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Formation of fine particles enriched by V and Ni from heavy oil combustion: Anthropogenic sources and drop-tube furnace experiments

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Abstract

The present study attempts to investigate the emission characteristics of fine particles with special emphasis on nickel and vanadium metal elements emitted from the heavy oil combustion in industrial boilers and power plant, which are typical anthropogenic sources in Korea. A series of combustion experiments were performed to investigate the emission characteristics of particles in the size range of submicron by means of drop-tube furnace with three major domestic heavy oils. Cascade impactors were utilized to determine the size distribution of particulates as well as to analyze the partitioning enrichment of vanadium and nickel in various size ranges. Experimental results were compared with field data of particle size distribution and metal partitioning at commercial utility boilers with heavy oil combustion. Such data were interpreted by chemical equilibrium and particle growth mechanism by means of computational models. In general, fine particles were the major portion of PM_{10} emitted from the heavy oil combustion, with significant fraction of ultra-fine particles. The formation of ultra-fine particles through nucleation/condensation/coagulation from heavy oil combustion was confirmed by field and experimental data. Vanadium and nickel were more enriched in fine particles, particularly in ultra-fine particles. The conventional air pollution devices showed inefficient capability to remove ultra-fine particles enriched with hazardous transition metal elements such as vanadium and nickel.

Keywords: Combustion; Heavy oil; Vanadium; Nickel; Ultra-fine particles

1. Introduction

Airborne particulate matter has been the primary focus of several epidemiological studies, which reported a correlation between adverse health effects and the particle concentration levels

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(Dockery et al., 1993; Ozkaynak et al., 1993). US Environmental Protection Agency (EPA) established National Ambient Air Quality Standards (NAAQS) for the six major criteria air pollutants, among which particulate matters less than 10 μm (PM_{10}) and particulate matters less than 2.5 μm ($PM_{2.5}$) in aerodynamic diameter are associated with adverse health effects such as asthma, respiratory disease, and mortality (US EPA, 1997). World Health Organization (WHO regional office for Europe) reported various exposure studies designed for the evaluation of toxic effects associated with physico-chemical properties of fine particulates (WHO Europe, 2000). Recent epidemiological studies have also indicated a strong correlation between lung cancer-induced mortality and the concentration level of fine particulates (Burnett et al., 2001; Pope et al., 2002; Krewski et al., 2005). Both the size and the chemical composition of the particulates are attributed to the adverse health effects. Adverse health effects of particulates becomes severer as particulates are enriched by hazardous metal elements such as vanadium and nickel, which are usually originated from the fuel combustion of heavy oils (Campen et al., 2001; Kodavanti et al., 2001).

Heavy oil combustion facilities produce fine particles in the size range of submicron, which could be enriched by heavy metals such as vanadium, nickel and zinc contained in liquid fuel. The very small size of these ultra-fine particulates makes it difficult to remove them by existing air pollution control devices from the flue gas. Industrial boilers and electricity generation boilers consuming heavy oil are regarded as one of the main sources of such fine particulate pollutants, and cause adverse health effect by emitting particulates enriched with heavy metals into the atmosphere. Some advanced countries have proved hazardousness of nickel and vanadium in heavy oil and the concentration of these elements have been limited by emission standard. Particulates from combustion process are formed when inorganic compounds and metals in fuel evaporate at high temperature and then condensate or coagulate. Linak et al. (2000, 2003, 2004) have reported a series of studies on the size distribution and chemical properties of fine particles formed in the combustion process of heavy oil. According to Linak et al., the combustion of heavy oils resulted in relatively pronounced fraction of ultra-fine particles smaller than 0.1 μm, in the size range of which transition metals such as nickel and vanadium were mostly enriched. Anthropogenic sources such as heavy oil combustion facilities or electricity generation plants release fine particles containing mainly vanadium and nickel, due to the limited removal efficiency of the existing air pollutants control devices (APCD) for these small particles (Lighty et al., 2000). Fine particles are thought to be originated from the metal vapor at high combustion temperature and formed via nucleation, condensation, coagulation processes (Linak and Wendt, 1993). The temperature of the furnace and the residence time were the controlling factors and the particle size distribution depended on the interaction between chemical reactions, nucleation, condensation, and coagulation (Biswas and Wu, 1997).

There is a strong relationship between the size distribution and the chemical properties of atmospheric particulates mainly originated from such an anthropogenic source. Shaheen et al. (2005) carried out a measurement of the atmospheric concentration of 10 heavy metals (Na, K, Fe, Zn, Pb, Mn, Cr, Co, Ni, and Cd) in the four size ranges (<2.5 μm, 2.5–10 μm, 10–100 μm, >100 μm), and reported that transition metals such as nickel existed mainly in fine particle mode (<2.5 μm) and coarse mode (2.5–10 μm) of airborne particulates. Espinosa et al. (2001), who measured the size distribution of total suspended particles (TSP) and heavy metals in Spain, reported that PM_{10}, $PM_{2.5}$, $PM_{0.61}$ constituted 85%, 61%, 50% of TSP, respectively. More than 60% of Ni, V, Pb, Cd, Pb, and Cd among the 11 metals analyzed were contained in ultra-fine particles less than 0.61 μm in aerodynamic diameter. According to Singh et al. (2002), particulate matter in the size range of 1–2.5 μm were constituted mainly by organic carbons, heavy metals, nitrate, and sulfate. And the smaller particle size was more associated with heavy metals such as Pb, Sn, Ni, Cr, V, 70–85% of such metals were distributed in the submicron diameter and 40% of which in particle size less than 0.35 μm. The strong correlation between the size distribution of airborne particles and heavy metal contents was attributed to the anthropogenic source emission (Espinosa et al., 2001; Singh et al., 2002). According to source apportionment study by Vallius et al. (2003), heavy oil combustion contributed 13% of $PM_{2.5}$ and vanadium, nickel, and SO_2 were recognized as index materials for heavy oil combustion. Li et al. (2004) reported that $PM_{2.5}$ in New York City was apportioned to six major factors of heavy oil combustion, automobile, suspended particulates, sea salts, and two secondary sources as sulfate and nitrate.