



Short communication

Characterization of vanadium in oil sands fluid petroleum coke using electron microscopy



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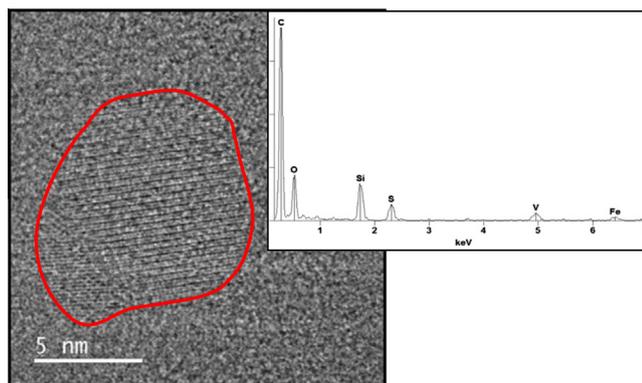
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HIGHLIGHTS

- Inorganic vanadium nanocrystals are identified in oil sands fluid petroleum coke.
- Vanadium is present in distinct nanocrystals with silicon, oxygen, sulfur, and iron.
- Nanocrystals embedded in carbon matrix are nearly spherical with crystal lattices.
- Long-term fate of mineral vanadium nanocrystals in coke stockpiles may be modeled.
- Efficient extraction methods can be developed to make a saleable vanadium product.

GRAPHICAL ABSTRACT



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ABSTRACT

Naturally occurring vanadium is found in many heavy oils and bitumen, which are upgraded to synthetic crude oil via the coking process. During coking the vanadium concentrates in the solid heavy oil product, petroleum coke. However, potential releases of this toxic vanadium, either due to long term natural leaching from stockpiles or during combustion, presents environmental and health concerns. In this study, the vanadium present in petroleum coke was characterized using high resolution transmission electron microscope imaging with energy-dispersive X-ray spectroscopy. Vanadium was observed in nanocrystalline mineral clusters, and is consistently associated with silicon, oxygen, sulfur, and iron. A distinct lattice structure is observed in these nanocrystals. This result is different from previous theories, which predicted that the coking process did not decompose the vanadyl porphyrins present in bitumen. By identifying the vanadium nanocrystals in petroleum coke, the long term fate of vanadium in petroleum coke stockpiles in reclaimed land may be predicted.

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Abbreviations: PC, petroleum coke; BF, bright field; TEM, transmission electron microscope; ADF, annular dark field; OSFPC, oil sands fluid petroleum coke; EDS, energy-dispersive X-ray spectroscopy; ICP-OES, inductively coupled plasma optical emission spectroscopy.

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1. Introduction

Vanadium metal has a variety of naturally occurring forms, including vanadium oxides, organometallic vanadyl compounds, and naturally occurring minerals. It is commonly used in steel alloys to increase strength and corrosion resistance [1,2]. Naturally occurring vanadium is known to be present in crude oil deposits,

first identified by Treibs in 1934 [3]. Compared to lighter crude oils, it has been observed that larger quantities of vanadium are present in heavier oils [4–6], including bitumen found in the Canadian oil sands. The Canadian oil sands are a naturally occurring bitumen deposit located in northern Alberta and Saskatchewan. The concentration of vanadium in Canadian oil sands bitumen is approximately 225 ppm [7]. The vanadium present in crude oils and bitumen is in the form of organometallic vanadyl compounds, including porphyrin ring vanadyl compound, where vanadium is chelated with nitrogen [4,6,8–10] and non-porphyrin organometallics, with vanadium chelated with nitrogen and oxygen [11,12].

Naturally occurring vanadium in heavy oils and bitumen must be removed prior to upgrading, since it will cause significant corrosion and deactivation of the catalysts during processing [4–6]. There are several techniques to remove vanadium from bitumen; one of the common techniques is coking: a process that removes carbon from bitumen producing petroleum coke (PC). There are two coking processes, fluid coking, which is a continuous coking process, and delayed coking, which is a batch coking process [10,13]. It has been shown that coking removes the majority of the vanadium within the bitumen, thus concentrating the vanadium in the PC [14,15]. The average vanadium concentration within fluid petroleum coke (FPC) is estimated to be 0.135 wt.% [13]. The average vanadium concentration in delayed petroleum coke (DPC) is approximately 0.093 wt.% [16]. However, the concentration of vanadium in PC samples will vary depending on the concentration of vanadium in the bitumen ore. Furimsky estimated that between 1979 and 1995, the variation in vanadium content in FPC was 0.129–0.141 wt.% [13]. Stuart and Pippin estimated the vanadium content of fluid coke to be 0.034 wt.%; however, they did not specify the source of bitumen used to prepare the coke [17].

