systems (LCS) are placed above lining systems in municipal solid waste (MSW) landfills to collect leachate for treatment and to control the leachate head on the liner. LCS clogging has traditionally been associated with accumulation of biological matter, inorganic particulate, and chemical precipitates in the pores of the leachate collection layer (Rowe and Yu 2010, Yu and Rowe 2012, Liu et al. 2018, Tang et al. 2018, Wang et al. 2021). In the last decade, however, black sticky solids have been accumulating in leachate collection systems in the humid regions of North America, causing extensive and frequent clogging (Fig. 1). These solids are unlike historical clogging materials, and consist of a sticky organic material that also contains a variety of other matter entrained in the matrix. Anecdotally referred to as "black goo," this sticky material fills pores within waste, leachate collection layers, and sumps. This material also accumulates in pumps, pipes, and other appurtenances.

Clogging caused by black goo affects leachate and gas management adversely, requiring costly and frequent maintenance to ensure systems operate properly. For example, pumps in dual-phase extraction wells often become clogged by the black sticky material, requiring removal and rebuilding, sometimes on a weekly basis. Similarly, sumps and risers have become clogged with mats and plugs of black goo, preventing removal of leachate and causing head buildup on the liner. In some cases, the LCS has become completely and irreversibly clogged by black goo. Black goo has been treated with physical methods (e.g., ultrasonic treatment) and/or in situ flushing with chemical solutions (e.g., acidic or alkaline flushes) with various levels of success.

Common special waste streams accepted at MSW landfills that have black goo problems include wastewater treatment plant (WWTP) sludges, dredge spoils, and rendering waste. However, black goos have also been encountered at MSW landfills with no unusual waste stream. Thus, the source of black goo remains a mystery.



*Figure 1.* Black goo bound to a leachate extraction pump (a and b) and fresh black goo samples (c and d) from two different MSW landfills.

In this study, black goo samples were collected from two MSW landfills in North America, one in Michigan and the other in Florida. The black goos were analyzed using Fourier-transform infrared (FTIR) spectroscopy and solid-state nuclear magnetic resonance (ssNMR). Loss-on-ignition tests and thermogravimetric analysis (TGA) were conducted to determine the organic matter content as well as the thermal stability of the samples. The FTIR and NMR spectra were used to evaluate similarities in the bonding structures within the goo, which can provide clues to the composition and source of black goos.

# 2 MATERIALS AND METHODS

# 2.1 Sample Collection and Preparation

Black goo samples were collected from two landfills in the United States that have been experiencing black goo problems: sample BG-1 from a landfill in Michigan and sample BG-2 from a landfill in Florida. The black goo samples were placed in 2-L plastic zip-top bags with the head space evacuated, and shipped on ice overnight to the Wisconsin Geotechnics Laboratory at the University of Wisconsin-Madison. The samples were stored in a cold room prior to testing.

The black goo samples were oven-dried prior to the analysis. Approximately 100 g of each black goo was dehydrated at 60 °C for 48 hr. Low temperature was used preserve the organic structure and prevent carbon mineralization. The dried samples were finely pulverized prior to analysis.

# 2.2 Analytical Methods

Both black goos were examined using loss on ignition (LOI), Fourier transform infrared (FTIR) spectroscopy, solid-state nuclear magnetic resonance (ssNMR), and thermogravimetric analysis (TGA). FTIR and NMR provide information about functional groups and bonds within the material, and are particularly valuable in identifying the composition of gel-like polymeric materials (Tian et al. 2019, Gustitus and Benson 2020, 2021).

LOI tests were conducted in accordance with ASTM D7348 using 10 g of dehydrated black goo. Black goo samples were placed in crucibles in a muffle furnace for 8 hr at 550 °C. The organic matter content was 65.2% for BG-1 and 52.1% for BG-2, indicating that more than half of the black goo is organic material.

Solid state FTIR analyses were conducted using a Bruker FTIR PMA 50 to obtain an infrared spectrum describing bond structures and functional groups in the black goos. Approximately 10 g of sample was used in the analysis, which was sufficient to cover the emitting beam. The sample was analyzed using attenuated total reflectance (ATR). After collecting a background spectrum, samples were analyzed in the wavenumber range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. Transmittance data were collected in wavenumber-transmittance format. The spectra were evaluated by assigning the observed absorption frequency bands in the sample spectrum to appropriate normal modes of vibrations in the molecules.

