

Environmental Assessment of Bottom Ash from Canadian Coal-Fired Power Plants

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Abstract: Bottom ashes collected from ESP and baghouse of seven pulverized coal-fired power plants using subbituminous and bituminous coal and a fluidized bed combustor using crushed bituminous coal were examined for their mineralogy and elemental composition. The results presented in this paper are based on the average of three samples collected from each power plant. The mineralogy of each sample was determined using XRD and SEM/EDX; Elemental content was determined using INAA, ICPMS, and CVAAS; and the speciation of As, Cr, and Ni was determined by XANES. Bottom ash from the pulverized power plants consists of granular particles with a minor input of melted glassy fragments, while the bottom ash from the fluidized bed combustor consists entirely of granular particles. The sulphur and carbon contents of pulverized bottom ashes range from 0.03 to 2.32 wt % and 0.19 to 6.62 wt %, respectively. For the fluidized bed combustor, the sulphur and carbon contents were 5.27 wt % and 10.72 wt %. The concentrations of As, Cr, Hg, Ni, and Pb in bottom ash are related to sulphur content of coal and are higher for bottom ashes from high sulphur feed coals. Most of the elements associated with S (As, Hg, and Pb) are captured from fluidized bottom ash, more so than by the corresponding ESP fly ash. Most of the elements in bottom ash have enrichment (RE) factors of less than 0.7 indicating that they are not enriched in the bottom ashes as compared to the feed coals. Arsenic, Cd, Cr, Ni, and Pb have higher concentrations in granular bottom ash as compared to glassy bottom ash of the same power plant. The feldspars and quartz of feed coal are health hazards and are captured mostly by bottom ash and therefore prevent their emission from stack. The As, Cr, and Ni in form of: non-toxic As^{+3} , mostly beneficial Cr^{3+} , and non-carcinogenic Ni^{2+} are in coordination predominantly with oxygen. Mercury and Pb are low and have very little environmental impact. The hazardous elements (As, Cr, Ni, and Pb) are only leached by HCl, indicating that under normal condition they remain immobile and their impact on environment can be considered low.

Key Words: Bottom ash, coal fired power plants, elements, Canada

1. INTRODUCTION

Coal-fired power plant ash consists mostly of products from the decomposition and alteration of mineral matters in coal, a small amount of unburnt carbon (Clarke ICEA 1992 [1], Cloke Fuel 1994 [2] Goodarzi GSC 2002 [3], Helle FPT 2003 [4]). Bottom ash forms up to 25% of the total ash while ESP fly ash forms the remaining 75% (Stultz BWC 1992) [5].

In general, the bottom ash consists of two fractions: bulk, which is granular and porous particles; and minor (boiler slag), which consists of melted glassy fragments (Goodarzi GSC 2002) [3]. Bottom ash is used mostly for snow and ice control, as an aggregate in lightweight concrete masonry units, as raw feed material for production of Portland cements, for road base and sub base aggregate, as structural fill material, and as a fine aggregate in asphalt paving. Boiler slag is mainly used as blasting grit or roofing shingle granules (Hecht USEPA 1975 [6] Moulton USBM 1973 [7] ASTM 1997 [8] Lovell AMTRB 1991 [9] Moulton TRB 1973 [10]). Therefore, bottom ash has direct contact with our

living environment and its environmental impact is important. Bottom ash has low concentrations of volatile elements such as Hg and others, compared to ESP fly ash Sawine KAP 1995 [11]. It may also contain some unburnt coal and/or char fragments (Goodarzi GSC 2002) [3]. In general, for the pulverized coal-fired power plants the elemental concentrations in bottom ash are lower than that in ESP fly ash for most of elements (Goodarzi GSC 2002) [3]. Mineralogy of most bottom ash consists of silicates, with unburnt carbon/char contributing only a small fraction (Goodarzi GSC 2002) [3].

2. ANALYTICAL METHODS

Sampling: Bottom ash samples examined in this study were produced from seven pulverized coal power plants using low sulphur subbituminous feed coals (five samples) and one each from low sulphur bituminous feed coal, a high sulphur bituminous feed coal, and a fluidized bed combustor. Sampling was carried out according to the recommendations of the Electric Power Research Institute (EPRI 1994) [12]. Samples were collected over a period of three days at two-hour intervals. These samples were then combined to produce a single sample for each day. Samples of bottom ash for each day were analyzed in duplicate, and then an average of

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analytical results was made of all three days to represent the bottom ash from each power plant.

Elemental Analyses: The carbon and sulphur analyses of ESP fly ash were performed according to ASTM specifications (ASTM 1978) [13]. Elemental composition of samples was determined using some of the techniques recommended by (EPRI 1994) [12]; these included INAA, GFAA, CVAA, and ICPEs. The ESP fly ash materials used for comparison were NIST1633b and SARM 19 and 20.

Relative Enrichment Index (RE): The power plant ashes can be classified into three classes based on their Relative Enrichment index (RE) and the degree of volatilization during combustion (Meij IT 2000) [14]. The RE is defined as:

$$RE = \frac{E_{ash}}{E_{coal}} \times \frac{\% Ash_{coal}}{100}$$

E_{ash} = Elemental concentration in ash

E_{coal} = elemental concentration in coal

$\% Ash_{coal}$ = percent of ash in coal

Class I. This includes the non-volatile elements and consists of major and rare earth elements, as well as Cs, Hf, and Sc. These elements have RE factors of >1 and are enriched in ash.

Class II. This includes elements that volatilize during combustion such as As, Ni, Pb, and S. These elements show RE factors of <0.7 and are redistributed into both the bottom and ESP fly ashes, and then they condense en-route to the stack (Goodarzi IJCG 2006 [15] Meij 1995 KAP [16]).

