

LEGISLATIVE AND METHODOLOGICAL DISAGREEMENTS RELATING TO HEAVY METALS FROM FLY ASH

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ABSTRACT

Fly ash resulting from coal combustion escapes in small amounts into the air as particulate emissions. The majority of these particulates are deposited in the area around the power station. The airborne particulates spread over a large area and then are removed by dilution, moisture and rain. Legislation or other regulations restrict both deposited particulates and airborne particulates. Legislation regarding air particulates does not take into account the heavy metal content. These particulates are laid down by dry deposition on the topsoil close to the power station. Over several years, the soil will accumulate large amounts of fly ash together with the associated heavy metals. These metals are mainly in the form of silicates and they are not covered by regulations that specify limits for leachable metals, those which can be extracted in chloride acid or aqua regia. However, some very hazardous metals such as lead and cadmium are restricted by total content in soil. Over time these metals will certainly exceed the legal limits. A case study for a power station in Romania will be presented.

For a number of years, our team has worked on a great number of environmental impact assessments, especially in the mining field. By processing statistical data obtained from environment quality monitoring, we have observed that, in some cases, there is a lack of correlation between different legislation regarding environment protection. This lack of correlation becomes evident when pollution spreads, affecting successively more environmental media.

This lack of correlation appears between two areas of legislative regulation:

1. Laws that impose environmental quality and limit values for pollutant effluents;
2. Soil and other environmental standards.

Pollutants can spread between environmental media, for example moving from air to soil. There is therefore a chain of legislation that may be appropriate and a legal limit may be exceeded at any time. In order to test this theory we carried out a case study of bituminous coal burning in power stations.

1 COAL QUALITY

It is well established that coal is composed of both organic and inorganic mass. Organic mass is composed of carbon, hydrogen, oxygen, sulphur and nitrogen and inorganic mass of silica, aluminium, oxygen, iron, calcium, magnesium, sodium, potassium, heavy metals and radioactive metals.

Coal quality is only determined by standards relating to combustion characteristics. The sulphur concentration is limited in order to protect the environment. But this regulation may be also imposed to protect the equipment from corrosion during coal combustion (a similar situation is seen with vanadium in oil). The ash content is also restricted, not only for environmental protection but also to increase the combustion process efficiency.

The heavy metal content of coal is shown in Table 1. There is no legislation regulation regarding heavy metal content of coal for energy production.

Table 1. Heavy metal content of coal ash [1].

Nr	Mine	Heavy metal content (mg/kg)						
		Cu	Pb	Zn	Ni	Cd	Cr	Mn
1	Valea de Brazi	100	29	200	240	280	190	850
2	Barbateni	400	34	170	300	300	140	550
3	Petrila Sud	600	34	135	180	300	200	600
4	Livezeni	600	50	170	240	420	200	850
5	Uricani	400	50	220	400	300	225	650
6	Petrila	400	29	150	260	380	200	800
7	Lupeni	180	35	200	200	280	160	850
8	Paroseni	240	34	170	250	320	200	950
9	Câmpu lui Neag	100	34	160	170	200	140	650
10	Aninoasa	400	90	320	320	320	280	620
11	Lonea	100	78	200	300	500	230	900
12	Dâlja	400	60	200	290	400	200	860
13	Vulcan	600	60	340	390	800	550	900

For this study we chose to concentrate on the behaviour of cadmium during the spreading of effluents in the environment.

2 COAL COMBUSTION

Coal undergoes major transformations during combustion. Organic mater is almost entirely transformed into gases such as carbon dioxide, carbon monoxide, sulphur dioxide, nitrogen oxides, water and other products.

At the same time it is possible for some coal particles to remain unburned and, at the high temperature in the furnace, lose their volatile compounds and acquire very good absorbance properties.

Inorganic mass also undergoes transformations that are not obviously like the organic mass transformations. For example, alumino-silicates may undergo dewatering and vitrification processes. Sulphides are decomposed to metallic oxides and sulphur dioxide. The trace elements in coal, by burning, are also transformed into oxides. These oxides may remain as such or they may be transformed into alumino-silicate compounds during vitrification processes.

