

## Flotation of river-born sediment from the old ecological load of Černý příkop in Ostrava, Czech Republic

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### Abstract

The paper deals with an evaluation of the flotation application suitability in the sludge decontamination from the Černý příkop situated in the city of Ostrava. We used Montanol 551 as a flotation collector, which are commonly used in coal mineral processing. The water quality in the Černý příkop is predominantly determined by the quality of the discharged water from the Ján Šverma Coking Plant, MCHZ (chemical industry) and the water from the Central Waste Water Treatment Plant for Ostrava, which participate in the course aquosity with two thirds. Application of the flotation is used as a new quick method of decontamination of organic pollutants as PAHs, PCBs and petroleum hydrocarbons  $C_{10} - C_{40}$ . Flotation of organic pollutants is very effective and more than 90 % of hydrocarbons  $C_{10} - C_{40}$ , 70 % of PCB and 70 % of PAH from the sediments was removed.

**Key words:** flotation, PAHs, PCBs, Petroleum hydrocarbons  $C_{10} - C_{40}$

### Introduction

Organic pollutants belong among the most ubiquitous in our environment. They have accumulated because of a variety of anthropogenic causes and because of their greater hydrophobicity (i.e., their lack of solubility in the water). The organic chemical industry, which manufactures the carbon-containing chemicals, produces an enormous number of materials that are essential to the economy and to the modern life. This industry obtains raw materials from the petroleum industry and converts them to the intermediate materials or basic finished chemicals. Organic chemical industries are among the largest producers of the toxic wastes (Mukesh et al., 2005). The high content of organic pollutants such as PAHs, PCBs and petroleum hydrocarbons  $C_{10} - C_{40}$  in the sediments is real problem in the city of Ostrava. These pollutants have entered into the sediments predominantly from the waste water from both the above mentioned sources, larger part being from the Ján Šverma Coking Plant and probably there is a seepage from the industrial premises of the Ján Šverma Coking Plant and the near-by petroleum oil lagoons Ostramo, which affect the content of hydrocarbons  $C_{10} - C_{40}$  and PCB in the sediment.

Organics, which include polycyclic aromatic hydrocarbons (PAHs), chlorinated aromatic hydrocarbons, chlorinated aliphatic hydrocarbons, halogenated hydrocarbons, biphenyls, phenols, aniline derivatives, phenol ethoxylates, and benzoic acid derivatives, are ubiquitous in our environment. Both anthropogenic and natural causes are known for their accumulation. They are found in the water, marine systems, soil, sewage, and air.

These are the most common pollutants and are known to persist in the environment. Some of them, such as the PAHs, are potential carcinogens. All of them are reported to have adverse effects on the human and animal health. Some of these, like the polyhalogenated aromatics, are chemically inert and therefore can only be degraded by biological means. The degradation could be either by aerobic or anaerobic pathways. A brief outline of both these pathways is necessary to be able to design suitable degradation pathways for a given contaminant (Simpson et al., 1995). Hydrocarbons  $C_{10} - C_{40}$  represent a term used to describe a several hundred chemical compounds that originally come from the crude oil. Crude oil is used to make petroleum products, which can contaminate the environment. Because there are so many different chemicals in the crude oil and in other petroleum products, it is not practical to measure each one separately. However, it is useful to measure the total amount of hydrocarbons  $C_{10} - C_{40}$  at a site. Hydrocarbons  $C_{10} - C_{40}$  are a mixture of chemicals, but they are all made mainly from the hydrogen and carbon, called hydrocarbons. Scientists divide hydrocarbons  $C_{10} - C_{40}$  into groups of petroleum hydrocarbons that act alike in soil or water. These groups are called petroleum hydrocarbon fractions. Each fraction contains many individual chemicals. Some chemicals that may be found in hydrocarbons  $C_{10} - C_{40}$  are hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorene, as well as other petroleum products and gasoline components (Li et al., 2002).

Polychlorinated biphenyls (PCBs) are mixtures of up to 209 individual chlorinated compounds (known as congeners). There are no known natural sources of PCBs.

Tab. 1  
Organic pollutant content in the sediment solids from the Černý příkop (mg · kg<sup>-1</sup> solids)

Benzene	BTEX	EOX	C <sub>10</sub> – C <sub>40</sub>	Tetrachlorethene	Trichlorethene	PAH(15)	PCB(6)
3.58	8.722	14.4	2880	0.76	1.06	541	0.644

Notes: PCB (congeners 28, 52, 101, 138, 153, 180), BTEX (volatile organic compounds – benzene, toluene, ethylbenzene and xylenes), EOX – organic halides extractable by a specified organic solvent

PCBs are either oily liquids or solids that are colourless to light yellow. Some PCBs can exist as a vapor in air. Flotation has not been applied in the cleaning of organically contaminated soils and sediments in the Czech Republic so far. In the CR there are only references on the application of flotation predominantly in the cleaning of oiled water which can be found in the textbooks on the theory of flotation (Kmeř, 1986; Fečko et al., 2009).