Class III. These are highly volatile elements (Cl, Hg, and Se), which almost entirely volatilized and emitted from the stack except for the portion that is captured by the carbon in the ESP fly ash (Hower IJCG 1993) [17] (EPRI 1994) [12]). These elements have very low RE factors.

Speciation of As, Cr, and Ni: X-ray Absorption Near Edge Structure (XANES) and X-ray Absorption Fine Structure (XAFS) spectroscopies were used to determine the oxidation states and modes of occurrence of arsenic, chromium, and nickel in bottom samples. For details of these procedures please see Goodarzi and Huggins (Goodarzi JEM 2004 [18] EF 2005ab [19, 20]).

Data Treatment: The data processing was same as described by (Goodarzi 2002 GSC) [3], which is consistent with the EPRI data collection procedures (EPRI 1994) [12]. Enrichment indices of the elements were determined according to Meij (KAP, 1995) [16].

Semi-quantitative Mineralogy: Semi-quantitative XRD analyses were carried out using corundum (Al_2O_3) as an internal standard. This analytical technique is known as the reference intensity ratio (RIR) method and was developed by Chung (JAC 1974 1975 [21, 22]). This internal standard method is based on eliminating matrix absorption effects. SED/EDX study was carried out on carbon-coated samples. Oxide percentages were determined by X-ray fluorescence.

Leaching: Leaching of elements were carried out using a modified version of method described by Finkelman EF 1990 [23] in that only bottom ash were leached by deionized

water (H_2O), ammonium acetate (NH_4OAc), and hydrochloric acid (HCl). The elemental content (As, Cr and Ni and Pb) of leachates were determined using ICAPES.

3. RESULTS AND DISCUSSION

Bottom ash is a valuable product of coal combustion and it helps to retain some hazardous air pollutants and particles such as quartz and feldspar (Meij IT 2000 [14] Finkelman EF 1990 [23] Goodarzi Fuel 2006a [24]), thus, lowering their emission from stack. However, little attention is paid to the mineralogy and elemental composition of bottom ash as compared to ESP fly ash. The bottom ash in the present study is from seven pulverized coal power plants and a fluidized combustor. It consists of granular particles, which constitute bulk, and boiler slag, which is melted, glassy fragments and form minor part of samples. The fluidized combustor sample is composed entirely of granular particles.

3.1. Variation of Quartz and Feldspar

Table 1 is a comparison of quartz and feldspar content of bottom and ESP fly ash for same stations. The results indicate that quartz content of bottom ash produced from subbituminous coal is lower and that for bituminous coal and is higher compared to the corresponding ESP fly ash (Table 1). The feldspars are also higher in bottom ash compared to ESP fly ash (Table 1). In general, mineral matter such as quartz and feldspars remain unchanged during combustion due to their high melting point (quartz: $1710^\circ C$) and their emission from stack is considered as possible human health hazards (Goodarzi Fuel 2006a [24] Puntis E 1980 [25]).

3.2. Variation of Elements

The bottom ash makes up approximately 25% of coal ash in power plants while the rest is captured as ESP fly ash and a minor amount (0.5%) is emitted from stack as particulates (PM) (Goodarzi Fuel 2006b) [26]. The elements in coal and coal ashes are classified into various groups depending on their environmental impacts (Goodarzi IJCG 2006) [15]. For the bottom ash samples, five elements (As, Cr, Hg, Ni and Pb) are designated as "toxic substances" under the terms of the Canadian Environmental Protection Act (CEPA 1995) [27]. The enrichment of elements in bottom ashes is an indication of redistribution of elements from the feed coals (Table 2) into both bottom (Table 3) and ESP fly ashes upon combustion (Meij KAP 1995) [16].

3.3. Carbon and Sulphur Content

The C and S contents of bottom ash range from 0.68 to 6.6 wt% and 0.03 to 10.72 wt%, respectively (Table 3). The subbituminous coals have low S contents while bituminous coals have high S contents, except bituminous coal #6 from western Canada, which has a low S content (Table 2), indicating that most of S in station #6 is captured by bottom ash in this sample. The fluidized bed ash has the highest S content in bottom ash samples (Table 3).

3.3.1. Bottom Ash from Pulverised Coal

These bottom ashes have lower concentrations of most of elements as compared to ESP fly ash (Goodarzi GSC 2002) [3] (Hower IJCG 1993) [17]. In general, the As content of bottom ash produced from high S feed coal is greater than

Table 1. Percentage of Quartz and Feldspars in Granular Bottom Ash and ESP Fly Ash from Same Station

Minerals	1	2	3	4	5	6	7	8
Quartz,								
Bottom ash	9.20	15.0	8.40	10.30	12.50	8.15	1.30	2.20
ESP fly ash	1.25	9.3	3.40	8.75	N/D	10.80	2.70	4.20
Feldspars								
Bottom ash	15.50	13.00	7.20	10.1	8.30		1.70	11.2
ESP fly ash	1.15		0.10	0.30	N/D	0.25	2.50	1.10

Table 2. Variation of Sulphur and Ash (wt %) and Elements (mg/kg) in Canadian Feed Coals

Elements	Subbituminous					Bituminous		
	1	2	3	4	5	6	7	8
S*	0.51	0.73	0.36	0.37	0.32	0.66	2.90	3.60
As	1.77	3.63	1.60	2.40	2.20	4.39	54.4	84.4
Cr	4.47	29.3	11.7	13.3	6.00	51.7	10.3	9.90
Hg	0.03	0.06	0.03	0.04	0.05	0.19	0.20	N/D**
Ni	5.30	5.67	6.30	7.30	4.30	15.20	8.30	13.6
Pb	9.80	11.2	12.0	9.60	13.00	9.70	24.0	43.0
Ash	15.3	16.6	22.2	18.80	20.4	27.4	29.4	33.2

*Dry ash free; **N/D: Not determined.

