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Fuel xxx (2011) xxx–xxx

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Short communication

Heavy metal content of bottom ashes from a fuel oil power plant and oil refinery in Cuba

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A R T I C L E   I N F O

Article history:
Received 13 December 2010
Received in revised form 8 March 2011
Accepted 10 March 2011
Available online xxxx

Keywords:
Heavy metals
Ash
Hazardous waste
Cienfuegos
Cuba

A B S T R A C T

Fly and bottom ashes from fuel oil power plants and oil refineries may contain hazardous trace elements, such as heavy metals, which have a negative impact on the environment with time due to potential leaching through acid rains and into groundwaters. This study provides levels of As, Cr, Cu, Hg, Mn, Ni, Pb, Ti, V and Zn of bottom ashes from a thermal power plant and an oil refinery placed in Cienfuegos Bay, Cuba. Trace elements were measured using X-ray fluorescence (XRF) with a SPECTOR X-LAB PRO 2000 system. High contents of Cr, Ni, Pb, Ti, V and Zn were found in the ashes, with values significantly higher than those reported in literature. According to Cuban regulations these ashes are classified as hazardous waste. For this reason we discuss some management alternatives.

This study represents the first report of heavy metals in bottom ashes from power plants and oil refineries in Cuba.

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1. Introduction

Environmental pollution due to release of smoke, gases, effluents and solid wastes from industries is one of the major issues of global concern. Combustion of fuel oil and coal for electricity production in thermal power plants and for refinery processes, produces a complex mixture of pollutants in the atmosphere, even when employing pollution control devices, that includes: SO_x, NO_x, CO, acid gases, organic compounds and solid wastes such as fly ashes and bottom ashes. The relative amount of each residue depends on the industrial configurations and on the mission control devices available. Bottom ash is a waste material that is discarded continuously from thermal power plants. It is made from agglomerated ash particles that are too large to be carried in the flue gases and fall through open grates to an ash hopper at the bottom of the furnace. Due to the minute particle size and the presence of potentially toxic elements like Arsenic, Chromium, Lead, Vanadium and Zinc, this ash has been considered hazardous for living organisms.

Several authors have reported concentrations of heavy metals in fly and bottom ashes from coal thermal power plants [1–6], however few data are available for these elements in ashes from fuel oil power plants and oil refineries. In Cuba, very few studies exist on the levels of heavy metals in the residual ash from these industries, but none from the Cienfuegos province where a petrochemical pole was developed. An oil refinery producing 65,000 barrels per day and a power plant of 370 MWh were established on the littoral zone of Cienfuegos Bay. Studies carried out in sediments from the bay indicate high contamination in the coastal area where these industries are located [7–9]. Lack of information on the levels of heavy metals in ashes from these industries limits the effectiveness of waste management.

The present study investigates selected heavy metal contents of bottom ashes from thermal power plants and oil refineries located in Cienfuegos and compares those to data available in literature for ashes from other areas. Possible management alternatives are discussed.

2. Materials and methods

Oil ashes were collected from disposal sites of waste materials from the thermal power plant "Carlos M. de Cespedes" (TER) and the refinery "Camilo Cienfuegos" (REF) in Cienfuegos, Cuba.

The oil ash was dried at 110 °C to reach a constant weight and a water content close to 1%. The powder was then sieved and the fraction below 250 μm used in the XRF analysis. Trace elements were measured using X-ray fluorescence (XRF) with a SPECTOR X-LAB PRO 2000 system. The system was calibrated for 4 g samples in sample cups with premounted 4 μm thick Prolene thin-film. Cups were filled with 4 g of dry and sieved (250 μm mesh size) sediment. The XRF analysis was performed by combining measurements with three different targets, which enabled the determination of elements from atomic number 13 (Al) to 92 (U). In

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0016-2361/$ - see front matter © 2011 Published by Elsevier Ltd.
doi:10.1016/j.fuel.2011.03.014

Please cite this article in press as: Alonso-Hernández CM et al. Heavy metal content of bottom ashes from a fuel oil power plant and oil refinery in Cuba. Fuel (2011), doi:10.1016/j.fuel.2011.03.014

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Table 1
Trace elements concentrations in Certified Reference Materials.

