Black goo: What is this stuff and what can we do about it?

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Kappe Lecture

20 March 2025

In Memoriam

Mehmet Yilmaz, PhD

Dr. Mehmet Yilmaz was a research scientist in my group in 2022 and 2023, leading our research on **black goo**.

Mehmet received the PhD from the University of Wisconsin-Madison in 2018.

Mehmet was unexpectedly diagnosed with an aggressive cancer in late September 2023.

Mehmet left this world on 29 January 2024.

We all miss Mehmet. He lives on through his son Kai and his wife Sue Mun.

May Mehmet rest in peace.

UW-Madison Black Goo Research Team

Mehmet Yilmaz - Post Doctoral Associate (*in memoriam*)

Yu Tan - Post Doctoral Associate

Craig H. Benson – Wisconsin Distinguished Professor Emeritus

Sabrina L. Bradshaw – Research Scientist and Manager

Tuncer B. Edil – Professor Emeritus

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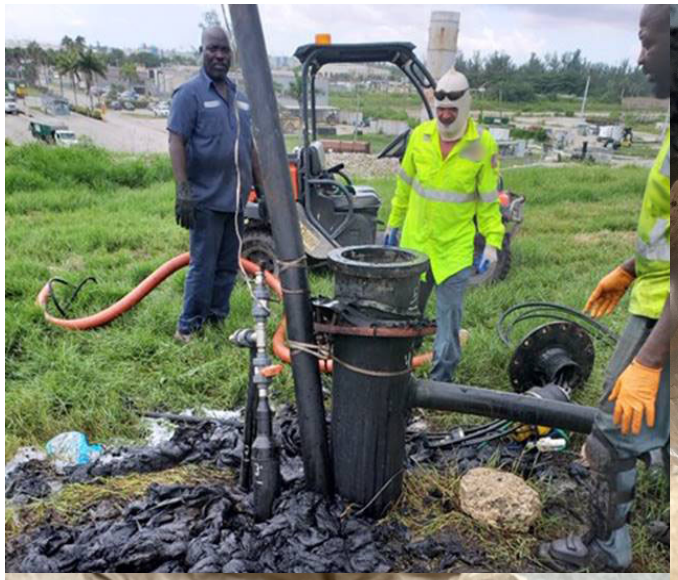
Lighting the way towards a more circular economy



Visual, Textural, and Olfactory Characteristics

- Very sticky, stretchy, rubbery with strong odor (sulfur smell)
- Same physical appearance for samples from different landfills

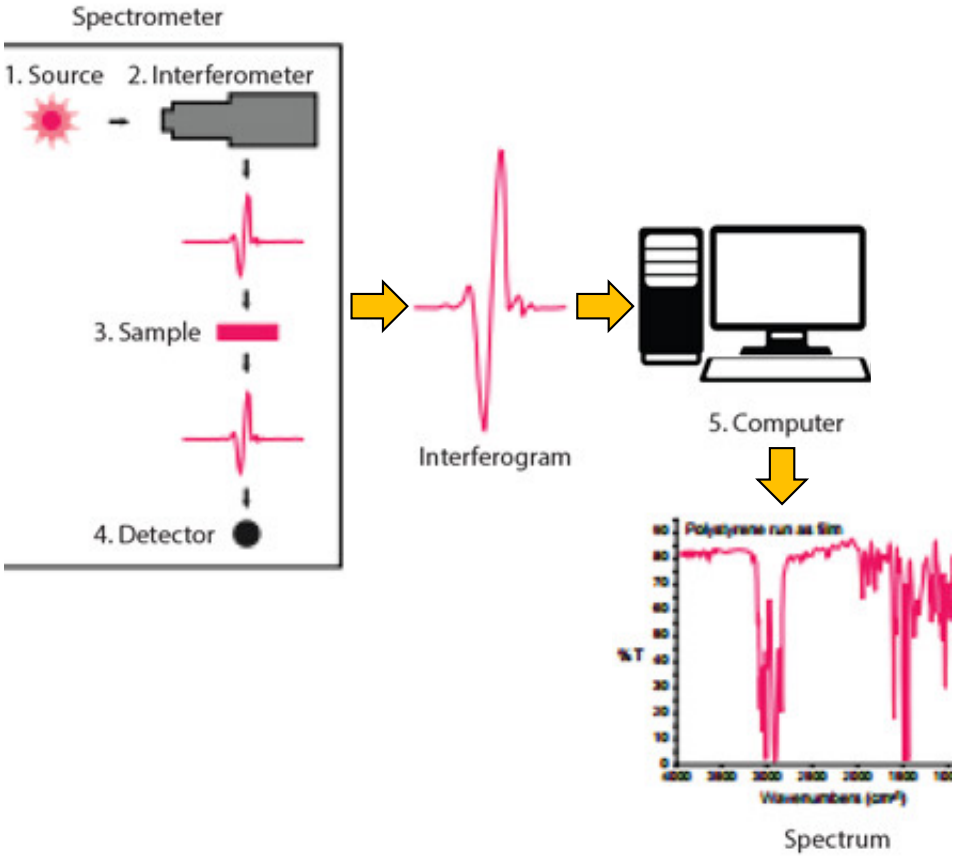
Where Do We See Black Goo?
28 Samples Primarily from Landfills in North America