Table 3. Variation of Carbon and Sulphur (wt %) and Elements (mg/kg) in Canadian Bottom Ash

Elements	Subbituminous										Bituminous					
	1	RE*	2	RE	3	RE	4	RE	5	RE	6	RE	7	RE	8	RE
C	0.19	N/D [#]	6.62	N/D	0.44	N/D	1.47	N/D	1.14	N/D	0.55	N/D	5.80	N/D	5.30	N/D
S**	0.03	0.01	0.15	0.03	0.04	0.02	0.02	0.00	2.32	1.48	0.05	0.02	0.19	0.02	10.7	1.00
As	3.63	0.31	6.00	0.27	1.60	0.22	3.70	0.29	1.70	0.16	0.30	0.02	34.0	0.18	445	1.75
Cr	28.0	0.96	156	0.88	29.0	0.55	54.0	0.76	43.0	1.46	344	1.82	45.0	1.28	22.0	0.74
Hg	0.01	0.05	0.02	0.06	0.01	0.07	0.01	0.05	0.01	0.04	0.05	0.07	0.02	0.04	0.08	N/D [#]
Ni	30.3	0.87	22.3	0.65	23.0	0.81	30.0	0.77	21.0	1.00	39.6	0.71	44.3	1.57	15.7	0.38
Pb	17.7	0.28	11.3	0.17	24.0	0.44	8.70	0.17	4.30	0.07	6.33	0.18	12.7	0.16	16.0	0.12

*RE: Relative Enrichment Index; **Dry ash free; #N/D:Not Determined.

those produced from low S feed coals (Tables 2 and 3) indicating that As and S have similar source (sulphides, such as pyrite) and some of As of feed coals is captured by bottom ash; therefore, prevented from being emitted to the environment.

Most of the elements in the bottom ashes have RE factors less than 0.7 indicating that they are not enriched in the bottom ash as compared to the feed coals (Tables 2 and 3). There are differences in elemental contents of granular particles of bottom ash as compared to the glassy melted fragments. Generally, the granular bottom ash particles have

higher concentrations of some elements as compared to the glassy slag for pulverized coal fired power plants (Table 4); for example, the concentrations of As and Ca are three times higher for bottom ash particles compared to the slag (Table 4).

3.3.2. Bottom Ash from Fluidized Bed

The bottom ash from fluidized combustor has the highest content of As than that in ESP fly ash, which associated with high S in this ash (Table 3), indicating that the lime (CaO) in the system has successfully removed the As and S from the system, possibly through the reaction between As and CaO (As_2O_3) or by iron oxides (Gutberlet VGBK 1988) [28]. This is the only bottom ash that has a higher concentration of As than its corresponding ESP fly ash (Table 4) indicating that this bottom ash was able to capture high percentage of As due to the presence of CaO.

There is also similar relation to that of pulverized coal bottom ash between the particulate and glassy melted for this sample (Table 4). The concentration of As is 3.3 times greater than the larger glassy particles in smaller granular ash (Table 4). What is important is that the glassy bottom ash has higher concentration of metallic elements such as Cr, Ni, and Pb (Table 4), which is related to high concentration of metallic particle in this ash (Fig. 1).

4. SPECIATION OF ELEMENTS IN BOTTOM ASH

4.1. Arsenic

The toxicity of As depends on its chemical form and decreases in the order of $\text{As}^{3+} > \text{As}^{5+} >$ organo-arsenic (Fergusson PP 1990) [29] and does not serve any known useful biological function (Ashby PCEC 1993) [30]. It is usually ingested as arsenate As^{5+} , then, it is reduced in the body to the more toxic form of As^{3+} , where it can interfere with enzymes and results in a highly toxic effect in the body (Ashby PCEC 1993) [30] (Harte UCP 1991) [31]. Arsenic at higher concentrations can cause liver and kidney damage (Fergusson PP 1990) [29]. Therefore, it is one of the elements that is listed as "Toxic substance" by EPRI (EPRI 1994) [12] and CEPA (EC 1995) [27] as carcinogenic health risk. The adverse effect of arsenic "arsenosis" is sometimes evident when coal with high As contents is burnt such those documented in Czechoslovakia and China (Swaine B 1990) [32] (Finkelman IJCG 2002) [33]. Arsenic in coal is generally associated with pyrite, most likely in solid solution (Swaine B 1990 [32] Finkelman IJCG 2002) [33]) Goodarzi IJCG 1993 [34].

The arsenic content of bottom ash increases with increasing sulphur content and the highest arsenic is found in the bottom ash (#7) from the fluidized bed combustor. In addition, As is greater in granular ash than in the fused glassy type in this bottom ash (Table 4). The granular bottom ash contains metallic-like particles of hematite and magnetite, which may provide surface for deposition of arsenic (Fig. 1). In general, the arsenic content of the bottom ash is much lower than that of the corresponding ESP fly ash (1.75-54.0 mg/kg), sometimes by a factor of 10. This is consistent with arsenic being a class II element (Meij KAP 2005) [16]. However, the relationship of bottom/ESP fly ash established for pulverized coal-fired power plant (#1-7) does not appear to apply to ash from the fluidized bed combustor (#8), where the concentration of As in ESP fly ash is 146

mg/kg and for bottom ash is 445 mg/kg (Table 3). Arsenic in bottom ash from low sulphur subbituminous coal and high sulphur bituminous coal is not leachable by water and ammonium acetate (NH_4OAc). Arsenic is only leached by HCl at 35% and 37% for subbituminous, 24% for bituminous ashes and 74% from fluidized bed bottom ash (Table 5).