Currently PC is largely a stockpiled coking product because it is enriched in environmentally harmful elements, primarily sulfur, which would be released if the coke were combusted as a traditional fuel similar to coal [13,18]. In FPC, the sulfur content is estimated to be 6.6 ± 0.27 wt.%, while in DPC, the sulfur content is estimated to be 5.8 ± 0.18 wt.% [13]. Another key concern with the combustion of PC is the toxicity of the vanadium pentoxide compounds formed and released during combustion [19]. At the end of 2013, it was estimated that 84 million tonnes of PC had been stockpiled [18]. However, stockpiling PC is not a long term solution, due to the high production rates [20]. One of the proposed solutions is to use PC for future land reclamation. However, it has been shown that moderate amounts of metal contaminants, including vanadium, may naturally leach from the PC, resulting in contamination of the reclaimed land above current toxicity guidelines [21–24].

The potential environmental and toxic impacts of stockpiling, and further processing PC can be addressed by identifying the chemical structure of vanadium in the PC. This knowledge can be used to predict the fate of vanadium under natural land reclamation conditions or to develop an economical and efficient extraction process, to produce a saleable product.

The current study uses high resolution transmission electron microscope (TEM) imaging and analysis to identify the structure of the vanadium deposits within FPC.

2. Experimental

2.1. Raw materials

Fluid petroleum coke (FPC), supplied by Syncrude Canada Ltd., was sampled randomly from the drum, and then was sieved to particles between 150 and 212 μm . Sample characterization was

performed using two methods. Ultimate chemical analysis of the FPC was performed using the Exeter Analytical CE-440 Elemental Analyzer, which determines the carbon, nitrogen, hydrogen, and sulfur content of the sample by combustion. The metals content of the FPC was determined using ASTM standard ashing techniques and acid digestion, followed by inductively couple plasma optical emission spectrometry (ICP-OES), as outlined below. Other techniques to perform this analysis are available such as microwave assisted wet acid digestion [5,6,25,26]. Ashing was performed using the American Society of the International Association for Testing and Materials (ASTM-International) standard designation D4422-13, Standard Test Method for Ash in Analysis of Petroleum Coke [27]. Approximately 5 g of FPC was crushed and then weighed into ceramic crucibles and placed in a 700 °C muffle furnace for 24 h. The ash samples were then transferred to aqua regia solutions, of 3 parts hydrochloric acid and 1 part nitric acid, and digested at 50 °C for 48 h, using a hot water shaker at 150 rpm. The acid digested samples were diluted and the concentration of vanadium in the samples were analyzed using a Perkins Elmer Optima 7300 Dual View ICP-OES.

2.2. Transmission electron microscope sample preparation and observation

A small amount of FPC was placed in ethanol and crushed using a mortar and pestle to make thin coke flakes. The ethanol-coke suspension was dropped on a copper TEM grid and allowed to dry at ambient conditions. To avoid artifacts in the results and maintain the composition of the FPC, heating and Ar-sputtering were not performed during TEM specimen preparation.

The TEM used for imaging and analysis was supplied by Japan Electron Optics Laboratory Company, Limited.; the TEM model is JEOL-ARM200CF, with aberration corrector on the probe side. An electron accelerating voltage of 200 kV and a probe forming aperture of 24.5 mrad were used during analysis. Both annular dark field (ADF) and bright field (BF) images were observed and the spans for those images were 68–280 and 0–17 mrad, respectively. Energy-dispersive X-ray spectroscopy (EDS) signal was detected using a silicon drift detector, with a detection range around 0.8 steradians, which is a detection angle almost four times greater than conventional Si–Li detector. Furthermore, since this instrument uses a cold field emission gun, the energy spreading is around 0.3 eV and a spatial resolution of 0.07 nm can be achieved.

3. Results and discussion

3.1. Chemical composition of fluid petroleum coke

Table 1 presents the carbon, hydrogen, nitrogen, sulfur, and ash content, and the metallic components of the ash, in FPC. Carbon,

Table 1
Chemical composition of oil sands fluid petroleum coke. Analysis performed using elemental analysis, and acid digestion with ICP-OES analysis.

Ultimate analysis	Oil sands fluid coke composition
Carbon content (wt.%)	84.43 ± 1.27
Hydrogen content (wt.%)	1.85 ± 0.07
Nitrogen content (wt.%)	1.78 ± 0.35
Sulfur content (wt.%)	7.54 ± 0.65
Ash content (wt.%)	3.72 ± 0.03
<i>ICP-OES analysis</i>	
Vanadium content (wt.%)	0.11 ± 0.01
Iron content (wt.%)	0.13 ± 0.02
Calcium content (wt.%)	0.12 ± 0.01
Nickel content (wt.%)	0.011 ± 0.001

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