NMR tests were conducted on the black goos using a Bruker ssNMR 4 mm iProb to obtain a spectrum for characterization of atomic level structure. Analysis was conducted on 10 g of dehydrated and finely ground black goo. Ground samples were placed in 4 mm Bruker ZrO<sub>2</sub> MAS rotors and compacted to eliminate spinning failures. The samples were spun at 10 kHz for 4 hr.

TGA was performed using a TA Instruments Q500 thermogravimetric analyzer (TGA) on 10-15 mg dried samples. The samples were heated from 25 to 1000 °C.

# 3 RESULTS AND DISCUSSION

The FTIR spectra are shown in Fig. 2. The peaks identified at 3243 cm<sup>-1</sup> correspond to O-H bonds associated with water in the goo and the peaks at 2921 cm<sup>-1</sup> correspond to C-H bonds. The peaks at 1637 cm<sup>-1</sup> and 1411 cm<sup>-1</sup> correspond to C=O bonds of a carbonyl group, the peak at 1547 cm<sup>-1</sup> corresponds to asymmetric C-O stretching, the peak at 1029 cm<sup>-1</sup> corresponds to C-H and C-O deformation, and the peaks at 876 cm<sup>-1</sup> and 786 cm<sup>-1</sup> indicate C-H bending.

The <sup>13</sup>C NMR spectra obtained for the dehydrated specimens of BG-1 and BG-2 are shown in Fig. 3. Peak intensities occur at 35 ppm, 45 ppm, and 185 ppm for both black goos. The peaks at 35 ppm and 45 ppm correspond to C-H and C-H<sub>2</sub> structures. The peak at 185 ppm corresponds to a C=O bond.



Figure 2. FTIR spectra of the black goo samples.



Figure 3. NMR spectra of the black goo samples.

The TGA curves for BG-1 and BG-2 are shown in Fig. 4. Both black goo samples exhibit similar response to thermal decomposition, with a gradual loss of mass from 25 to 480 °C due to the volatilization of organic matter followed by a steep loss of mass between 480 and 550 °C. Sample BG-1 lost 26% of the mass between 480 and 515 °C, while BG-2 lost 12% of the mass between 530 and 550 °C. After the steep loss of mass, both samples degraded gradually until reaching 700 °C, when another increase in degradation rate occurred. After this second steep loss of mass, the samples degraded gradually until reaching 1000 °C where approximately 40% of the mass remained as ash. The steep mass losses around 500 and 700 °C indicate both samples contained a substantial fraction of synthetic material or polymer. If the mass had been predominantly natural biopolymers, degradation would have occurred around 250 to 350 °C.



Figure 4. TGA degradation curves for the black goo samples.

The consistency between the FTIR and NMR spectra as well as the TGA curves for BG-1 and BG-2 is striking, given they are from two different landfills in very different parts of the United States. The bond structures suggest that black goos are a hydrocarbon, and their similarity suggests that a common component exists in both black goos that likely originates in the waste. Comparison with FTIR and NMR spectra for known materials indicates that black goos are very similar in chemical structure to anionic polymers, such as sodium polyacrylate, a hydrophilic superabsorbent polymer (SAP). SAPs are used in a broad range of products to absorb moisture, such as meat packaging, feminine hygiene products, and incontinence garments. All of the products are common in waste streams disposed in MSW landfills.

Biological materials are likely commingled with the goos due to exposure in the MSW within the landfill, and may colonize the black goo as a substrate. Biological materials likely are responsible for the black color of black goos, as the microbial communities in MSW landfills induce reducing conditions known to precipitate sulfide salts with dark color. The relative importance of these biological materials relative to the synthetic abiotic polymers in the goo is an area of future study.

# 4 SUMMARY AND CONCLUSIONS

This paper has described tests conducted on two black goos from landfills in North America, one in Michigan and the other in Florida. Both are comprised of more than 50% organic matter, with similar bonding structures identified through FTIR and NMR that are characteristic of hydrocarbon molecules. The FTIR and NMR spectra of the goos indicate that the molecular structure is very similar to the structure of hydrophilic anionic polymeric materials, which are commonplace in consumer products that are disposed in the MSW stream. Thermogravimetric analysis of the samples revealed similar degradation curves indicative of synthetic materials or polymers. Identifying materials in the waste stream with polymers having similar bonding structures may provide clues to the source and mechanisms contributing to the formation of black goos.

Although this research has focused on the physical and chemical characterization of black goos, additional research should be conducted to evaluate the role of microbial communities in the formation and persistence of black goos in MSWs.

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