Black Goo from Brazil

ECOPARQUE
SÃO GONÇALO

Black Goo from Finland

Forensic Chemistry Tools: FTIR Spectroscopy

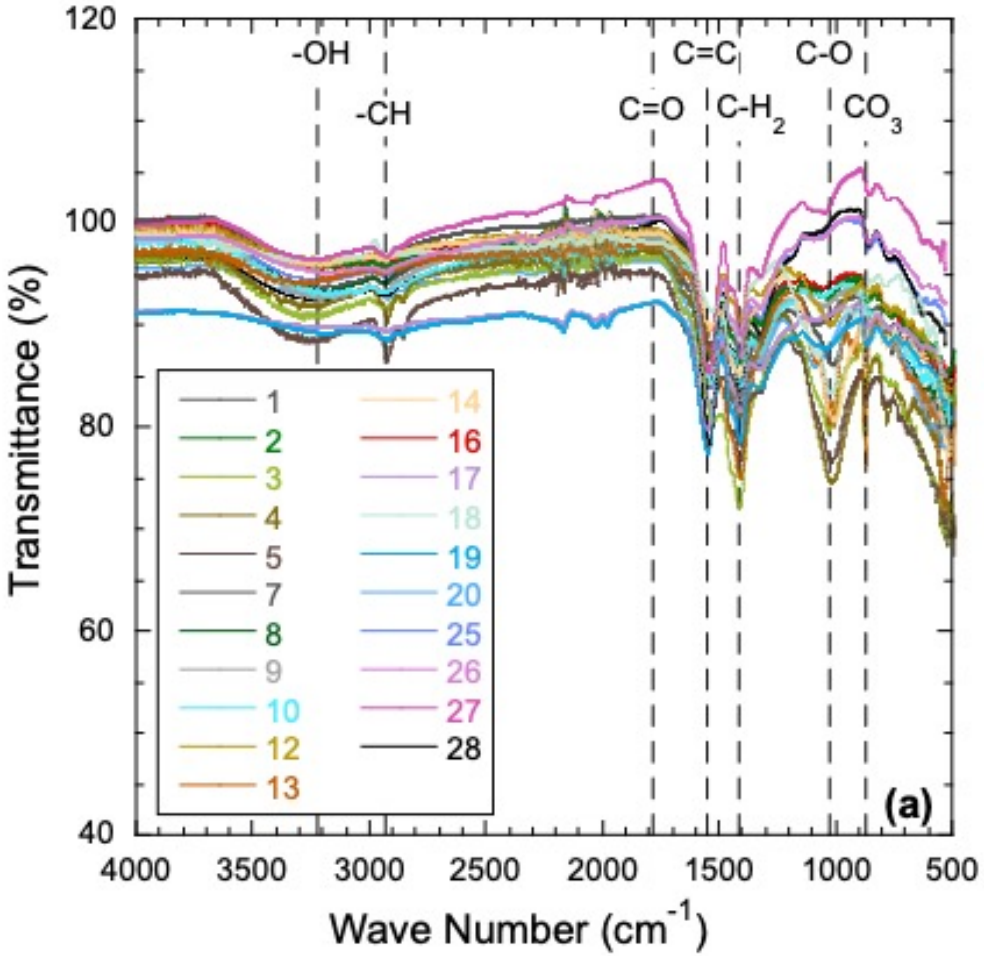


- Broad spectrum infrared source directed at specimen to obtain "**chemical fingerprint**."
- Interactions with bonds between elements absorbs fraction of light.
- Absorption of different wavelengths for different chemical structures.
- Process to get a FTIR "spectrum."

Forensic Chemistry Tools:
Solid-State Nuclear Magnetic Resonance (ssNMR)

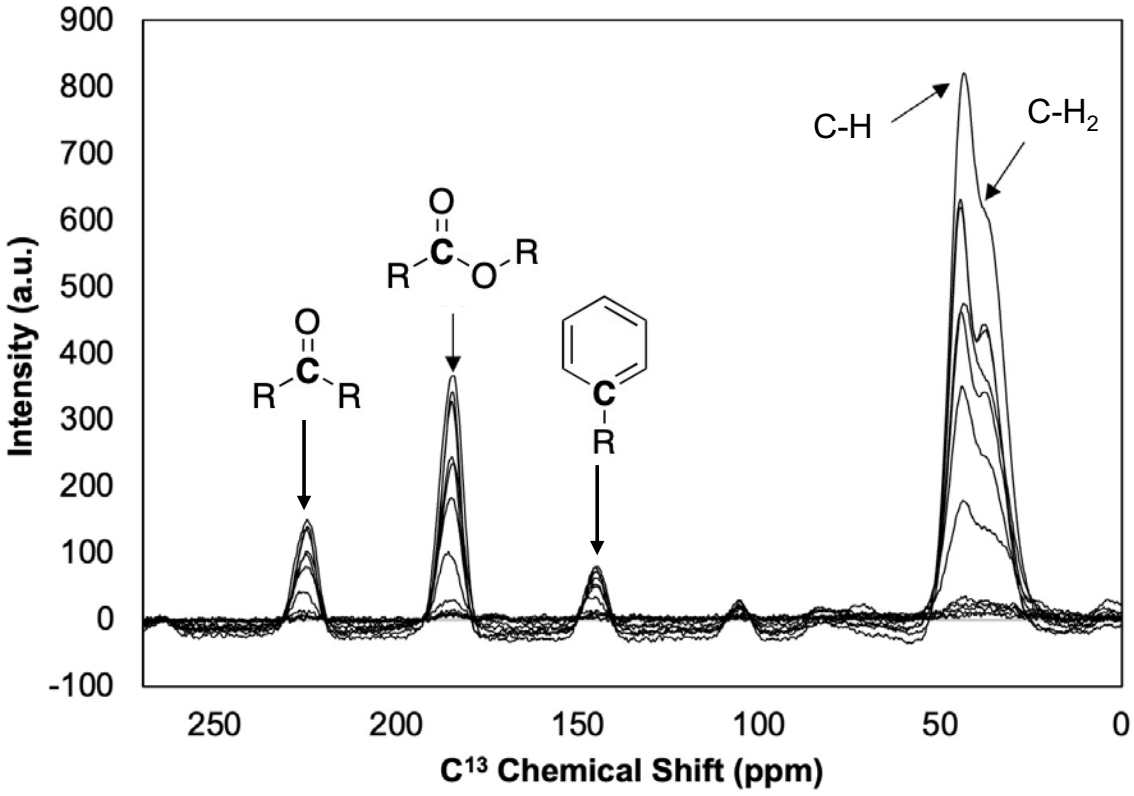
- Nuclei in strong constant magnetic field perturbed by weak oscillating magnetic field.
- Produce EM signal with a frequency characteristic of magnetic field at nucleus.
- Response unique to specific atomic structure.
- Solid-state NMR allows evaluation of as-received black goo (not dry, not solution).

FTIR Spectra of Dry Black Goos



- Consistent peaks in “fingerprint” region indicate C-H and C-H_2, C-O, C=O, C=C, and CO_3 bonds.
- Remarkably similar FTIR spectra from goos collected from broad range of landfills from disparate locations.

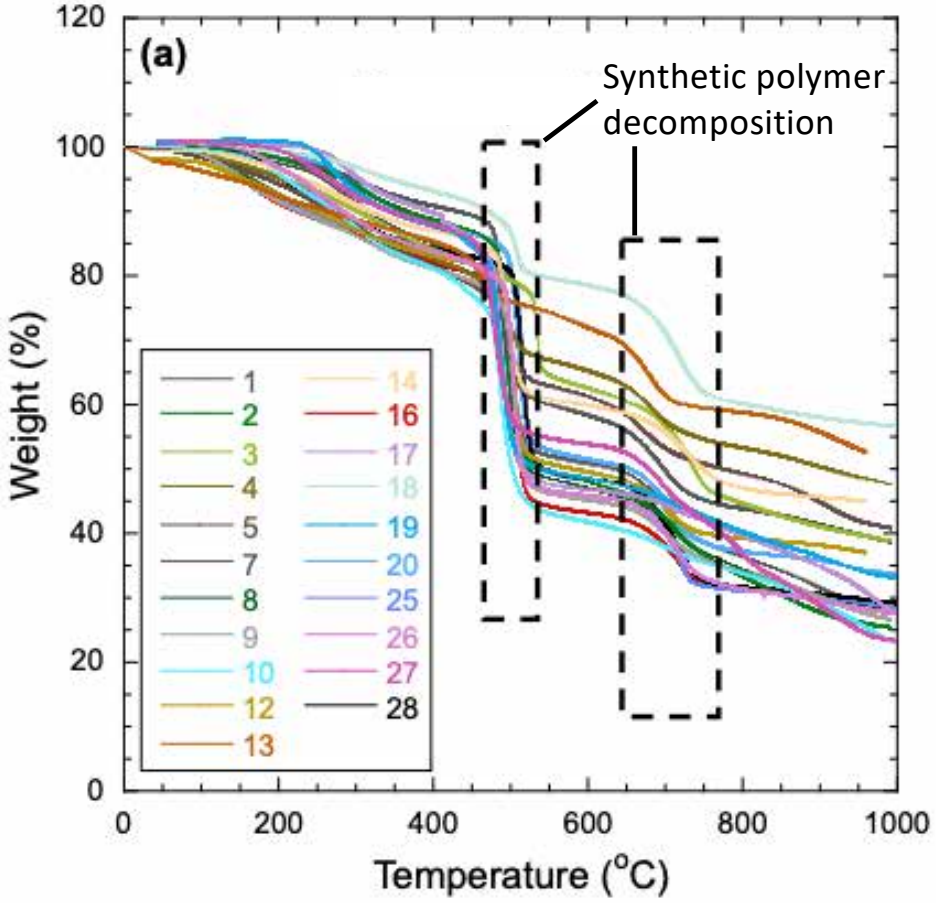
Solid-State Nuclear Magnetic Resonance (ssNMR)



- Spectra indicate black goo has C-H_2, C-H, and C=O bonds.
- Structures observed in NMR spectra match bonds indicated by FTIR spectra.
- Remarkable similarity between goos.

