Characterization of Solids from Oilfield Emulsions

Richard W. Cloud,[†] Rebecca L. Ramsey,[‡]
Robert A. Pultz,[‡] and Michael K. Poindexter[‡]

[†] Nalco Company, Naperville, Illinois; [‡] Nalco Energy Services, Sugar Land, Texas

rcloud@nalco.com

Introduction

Production of crude oil is generally accompanied by several other product phases, namely water, gas and solids. Pressure drops across chokes, concomitant gas evolution (due to pressure drops) and turbulence caused by various pipeline configurations can create difficult-to-resolve emulsions. Natural crude oil surfactants and solids exacerbate the problem further by migrating to the newly created oil-water interface and stabilizing the unwanted emulsions. Once the fluids arrive at the production facilities, a variety of vessels are employed to separate the oil, gas and water. Depending on the wettability of the solids, they will exit via one or both of the liquid phases. In a worse case scenario, the solids will accumulate at the oil-water interface.

Production treatment facilities feature a combination of increased residence time, gravity settling (to utilize the density differences of the phases), heat, centrifugation, and/or chemical treatment (*i.e.* demulsifiers) to help resolve the incoming emulsion. Producing and ultimately transporting oil within certain water specifications is critical to prevent pipeline corrosion damage. Additionally, shipping water down pipelines is not economical. Understanding the primary factors that contribute to emulsion stabilization remains a challenging endeavor due to the complexity of the mixtures. Solids, along with other constituents, are known to enhance emulsion stability.[1] With the aid of scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS), inorganic solids from various unresolved water-in-oil emulsions were characterized. In one instance, highly structured "salt scaffolds" were identified. These scaffolds appear to outline once existent droplets. From our knowledge and search of the literature, such structures have not been reported until now.

Characterization of Oilfield Emulsions

Compositionally, petroleum is one of the most complex organic mixtures known, as demonstrated by recent ultrahigh-resolution mass spectrometry studies.[2] Classification of crude oil typically involves fractionation into four broad polarity classes – saturates, aromatics, resins and asphaltenes (SARA).[3] Figure 1 illustrates these four organic fractions.

For most crude oils, the asphaltenes and resins constitute the natural surfactants. However, these fractions do not have the head-to-tail (hydrophilic-hydrophobic) molecular framework that is often characteristic of synthetic surfactants. Asphaltenes, which are defined by solubility properties (*i.e.* material that is aromatic soluble and aliphatic insoluble), constitute the highest molecular weight fraction and have garnered most of the attention regarding crude oil characterization. Model emulsion studies have clearly revealed the surface activity of this highest molecular weight crude oil fraction. However, asphaltenes and their properties alone have not been able to model and adequately describe emulsion stability as observed in the field. Other compositional factors clearly play a role in emulsion stabilization including, but not limited to, the often more abundant resin fraction as well as naphthenic acids, waxes (problematic at lower process temperatures), overall aromaticity of the dispersion media (*i.e.* the saturate and aromatic fractions) and solids. Inherent physical properties of an emulsion, which are clearly derived from the chemical make-up and process conditions, are also used to probe emulsion stability. Bulk viscosity of the external phase, as well as interfacial elasticity and viscosity, are useful parameters in quantifying emulsion strength. Recent work in our lab has shown that a variety of emulsion stability parameters correlate strongly with inorganic solid content.[4]

To identify the inorganic solid constituents that reside at or near the interface, unresolved emulsion from process facilities was isolated. Following the ASTM D4807-88 procedure,[5] emulsions were diluted with hot toluene, filtered through a 0.45 μm filter membrane and rinsed further with hot toluene. Washing with toluene removed most of the residual organic material that was associated with the solids. Solid samples were then dried and their content determined gravimetrically.

A detailed characterization of the filtered solids was accomplished via scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Images of these solids were taken in backscatter electron mode (BEI) to best highlight differences in elemental composition using atomic number contrast and to indicate distinct variations in morphology. EDS analyses for composition are shown of selected solid components. All analyses were run after coating the filtered solids with conductive graphite and collected at a 20kV excitation voltage. Below are SEM and EDS results from a few of these materials.

