

BERYLLIUM POLLUTION FROM SLAG AND ASHES FROM THERMAL POWER STATIONS

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Abstract. Beryllium enters the environment principally from coal combustion. Be contents in the ashes from a Czechoslovak power plant were determined. The ashes used in the experiment were as follows: coarse (> 2.0 mm) and fine (2.0 to 0.2 mm) fraction from dump, and fine (< 0.2 mm) fraction from electrostatic precipitators. It was discovered that the acidic and the alkali aqueous extracts of these ashes contain various concentrations of Be (1 to 17% of total concentration). Wastewater has shown 3.15 and $3.4 \mu\text{g Be L}^{-1}$. Thus, secondary long-term Be pollution emerges from the slag and ash dumps.

1. Introduction

Beryllium exhibits toxic and carcinogenic effects (Groth *et al.*, 1980; Reeves, 1979; Sunderman, 1984; IARC, 1980; SCTM, 1981). Its threshold limiting value is $2 \mu\text{g Be m}^{-3}$ and MAC occupational exposure value is $1 \mu\text{g Be m}^{-3}$. Experimental evidence of carcinogenic effects of Be on mammals has been reviewed by Kuschner (1981); the phytotoxicity of this element is not yet fully understood (Lepp, 1981).

The amount of Be present in the environment has increased dramatically over the past 50 yr. The world production of Be was about 20×10^3 tonne in 1979. The annual emissions of Be have been estimated to be 30 tonne. About 2 tonne of Be pollution results from special extraction plants and in the nuclear, electrotechnical, metal working, machinery, and ceramic industries.

The amount of atmospheric emissions of Be in Czechoslovakia is estimated to be $3.1 \text{ tonne yr}^{-1}$; in this respect this country assumes fifth place in Europe after USSR, Poland, GDR, and FRG (Pacyna, 1984). The main source of pollution is thermal power stations which burn coal containing Be, particularly brown coal mined at the North Bohemia Brown Coal Mining District which contains Be in amounts of 1.5 to $30 \mu\text{g g}^{-1}$ (annual extraction of coal about 1×10^8 tonne) (Bouška 1981).

In 1976 to 1980 we monitored environmental pollution in the vicinity of a thermal power station burning coal from that mining district, and measured the concentration of Be and other potentially toxic elements along the chain: coal-slag-ashes-dust fallout-wastewater from the light ashes dumping ground-soil-plants within a distance of 15 km from the power station. We observed no significant changes in the accumulation of trace elements in crop plants, which are the first link of the food chain (Švácha *et al.*, 1979, 1980).

The aim of the present work was to estimate the Be content of the solid matter of the wastewaters, and to examine the liberation of this pollutant from the solid matter by acid and alkaline solutions at various pH.

2. Materials and Methods

The Mělník power station is a condensation type, with installed capacity of 1333 MW; its annual fuel consumption is about 5×10^6 tonne of brown coal with medium S content and about 30% ash. The dump, located to the west of the station, is a horizontal type and is divided into two parts by an hydraulic-fill earth dam. The situation is depicted in Figure 1.

The samples were ground and homogenized in a ball grinder (Fritsch, FRG), their wet decomposition was performed in a home made Teflon-lined autoclave.

Beryllium was determined fluorometrically with morin on a Flaphokol III instrument equipped with a fluorometric adapter (Zeiss, Jena, GDR). The acidity of the solutions treated was measured on an OP-265/1 digital pH-meter (Radelkis, Hungary).

A reference stock solution of Be was prepared by dissolving 0.4506 g of Be in 50 mL of 1M- H_2SO_4 and diluting to 500 mL with water. A 0.064% solution of morin in ethanol was made up from the purified chemical (Koch-Light, U.K.). The other chemicals used of reagent grade purity were purchased from Lachema, Czechoslovakia.

Samples were collected in polyethylene bags, dried at 105 °C, and screened using 2.0 and 0.2 mm sieves to obtain a coarse fraction from the dump, a fine fraction (fly ashes) from the dump, and a fine fraction from an electrostatic precipitator in the power station.

