# EMISSION CONTROL, ABATEMENT TECHNOLOGIES AND REMEDIATION - POSTERS

### OXIDATIVE-GEOCHEMICAL BARRIER AGAINST DIOXIN-POLLUTION AS GROUNDWATER REMEDIATION METHOD

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#### Introduction

It is known that, dioxins have a low solubility in water (2 - 200 ng/L) and their high sorbability in soil (coefficient of interfacial distribution in a system soil/water is on the order of 10<sup>4</sup> magnitude). However, they are found in groundwaters in the quantities that greatly exceed allowed standards ("top allowed concentrations"). Migration of dioxins in groundwater-aquifer to significant distances from the ground surface - which is an original place of their appearing in the groundwaters - is explained by their transport by carrier substances (organic acids and solvents, oil industry spills, landfills filtrates, waste waters of municipal and industrial sewerage systems)<sup>11</sup>. High enough mobility of the dioxins in the groundwaters determines necessity of developing of actions for limiting their migration and, furthermore, artificially creating physico-chemical conditions on the ways of dioxins migration in order to decrease their toxicity up to complete decomposition. Based on the properties of the dioxins and the real geological environment, the easiest and the most reliable method is creation for this purpose of oxidative-geochemical barriers on which oxidation of dioxins would take place. This oxidation would yield non-toxic intermediate products of this reaction and absolutely harmless final products in the form of carbon dioxide gas, water, etc.

Oxidative barriers are created by a treatment of the site of the groundwater-aquifer, chosen for this purpose, with oxygen-containing water from the same aquifer. Pumping this water out, saturating it with oxygen (or air) and pumping water with dissolved oxygen back is done through pit-holes. There are using technical means, widely used for these purposes during mining (copper, uranium and other metals) by the underground leaching method<sup>2</sup>.

### **Methods and Materials**

Commercial eosin (2',4',5',7'-tetrabromofluorescein) was utilized. Eosin oxidation was realized by barbotage of atmospheric air in presences of two hydrated forms of Fe(III). The fine disperse material was prepared by special treatment of commercial  $Fe_2O_3 \cdot nH_2O$ . Initial concentration of eosin solution was 5 mg/L.  $Fe_2O_3$  was added in amount of 50 g/L. Experimental volume was 100 mL. Eosin concentration was controlled by electronic absorption spectra. Electronic absorption spectra were obtained on a Specord-UV-Vis spectrophotometer. The solution was intermixed by a magnetic agitator at carrying out of processes with usage of eosin.

#### **Results and Discussion**

The groundwater-bearing rock contain in noticeable amounts (more than 0.5%) Fe(II). The oxidation of Fe(II) to Fe(III) takes place during the filtration of the oxygen-containing water bed through a sand medium. Various hydrated forms of Fe (III) occur. The chemical modelling of

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oxidative process was proceeding. Eosin (2',4',5',7'-tetrabromofluorescein) was utilized as dioxin simulator. The structure of eosin is similar to the same of dioxin. The simulator was oxidized by barbotage of atmospheric air in presences of two hydrated forms of Fe(III). The fine disperse material was prepared by special treatment of commercial Fe<sub>2</sub>O<sub>3</sub> nH<sub>2</sub>O. The both samples (fine disperse and commercial) was used in experiments. The results of oxidation on modelling barrier are summarised in Table 1. Oxidative conversion rating of dioxin simulator increases in the case of using fine disperse material. Spectroscopic researches allow to propose the mineralization of dioxin simulator in modeling geochemical barrier.

	1	2	
Time of air barbotage	Oxidative conversion	Time of air	Oxidative conversion
(hour)	rating (%)	barbotage (hour)	rating (%)
0	0	0	0
4.5	8.0	4.5	10.0
7.5	12.5	12.5	13.0
15.5	21.0	20.5	17.0
23.5	46.0	28.0	20.0
31.5	67.0	35.0	25.0

Table 1. Oxidative conversion rating of dioxin simulator on hydrated forms of Fe(III). Fine disperse material (1). Commercial Fe<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O (2).

During the filtration of the oxygen- containing water bed through a sand medium, the oxidation of Fe(II) which is almost always present in this water in noticeable amounts (more than 0.5%), to Fe(III) takes place. The oxidation is accompanied by the formation of various hydrated forms, and the formation of the oxidative barrier is completed in general. In such geochemical barrier a heterogeneous-catalytic system is created, which is able to oxidize the dioxins themselves, as well as the carrier-substances. When the groundwaters contaminated with dioxins reach such a barrier, their oxidative decomposition starts. It is fully completed by the time when the pollutants passed through the whole thickness of the barrier. It is known that the dioxin half-life in an aqueous phase is 1 - 2 years<sup>3</sup>. It was shown that in modelling system the dioxin simulator half-life is about 25 hours.

There is proposed philosophy of oxidative-geochemical barrier against dioxin-pollution of groundwater. The chemical model confirms this conception.

It will be observed that the oxidative-geochemical barriers possess few additional positive features: they are soft for environmental, there is possibility of oxidation of a range of harmful organic pollutants of the groundwaters (related to oil spills from the pipe-lines, oil storage tanks, etc.) on the barriers. Besides oxidation of Fe(II) dissolved in the groundwaters and its conversion in a practically insoluble trivalent form, accomplishes a de-ironing of the drinking water supply, which is a necessary operation in the water treatment.

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