Comprehensive Analysis of Changes in Crude Oil Chemical Composition during Biosouring and Treatments

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Introduction

Biosouring in crude oil reservoirs by sulfate-reducing microbial communities (SRCs) results in hydrogen sulfide production, precipitation of metal sulfide complexes, increased industrial costs of petroleum production, and exposure issues for personnel. Potential biosouring treatment strategies include nitrate or perchlorate injections into reservoirs. This study uses gas chromatography combined with vacuum ultraviolet ionization, as well as Fourier transform ion cyclotron resonance mass spectrometry, to characterize biodegradation changes in the oil's chemical composition in sulfate, nitrate, and perchlorate reducing environments.

Experimental

Ultra-high-resolution 9.4T FT-ICR MS analysis was used at the NHMFL in this study.

Results and Discussion

Crude oil hydrocarbons were selectively transformed based on molecular weight and compound class in the biosouring control environment. Both the nitrate and the perchlorate treatments significantly reduced sulfide production; however, the nitrate treatment enhanced crude oil biotransformation, while the perchlorate treatment inhibited crude oil biotransformation. Nitrogen- and oxygen-containing biodegradation products, particularly with chemical formulas consistent with monocarboxylic and dicarboxylic acids containing 10−60 carbon atoms, were observed in the oil samples from both the souring control and the nitrate-treated columns but were not observed in the oil samples from the perchlorate-treated column. These results demonstrate that hydrocarbon degradation and product formation of crude oil can span hydrocarbon isomers and molecular weights up to C_{60} and double-bond equivalent classes ranging from straight-chain alkanes to polycyclic aromatic hydrocarbons. Our results also strongly suggest that perchlorate injections may provide a preferred strategy to treat biosouring through inhibition of biotransformation. Microbial communities structures shifted towards nitrate reducing and perchlorate reducing bacteria upon the introduction of alternate nitrate and perchlorate ions, respectively. Figure 1 (attached in jpeg) illustrates isoabundance-contoured plots of double-bond equivalents (N_{DBE}) vs carbon number for the parent North Sea crude oil, oil from 70 days into souring, oil from 70 days into the nitrate treatment, and oil from 70 days into the perchlorate treatment measured by (a) positive electrospray ionization and (b) negative electrospray ionization combined with FT-ICR MS. Each compositional image is normalized to the most abundant species within that heteroatom class for each mass spectrum

Conclusions

The differences in transformation patterns observed in the oils from the souring control environment, the nitrate-treated environment, and the perchlorate-treated environment demonstrate that the degree of microbial biotransformation of crude oil is specific to the presence of a dominant electron acceptor, the relative abundances of microbial communities, and the availability of specific crude oil components as electron donors and carbon sources. This study reveals that hydrocarbon degradation and product formation of crude oil is not limited to a narrow range of compound classes or molecular weights. Isomers of hydrocarbons from C_{10}−C_{30} were degraded, and carboxylic acid products were formed up to molecular sizes of C_{60}. The biotransformation patterns and product formations revealed in this work can constrain and strengthen existing models of crude oil degradation patterns for industrial and environmental applications.

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References (citation of this publication)

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