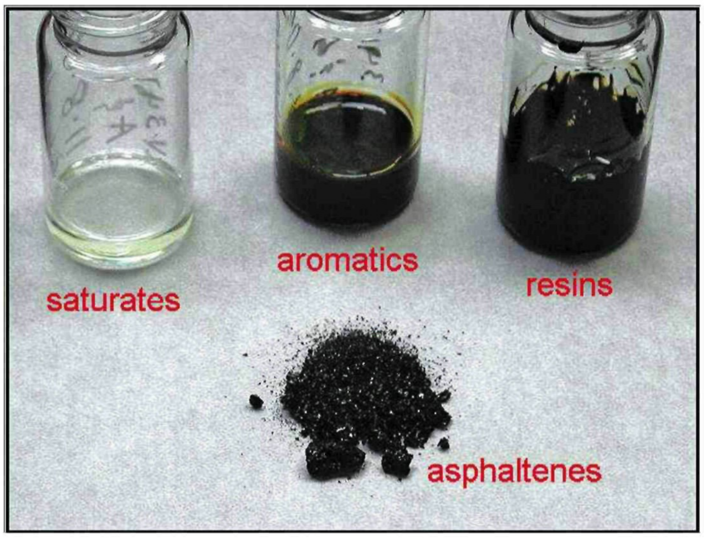


Figure 1. *Illustration of four main fractions isolated from an asphaltenic crude oil.*

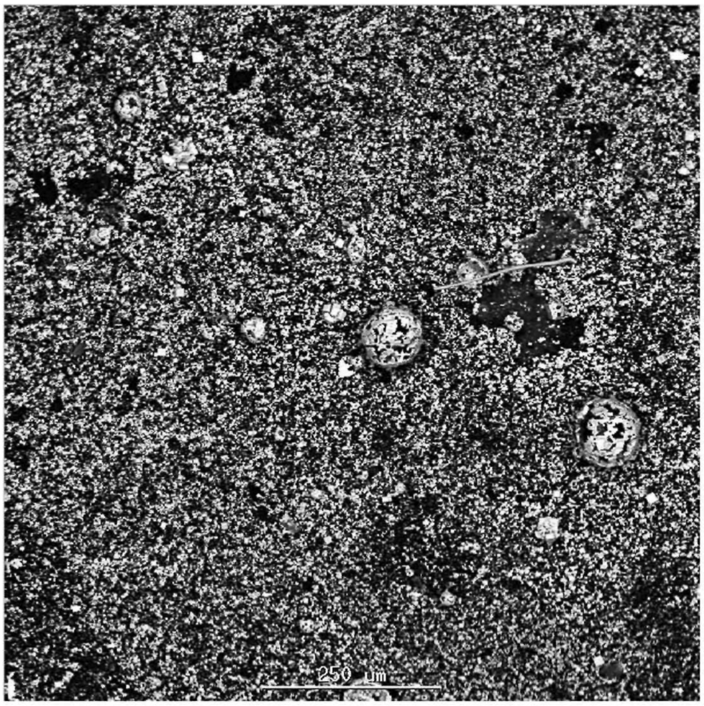


Figure 2. *BEI (100x) of solids isolated from a Gulf of Mexico emulsion.*

2006 MICROSCOPY COURSES

McCRONE RESEARCH INSTITUTE

2820 SOUTH MICHIGAN AVE., CHICAGO, IL 60616-3292
312-842-7100 ~ www.mcri.org ~ registrar@mcri.org

METHODS IN FORENSIC AND TRACE EVIDENCE ANALYSIS

Applied Polarized Light Microscopy (1201)
same as Forensic Microscopy (1204)
Jan 23-27 March 20-24 April 24-28
June 5-9 July 17-21 August 14-18
Sept. 11-15 Nov. 13-17 Dec. 4-8

Advanced Polarized Light Microscopy (1251*)
Same as Adv. Forensic Microscopy (1701*)
Feb. 6-10

Chemical Microscopy (1202)
(taught in Ithaca, NY at Cornell University)
July 31-August 4

Forensic Hair and Fiber Microscopy (1207)
June 12-16

Forensic Microscopy of Glass (1712)
INQUIRE

Microscopy of Illicit Drugs and Excipients (1726*) INQUIRE

Forensic Paint Microscopy (1715*)
Aug. 7-11

Microscopy of Explosives (1722*)
March 13-17 Oct. 9-13

Microchemical Methods (1270A*)
Oct. 2-6

Microscopical Identification of Asbestos (1608A)
Jan 9-13 Feb. 20-24 April 10-14
May 1-5 July 24-28 Aug. 21-25
Oct. 9-13 Dec. 11-15