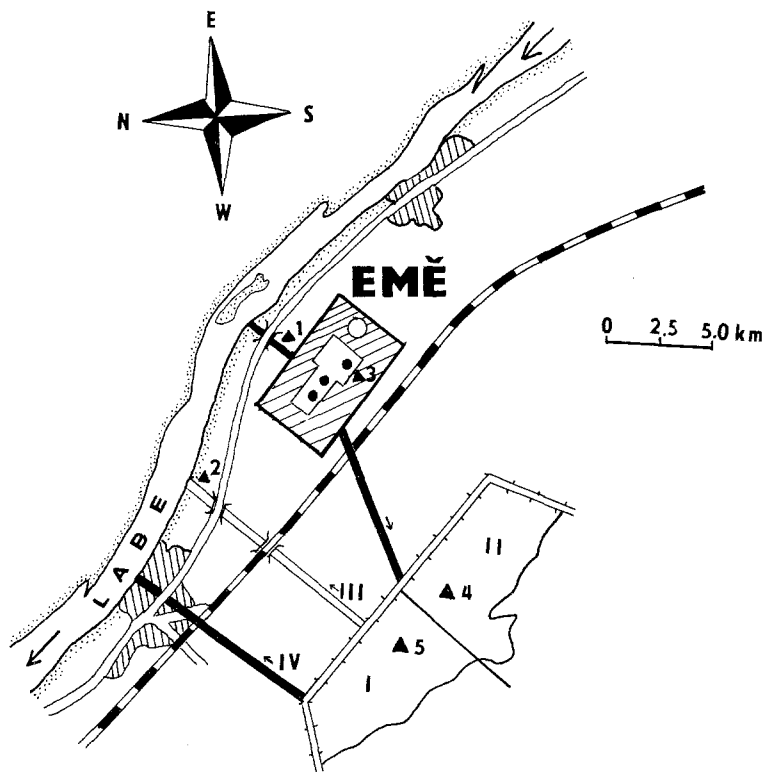


Fig. 1. Location of sampling sites in the surroundings of the Mělník thermal power station.

For determining the total Be content, about 0.2 g samples were decomposed by pressure digestion with 8 mL of concentrated HCl and 2 mL of concentrated HNO₃ for 1 hr at 150 °C. The system was filtered through a Synpor filter, the filtrate was diluted and Be was determined (details concerning the optimized fluorometric determination of Be in environmental samples can be found in Kubizňáková, 1983).

Wastewater samples (1000 mL) were stored with 10 mL additions of concentrated HCl as a preservative. The polyethylene bottles were cleaned with 1M-HNO₃, and perfectly rinsed with redistilled water prior to use.

In order to see how easily Be can be released from actual samples by acidity in alkalinity, 50 mL volumes of 10⁻³, 10⁻⁴, and 10⁻⁵ M solutions of H₂SO₄ and sodium hydroxide were added to 5 g samples in polyethylene bottles, and the systems were allowed to stand for 40 days with occasional stirring. The suspensions then were filtered, pH of the filtrate was measured and the concentration of Be was determined.

3. Results and Discussion

The results are given in Table I. The long-term action of weakly acid or weakly basic solutions leads to a partial liberation of Be from the ashes. The total available Be concentrations in the coarse fraction from the ash dump (sample A), in the fly ash from the dump (sample B), and in the light ashes from the electrostatic precipitator (sample C) were 1.80, 1.87, and 1.58 µg g⁻¹, respectively. Acid medium releases Be best from the light ash from the precipitator (samples Nos. 16 to 18), whereas the coarse fraction from the dump is better attacked by alkaline solutions (samples Nos. 5 to 7). Virtually no Be was extracted from the ash on the dump (sample B), which is a fine fraction formed by abrasion. This fly ash contained Be in the highest amounts, and also has the highest pH (in the most basic medium).

During the hydraulic transport of the slag-ash slurry to the dump, the ash interacts with the water used, whereby the quality of the latter is markedly affected. Therefore, we also measured the average amounts of insoluble and soluble matter, pH, and Be concentrations in this water. The results are given in Table II. The pH was found to be higher by 0.3, and also the amount of insoluble and soluble matter was about 3 and 12%, respectively, higher in the wastewater than in the initial water source. (These values, naturally, refer to our specific case and cannot be generalized.)

Beryllium concentrations were determined both in the outflowing (recurrent) water from the dump and in the stagnant water directly on the dump. The values obtained were 3.15 and 3.4 µg L⁻¹, respectively. It should be noted that the dump comprises a variety of materials of different chemical composition, granularity, etc., and a number of local equilibria, influenced by diverse external factors, are involved.