	IAEA-356		IAEA-405		IAEA-158	
	Certified	Measured	Certified	Measured	Certified	Measured
Al (g kg^{-1})	39 ± 5.1	34.9 ± 2.0	77.9 ± 5.2	82 ± 1		
As (μg g^{-1})					11.5 ± 1.2	11.5 ± 0.88
Br (μg g^{-1})	76.1 ± 12	77.1 ± 2.3	85 ± 25	77 ± 2		
Cu (μg g^{-1})					48.3 ± 4.2	46.3 ± 1.48
Fe (g kg^{-1})	24.1 ± 2.6	26.9 ± 1.2	37.4 ± 2.20	38 ± 3		
Mn (μg kg^{-1})					356 ± 24	352 ± 8
Ni (μg g^{-1})					30.3 ± 2.9	29.1 ± 1.7
Pb (μg g^{-1})	347 ± 33	311 ± 8	74.8 ± 2.3	77 ± 1	39.7 ± 4.7	41.8 ± 1.18
Se (μg g^{-1})			0.44 ± 0.12	0.40 ± 0.09		
Ti (g kg^{-1})	2.19 ± 0.44	2.03 ± 0.40			0.34 ± 0.01	0.33 ± 0.02
Zn (μg g^{-1})					140 ± 9.5	132 ± 1.9
Sr (μg g^{-1})	170 ± 16	177 ± 10	118 ± 14	130 ± 4	473 ± 25	471 ± 1.14
V (μg g^{-1})					73 ± 3.7	75.6 ± 13.6

addition, IAEA Reference Materials (IAEA-356, IAEA-405, IAEA-433) were used to validate the measurements. Results for the analysis of Reference Materials are reported in Table 1.

3. Results and discussion

3.1. Heavy metals content

Results of the heavy metals content of bottom ash samples from the Cienfuegos power plant and refinery are presented in Table 2.

In the power plant, Vanadium displayed the highest concentrations (14,350 mg kg^{-1}) while Mercury the lowest (0.19 mg kg^{-1}). All tested elements were distributed as follows: V > Ni > Ti > Zn > Mn > Cu > Cr > Pb > As > Hg (see Fig. 1). Results from this study were compared with the ranges of heavy metals reported in literature for fly and bottom ashes from other countries (Table 3). With the exception of As, Hg and Pb, the rest of the elements quantified in the bottom ashes from the Cienfuegos power plant showed higher levels than those reported in literature, especially in the case of V, Ni and Ti. Fig. 2 shows the elemental distribution obtained for bottom ashes from the power plant: Vanadium represents 73% of total quantified elements, while Ni and Ti are both 9%.

Different results are obtained for bottom ashes originated from the oil refinery (Fig. 3). The highest concentration, 14,350 mg kg^{-1}, was recorded for Lead, followed by Vanadium (4779 mg kg^{-1}), Zinc (1928 mg kg^{-1}) and Nickel (1601 mg kg^{-1}). Also in this case the lowest concentrations were reported for Mercury, 0.1 mg kg^{-1}. As for the power plant, the concentrations of metals recorded in ashes from the oil refinery were significantly higher than those reported in literature (Table 2), especially for the Pb, Cr, Mn and V. Fig. 4 shows the elemental distribution in bottom ashes from the oil refinery where: 50% of the analyzed elements is Lead, followed by Vanadium (17%) and Chromium (14%). Manganese, Titanium, Copper, Arsenic and Mercury represent only 3% of the total concentrations of heavy metals in the bottom ashes from the oil refinery.

Table 2
Concentration of elements in bottom ash from power plant (TER) and refinery (REF) in Cienfuegos (values in mg/kg).