Advanced Asbestos Identification (1608B*)
Jan. 16-20 May 8-12 Aug. 28-Sept. 1
Oct. 16-20

Microscopy of White Powders (1550*)
Jan. 30-Feb. 3 April 3-7 June 19-23
Sept. 25-29 Dec. 18-22

Sample Preparation and Manipulation for Microanalysis (1501E)
May 15-19 Sept. 25-29

METHODS IN MATERIALS SCIENCE

Applied Polarized Light Microscopy (1201)/
same as Forensic Microscopy (1204)
Jan 23-27 March 20-24 April 24-28
June 5-9 July 17-21 August 14-18
Sept. 11-15 Nov. 13-17 Dec. 4-8

Advanced Polarized Light Microscopy (1251*)
Same as Adv. Forensic Microscopy (1701*)
Feb. 6-10

Fluorescence Microscopy (1210)
April 12-14 June 28-30 Oct. 4-6

Practical Infrared Microspectroscopy - FTIR (1422)
March 27-31 June 12-16 Sept. 18-22
Dec. 11-15

Raman Microscopy (1430)
Feb. 20-22 Aug. 14-16

Scanning Electron Microscopy and X-Ray Microanalysis (1402)
May 22-26 Nov. 6-10

Polymer Microscopy (1205)
INQUIRE

DIGITAL IMAGING

Digital Imaging and Photomicrography (1105)
March 6-10 Oct. 30-Nov. 3

A custom-designed course held at your facility can be conducted.
Contact the registrar for further details.

*Prerequisites: Course 1201/1202/1204 (Applied Polarized Light Microscopy/Chemical Microscopy/Forensic Microscopy) or consent of instructor; 1608A for 1608B; 1630 for 1631 or 1632.

CHEMICAL, ENVIRONMENTAL AND BIOLOGICAL HAZARDS

Microscopy of White Powders (1550*)
Jan. 30-Feb. 3 April 3-7 June 19-23
Sept. 25-29 Dec. 18-22

Microscopy of Explosives (1722*)
March 13-17 Oct. 9-13

Indoor Air Quality: Fungal Spore Identification (1630)
Feb. 13-17 May 15-19 Aug. 28-Sept. 1
Nov. 27-Dec. 1

Advanced Indoor Air Quality: Fungal Culture Plate Identification (1632*)
INQUIRE

Indoor Air Quality: Identification of House Dust and Indoor Particles (1633)
INQUIRE

Microscopical Identification of Asbestos (1608A)
Jan 9-13 Feb. 20-24 April 10-14
May 1-5 July 24-28 Aug. 21-25
Oct. 9-13 Dec. 11-15

Advanced Asbestos Identification (1608B*)
Jan. 16-20 May 8-12 Aug. 28-Sept. 1
Oct. 16-20

Asbestos Fiber Counting (NIOSH 582) (1616)
Feb. 27-March 3 June 26-30 Sept. 23-27

SPECIALTY COURSES

Sample Preparation and Manipulation for Microanalysis (1501E)
May 15-19 Sept. 25-29

Raman Microscopy (1430)
Feb. 20-22 Aug. 14-16

Pharmaceutical Microscopy (1203)
Feb. 27-March 3

Microscopy for Art Conservators (1206)
April 17-21 Oct. 23-27

Microscope Cleaning, Repair and Adjustment (1301) Feb. 16-17

More Information about McCrone Research Institute, microscopy courses, the Microscope publications and INTER/MICRO-2006 can be found on our website at: WWW.MCRI.ORG

Figure 2 shows a general view of collected solids from a Gulf of Mexico emulsion. These solids display both loose, single crystals on the membrane surface and intimately joined crystals within a spherical framework, *i.e.* as salt scaffolds.

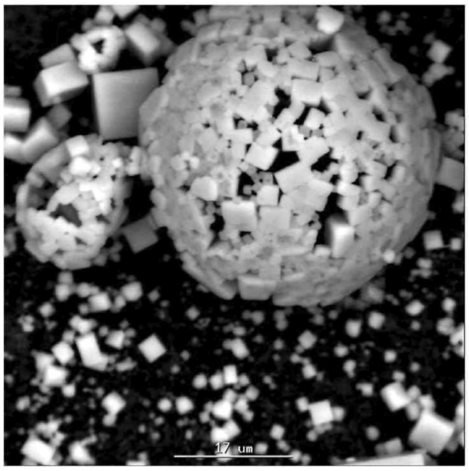
Figure 3a shows an enlarged view from a second portion of the Gulf of Mexico emulsion. In this instance, the large salt scaffold is intact where both the size and form of the structure is apparent, while the small salt scaffold to the left has partially collapsed. **Figure 3b** shows that the cubic shaped crystals are sodium chloride.

