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TRACE ELEMENT EMISSIONS FROM SOME CEMENT PLANTS IN TURKEY

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Abstract

Air pollution regulation of Turkey deals with the problem of trace element pollution by categorizing inorganic material in two groups and three different classes each and by issuing different emission limits for each class. In the present study, dust samples obtained from main stacks of three cement plants located in three different geographical areas are analyzed for their trace elements including Be, Cd, Cr, Pb, Ni, Se, Te, Tl, V, Sb, Ba, Zn, Co, Sr, Cu, Bi, Ca, Mg and Mo. Sequential plasma type AtomScan 25 inductively coupled plasma spectrophotometer of Thermo Jarrell Ash Corporation has been used in the final analysis of the elements. The samples have been prepared by the modified TJA Portland cement analytical method.

The trace element emission factors which have been calculated for the three cement plants located in different regions of Turkey agree to a great extent with the values given in literature. On the other hand, the trace element emissions of all the plants considered are well below the limits set in the Turkish Air Quality Protection Regulation.

Key words : Trace element, emission, cement, ICP.

INTRODUCTION

Cement production is one of the industries which process high amounts of solid material in a great variety of equipments. The modern concrete roads, buildings, structures like dams etc. indicate the growth and development of this industry in the century which is about to end. Environmental pollution, however, has also developed along with it. This has been a major environmental problem in Turkey in the past. The Turkish cement industry has voluntarily taken precautions to minimize the adverse effects of the air pollution on the natural environment, on human health, and on the equipments, structures etc. Application of efficient control techniques have decreased the dust emissions below the voluntarily set emission limits which are lower than the national limits set in the Turkish Air Quality Protection Regulation (AQPR) of 1986.

The raw materials used for the production of cement clinker are limestone or chalk and clay or their mixture which occur naturally or calcareous marl. Clinker is then blended with various additives to produce different cement types. Chemical compositions of the raw materials used in the cement production in general do not contain harmful substances. Trace elements, however, may cause severe problems because of high production capacities and emission rates and large number of sources involved, especially from the plants which are located in urban areas.

AQPR deals with this problem by categorizing inorganic materials in two groups of noncarcinogenic and carcinogenic elements and in several classes. The limits of these trace elements are given as concentrations in the stack gas provided their emission rates exceed the set flow rates (Table 1). If more than one trace element is present, the set limits of the highest class present apply to their sum. Calcium and magnesium oxides are listed in the third class of noncarcinogenic trace elements although their concentration is quite high in the solid materials dealt with in cement plants.

Table 1. Limits of trace element emissions in the Turkish AQPR.

Class	Total flow rate	Concentration limit
Noncarcinogenic I	> 0.1 [kg/h]	20 [mg/Nm^3]
Noncarcinogenic II	> 1.0 [kg/h]	50 [mg/Nm^3]
Noncarcinogenic III	> 3.0 [kg/h]	75 [mg/Nm^3]
Carcinogenic I	> 0.5 [g/h]	0.1 [mg/Nm^3]
Carcinogenic II	> 5.0 [g/h]	1.0 [mg/Nm^3]

In the presented study, samples of three cement plants located in three different geographical areas of Turkey are analyzed for their trace elements and the results are presented in comparison with the AQPR limits. Also emission factors are calculated and compared with those given in the literature.

METHODS

Samples obtained from the cement plants were analyzed for their composition using a modified version of the method given by Thermo Jarrell Ash. 0.1 to 0.5 grams of each sample was weighed out and placed in 100 ml polyethylene volumetric flask along with 5 to 25 ml of conc. HNO_3 and 3 to 15 ml of conc. HCl and heated for 10 minutes over a 90 °C water bath. Samples were cooled and 0.1 to 1 ml of HF was added. The bottles were capped, heated for 15 minutes at 90 °C, cooled and 0.5 to 1.5 grams of H_3BO_3 added and brought to 100 ml volume. The prepared solutions are then analyzed using Atomscan 25 inductively coupled plasma (ICP) spectrophotometer of Thermo Jarrell Ash.

This method does not differentiate between the carcinogenic and noncarcinogenic salts of Cr, Ni, and Co and their total concentrations are indicated both in the list for carcinogenic and noncarcinogenic compounds. The wavelengths at which emission of the trace elements were numerous. However, the presence of high amounts of calcium, magnesium, titanium, silica, aluminum, and iron limited the number of the wavelengths at which reliable readings could be made. These are given in Table 2.

Table 2. Analytical wavelengths considered.

Element	Symbol	Wavelengths [nm]
Cadmium	Cd	228.802
Chromium	Cr	267.716
Lead	Pb	220.353
Nickel	Ni	231.604, 341.476
Selenium	Se	196.090, 203.985, 206.279
Tellurium	Te	238.578
Titanium	Tl	351.921, 377.572
Vanadium	V	292.464, 310.230
Antimony	Sb	206.833, 217.582
Barium	Ba	455.403, 493.409
Zinc	Zn	206.200, 213.856
Cobalt	Co	237.862, 228.616
Strontium	Sr	407.771, 421.552
Copper	Cu	324.754, 327.396
Bismuth	Bi	190.241
Calcium	Ca	317.933
Magnesium	Mg	285.213, 280.270, 279.079
Molybdenum	Mo	204.598, 203.844
Beryllium	Be	313.042
Arsenic	As	189.042, 197.262

MATERIAL STUDIED

The three cement plants considered are in the Marmara, Aegean, and Central regions of Turkey. The samples are collected at the main stacks of the cement plants. The dust emission of these stacks and the total emissions as well as clinker production capacity of the plants are given in Table 3.