Element	TER	REF
As	12.8	16.5
Cr	228	3821
Cu	287	458.3
Hg	0.19	0.1
Mn	362	600
Mo	720	113.9
Ni	1861	1601
Pb	56.8	14,350
Ti	1800	473
V	14,840	4779
Zn	933	1928

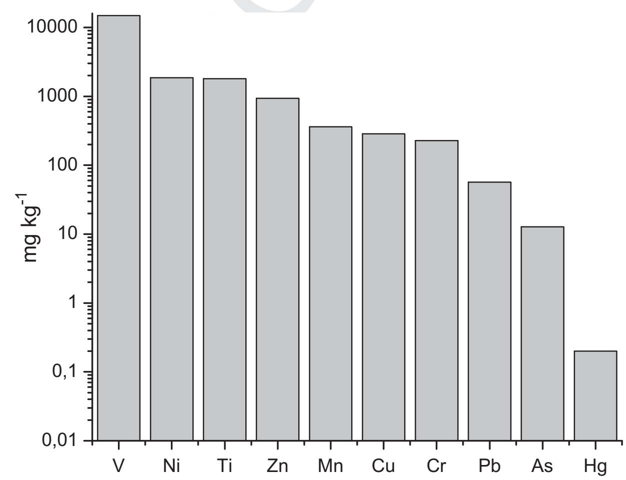

Fig. 1. Levels of heavy metals in bottom ash from fuel oil power plant in Cienfuegos.

3.2. Waste management alternatives

In Cuba, 100,000 tons of "hazardous waste" are generated annually, mostly corresponding to residuals of the petroleum industrial processes. Hence, the appropriate management of these wastes constitutes a priority for the environmental authority of the country.

The Basel Convention [10] was ratified by Cuba in 2008, establishing the regulations for the integral administration of the hazardous waste in the country, through the resolution 136/2009 [11]. This resolution regulates all management activities of hazardous waste from its generation. These are: collection, classification, transport, storage, economic use, treatment and final disposal. According to Annex I of the resolution, ashes from fuel oil power plants and oil refineries are classified as hazardous wastes, excluding the possibility of making final disposal of these ashes in the environment, particularly to the Cienfuegos Bay, common practice up to 1980.

Given the results obtained in this study, the levels of heavy metals in ashes collected from the power plant and refinery of Cienfuegos exceed Italian regulatory limits for their employment as composts for agricultural purposes [12], so limiting this common alternative use [13–17].

Q2 **Table 3**
Comparison of values of heavy metals concentration in this study with those reported in literature (values in mg kg^{-1}). TER: power plant, REF: oil refinery.

Location	As	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Ti	V	Zn	Zr	References
TER	13	228	287	0.19	362	720	1861	57	1800	14,840	933	48	Current study
REF	16	3821	458	0.1	600	114	1601	14,350	473	4779	1928	31	
India		145	83		339		56	54			69		[5,4,2]
China								843					[3]
UK	104							176					…ge et al. (1986)
Spain	60	134	72		324		88	52			221		
Greece		160			330			143			60		[4]
USA										3000–26,446			Hower et al. (2005)

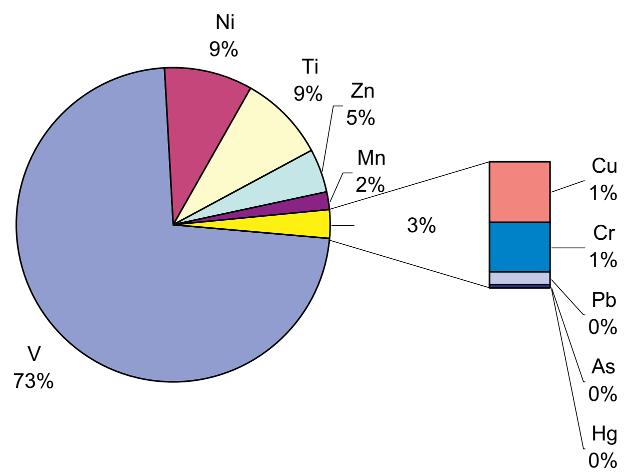

Fig. 2. Heavy metals composition of bottom ash from Cienfuegos power plant.