Figure 4a shows a general view of collected solids from an Eastern Montana emulsion. Here the emulsion solids appear to have formed in a distinct time sequence. The thin rod-like crystals appear to have solidified first and then later encapsulated within the cubic crystals. **Figure 4b** shows that the cubic crystals (line profile) are again sodium chloride, while the thin rods (solid profile) are enriched with calcium, sulfur and potassium. The sodium and chloride levels detected in the thin rods may actually result, in part or all, from the adjacent cubic crystals.

Figure 5a shows a general view of collected solids from an Alberta emulsion. These solids have formed a dendritic, mat-like structure of non-distinct individual crystals. Some of these dendrites appear to contain a generally uniform appearance. Other dendrites have a varied appearance where the internal portion displays a coarser and brighter (in BEI) structure. **Figure 5b** shows that the darker, outer dendrite (line profile) contains a mixed composition having sodium, silicon, chloride and low sulfur. The brighter, inner dendrite (solid profile) contains a nearly pure sodium chloride composition.

Conclusions

SEM/EDS analysis was used to characterize inorganic solids from oilfield emulsions. This analysis was able to provide key insights into the behavior of these emulsions and to better understand the relationship of these solids to emulsion stability. The solid structures illustrated in these examples reveal unique architectures that are often undetected in many crude oil emulsion analyses. ■



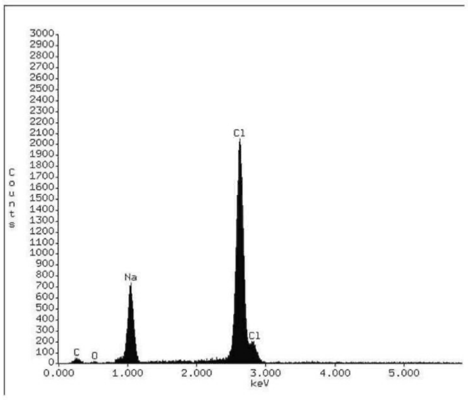
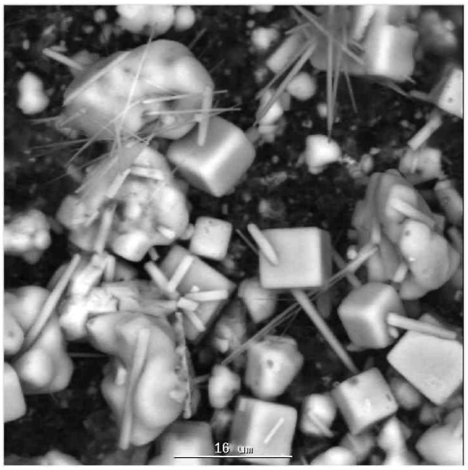


Figure 3a. *BEI (1,500x) of solids isolated from a Gulf of Mexico emulsion.*
Figure 3b. *EDS spectrum of crystal solids within intact 'salt scaffold' shell, i.e. sodium chloride.*



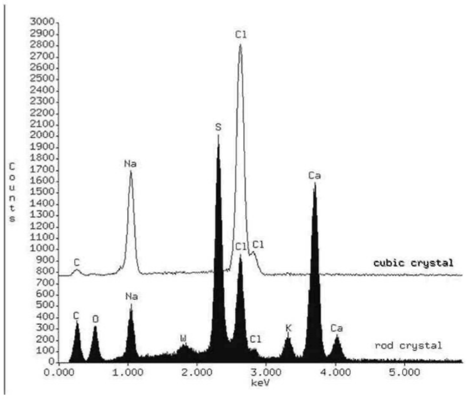
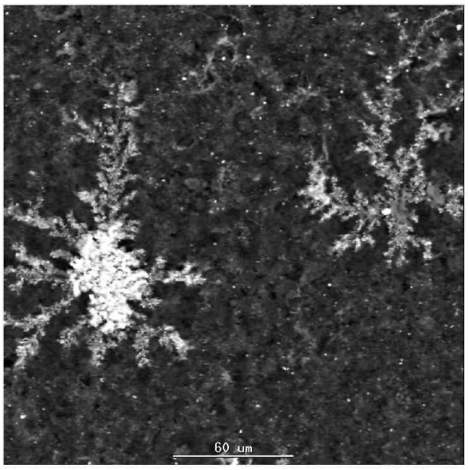