4.1.1. Speciation of As

Spectral data for the two major As oxidation states, As^{3+} and As^{5+} for a high pyrite coal used as standard are shown in Fig. (1). The XANES spectra of bottom ash #1-4 are similar and have greater signal/noise ratio (Fig. 2).

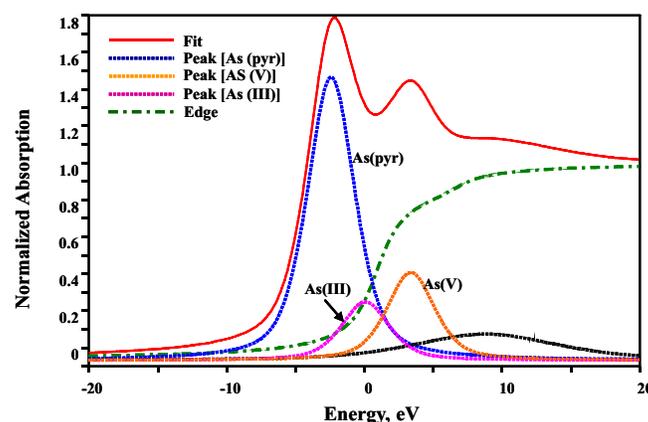


Fig. (1). The least square fitting of the XANES spectra for milled coal with high pyrite content. Peaks denoted by "A" and "P" arise from arsenic as arsenate (As^{5+}) and as As in pyrite (substitutes for sulphur in pyrite i.e. As_2^{2+} for S_2^{2+})

However, in the spectra of three-bottom ash #1-3, a fraction of the arsenic must be present in more than one oxidation states in order to account for the weak broad shoulder at about -0.5- 1.5 eV (Fig. 1). For these samples, the As^{3+} content varies from <10% to as much as 20%, while the As^{5+} content varies inversely. However, for bottom ash #4, the low-energy shoulder is broad and the position of the peak at about -1.4 eV is intermediate between that for arsenic associated with pyrite (-2.25 eV) and As^{3+} in oxygen coordination (0.0 eV) (Fig. 2); indicating that about 5-10% of the arsenic is in association with As^{3+} and 80-90% as As^{5+} and 5-10% as pyrite. The arsenic spectrum of the bottom ash for low sulphur bituminous coal (#5) is very weak and this indicates that virtually all the arsenic is volatilized during combustion and very little is incorporated into the bottom ash (Fig. 1). This is confirmed by the very low RE factor of 0.02 obtained for As in this bottom ash (Table 3). The feed coal 6 and 7 have similar and high sulphur coal (Table 1), but the speciation of As in bottom ash #6 is very different to that #7 (Fig. 1). This is due to the bottom #6 is from pulverized coal and that of #7 from fluidized combustion. The arsenic species in the bottom ash from fluidized combustion is mostly (85-90%) in the form of As^{5+} with 10-15% of the arsenic as As^{3+} (Fig. 2). In contrast, the arsenic XANES spectrum of the bottom-ash #7 produced from fluidized combustor is almost entirely As^{5+} , a small feature at about 15eV, which is indicative of the formation of crystalline arsenates in this

sample (Fig. 1). Possibly due presences of calcium arsenate/sulphate (Huggins EF 1994) [35] (Huffman JFPT 1994) [36] due to use of limestone in the fluidized-bed combustor, which transformed the pyrite to the arsenic compound.

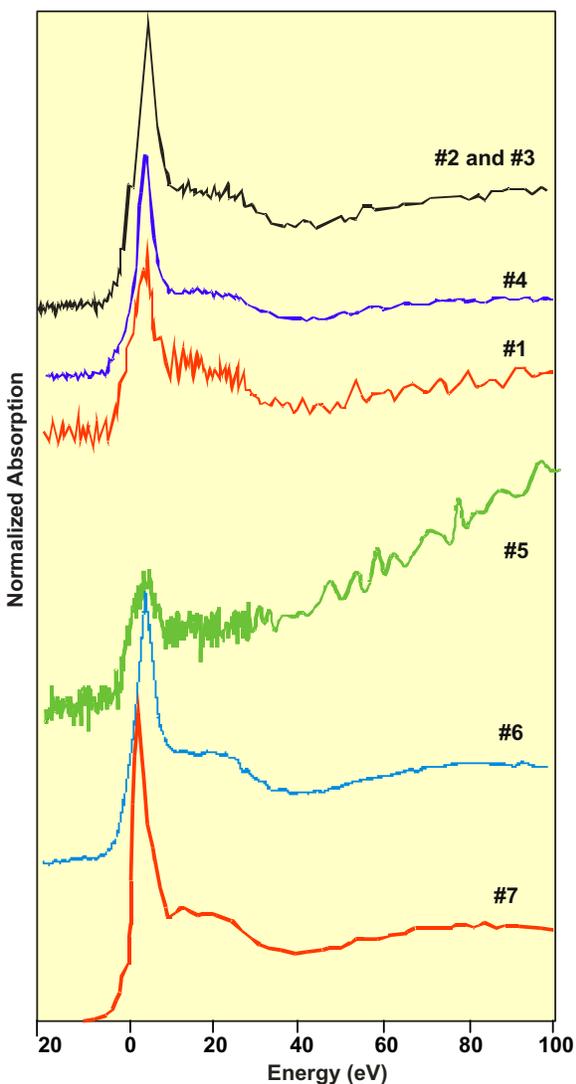


Fig. (2). Arsenic K-edge XANES spectra of bottom ash#1-4, produced by pulverized subbituminous coal combustion, bottom ash#5 from low sulphur and #6 and #7 from high sulphur bituminous coal. Bottom ash#5 and #6 are from pulverized coal combustion, while #7 is from a fluidized bed combustor.