### Description of the Černý příkop locality

The Černý příkop rises in Ostrava, the municipality of Mariánské Hory, located approximately 230 m above sea level. It runs through the city district of Moravská Ostrava and Přívoz and near the confluence of the Odra and Ostravice rivers it flows into the Odra river. The course is about 5 km long and Q355 is 0.074 m<sup>3</sup> · s<sup>-1</sup>. Waste water from the Ján Šverma Coking Plant and the Central Waste Water Treatment Plant for Ostrava (UCOV) is discharged into the Černý příkop. The average value of BSK5 in 2007 was 7.2 mg · l<sup>-1</sup> (4th quality class) and CHSK 37.5 mg · l<sup>-1</sup> (5th quality class). Also the parameter of ammoniated nitrogen of 3.28 mg/l places this water course into the 5th quality class. Out of the monitored parameters only total phosphorus (0.25 mg · l<sup>-1</sup>) and electrolytic conductivity of 122 mS · m<sup>-1</sup> are placed into the class 3. The water quality in the Černý příkop is predominantly determined by the quality of the discharged water from the Ján Šverma Coking Plant (0.014 m<sup>3</sup> · s<sup>-1</sup>) and the water from the Central Waste Water Treatment Plant for Ostrava (0.038 m<sup>3</sup> · s<sup>-1</sup>), which participate in the course aqosity with two thirds.

Within the construction of D 47 motorway a partial relocation of the water course into a new bed (2.47 km) had been planned below the waste water discharge from the Ján Šverma Coking Plant. The relocation of the water course also required a removal of the sediments. The sediment reached the thickness of 1.8 m, the average thickness of the sediment in the bed was 1.2 m and the minimum thickness of the sediment was 0.2 m (shipyard). The sediment comprised of organic pollutants in the concentrations (see Tab. 2), which prevented its dumping on a disposal site. Also the content of organic carbon in the sediment solids (30.82 %) was the second key parameter, which limited its dumping on a disposal site (5 % TOC). The content of heavy metals in the water extract meets the requirements of Regulation 294/2005 Coll. The problem sediment pollutants are mainly PAH, PCB and petroleum hydrocarbons C<sub>10</sub> – C<sub>40</sub>.

With regard to the fact that the content of the organic pollutants in the solids exceeded (see in Tab. 1) the limits for dumping this waste on disposal sites a suitable decontaminating technology had to be selected, which would permit a safe disposal of the waste on the disposal site or a new method of utilization of the decontaminated sediment (e.g. for land reclamation).

### Materials and methods

#### Mineralogical composition of the Černý příkop sediment

Four samples of sediments from different sampling points were taken. The mineralogical composition analysis of the samples was carried out on an all-levels sample. An X-ray diffraction analysis was done in the laboratories of the Institute of Geological Engineering at VŠB-TU Ostrava. The measurements were carried out on a modernized, fully automated diffractometer URD-6 (Rich. Seifert-FPM, SRN). The following phases were identified on the samples in question: ankerite, chlorite, kaolinite, muscovite, orthoclase, plagioclase, amorphous, quartz (see Fig. 1).

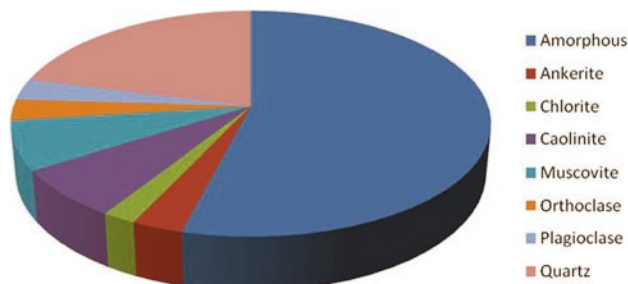


Fig. 1. Mineralogical composition of the Černý příkop sediments.

### Flotation experiments

The flotation experiments were carried out in the laboratories of the Institute of Environmental Engineering at the VŠB-TU Ostrava on a flotation machine VRF-1, a product of RD Příbram with an active capacity of 1 litre, under the following conditions:

- Condensation: 150 g · l<sup>-1</sup>
- Montanol 551 collector dose: 500 g · t<sup>-1</sup>
- Pulp collector agitation: 2 min.
- Flotation time: 10 min.