Table 3. Dust emission parameters of the cement plants (Kalafatoğlu et.al, 1996a, b, c).

Region	Plant		Main stack			Clinker production [kg/h]
	no. of sources	emission [kg/h]	no. of sources	emission [kg/h]	% of plant emission	
Marmara	27	39.19	3	19.89	51	228
Aegean	19	27.39	1	24.22	88	108
Central	17	3.16	1	2.99	95	48

RESULTS AND DISCUSSION

The results of the ICP analysis are given in Tables 4-6 for the noncarcinogenic trace elements and in Tables 7-9 for carcinogenic elements for the Marmara, Aegean, and Central region plants, respectively.

Table 4. Noncarcinogenic trace element concentrations of the main stack dust of Marmara Region plant as classified in AQPR (* includes carcinogenic compounds).

Class I Element		[ppm]	Class II Element		[ppm]	Class III Element		[ppm]
Cadmium	Cd	< 2	Antimony	Sb	< 30	Copper	Cu	< 2
Chromium	Cr	42*	Barium	Ba	52	Bismuth	Bi	< 60
Lead	Pb	< 25	Zinc	Zn	33	Calcium oxide	CaO	% 27.9
Nickel	Ni	< 5*	Cobalt	Co	< 3*	Magnesium oxide	MgO	% 0.45
Selenium	Se	< 30	Strontium	Sr	124	Molybdenum	Mo	< 8
Tellurium	Te	< 80						
Thallium	Tl	< 50						
Vanadium	V	16						
Total		< 250			< 242			< % 28.4

Table 5. Noncarcinogenic trace element concentrations of the main stack dust of Aegean Region plant as classified in AQPR (* includes carcinogenic compounds).

Class I Element		[ppm]	Class II Element		[ppm]	Class III Element		[ppm]
Cadmium	Cd	5	Antimony	Sb	< 30	Copper	Cu	< 2
Chromium	Cr	122*	Barium	Ba	87	Bismuth	Bi	< 60
Lead	Pb	< 25	Zinc	Zn	41	Calcium oxide	CaO	% 23.7
Nickel	Ni	87*	Cobalt	Co	< 3*	Magnesium oxide	MgO	% 0.85
Selenium	Se	< 30	Strontium	Sr	644	Molybdenum	Mo	< 8
Tellurium	Te	< 80						
Thallium	Tl	< 50						
Vanadium	V	27						
Total		< 427			< 805			< % 24.6

Table 6. Noncarcinogenic trace element concentrations of the main stack dust of Central Region plant as classified in AQPR (* includes carcinogenic compounds).

Class I			Class II			Class III		
Element		[ppm]	Element		[ppm]	Element		[ppm]
Cadmium	Cd	< 4	Antimony	Sb	< 60	Copper	Cu	< 84
Chromium	Cr	90*	Barium	Ba	123	Bismuth	Bi	< 116
Lead	Pb	< 50	Zinc	Zn	724	Calcium oxide	CaO	% 40.6
Nickel	Ni	50*	Cobalt	Co	< 6*	Magnesium oxide	MgO	% 0.97
Selenium	Se	< 60	Strontium	Sr	160	Molybdenum	Mo	< 16
Tellurium	Te	< 160						
Thallium	Tl	< 100						
Vanadium	V	31						
Total		< 545			< 1073			< % 41.6

Table 7. Carcinogenic trace element concentrations of the main stack dust of Marmara Region plant as classified in AQPR (* includes noncarcinogenic compounds).

Class I			Class II		
Element		[ppm]	Element		[ppm]
Beryllium	Be	< 1	Arsenic trioxide	As_2O_3	< 79
			Chromium	Cr	42*
			Cobalt	Co	< 3*
			Nickel	Ni	< 5*
Total		< 1			< 129

Table 8. Carcinogenic trace element concentrations of the main stack dust of Aegean Region plant as classified in AQPR (* includes noncarcinogenic compounds).

Class I			Class II		
Element		[ppm]	Element		[ppm]
Beryllium	Be	< 1	Arsenic trioxide	As_2O_3	211
			Chromium	Cr	122*
			Cobalt	Co	< 3*
			Nickel	Ni	87*
Total		< 1			< 423

Table 9. Carcinogenic trace element concentrations of the main stack dust of Central Region plant as classified in AQPR (* includes noncarcinogenic compounds).