4.2. Chromium

Chromium naturally occurs as three stable forms of, Cr^0 , Cr^{3+} , and Cr^{6+} , with Cr^{3+} being the most abundant (Harte UCP 1991) [31]. Chromium as Cr^{3+} is essential for carbohydrate metabolism and chromium deficiency may cause diabetes whereas Cr^{6+} is carcinogenic (Beliles M 1975 [37] Anderson STE 1981 [38]). The adverse effects of Cr^{6+} is also short lived and it rapidly changes to Cr^{3+} form (Harte UCP 1991) [31]. Chromium also does not bioaccumulate in the food chain (Harte UCP 1991) [31]. However, Cr can cause lung cancer, when inhaled as Cr^{6+} (chromates) as fine particulates (Piperino ACS 1975) [39]. Chromium in these bot-

tom ashes is low as compared to coal and ESP fly ash, which is evident by its low RE (Table 1). Chromium in bottom ash from low sulphur subbituminous coals and high sulphur bituminous coal is not leachable by water and ammonium acetate (NH_4OAc), and only leached by HCl at 12% and 96% for subbituminous and 12% for bituminous (Table 5). Bottom ash from fluidized bed has 17.3 leachable Cr (Table 5).

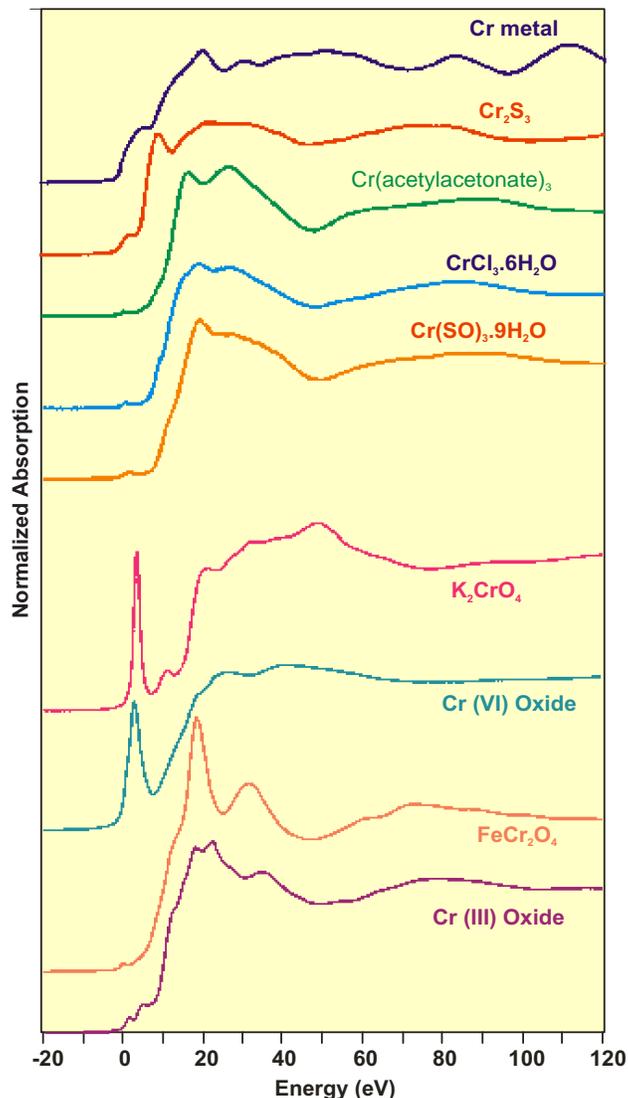


Fig. (3). Chromium XANES spectra of various standard materials; top five indicates special shapes for the metallic and sulfide chromium compounds and those compounds in which chromium is occasionally coordinated by oxygen whereas bottom four indicates two Cr^{3+} oxide minerals and for two Cr^{6+} oxide compounds. Note the prominent pre-edge peak at about 2 eV that is highly characteristics of hexavalent chromium.

4.2.1. Speciation of Chromium

The standards used for determination of species of Cr consists of compounds found in nature such as metallic and sulphide chromium, which have different XANES spectral than the compounds associated with oxygen with two major Cr oxidation states i.e. Cr^{6+} and Cr^{3+} (Fig. 3). There is always a prominent pre-edge peak $\approx 4\text{-}5$ eV associated with com-

pound containing Cr^{6+} , where as Cr^{3+} compounds does not display such peaks (Fig. 3). The Cr XANES spectra of the bottom ash samples from stations 1 to 4 do not show any evidence of a peak at 4-5 eV that can be attributed to Cr^{6+} (Fig. 4); therefore, their Cr is mostly (>95%) Cr^{3+} that is in association with aluminosilicate phases such as glass. The chromium XANES spectrum in this group of bottom ash often show broader peaks, which is dissimilar to the feed coal, indicating the transformation of Cr^{3+} /illite in coal to a range of distorted sites in the aluminosilicate (glass) matrix in the bottom ash. Chromium spectrum in sample #6 show a slight prominent pre-edge feature than other samples, indicating a minor presence of Cr^{6+} (Fig. 4). The spectrum of Cr for bottom ash #6 is similar to that for # 1 and consists mostly of the Cr^{3+} oxidation state (Fig. 4). However, this sample is produced from a coal with high pyrite/sulfur content and relatively featureless and flat spectra is observed that is more consistent with sulfide and metallic forms of chromium. The Cr spectrum for the bottom ash from fluidized bed combustor is quite weak and is entirely Cr^{3+} .