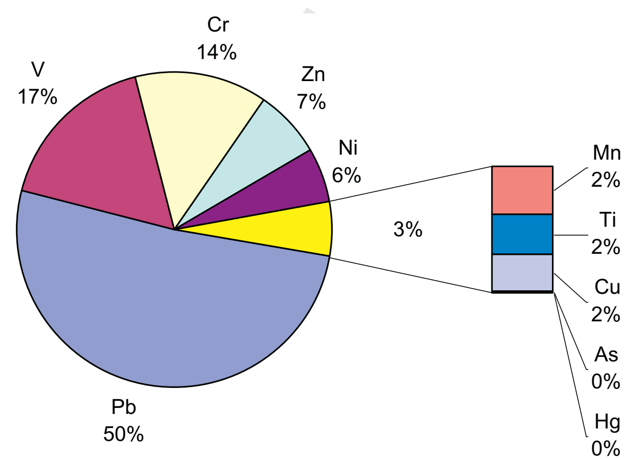

Fig. 4. Heavy metals composition of bottom ash from Cienfuegos oil refinery.

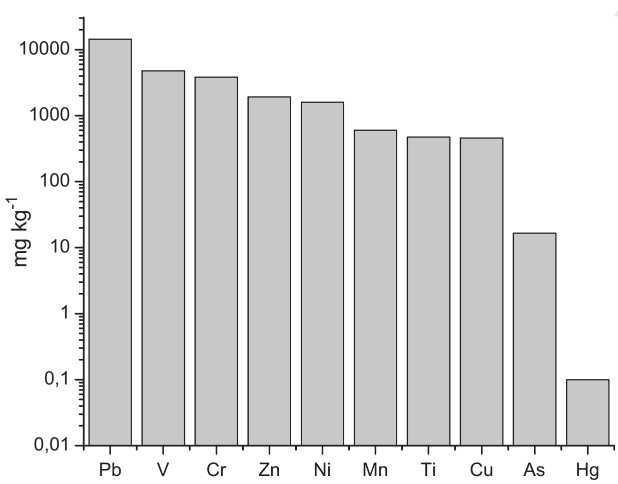

Fig. 3. Levels of heavy metals in bottom ash from oil refinery, Cienfuegos.

Internationally, approximately 45% of the produced bottom ashes are used and applied in many sectors [6,18], as a secondary source of high quantities of valuable metals. By applying mineral processing technologies and hydrometallurgical and biohydrometallurgical processes, it is possible to recover metals such as Al, Ga, Ge, Ca, Cd, Fe, Hg, Mg, Na, Ni, Pb, Ra, Th, V, Zn, etc., from bottom ashes. Recovery of metals from such wastes and their use are important not only for saving metal resources, but also for protecting the environment.

In Cuba, as shown by our results, the recovery of V, Ni, Ti, Pb and Cr could be a cost effective and attractive alternative to their disposal. However, the economic situation of the country does not allow the development of these technologies in the short or medium term.

Other possible uses of bottom ashes from power plants and oil refineries, probably more realistic in the short term, can include road structural fills and concrete/concrete products. Bottom ashes can be used as an aggregate in raw feed material for cement or in asphalt mixes. A cement plant is present in the Cienfuegos area very close to the petrochemical pole.

4. Conclusions

In this study levels of As, Cr, Cu, Hg, Mn, Ni, Pb, Ti, V and Zn of bottom ashes from a thermal power plant and an oil refinery placed in Cienfuegos, Cuba, are presented. The highest concentrations in bottom ashes from the fuel oil power plant were recorded for Vanadium (14,840 mg kg^{-1}), Nickel (1861 mg kg^{-1}), Titanium (1800 mg kg^{-1}) and Zinc (933 mg kg^{-1}). Ashes from the refinery displayed high concentrations of Lead (14,350 mg kg^{-1}), Vanadium (4779 mg kg^{-1}) and Chromium (3821 mg kg^{-1}). These values are significantly higher than those reported in the international literature.

We conclude that the most realistic alternative for the final disposal of bottom ashes from the investigated industries is the incorporation of these in lines of cement or asphalt production, both existent in Cienfuegos.

Acknowledgements

This research work has been undertaken in the framework of the IAEA TC Project CUB/7/008 “Strengthening the National System for Analysis of the Risks and Vulnerability of Cuba’s Coastal Zone Through the Application of Nuclear and Isotopic Techniques”. Special gratitude goes to Dr. Federica Pannacciulli for her great help during the elaboration of the manuscript.

Please cite this article in press as: Alonso-Hernández CM et al. Heavy metal content of bottom ashes from a fuel oil power plant and oil refinery in Cuba. Fuel (2011), doi:10.1016/j.fuel.2011.03.014

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