The water draining from the dump affects the underground waters by increasing their level and gradients, and possibly also by contaminating them with a number of elements, including Be. It was, indeed, observed that if no wet feed is added, rapid draining and drying of the dump take place.

The concentrations of Be in the outflow waters were compared with the highest

TABLE I
Extraction of Be from ashes with acid and alkaline solutions

No.	Extractant	Be extracted		pH
		ng L ⁻¹	%	
A. Coarse fraction from dump (sites 4, 5), grain size 2 mm, Be content 1.80 µg g ⁻¹				
1	Water	67.5	3.8	6.79
2	10 ⁻³ M-H ₂ SO ₄	45.0	2.5	6.33
3	10 ⁻⁴ M-H ₂ SO ₄	45.0	2.5	6.33
4	10 ⁻⁵ M-H ₂ SO ₄	78.8	4.3	6.75
5	10 ⁻³ M-NaOH	67.5	3.8	7.65
6	10 ⁻⁴ M-NaOH	146.3	8.1	6.55
7	10 ⁻⁵ M-NaOH	135.0	7.5	7.32
B. Fly ash from dump (sites 4, 5), grain size 2.0–0.2 mm, Be content 1.87 µg g ⁻¹				
8	Water	22.5	1.2	7.49
9	10 ⁻³ M-H ₂ SO ₄	45.0	2.4	8.11
10	10 ⁻⁴ M-H ₂ SO ₄	< 0.5	–	7.08
11	10 ⁻⁵ M-H ₂ SO ₄	< 0.5	–	7.11
12	10 ⁻³ M-NaOH	< 0.5	–	7.92
13	10 ⁻⁴ M-NaOH	< 0.5	–	7.35
14	10 ⁻⁵ M-NaOH	< 0.5	–	7.67
C. Light ash from electrostatic precipitator (site 3), grain size 0.2 mm, Be content 1.58 µg g ⁻¹				
15	Water	22.5	1.5	7.39
16	10 ⁻³ M-H ₂ SO ₄	22.5	1.4	7.39
17	10 ⁻⁴ M-H ₂ SO ₄	270.0	17.1	7.38
18	10 ⁻⁵ M-H ₂ SO ₄	135.0	8.5	7.38
19	10 ⁻³ M-NaOH	67.5	4.3	7.59
20	10 ⁻⁴ M-NaOH	67.5	4.3	7.48
21	10 ⁻⁵ M-NaOH	22.5	1.4	7.38

TABLE II
Characteristics of water of Mělník power station

Parameter	Labe river (site 1)	Waste channel (site 2)	Difference (%)
Insoluble matter, mg L ⁻¹	25.0	25.7	2.8
Soluble matter, mg L ⁻¹	280.0	314.0	12.1
Total dry matter, mg L ⁻¹	305.0	339.7	11.4
pH	7.1	7.4	–
Beryllium concentration, µg L ⁻¹	0.5	3.15	530.0

admissible values as per EPA, which are $11 \mu\text{g L}^{-1}$ for surface waters and $1.1 \mu\text{g L}^{-1}$ for underground waters (EPA-Be 1978), and was found to be lower than the former. (No Czechoslovak standard giving the highest admissible concentrations of Be in waters exists. A USSR standard requires less than $0.2 \mu\text{g Be L}^{-1}$ in drinking water.)

Balance calculations showed that the power station contributes daily 100 g of Be to the wastewater pollution. Air pollution by volatile beryllium compounds (chloride, fluoride) also occurs. It is estimated that about 1% of the total Be contained in the coal is released to the air, the majority, however, remains in the slag. Liberation of Be from power station ashes was observed by Jiřele as early as 1967.

Our present knowledge of the environmental situation with respect to the pollution by this dangerous element is still incomplete, and additional data concerning the normal and elevated levels of Be both in the natural ecosystems and in ecosystems disturbed by the activity of man are necessary for a comprehensive and thorough evaluation.

4. Conclusions

Thermal power stations, which burn coal with high Be contents, are the most serious sources of environmental pollution by this element. In addition to the primary pollution by emissions, secondary pollution emerges from the slag and ash dumps. These dumps give rise to long-term pollution, from which both surface and underground waters become contaminated. The experiments presented in this paper give evidence that Be can be released from the solid matter rather readily. In view of the high toxicity of this metal, these observations should stimulate further interest in its behavior and transport in the environment.

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