Forensic Chemistry: Thermogravimetric Analysis (TGA)

- TGA under N_2 atmosphere from 20 °C to 1000 °C
- Weight loss at 500 °C indicates **synthetic polymeric structures**.
- Natural biopolymers decompose 200-300 °C.
- Polymer content varies from 15% to 40%



Abiotic or Biotic?
Comparing Black Goo to Biomass

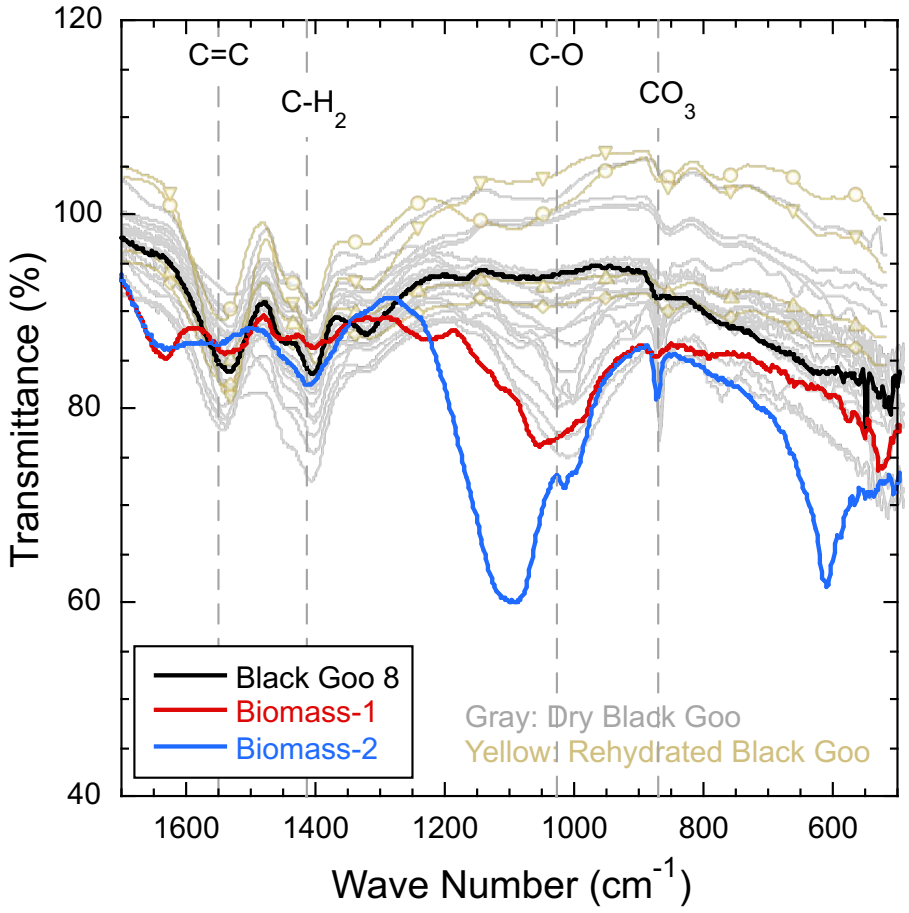
Black Goo

- Black
- H_2S smell
- Rubbery, sticky, stretchy
- Firm and stable under stress
- Heterogenous mixture when water added

Biomass

- Dark Purple (ink-like)
- Cheese smell
- Watery but not rubbery, sticky, stretchy
- Fragile under stress
- Homogeneous mixture when water added

FTIR Spectra: Black Goos and Biomass



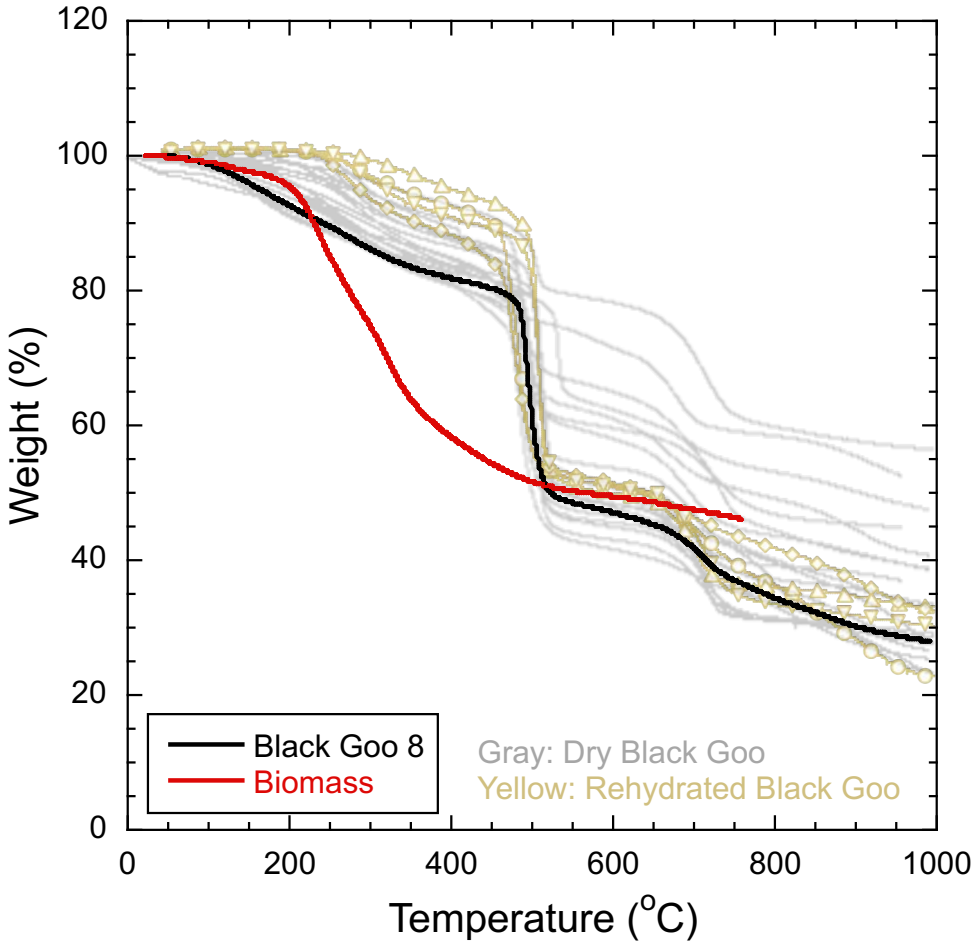
- FTIR analysis used to evaluate molecular and bonding structures.
- FTIR spectra for biomass (**red** and **blue**) very different than for black goo samples (including black goo from same site).

BG-11 from Biomass Site

Biomass

BG indicates black goo samples.

