

KAMIL P. BANASZKIEWICZ¹, TADEUSZ A. MARCINKOWSKI¹

CEMENTATION AS A METHOD OF REMEDIATION OF SOIL CONTAMINATED WITH XYLENE

The research was performed to evaluate usability of stabilization/solidification (S/S) processes in permanent separation of the surface of soil contaminated with xylene in order to reduce its emission to the environment. For the needs of the experiment, soil samples were prepared with the same amounts of solvent and then, after averaging their physicochemical composition, stabilized with Portland cement CEM II 32,5 R. In the course of stabilization/solidification process, all emitted gaseous contaminants were monitored. The effect of a binder dose on xylene emission was evaluated based on the momentary concentrations (C_8H_{10}) monitored above the surface of reactive mixture using a flame-ionization detector. Simultaneously, contaminated air was run through pipes filled with activated carbon. Then, based on chromatographic analysis of xylene vapors adsorbed on activated carbon, the measured momentary concentrations were verified.

1. INTRODUCTION

Chemical contaminations of soils are caused by uncontrolled events in the past, connected with activities of chemical plants but also with functioning of plants processing industrial and hazardous waste. Chemical contamination of soils has been the effect of activity of petroleum refineries, stores and transfer stations for fuels, motor and gear oils, paints and lacquers plants, used organic solvents refining plants, plants for dismantling and processing used or damaged transformers or accumulator batteries, places for storage and disassembling cars out of use, industrial machinery and installations, etc..

Contaminating substances, both organic (aliphatic and aromatic) and mineral, may be present in soils in liquid or solid form, sometimes pollutions are also caused by the presence of volatile organic compounds [1, 2].

¹Institute of Environmental Protection Engineering, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, e-mail addresses: kamil.banaszkiewicz@pwr.wroc.pl, tadeusz.marcinkowski@pwr.wroc.pl

Remediation of contaminated area may be performed by elimination, decomposition, immobilization or chemical transformation of contaminants into forms less toxic, less mobile and less reactive. Choice of the method for treating contaminated ground depends on amounts of contaminants present, as well as on their physicochemical properties and geohydrologic conditions [4, 5].

Recently, more common application of technologies based on so-called reactive materials in remediation of soils contaminated with metals or organic substances can be observed [4]. Processes of stabilization/solidification (S/S) are among the most often applied technologies of remediation of soils contaminated with inorganic substances. In the case of mineral contaminants, the S/S process is easier and less expensive as waste shows higher level of compatibility with binding materials based on cement. The situation is somehow different for stabilization/solidification of waste containing hazardous aliphatic or aromatic components [3]. Due to the effect of organics on the course of hydration of hydraulic binders, there are significant limitations in applying solidification techniques for neutralizations of such wastes [3, 6]. Depending on the composition of stabilizing-binding mixture, the process of immobilization of organic contaminants can be divided into three categories:

- direct physical immobilization of organic contaminants,
- sorption of organic contaminants (as a result of application of additional reagents, e.g. activated carbon, polymers or fly ashes),
- reduction of mobility of organic contaminants as a result of application of reagents characterized by oxidative-reductive properties.

Effectiveness of the processes of stabilization/solidification of organic compounds in cement matrices (with or without additional sorbents) depends significantly on possibilities of their physical immobilization [6–9]. Processes of stabilization/solidification of contaminated ground can be performed in situ – in the place where the pollution occurred, or ex situ, e.g. in a waste neutralizing plant [9]. Solidification of waste with hydraulic binders requires mechanical mixing in order to distribute them in the whole volume of waste and to dilute with water. Such a process creates (in the case of processing waste contaminated with aromatic hydrocarbons) a risk of releasing vapors of volatile organic compounds. This especially concerns the stage of material homogenization, as well as initializing the hydration process through introduction of diluting water [3, 10]. According to the directive of the Minister for the Environment [11], continuous and periodic measurements of emission of volatile organic compounds introduced to the air from installations should be performed using the method of continuous detection of flame ionization, determining the total organic carbon, or by the chromatographic method.