Tab. 2  
Flotation results – Sampling point 1

Product	Yield %	Content			Recovery		
		PAH	Σ PCB	C <sub>4</sub> –C <sub>10</sub>	PAH	Σ PCB	C <sub>4</sub> –C <sub>10</sub>
		mg · kg <sup>-1</sup>	mg · kg <sup>-1</sup>	mg · kg <sup>-1</sup>	%	%	%
K1	67.23	6 293	0.458	4 636	74.49	87.72	95.99
O1	32.77	293	0.396	1 812	25.51	12.28	4.01
P	100	5 061	0.351	3 065.4	100.00	100	100

Notes: K – concentrate, O – tailings, P – feed

Tab. 4  
Flotation results – Sampling point 3

Product	Yield %	Content			Recovery		
		PAH	Σ PCB	C <sub>4</sub> –C <sub>10</sub>	PAH	Σ PCB	C <sub>4</sub> –C <sub>10</sub>
		mg · kg <sup>-1</sup>	mg · kg <sup>-1</sup>	mg · kg <sup>-1</sup>	%	%	%
K3	57.12	1 082	0.330	4 607	68.75	69.56	78.647
O3	42.88	710	0.219	1 819	31.25	30.44	21.353
P	100	899	0.271	3 065.4	100.00	100.00	100

Notes: K – concentrate, O – tailings, P – feed

Tab. 3  
Flotation results – Sampling point 2

Product	Yield %	Content			Recovery		
		PAH	Σ PCB	C <sub>4</sub> –C <sub>10</sub>	PAH	Σ PCB	C <sub>4</sub> –C <sub>10</sub>
		mg · kg <sup>-1</sup>	mg · kg <sup>-1</sup>	mg · kg <sup>-1</sup>	%	%	%
K2	59.91	1 493	0.348	106	78.66	69.04	78.14
O2	40.09	934	0.206	50	21.34	30.96	21.86
P	100	1 276	0.302	85.15	100	100.00	100.00

Notes: K – concentrate, O – tailings, P – feed

Tab. 5  
Flotation results – Sampling point 4

Product	Yield %	Content			Recovery		
		PAH	Σ PCB	C <sub>4</sub> –C <sub>10</sub>	PAH	Σ PCB	C <sub>4</sub> –C <sub>10</sub>
		mg · kg <sup>-1</sup>	mg · kg <sup>-1</sup>	mg · kg <sup>-1</sup>	%	%	%
K4	61.10	641	0.327	< 0.5	78.96	58.08	–
O4	38.90	222.7	0.367	< 0.5	21.04	41.92	–
P	100	496	0.344		100.00	100.00	–

Notes: K – concentrate, O – tailings, P – feed

## Results and discussion

Having finished the flotation, the flotation products (both the concentrate and the tailings) were filtered, dried and underwent chemical analyses for PAHs, PCBs and hydrocarbons C<sub>10</sub> – C<sub>40</sub>, which were carried out in the laboratories of VÚHU, a. s. in Most. The flotation experiments were done on 4 samples from different sampling points. First sample was removed near from pollutant outlet water from the Ján Šverma Coking Plant and MCHZ Borsodcem. Another samples were removed in 200 m intervals. Fig. 2 shows first sampling point.

The results of flotation experiments (see Tabs. 2 and 5) imply that flotation applied on the samples in question is very effective and the obtained results are excellent. Applying flotation a high recovery of polluting material in the concentrates was succeeded in. The results confirm that the sediments drawn in closer sites to the industrial premises contain much larger proportions of pollutants than the sediments from more remote sites from the pollution sources. In the sample No. 1, in the case of which the highest pollutant concentrations were measured, the efficiency of flotation was 74 % for PAHs, 95 % for hydrocarbons C<sub>4</sub> – C<sub>10</sub> and 87 % for PCBs. In the sample No. 2, which was drawn from a site situated 200 m from the first sampling point, lower pollutant concentrations were measured. By means of flotation it was possible to remove 68 % of PAHs, 78 % of hydrocarbons C<sub>4</sub> – C<sub>10</sub> and 69 % of PCBs. The third sampling point was 400 m from the discharge. The efficiency of flotation was 78 % for PAHs, 78 % for hydrocarbons C<sub>4</sub> – C<sub>10</sub> and 69 % for PCBs. The fourth sampling point was situated 600 m from the



Fig. 2. First sampling point.

discharge. The efficiency of flotation was 74 % for PAHs and 58 % for PCBs. The content of hydrocarbons C<sub>4</sub> – C<sub>10</sub> was below the detection level.

## Conclusion

The objective of the work was to verify an application of separation by the flotation in the decontamination of sediment samples from Černý příkop situated in the city of Ostrava. The content of pollutants was over 80 %, which means that the given inexpensive technology would be able to treat the sediments which represent an immense ecological load for the city of Ostrava. It can be said that

setting the conditions right, froth flotation is positively a very effective tool how to decontaminate sediments. Despite the fact the experiment was carried out using sediments, it can be expected that the application of flotation shall be efficient also with other materials that may be polluted with similar substances.

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