Figure 4a. *BEI (1,500x) of solids isolated from an eastern Montana emulsion.*
Figure 4b. *EDS spectrum of crystal solids, line spectrum of cubic crystals, i.e. sodium chloride; solid spectrum of thin rods, i.e. calcium, sulfur and potassium enriched.*



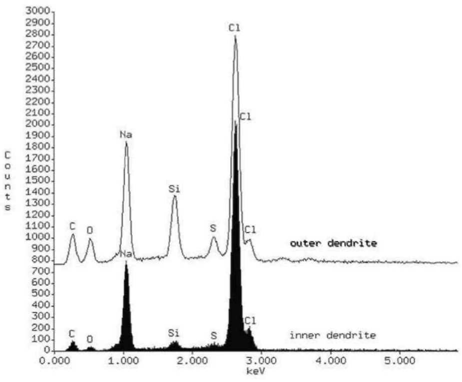


Figure 5a. *BEI (400x) of solids isolated from an Alberta emulsion produced by steam-assisted gravity drainage.*

Figure 5b. *EDS spectrum of crystal solids, line spectrum of outer dendrite formation; solid spectrum of inner (bright) dendrite formation.*

References

1. Aveyard, R.; Clint, J. H. Solid Particles at Liquid Interfaces, Including Their Effects on Emulsion and Foam Stability. In *Adsorption and Aggregation of Surfactants in Solution*; Surfactant Science Series, Marcel Dekker: New York, 2003; Vol. 109, Chapter 3, p 61-90.
2. Marshall, A. G.; Rodgers, R. P. Petroleomics: The Next Grand Challenge for Chemical Analysis. *Acc. Chem. Res.* **2004**, *37*, 53-59.
3. Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker: New York, 1998, p 269.
4. Poindexter, M. K.; Chuai, S.; Marble, R. A.; Marsh, S. C. Solid Content Dominates Emulsion Stability Predictions. *Energy Fuels* **2005**, *19*, 1346-1352.
5. ASTM D4807-88: Standard Test Method for Sediment in Crude Oil by Membrane Filtration, 1999.

Expertise and joie de vivre…

3rd Annual Microscopy Workshop
8 - 12 May, 2006

McGill University, Montréal, Canada

ADVANCED TECHNIQUES in MICROSCOPY for MATERIALS CHARACTERIZATION

Choose your sessions "à la carte":

SEM I	SEM II
X-ray Analysis I	X-ray Analysis II
Sample Preparation	Advanced Probe
Image Analysis I	Image Analysis II
EBSD, CL, EBIC/EBIV	

These topics will be covered :

High Resolution FESEM
Variable Pressure SEM
Spectrum Imaging
Focused Ion Beam
Dual Beam Systems
Thin Film Measurements
Monte Carlo Simulations
EBSD
Quantitative EDS
Stereology
Ion Beam Etching
3-D Atom Probe
Nano-SIMS

… AND MANY MORE!!!

The lecturers are renowned in their fields :

David Joy
Eric Lifshin
George Vander Voort
Rocco Cerchiara
Scott Sitzman
Brendan Griffin
Raynald Gauvin
Pierre Hovington
Marin Lagacé
Tom Kelly

McGill
Department of Mining, Metals and Materials Engineering

Hydro Québec
Institut de recherche

Regroupement Aluminium
REGAL
Réseau de recherche sur l'aluminium

Information : Prof. Raynald Gauvin
(514) 398-8951
raynald.gauvin@mcgill.ca

www.ebeamworkshop.com

INTRODUCING
The New High-Resolution Turbo Sputter Coater

the Polaron range

NEW!
Model SC5750

- Full Automatic Control
- Ultra High Resolution
- Turbo Molecular Pumping System
- Modular Control Electronics
- Suitable for Cr, Al, Ir, Au, Pt, etc.

EBSciences

ADDING BRILLIANCE TO YOUR VISION

800-992-9037 or 860-635-0411
e-mail: ebs@ebsciences.com
www.ebsciences.com

https://doi.org/10.1017/S1551929500053955 Published online by Cambridge University Press