In conclusion, during coal combustion there are two major solid products:

- furnace slag composed of large particles, with a high density, rich in oxides. This slag is deposited by hydraulic transportation to settling ponds.
- fly ash composed of small particles, of low weight, composed mainly of alumino-silicates. This ash is transported in the gaseous effluents and removed by electrostatic precipitators or other devices and transported to settling ponds. However, a small amount of this ash escapes from filtering devices and is spread in the atmosphere together with gaseous effluents.

Cadmium, studied in this paper, cannot demonstrate its chalcophile characteristics as sulphur is absent., and shows only lithophilic characteristics through association with alumino-silicates. Because of this, cadmium may exist in ash both as oxides that do not react with alumino-silicates and in great amounts like alumino-silicates.

It is important to remember the differences between the chemical properties of these compounds:

- Cadmium oxide, together with the other metallic oxides, is soluble in chloride acid, nitric acids solutions or aqua regia.
- Alumino-silicates are not soluble in acids, so heavy metals including cadmium cannot be extracted by acid leaching. Digestion requires fusion at high temperature with sodium carbonate and potassium carbonate.

- e.g. 1g ash contains 0.370 mg Cd (average content for all mines) from which
 0.055 mg is recoverable by acid digestion
 0.370 mg is recoverable by alkaline fusion

Even though coal quality is controlled to some extent to ensure environmental protection, atmospheric emissions are also restricted by legislation. These limits indirectly impose further coal quality restrictions. This legislation refers to both gaseous emissions and particulate emissions, including their chemical composition. Table 2 shows the legal limits regarding particulate emissions and their heavy metal content.

Table 2. Legislation regarding particulate emissions [2].

Pollutant	Emissions - legal limits	
	New equipment	Old equipment
Particulate	50 mg/m ³	125 mg/m ³
Heavy metals	0.5 mg/m ³	1.5 mg/m ³

The analysis of the cadmium content of these particulate emissions was performed in accordance with STAS 12731-89 which stipulates that particulate matter should be leached with nitric acid, then with perchloric acid and boiled until a white residue remains [3]. After dissolving, the solution is analysed by specific methods. Taking into account the properties of the cadmium compounds, as mentioned before, it is obvious that a part of cadmium will escape from this analysis.

- e.g. 0.125g ash contains 0.046 mg Cd from which:
 0.0069 mg is recoverable by acid digestion
 0.046 mg is recoverable by alkaline fusion

3 AIR QUALITY

In the case of atmospheric emissions, the Environmental Ministry Order no. 462/1993 rigorously limits air particulate concentration, especially in protected areas. This law refers to the gaseous pollutant and particulate concentration and the heavy metal content of particulates. Table 3 shows the main regulation of this law.

Table 3. Air quality regulations [4].

Pollutant	Maximum concentration (mg/m ³)			
	Short term		Long term	
	30 min	Daily	monthly	annual
Particulates	0.5	0.15	-	0.075
Cd	-	0.00002	-	-
Cr	-	0.0015	-	-
Mn	-	0.01	-	-
Pb	-	0.0007	-	-

In the case of cadmium, the focus of this paper, the concentration is determined in the same way as for atmospheric emissions. This means that part of cadmium will escape from the chemical analysis.

- e.g. 0.15 mg ash contains 0.000055 mg/m³ Cd from which:
 0.000008 mg/m³ is recoverable by acid digestion
 0.000055 mg/m³ is recoverable by alkaline fusion

4 SEDIMENTABLE PARTICLES.

Atmospheric immersions (deposition) are regulated by the same law, Order 462/1193, which refers in this case to particles that are deposited on the soil (Table 4).

Table 4. Legal limits for “sedimentable” particulates [3].

