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Assessment of elements, speciation of As, Cr, Ni and emitted Hg for a Canadian power plant burning bituminous coal

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Abstract

A detailed assessment of elements was carried out at a power plant rated at 150 MW burning western Canadian medium volatile bituminous coal with an ash content of 34 wt.%. The distributions of elements of environmental concern (As, Cd, Cr, Hg, Ni and Pb) in feed coals, ashes, and stack-emitted materials were determined using NAA, ICPES and ICP-MS, GFAA for Pb, and CVAA for Hg. The speciation of As, Cr, and Ni was examined using XANES spectroscopy.

The results show that the elements in the feed coal are within the same range for As, Hg and Pb and higher for Cd, Cr and Ni compared to other Canadian feed coals and within range for world coals. The combination of a Mechanical Cyclone Separator (MCS) and Fabric Filter (FF) removes a significant portion of the elements of environmental concern, as indicated by their relative enrichment (RE) ratios greater than 0.7. The fly ash from within the FF has a higher content of elements, such as Hg (1.58 mg/kg) than the MSC (0.13 mg/kg) due its lower temperature (130 °C) and the ability for finer particles to be captured by the baghouse.

Arsenic in the feed coal is dominated by arsenical pyrite and less toxic As^{+5} in arsenate forms. Arsenic is very low in the bottom ash, while in the fly ash it is largely (>90%) present as As^{+5}. Chromium in the milled coal is present as Cr^{+3} in association primarily with illite. This occurrence gives rise to an aluminosilicate association in ash materials, with the chromium oxidation state remaining as Cr^{+3}. Nickel in both the feed coal and ashes occurs as Ni^{+2} predominantly in coordination with oxygen. No evidence for carcinogenic Ni sub-sulfides was observed.

Mercury is emitted from the plant at a rate of 1.8 g/h and is mostly in the form of reactive gaseous mercury, followed by elemental mercury and particulate mercury.

The rates of input of elements of environmental concern, As, Cd, Cr, Hg, Ni and Pb, for this station were 10.45, 1.13, 123.3, 0.29, 36.3 and 23.1 kg/day, respectively, of which only 0.08, 0.01, 0.71, 0.04, 0.44, and 0.17 kg/day were emitted from the stack. Indicating that most of these elements (>99%) were captured by the particulate removing devices. The concentrations of elements in the air and in the vicinity of this power plant are low or within the range of published data for ambient air in urban and rural areas.

Keywords: Bituminous coal; Canada; Combustion; Speciation Environmental Assessment

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1. Introduction

There are limited published studies related to the distribution and speciation of elements in feed coal, combustion residues, and stack-emitted materials (Goodarzi, 2004; Goodarzi and Huggins, 2001, 2004, 2005a,b; Meij et al., 2002), particularly for Canadian coal-fired power plants (Goodarzi et al., 2002, 2005; Goodarzi, 2004; Goodarzi, 2006a,b,c). There is also little data regarding power plants burning bituminous coal (Evans et al., 1985; Mukhopadhyay et al., 1996; Hower et al., 1999; Mardon and Hower, 2004; Mastalerz et al., 2004; Sakulpitakphon et al., 2003, 2004). The combustion of coal results in a redistribution of elements into approximately 25% bottom ash, 75% fly ash (Stultz and Kitto, 1992), and less then 0.5% fine particles emitted from the stack (Goodarzi, 2006a). These figures may vary depending on the type of power plant and the configuration of the pollution control systems (Clarke, 1995; Briet et al., 1996, 1998; Goodarzi et al., 2002).

The detailed review of Kolker et al. (2006) describes the occurrence of mercury in coal emissions from power plants. The paper also outlines a number factors that influence mercury emissions such as the S and Cl content of coal, the rank, and the type of carbon in fly ash (Hower et al., 1999, 2000a,b; Senior and Johnson, 2005).

Elements in power plant ashes are grouped into three classes based on their degree of volatilization during combustion and their Relative Enrichment index (RE), which is defined as:

$$RE = \frac{(\text{elemental concentration in ash}) \times (\%\,\text{ash content of coal})}{(\text{elemental concentation in coal}) \times 100}$$

The non-volatile elements (Class I) consist of major and rare earth elements, as well as Cs, Hf, and Sc.

The elements that volatilize during combustion (Class II) include As, Ni, and Pb. These elements show RE factors of <0.7. The elements are redistributed into both the bottom and fly ashes, and then they condense en-route to the stack (Meij et al., 2002). The highly volatile elements (Cl, Hg, and Se) are almost entirely emitted from the stack (Class III), and have very low RE factors. Bottom ash from pulverized coal combustion has exceptionally low concentrations of volatile elements, especially As, Hg, Se, and halogens, when compared to fly ash (Goodarzi et al., 2002, 2006). In contrast, fly ash captures most elements (Hower et al., 1993, 1994, 1996; EPRI, 1994; Querol et al., 1999).

1.1. Health aspects of emitted elements

The elements that need monitoring are those considered as “toxic substances” under the terms of the Canadian Environmental Protection Act (CEPA, 1995). There are five elements of prime environmental concern (As, Cd, Hg, Ni, and Pb), as well as halogens. Chromium was added to this list in 1995 (EPRI, 1994) due to the possible presence of Cr^{+6}, a potentially carcinogenic form of Cr (Vela, 1993). It is recommended that elements such as As, Cr, and Hg to be monitored routinely for risk assessment due to the carcinogenic and other health risks associated with their emission (CEPA, 1995).

The objectives of this study are to provide detailed analyses of elemental concentrations of feed coal, bottom and fly ashes, and stack-emitted materials of environmental importance. This study focuses on Canadian power plants that burn bituminous coal. In addition, the speciation of As, Ni, and Cr in feed coal, bottom and fly ashes, and stack-emitted materials has been examined.

1.2. Speciation of stack-emitted mercury

Assessment of the environmental and physiological impact of mercury depends on its exposure levels and quantities, as well as its speciation. These factors are critical for evaluating the transport, deposition, and environmental impact of mercury emissions (Sloss, 1995; Goodarzi, 2004). Mercury in the atmosphere is found in both gaseous and particulate forms. The dominant form of the total gaseous mercury (TGM) is elemental mercury (Hg^0) (GEM) (Slemr et al., 1985). Mercury in anthropogenic emissions occurs in three main forms (Pacyna and Munch, 1991):

1. Gaseous elemental mercury (Hg^0), which is relatively non-reactive and insoluble;
2. Reactive gaseous mercury (Hg^{2+}), which is often soluble in water. This type is also known as “oxidized” mercury; a term that is commonly used for species of mercury (particularly $HgCl_2$) emitted from the stack of coal-fired power plants.
3. Particulate mercury (Hg^p), which is associated with particles (ash).

However, Cl and S in fly ash are two main elements that play a major role in the sorption of mercury in fly ash (Hg–Cl and Hg–S bond respectively (Meij, 1995; Meij et al., 2002; Pavlish et al., 2003). The temperature of the flue gas also plays an important role in determining the mercury sorption capacity (Meij, 1995, Goodarzi, 2004).