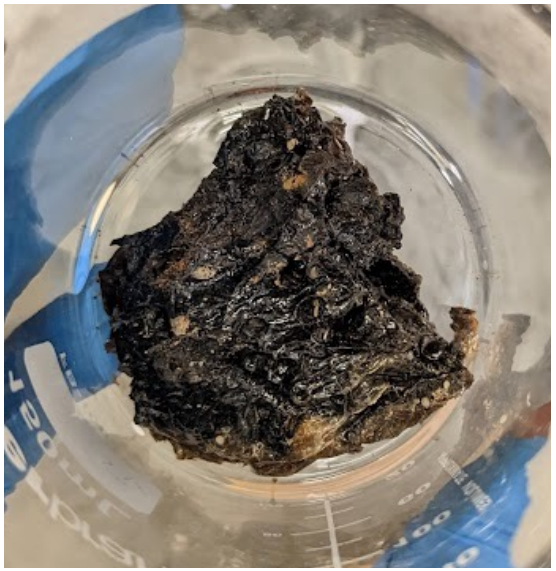
Thermogravimetric Analysis (TGA) of Goos & Biomass



- TGA evaluates thermal stability, particularly useful for polymeric materials.
- Mass decrease at 500 °C indicates synthetic polymeric content (e.g., acrylic materials), including black goo **from same site as biomass**.
- Gradual decrease at 250 °C for biomass (**red line**) indicates natural organic material.
- Biomass has no thermal response at 500 °C.

Rehydration of Black Goo & Phase Separation

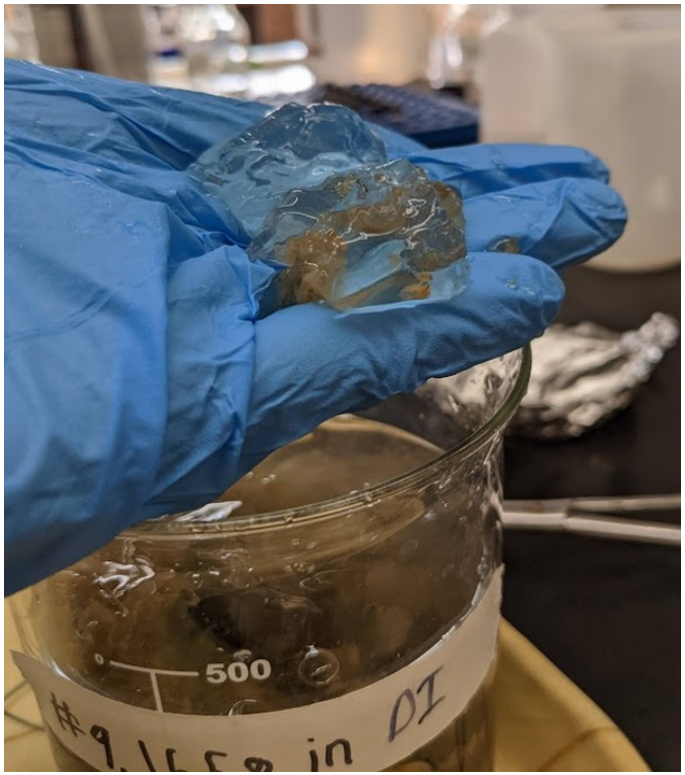
- Goo samples dried and rehydrated in DI water.
- Rehydrated samples absorbed water and released a transparent hydrophilic polymer.
- Polymer separated for further testing and analysis.



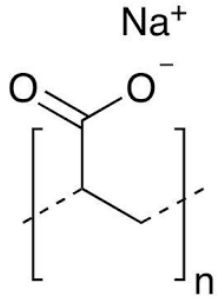
Dehydrated Black Goo

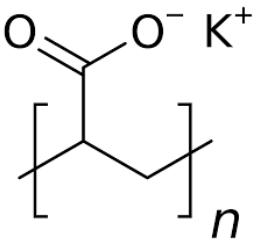
Rehydrated Black Goo

Isolated Polymer from Rehydration in DI Water



Key Findings: Observations, FTIR, NMR, TGA





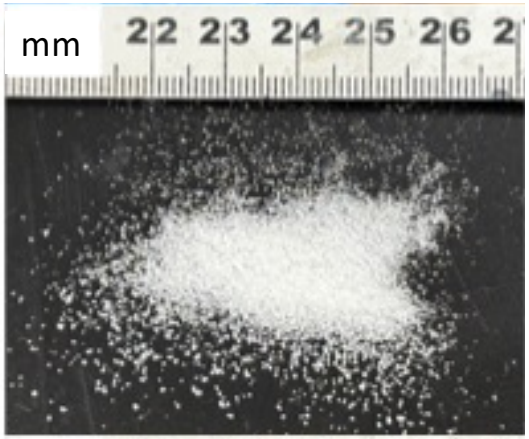
- C-H, C=O, C-H_2 bonds
- High temperature decomposition
- High organic content
- High water content and hydrophilic structure
- Predominantly abiotic
- Firm, stretchy, elastic texture
- Clear gelatinous texture & structure on rehydration

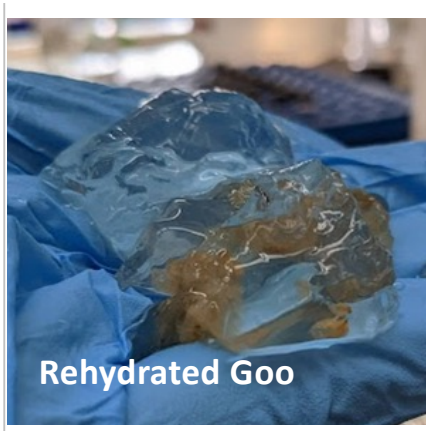
Similar to acrylate-based super absorbent polymers.

Superabsorbent Polymers & Rehydrated Goos

Diaper absorbent – dry particulate and hydrated with deionized water

Sodium polyacrylate (CAS No. 27599-56-0) – dry particulate and hydrated with deionized water

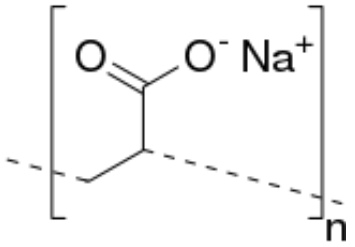




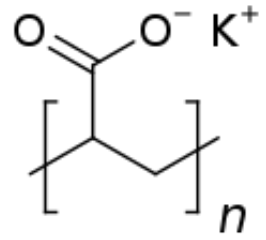
Where are Polyacrylates Used?