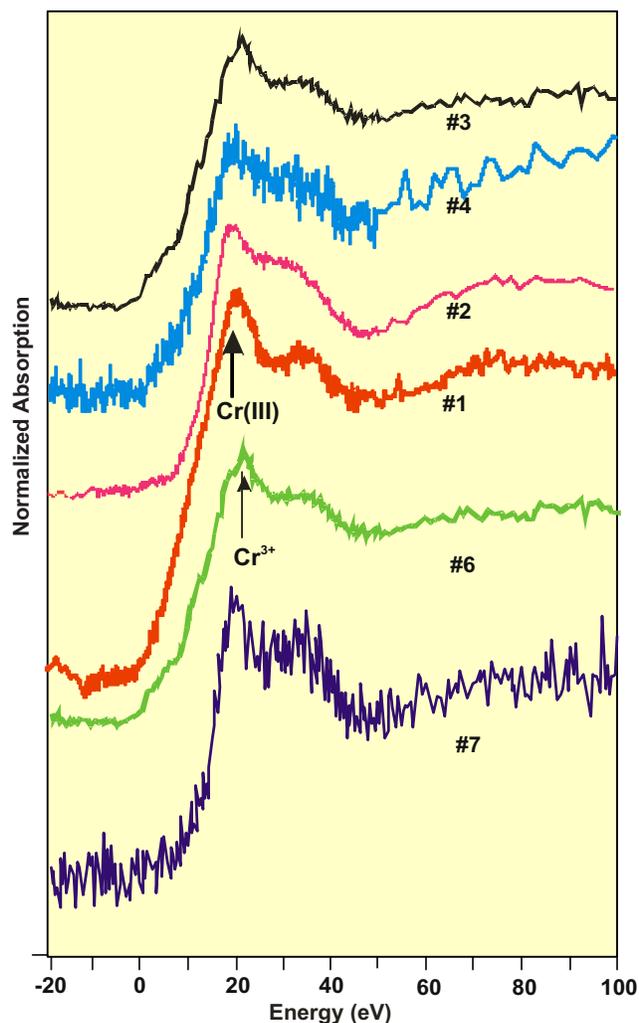


Fig. (4). Comparison of chromium XANES spectra of bottom ash from coal-fired power plants, subbituminous feed coals (#1, 2, 3, and 4), bituminous coal (#6), and fluidized bed combustor (#7). Zero point of energy corresponds to 5989 eV.

4.3. Mercury

Mercury in coal is a volatile element and is mostly emitted due to combustion from stack and partially captures by carbon in ESP fly ash (Goodarzi IJCG 2004, 2006 [40, 41] JEM 2004 [42] Hower EF 2000 [43]). Mercury has higher priority than any other elements due to its inherent toxic effects on humans and wildlife (Fergusson PP 1990 [29] Moore AP 1976 [44] USEPA 1997c [45]). The adverse health and environmental effects of Hg is mostly associated with organic Hg compounds such as methyl mercury, which is a potent neurotoxin (Fergusson PP 1990 [29] Moore AP 1976 [44] USEPA 1997c [45] WHO 1996 [46]). Most of mercury in soil, sediments, water, plants, and animals is in the forms of inorganic Hg salts and organic forms of Hg, primarily methyl mercury (Ashby RSC 1993 [30] USEPA 1997a, 1997b [47,48]).

In general, the total amount of mercury in the environment is not changed since Hg is an element that is part of the earth system (Lindberg EST 1998) [49] and cycles because of natural and geogenic activities (Rasmussen GSC 1996) [50]. However, the redistribution of mercury from geogenic sources into the air, water, and topsoil have been influenced by anthropogenic activities such coal burning, where it may more readily enter the food chain (Goodarzi GSC 2002, JEM 2001 [3, 51]). Mercury in bottom ash (Table 3) has a very low Hg content compared to feed coal and ESP fly ash (Goodarzi GSC 2002) [3].

4.3.1. Role of Bottom Ash in Mass Balance of Mercury

The role of bottom ash in capture of mercury during the combustion of coal is not well understood. This is due to low Hg content of bottom ash (Hower JCQ 1993 [5] Goodarzi JEM 2004 [42]). Mercury is mostly captured by carbon in ESP ash (Goodarzi IJCG 2005 [41] Hower EF 2000) [43]. The relation between carbon and mercury in bottom ash is not same as ESP fly ash, since an increase of carbon in ESP fly ash particularly from subbituminous to high volatile bituminous coal is generally accompanied by increase in Hg content of ESP fly ash (Goodarzi Fuel 2007) [52]. However, in bottom ash such a relation is not evident (Table 6). This is clearly demonstrated by the bottom ash from Canadian power plants having carbon content of 0.11-16.5 % (Table 6). The data present in this table indicates that bottom ash contribute between 1-16% Hg captured for power plants that are equipped with cold side ESP (Table 7); but for power plants equipped with hot side ESP, the capture of Hg by both ash is low and almost equal (Table 7).

4.4. Nickel

Nickel is an element that in small amount is beneficial to health (Harte UCP 1991) [31] some of its compounds are considered as possible human carcinogens (IARC 1980) [53]. The carcinogenic compounds of nickel consists of sub sulphides (Ni_{1+x}S , where $x = 0$ to 0.5) and nickel tetracarbonyl [$\text{Ni}(\text{CO})_4$] (Beliles M 1975 [37] Linton RSC 1993 [54]). Another toxic form of Ni is Nickel carbonyl, which forms due to reaction between CO and Ni (Beliles M 1975 [37] Linton RSC 1993 [54]).