Pollutant	Admissible value g/m ² /month
Sedimentable particulates	17

e.g. 17 g/m²/month ash contains 6.29 mg/m²/month Cd from which:
6.29 mg/m²/month Cd is recoverable by alkaline fusion

5 SOIL QUALITY

Soil quality is rigorously regulated in accordance with Order no. 756/1997. This Order differentiates between different soil use categories. Table 5 presents some heavy metal content limits for soil.

Table 5. Heavy metal admissible contents in soil [5].

Heavy metal	Normal value	Alert limit / Using category		Intervention limit / Using category	
		Sensitive	Less sensitive	Sensitive	Less sensitive
Cd	1	3	5	5	10
Co	15	30	100	50	250
Cr:					
Cr _{total}	30	100	300	300	600
Cr ^{VI}	1	4	10	10	20
Cu	20	100	250	200	500
Mn	900	1500	2000	2500	4000
Ni	20	75	200	150	500
Pb	20	50	250	100	1000
Zn	100	300	700	600	1500

The same Order provides the regulations regarding soil sampling. For example, the Order provides the number of samples related to the site surface and the sampling methods to be used. For this study, the sampling method is of special interest.

These sampling methods comprise:

1. Removal of top layer of soil that is very rich in roots. It is obvious that in the case of uncultivated soils, the majority of the particles from air will be removed from the sample by doing this.
2. The first soil sample is taken from five centimetres depth in the soil. This sample contains “sedimentable” particulates in cultivated soil when the earth is ploughed.
3. A second soil sample is taken from thirty centimetres depth to assess the extent of the soil contamination. In the case of deposited particulates, this soil portion cannot be affected other than by leaching products.

As a result of particulate deposition during the working lifetime of the power station, it is expected that significant quantities of heavy metals from this dust will accumulate in the soil.

The analysis of soil samples is made in accordance with a method approved by the Health Ministry.

In case of soil samples, these methods assume total samples breakdown involving alkaline fusion. In this way the entire heavy metal content, including alumino-silicates, reaches the analysis solution.

e.g. 17 g/m²/month ash contains 6.29 mg/m²/month Cd added to 1 m² of soil from which:

6.29 mg/m²/month Cd is recoverable by alkaline fusion

In case of uncultivated soils this means:

per month - 6.29 mg/m²/month Cd / 0.050m depth · 1m² · 2100 kg/m³
result 0.060 mg/kg Cd

per year 12 x 6.29 mg/m²/month Cd / 0.050m depth · 1m² · 2100 kg/m³
result 0.69 mg/kg Cd

during power station life time

(40 years) 40 x 12 x 6.29 mg/m²/month Cd / 0.050m depth · 1m² · 2100 kg/m³
result 28.7 mg/kg Cd

In case of cultivated soils (30 cm plough depth) this means:

per month 6.29 mg/m²/month Cd / 0.300m depth · 1m² · 2100 kg/m³
result 0.010 mg/kg Cd

per year 12 x 6.29 mg/m²/month Cd / 0.300m depth · 1m² · 2100 kg/m³
result 0.120 mg/kg Cd

during power station life time

(40 years) 40 x 12 x 6.29 mg/m²/month Cd / 0.300m depth · 1m² · 2100 kg/m³
result 4.79 mg/kg Cd

All the cadmium be analysed by using this method. In this way is very likely that the cadmium content of the soil will be greater than the legal limits in the case of cultivated soils, even if the average values do not exceed the admissible limits.

6 CONCLUSION

1. Even if legal limits for pollutant emissions are respected, other environmental limits may be exceeded due to a lack of correlation between legislation relating to different environmental media.
2. The first area of disagreement is between legislation regarding emissions, immision (deposition) or soil pollutant content.
3. The second area of disagreement is in the different analysis methods specified within the legislation.
4. This paper shows that, in some cases, it is possible to exceed permitted pollutant values in one or more environment media even when abiding by the law.

References

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I am a graduate of Timisoara Polytechnic University, Chemical Engineering Faculty, specialising in Inorganic Chemistry Engineering. I am also a postgraduate of Oxford Brookes University, School of Planning, in

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