Applications

- Diaper, sanitary pad, pet pad, meat pad
- Paint hardener (latex paints)
- Dewatering agent (e.g., dredged sediments)
- Wastewater treatment flocculating agent
- Drilling slurry, concrete protection, quenching
- Gardening as waterlock
- Wire and cable water block
- Growing toys
- Fragrance and detergent carrier
- Hot/cold gel pack



Na polyacrylate



K polyacrylate

Byproduct of Holiday Barbeque

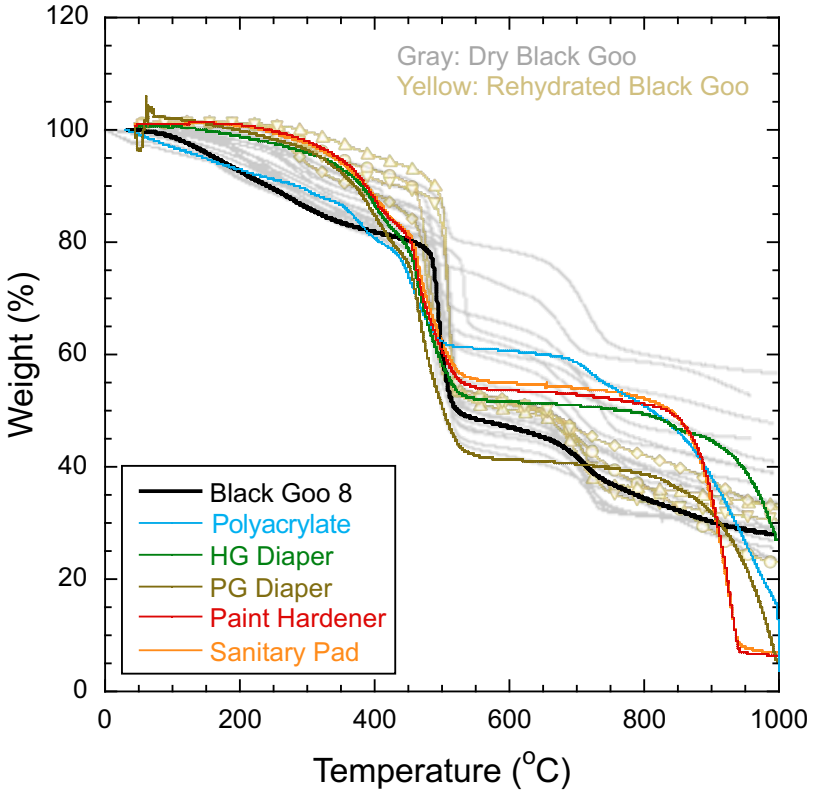
Paint Hardener – Sodium Polyacrylate

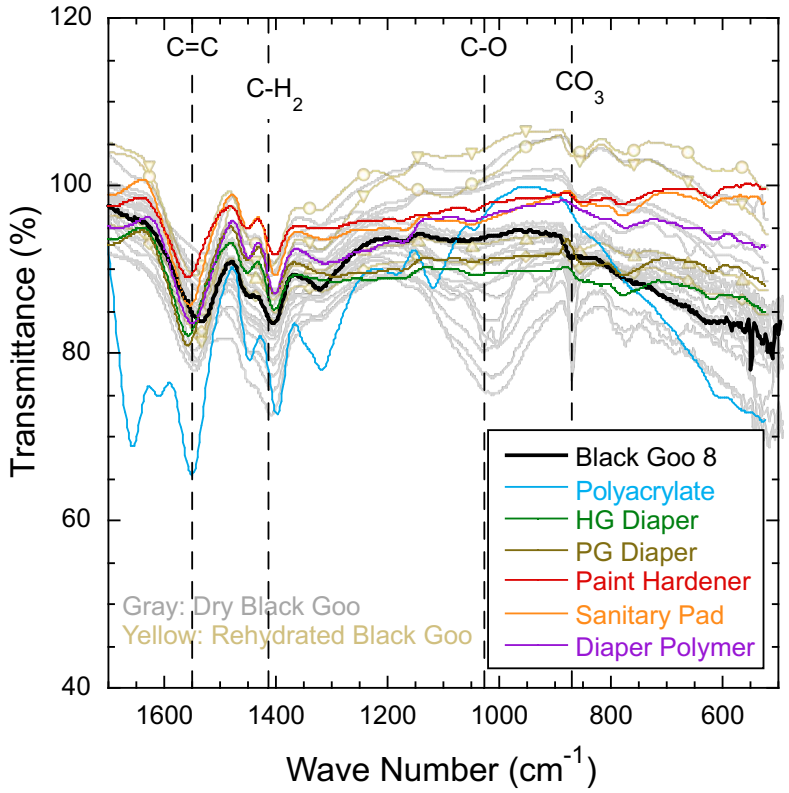
Super Absorbent Polymers (SAPs)

- Over 12.2 billion lbs of SAP produced in 2020.
- Water soluble and hydrophilic. Bind 100 – 1000x mass in water.
- SAPs used in diapers, sanitary products, absorbent meat and produce packaging.
- 85% of SAPs by mass are used in low-fluff diapers sent to landfills.
- **Sodium polyacrylate is the most common SAP produced**.

Water added to sodium polyacrylate

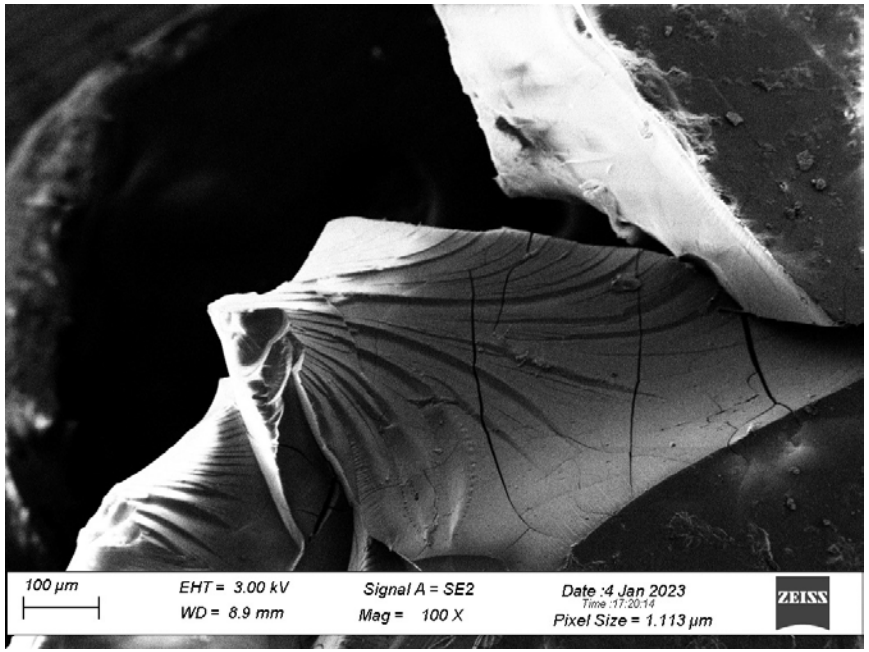
FTIR of Hydrated Black Goos & Anionic Polyacrylates