The oxidation state of Nickel carbonyl is (0) and for nickel sulphide it is (II). Nickel has a detrimental effect on the health of mammals in particulate form (Fergusson PP

Table 4. Variation of Elements (mg/kg) in Particulate Bottom Ash and Slag for Stations #1 and Large and Small Particles for Station #8 and their Corresponding ESP Fly Ash (mg/kg)

Elements	Pulverized Coal-Fired #1			Fluidized Bed Combustor #8		
	Bottom Ash		ESP Fly Ash	Bottom Ash		ESP Fly Ash
	Particle	Glassy Slag		Particle	Glassy Slag	
As	3.6	1.1	20.7	445	12.7	146
Cr	28.0	25.0	31.5	22.4	99.3	23.0
Hg	0.01	0.01	0.03	0.08	N/D*	2.37
Ni	30.3	27.7	38.8	15.7	55.3	32.0
Pb	17.7	10.8	48.7	16.0	92.2	177
Ca	52200	45555	60000	376000	36300	199000

*N/D: Not determined.

Table 5. Percent of Elements Leached from Bottom Ash by Water, Ammonium Acetate, and HCl

Elements	1		3		7		8	
	H ₂ O & NH ₄ OAc	HCl	H ₂ O & NH ₄ OAc	HCl	H ₂ O & NH ₄ OAc	HCl	H ₂ O & NH ₄ OAc	HCl
As	3	35	0	37	0	24	1	74
Cr	0	23	0	96	0	12	0	17
Ni	0	19	0	74	2	15	0	1
Pb	0	23	0	0	0	7	0	0

Table 6. Role of Bottom Ash in Mass Balance of Mercury for Some of Canadian Power Plants Using Subbituminous Coals

Power Plants	#1	#2	#3*	#4	#5	#6**
Inlet mercury mass flow rate (g/h)	9.47	19.52	20.48	26.15	29.44	7.1
Ash content of the coal (Dry Base, carbon-free) (%)	16.37	17	29.53	23	23.67	19.33
Dry base carbon-free ash mass flow rate (Mg/h)	23.31	36.45	103.7	79.8	94.7	26.71
Dry Base carbon content of bottom ash (%)	2.89	6.25	2.93	2.32	16.5	1.22
Dry Base carbon content of ESP fly ash (%)	0.13	0.19	0.11	2.72	1.32	1.27
Total estimated ash flow, including carbon (mg/h)	23.43	50.3	105	81.99	99.53	28.46
Bottom ash mass flow rate (mg/h), at 25% of total ash	5.86	14.39	42*	20.49	24.88	6.76
Mercury released in the bottom ash (g/h)	0.12	0.20	0.17	0.07	0.27	0.12
ESP fly ash mass flow rate (mg/h), at 75% of total ash,	17.57	43.15	63*	61.46	74.6	20.29
Total outlet mercury mass flow rate (g/h)	11.65	18.8	21.9	22.7	30.83	7.2
Mercury released in ESP ash (g/h)	0.64	2.46	8.38	9.8	17.82	0.13
Total outlet mercury mass flow rate in ash (g/h)	0.76	2.66	8.55	9.87	18.09	0.25
Mercury emission rate in flue gas (g/h)	10.89	15.66	12.74	12.84	12.74	6.95
Fraction found in the ash (%)	6.17	13.55	40.3	42.45	57.58	3.33
Fraction found in the flue gas (%)	93.83	86.45	59.7	57.55	42.42	96.67

*Station #3 has split of 40% bottom ash and 60% ESP ash.

**This power plant is equipped with hot side ESP.

Table 7. Role of Bottom Ash in Capture of Mercury in Some Canadian Power Plants Using Subbituminous Coals

Power Plants	#1	#2	#3*	#4	#5	#6**
Mercury released in the bottom ash (g/h)	0.11	0.2	0.17	0.06	0.27	0.12
Mercury % in bottom ash as in total ash	16	8	2	1	2	48
Mercury released in ESP ash (g/h)	0.64	2.46	8.38	9.8	17.82	0.13
Mercury % in ESP ash as in total ash	84	92	98	99	98	52
Total outlet mercury mass flow rate in ash (g/h)	0.76	2.52	8.54	9.87	18.09	0.25
Normalized to 100%, fraction found in the ash (%)	6.17	13.55	40.3	42.45	57.58	3.33

*Station #3 assumes a split of 40% bottom ash and 60% ESP ash.

**This power plant is equipped with hot side ESP.

1990) [29]. Nickel in bottom ash from low sulphur subbituminous coal and high sulphur bituminous coal is not leachable by water and ammonium acetate (NH_4OAc), and only leached by HCl at 19% and 74%, for subbituminous and 15% for bituminous coal. Bottom ash from fluidized bed has very little leachable Ni (Table 5).

4.4.1. Speciation of Nickel

The standard for Ni is shown in Fig. (5), which consists of the metallic, sulphide of Ni and compounds in which Ni is coordinated with oxygen (Fig. 5). Nickel is designated as a "toxic substance" by the Canadian Environmental Protection Agency (CEPA 1995) [27]. Therefore, it is necessary to determine the speciation of Ni in any products associated with anthropogenic activities such generation of energy from coal-fired power plants and residual oil combustion (Goodarzi JEM 2004 [18]).

Another toxic Ni compounds is Nickel carbonyl, which forms due to reaction between CO and Ni. The subbituminous coals produced bottom ash that show a fairly strong peak with Ni^{2+} in coordination predominantly with oxygen anions, at about 20 eV (Fig. 6). The nickel for the bottom ash samples #1, #3, and #4 have higher Ni contents (23 to 30 mg/kg) and/or lower iron contents and better quality XANES spectra. The Ni XANES spectra for bottom ash produced from the bituminous feed coals (Fig. 6) is also showing a strong peak at about 20 eV, consistent, indicating of Ni^{2+} in coordination predominantly with oxygen (Fig. 6). The spectra for bottom ash produced from fluidized bed combustor are very weak (Fig. 6). Nickel in these bottom ash samples appears to be in an oxygen environment similar to that reported for silicate glasses and carcinogenic Ni sulphides are not present in these bottom ashes.

