Chapter 2
Sulfur and Nitrogen Chemical Speciation in Crude Oils and Related Carbonaceous Materials

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ABSTRACT

This chapter gives an overview of sulfur x-ray absorption near edge spectroscopy (XANES) studies performed on some carbonaceous materials, viz. crude oil and related materials (asphaltenes, kerogens, bitumens, and resins), and coals. Thiophene, sulfide, sulfoxide, sulfone, pyrite, and sulfate are found in varying amounts in these materials. In source rock bitumens, sulfoxide is more abundant than in the kerogens, while within the kerogens, the less aromatic Type I samples show a smaller ratio of thiophenic/sulfidic sulfur than in Type II samples. Petroleum asphaltenes have a similar sulfur chemistry, regardless of the source or the burial depth. Resins and oil fractions retain the polar sulfoxide species of the parent oil similar to the more polar asphaltenes fractions. More aromatic sulfur species also dominate in the more matured coals than in the younger coals. Studies of nitrogen XANES also reveal that aromatic forms of nitrogen prevail in samples with increased aromatic carbon.

INTRODUCTION

Sulfur has been an age old impediment in the processing and utilization of fossil fuels, such as crude oil. The presence of sulfur in crude oil and its by-products can make refining tasks very difficult, as it reacts with catalysts and produces corrosive poisons. Noble metal catalysts used in refining processes form corrosive agents in the presence of sulfur, as sulfur can bond strongly with the catalysts (Ruiz-

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Figure 1. Sulfur removal from Athabasca bitumen is stored as elemental sulfur in exposed enormous yellow mounds

Guerrero, 2006), and corrode refining equipment (Manning & Thompson, 1991). Sulfur is sometimes found in the form of H_2S in crude oils, and is lethal even at small concentrations (~100 ppm) and is a major concern in creating extreme brittleness in many metals. In addition, burning of fossil fuels with significant amounts of sulfur releases sulfur dioxide into the atmosphere causing environmental hazards (Orr & White, 1990). The presence of sulfur in fuels serves no useful purpose (Orr, 1990), as some of them contain only minor quantities of sulfur and generally removal of sulfur from fuels is a primary objective in processing. Sulfur removal for Athabasca bitumen has led to storage of elemental sulfur in huge yellow mounds as seen in Figure 1.

Sulfur chemistry also gives us a picture of the geochemical environment of the deposition of the source materials for the fossil fuel energy resources (Orr, 1990). Organo-sulfur compounds in crude oils provides information about the formation, migration, and thermal maturity of the oil. (Hughes, 1989; Lin, 1988; Wang, 2005; Radke, 1982). Sulfur content in kerogen and bitumen is an important indicator of how these fractions ultimately produce oil and gas (Pomerantz, 2013; Lewan, 1985, 1998; Seewald, 1998; Sinninghe, 1989, 1990; Gransch, 1974). The presence of sulfur also affects solubility and other characteristics of the important fractions of crude oils, such as asphaltenes (Mitra-Kirtley, 2007).

Sulfur content in crude oils and bitumens ranges from a fraction of a percent to 14% (Orr 1990), making it generally the most abundant element after carbon and hydrogen. The world reserves of sweet crude oils (crude oils with low sulfur content) are becoming more limited as time progresses, making the refining of more sour (high sulfur content) varieties a necessity (Purcell, 2007; Swain, 1998). Atmospheric and vacuum bottom residues are increasingly converted to lighter products (Purcell, 2007), and desulfurization of these reserves is becoming increasingly favored.

Sulfur in coal also reveals a wealth of information about the depositional environment. Much of the sulfur in low sulfur coals is derived from the deposited plant material. The presence of a brackish envi-