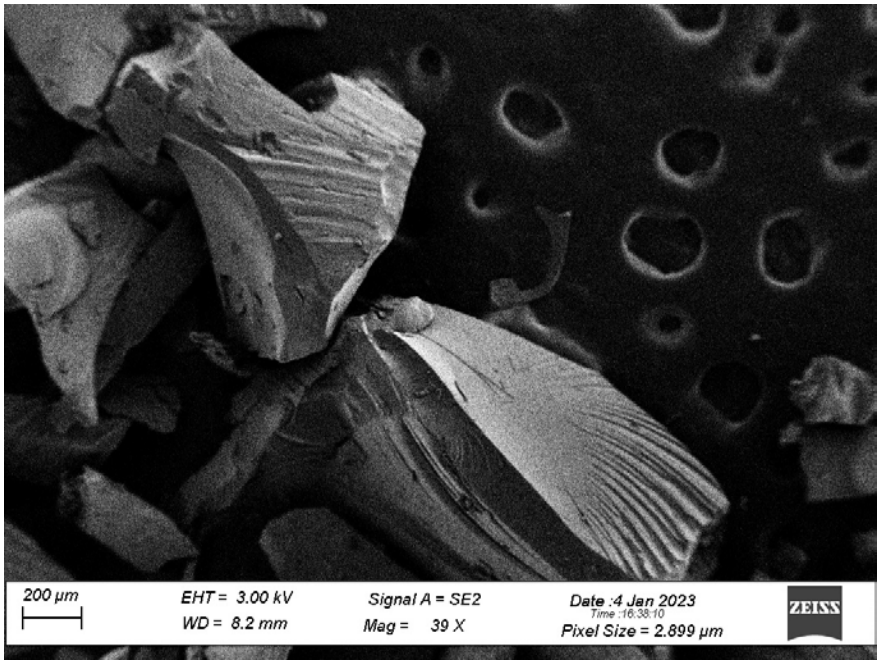


TGA and FTIR of Goos Very Similar to Products with Sodium Polyacrylate

SEM Images:
Black Goo Polymers & Na Polyacrylate



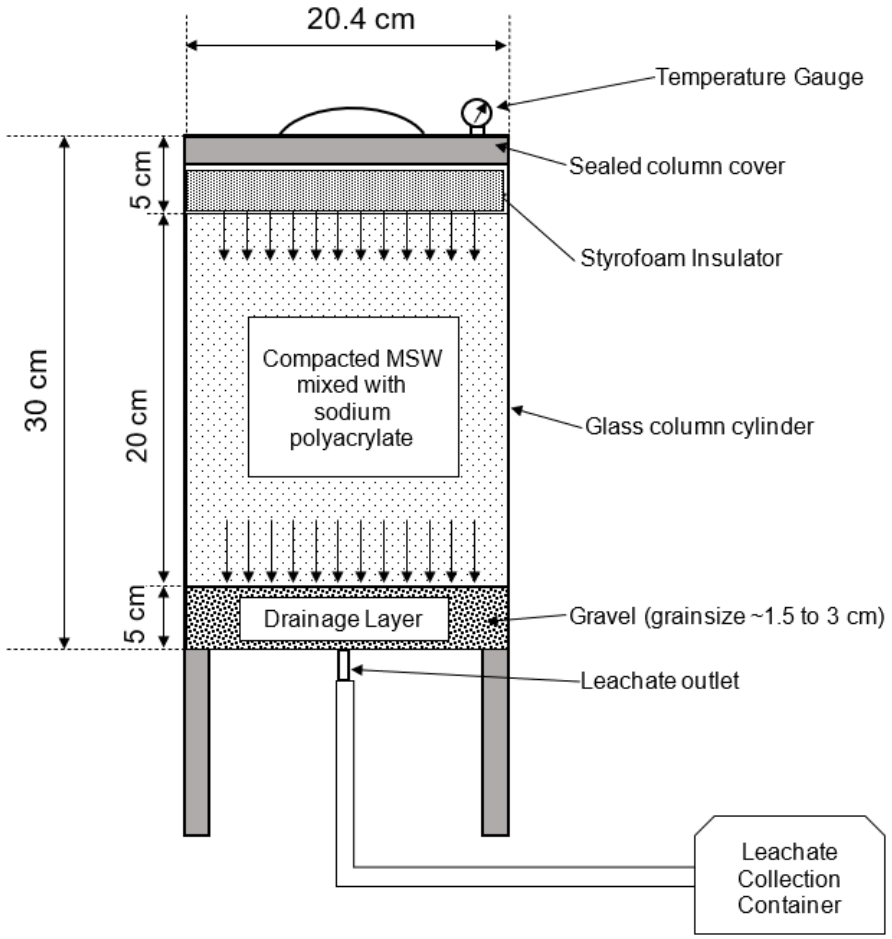
Isolated Polymer from “Black Goo”



Sodium Polyacrylate

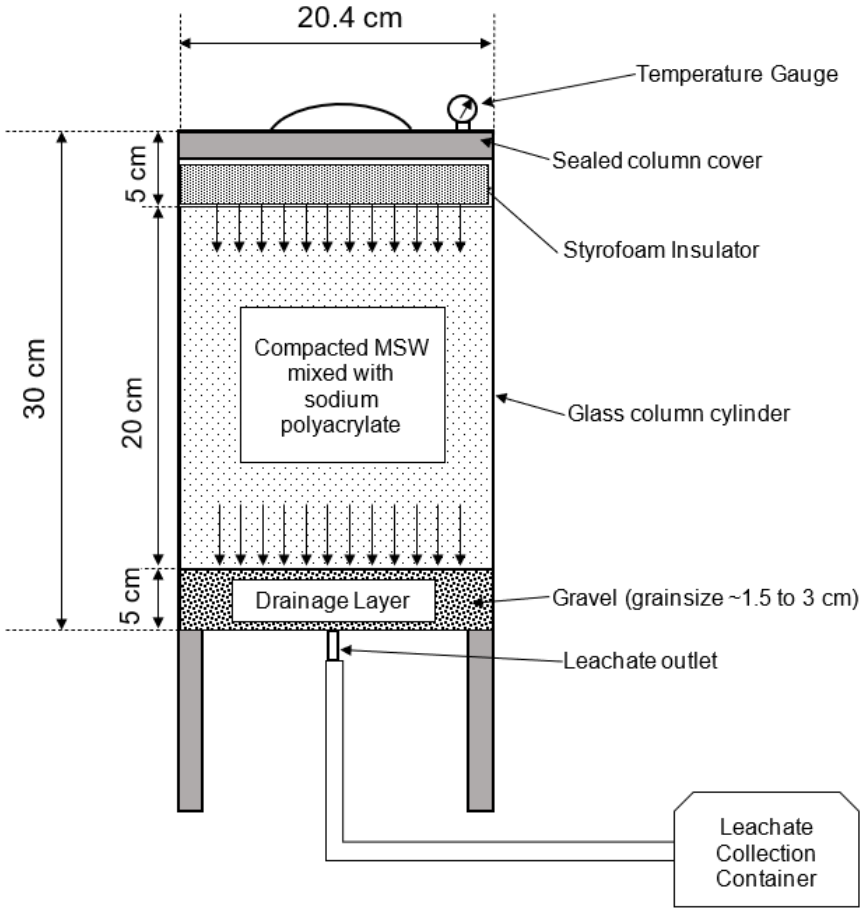
Waste Column Tests – MSW Spiked with Polyacrylate

- Waste shredded and spiked with 0, 1% and 5% dry polyacrylate particulate (by mass).
- Columns dosed with MSW leachate.
- Waste and leachate collected from MSW landfill in Madison area.