4.5. Lead

Lead is naturally occurring mineral and is widespread in soil, water, and air. Lead is associated with sulphides in coal (Finkelman KAP 1995) [55]. Its effects on human are both physiological and neurological (Fergusson PP 1990) [29]. Its health effects are severe even at low doses and mostly on brain and blood forming system (Harte UCP 1991) [31]. It may cause irreversible brain damage. In general, Pb is a volatile element and does not concentrate in bottom ash (Goodarzi GSC 2002) [3] as indicated by low RE value (Ta-

ble 3). In addition, it is not leached by water, ammonium acetate (NH_4OAc) and only 23 % of Pb is leached by HCl from subbituminous and 7% from bituminous coal (Table 5).

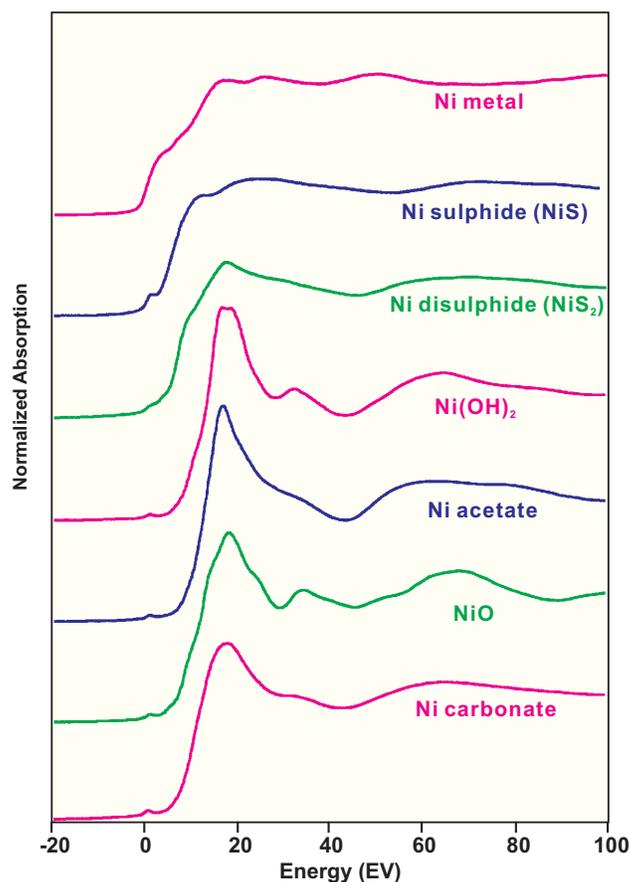


Fig. (5). Nickel XANES spectra of various standard materials. Note how the overall spectral shapes for the metallic and sulphide nickel compounds differ from those compounds in which nickel is coordinated with oxygen. The zero-point of energy for these and subsequent Ni XANES spectra corresponds to 8333 eV.

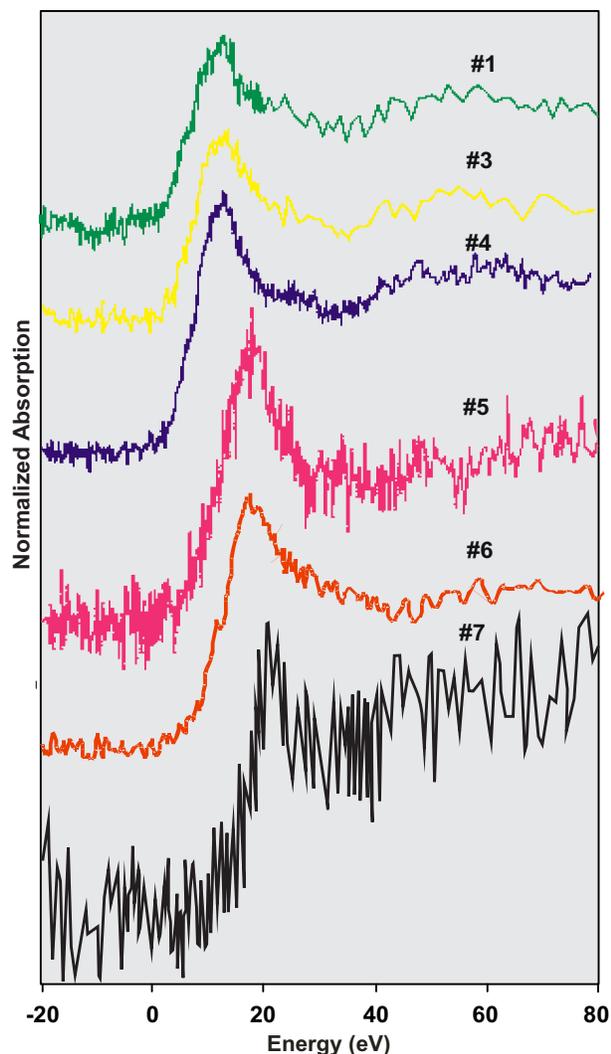


Fig. (6). Ni XANES spectra of bottom ash from combustion of bituminous feed coal #1-7

5. ENVIRONMENTAL ASSESSMENT

The present results indicate that feldspars and quartz of feed coal are mostly captured by bottom ash, particularly in bituminous coal (Table 1), this is important since both emitted quartz and feldspars particles (PM) are considered as possible occupational hazards.

The environmental impact of the As, Cr, Hg, Ni and Pb is low and they are in form of; non toxic As^{+3} , mostly beneficial Cr^{3+} , and non carcinogenic Ni^{2+} in coordination predominantly with oxygen. Mercury and Pb are low and have very little environmental impact.

Arsenic, Cr, Ni and Pb become only mobile under strong acidic condition, which generally is not occur naturally and in the bottom ash storage facilities. Therefore, the environmental impact of Bottom ash is considered very low.

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