Class I			Class II		
Element		[ppm]	Element		[ppm]
Beryllium	Be	< 2	Arsenic trioxide	As_2O_3	< 153
			Chromium	Cr	90*
			Cobalt	Co	< 6*
			Nickel	Ni	50*
Total		< 2			< 299

There are no detailed data available for the trace elements emission from cement plants. The emission factors given in the literature are listed in Table 10.

Table 10. Some emission factors of trace elements from cement plants.

Element		I	II	III	IV	V	VI
Arsenic trioxide	As_2O_3	0.000-0.004	-	-	-	0.016	-
Lead	Pb	0.000-0.033	0.006	0.012-0.2	1.1	0.216	≤ 0.033
Selenium	Se	-	-	-	-	0.002	-
Chromium	Cr	0.010-0.011	0.006-0.02	0.02-0.3	-	0.105	-
Nickel	Ni	0.003-0.020	-	-	-	0.111	-
Vanadium	V	0.001-0.020	-	-	-	-	-
Zinc	Zn	0.003-0.047	-	-	11	0.293	0.003-0.47
Cadmium	Cd	0.000-0.001	-	-	0.04	0.008	≤ 0.001
Thallium	Tl	0.000-0.228	-	-	-	-	-

I Sprung (1988); as mg element/kg clinker
II Coal and oil fired, ATMOS 9/10/2; as mg element/kg cement
III Larger proportion of waste oil, ATMOS 9/10/2; as mg element/kg cement
IV Fuel unknown, Pacyna (1990); as mg element/kg cement
V Jockel and Hartje (1991); as mg element/kg cement
VI Dombrowski (1992); as mg element/kg cement

The trace element emission factors for the cement plants under investigation have been calculated on the basis of clinker production because some of the clinker produced is not converted to cement at the site and sold to other cement plants. The results are given in Table 11.

Table 11. Calculated emission factors of trace elements (mg metal/kg clinker).

Element		Marmara region	Aegean region	Central region	Range		
Cadmium	Cd	< 0.0002	0.001	< 0.0002	< 0.0002	-	0.001
Chromium	Cr	0.004	0.027	0.006	0.004	-	0.006
Lead	Pb	< 0.002	< 0.006	< 0.003	< 0.002	-	< 0.006
Nickel	Ni	< 0.0004	0.020	0.003	< 0.0004	-	0.020
Selenium	Se	< 0.003	< 0.007	< 0.004	< 0.003	-	< 0.007
Tellurium	Te	< 0.007	< 0.018	< 0.010	< 0.007	-	< 0.018
Thallium	Tl	< 0.004	< 0.011	< 0.006	< 0.004	-	< 0.011
Vanadium	V	0.001	0.006	0.002	0.001	-	0.006
Antimony	Sb	< 0.003	< 0.007	< 0.004	< 0.003	-	< 0.007
Barium	Ba	0.005	0.020	0.008	0.005	-	0.020
Zinc	Zn	0.003	0.009	0.045	< 0.0003	-	0.045
Cobalt	Co	< 0.0003	< 0.0007	< 0.0004	0.001	-	< 0.0007
Strontium	Sr	0.001	0.144	0.010	0.001	-	0.144
Copper	Cu	< 0.0002	< 0.0004	0.005	< 0.0002	-	0.005
Bismuth	Bi	< 0.005	< 0.013	< 0.007	< 0.005	-	< 0.013
Molybdenum	Mo	< 0.0007	< 0.002	< 0.001	< 0.0007	-	< 0.002
Beryllium	Be	< 0.00009	< 0.0002	< 0.0001	< 0.00009	-	< 0.0002
Arsenic trioxide	As_2O_3	< 0.007	0.047	< 0.010	< 0.007	-	0.047

The emission factors calculated agree in general with the values given in literature with the exception of arsenic trioxide emission from the plant in the Aegean region. This is most probably caused by the relatively higher As_2O_3 content of the raw materials used.

However, the trace element emissions of the plants mostly are below the limits set by AQPR for each element as well as for each class (Table 12). In the case of the Aegean plant, total class III emissions of noncarcinogenic elements and total class II emissions of carcinogenic elements and in the case of the Marmara plant total class III emissions of noncarcinogenic elements are above the flow rates given in AQPR (Table 1). Their emission concentrations, however, are 26 mg/Nm^3 and 0.04 mg/Nm^3, respectively, for the Aegean plant and 9 mg/Nm^3 for the Marmara plant and all are below the limits.

Table 12. Trace element emission flow rates of the cement plants.

Noncarcinogenic elements [kg/h]				
Class	Marmara region	Aegean region	Central region	Limit
I	0.00499	0.0163	0.00163	0.1
II	0.00480	0.0195	0.00321	1.0
III	5.65	6.00	1.243	3.0
Carcinogenic elements [g/h]				
Class	Marmara region	Aegean region	Central region	Limit
I	0.020	0.084	0.00593	0.5
II	0.257	10.25	0.3934	5.0

CONCLUSIONS

The trace element emission factors which have been calculated for the three cement plants located in different regions of Turkey agree to a great extent with the values given in the literature. On the other hand, the trace element emissions of all the plants considered are well below the limits set in the Turkish Air Quality Protection Regulation.

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