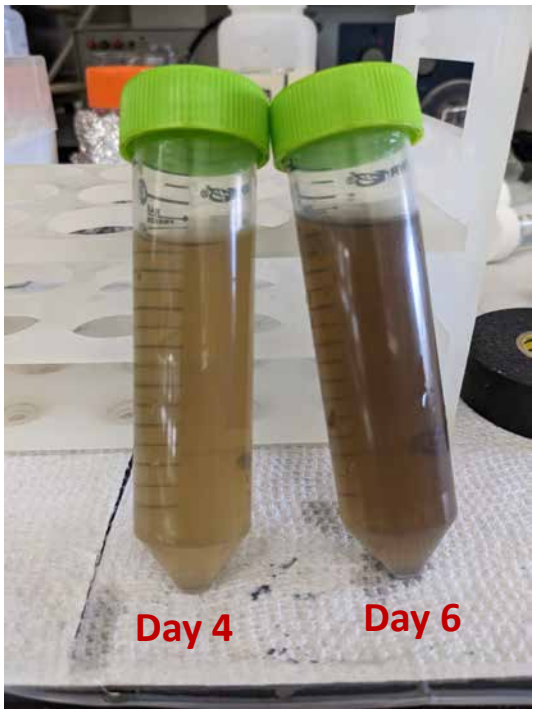


Waste Column Tests – MSW Spiked with Polyacrylate

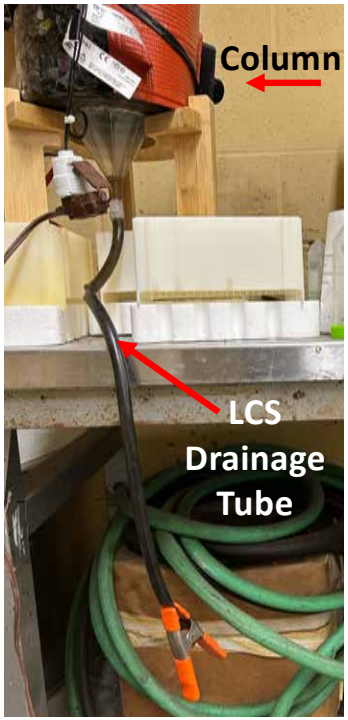
Waste column before and during testing



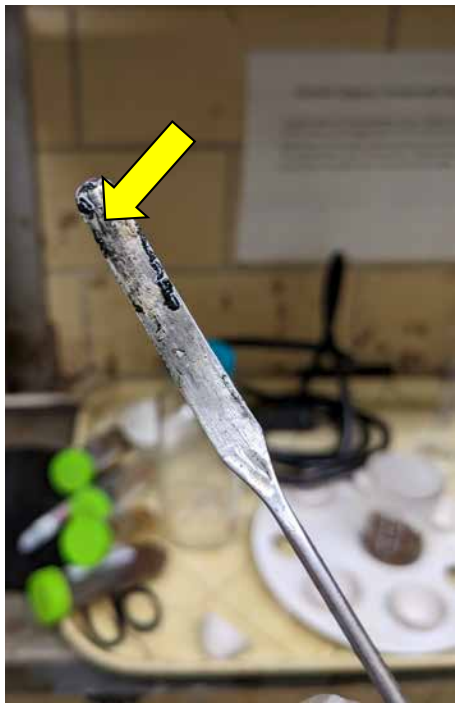
We Created Black Goo – At Least it Looks Like Goo!



Leachate collected from column



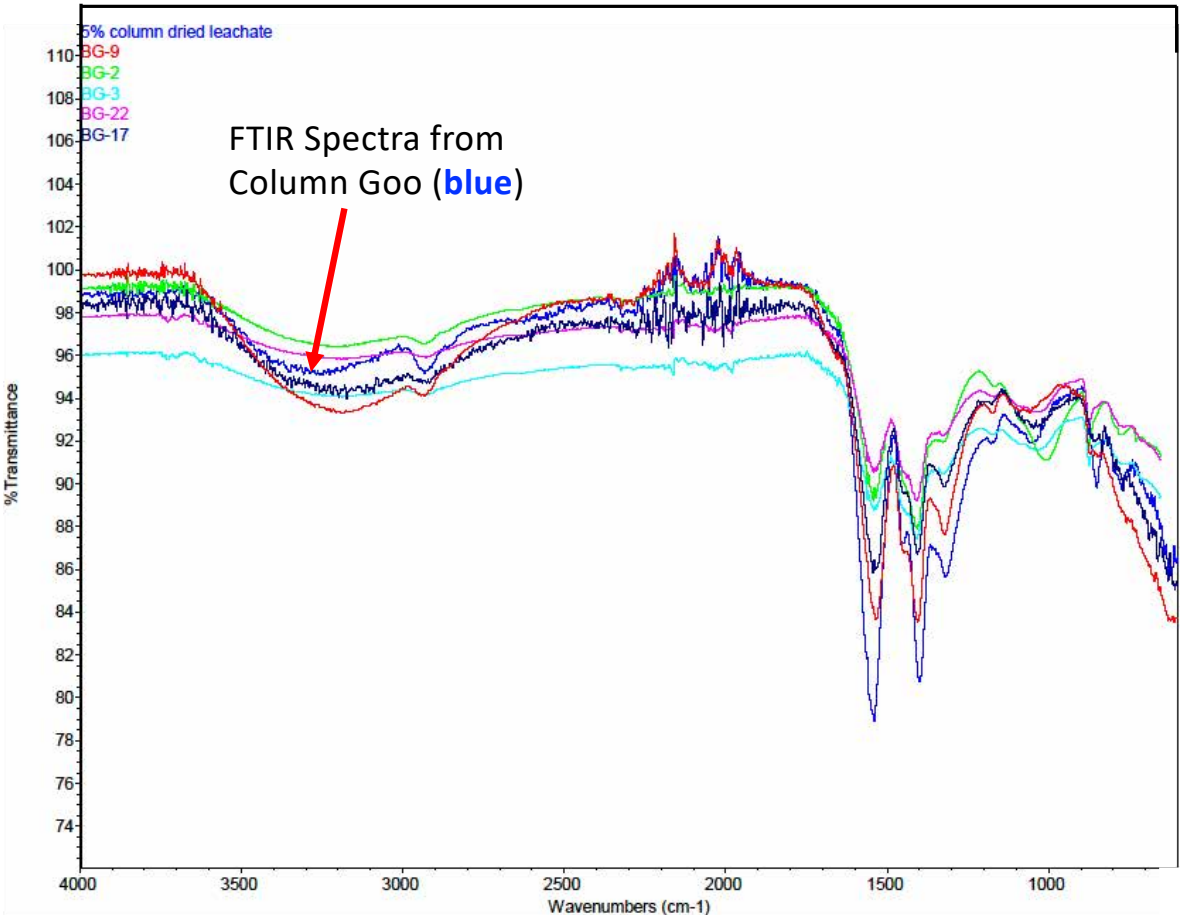
LCS tubing accumulating dark material



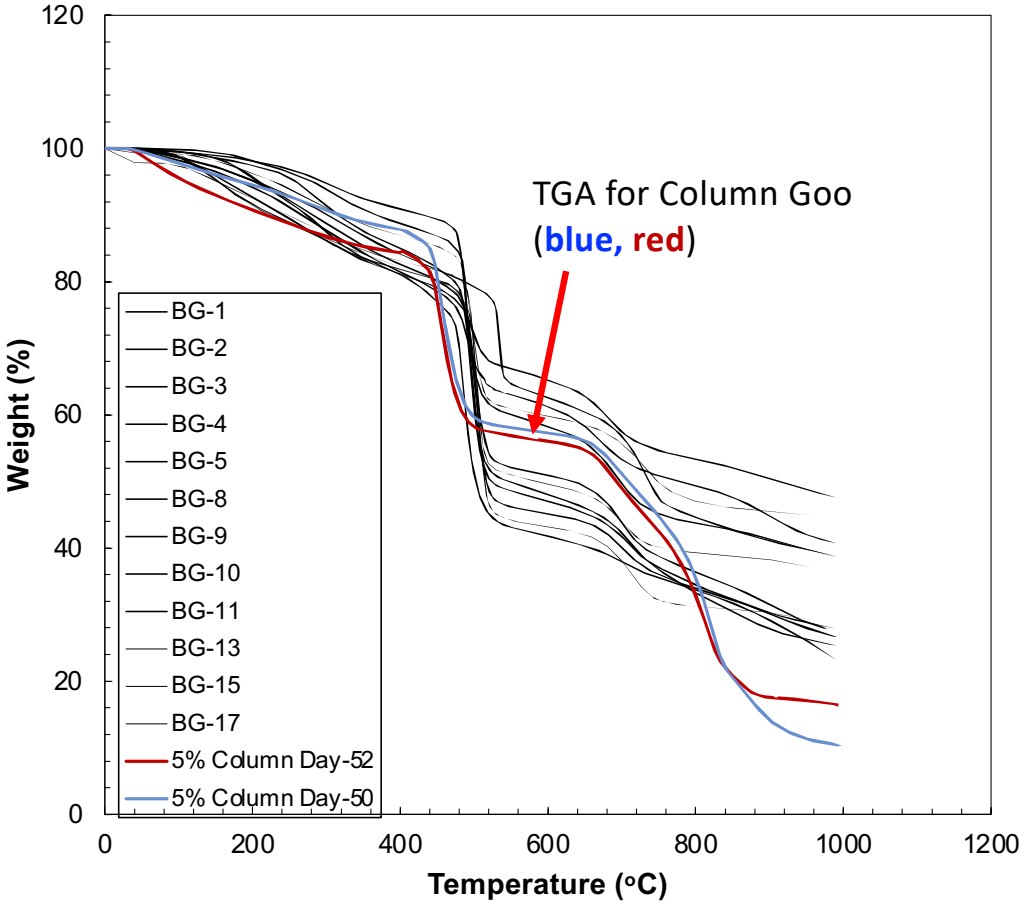
Sample of dark material in LCS tubing

FTIR Analysis on Black Goo from Column LCS

- Sample of black goo collected after 50 days of testing column spiked with 5% Na-polyacrylate.
- Compared with black goos BG-2, BG-3, BG-9, BG-17, and BG-22.



TGA on Goo from Column LCS

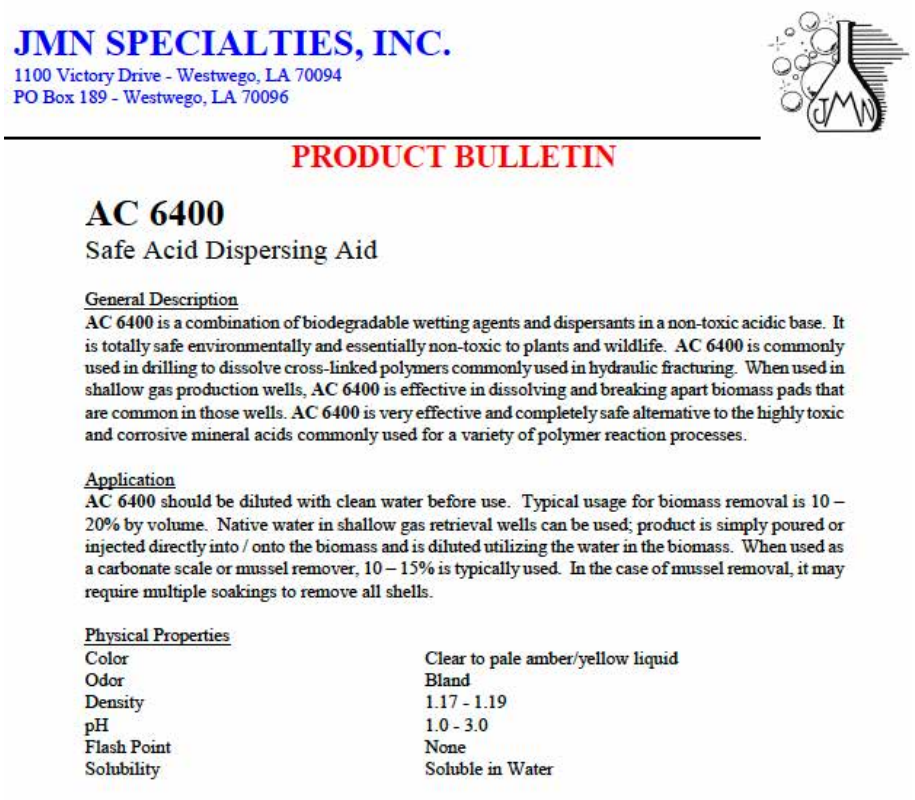


- TGA conducted on goo samples collected on days 50 and 52.
- Compared with 12 other goos.
- TGA similar. Somewhat lower loss at 500 °C may be due to entrained organic matter in actual goos.

Not All Black Liquids in Landfills are Black Goo

Black Goo vs. ETLF Black Liquid

How to Remedy Black Goo Problems?



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PRODUCT BULLETIN

AC 6400
Safe Acid Dispersing Aid

General Description
AC 6400 is a combination of biodegradable wetting agents and dispersants in a non-toxic acidic base. It is totally safe environmentally and essentially non-toxic to plants and wildlife. **AC 6400** is commonly used in drilling to dissolve cross-linked polymers commonly used in hydraulic fracturing. When used in shallow gas production wells, **AC 6400** is effective in dissolving and breaking apart biomass pads that are common in those wells. **AC 6400** is very effective and completely safe alternative to the highly toxic and corrosive mineral acids commonly used for a variety of polymer reaction processes.

Application
AC 6400 should be diluted with clean water before use. Typical usage for biomass removal is 10 – 20% by volume. Native water in shallow gas retrieval wells can be used; product is simply poured or injected directly into / onto the biomass and is diluted utilizing the water in the biomass. When used as a carbonate scale or mussel remover, 10 – 15% is typically used. In the case of mussel removal, it may require multiple soakings to remove all shells.

Physical Properties

Color	Clear to pale amber/yellow liquid
Odor	Bland
Density	1.17 - 1.19
pH	1.0 - 3.0
Flash Point	None
Solubility	Soluble in Water

Be careful regarding H&S using treatments. Know composition of treatment agent.

- Appropriate solution and removal methods not yet clear, as goo composition had not been defined previously.
- Some have found that acid washes with “AC 6400 Safe Acid Dispersing Aid” have been effective. 20% acid solution in sump using leachate in sump for dilution.
- Others have used a hot water flush. We are exploring hot saltwater flushes.

Keep it Moving

- Goo tends to accumulate in cooler quiescent zones (low shear)
  - LCS on surface of liner
  - Leachate sump
  - Dual-phase extraction pumps
  - Check valves
  - Pump chamber

- Polyacrylates dissolve in solution, but will agglomerate as concentration increases and temperature and fluid shear decrease.

- Keep the fluid moving (shear stresses) to keep the polymer flowing with liquid and not as separate sticky phase.

Black Goo: What is this stuff?

- Forensic chemical analysis suggests that black goos are predominantly hydrophilic superabsorbent polymers (polyacrylates, polyacrylamides).
- The “black” component appears to be from the reducing environment in which black goo is found, and is not intrinsic component.
- Black goos are largely abiotic (not biological), but microbial communities that live on black goos probably affect their physical behavior (stickiness, stretchiness).
- Breaking down black goo is complicated – brute force destruction of bonds in molecule. May affect containment system, health and safety.
- There is no magic solution – the primary components are ubiquitous in our economy (industry, homes, schools, etc.) and in our waste stream. Keep leachate moving appears to be critical.

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