The reported research focused on the analysis of xylene evaporation from soil during the process of stabilization/solidification with Portland cement. Measurements of continuous concentrations of gaseous contaminants emitted from the reactive mixture were performed using a flame-ionization detector MicroFID (Photovac). Simultane-

ously, contaminated air was run through pipes with activated carbon. Then, based on chromatographic analysis of xylene vapors adsorbed on activated carbon, the measurements of momentary concentrations was verified.

2. MATERIALS AND METHODS

Contaminated soil samples. Material used in experiments was mineral (sandy) soil, characterized by low content of organic matter (below 2 wt. %) and low hydration level (ca. 4%). For the needs of the experiment, 200 g soil samples containing 0.5 cm³ of xylene were prepared. Hermetically closed containers with contaminated material were then shaken for ca. 2 min in an overhead shaker (Heidolph Reax 20/8). Loose basement soil enabled uniform distribution in a whole volume of samples. Such prepared samples, after 24 h of stabilization at 21 °C, were solidified with cement.

Binder. Portland cement CEM II 32,5R, being a mixture of Portland cement CEM I 42,5 R (main component – Portland clinker) and fly limestone ash (ca. 65/35 mass ratio) was used in the experiments.

Neutralization process. The process of cementation of soil contaminated with xylene was performed in a cement mortar reactor Tecnotest B205/X5. Contaminated soil material (200 g) was solidified with 100, 200 and 400 g of Portland cement CEM II 32,5 R. In order to evaluate repeatability and stability of the process, all samples were tested twice. Table 1 presents the composition of composites produced using contaminated soil material.

Table 1

Material composition of composites produced from soil contaminated with xylene and initial ambient conditions of the experiment

Sample	Volume of C ₈ H ₁₀ [cm ³]	Binder dose [g]	Water (diluent) dose [cm ³]	Initial temperature [°C]	Initial humidity [%]
Xylene 200 + 0	0.5	0	80	30.4	25.5
Xylene 200 + 100		100	80		
Xylene 200 + 200		200	125		
Xylene 200 + 400		400	200		

The stabilization/solidification process covered the following stages: background measurements, loading the reactor (simultaneous introducing of waste and binding medium), mechanical mixing of components (homogenization phase), introducing diluent water to initiate the process of hydration of cement components and for further

mixing (so-called hydration phase), unloading the reactor and forming waste-cement composites. In total, the phase of homogenization and hydration took 10 min (5 min each of them). In order to limit the effect of external factors on the volume of the emission of gaseous contaminants, all materials (binders and waste) were mixed with a constant rotational speed of 140 rpm. The amount of water introduced into reacting mixture was closely related to the hydration level of soil material and the dose of binder (Table 1).

The effectiveness of immobilization of xylene was evaluated in relation to the sum of concentrations of volatile organic compounds measured above the surface of the zero sample. The reference was a 200 g sample of soil contaminated with the same amount of xylene (0.5 cm^3). In this instance, cement was not introduced into the reactor, while the rest of technological parameters remained unchanged. In order to determine complete characteristics of emission of gaseous contaminants, 80 cm^3 of water was introduced into the reactor during the phase of hydration.

Measurement of concentration of emitted contaminants. Continuous monitoring of emitted gaseous contaminants was performed using a portable flame ionization analyzer. Samples of gas were taken from the bowl of the reactor and transferred to the measuring device through a teflon pipe. The flame ionization detector MicroFID (Photovac) was calibrated before each measuring session and xylene concentration was calculated based on the response factor, provided by the manufacturer. The air flow rate inside the device was $0.6 \text{ dm}^3/\text{min}$. Concentrations of contaminants were recorded in 1 s intervals. After each measurement, data was sent to a computer for further analysis.

Simultaneously emitted gaseous contaminants were transferred through pipes filled with activated carbon (SCK, Anasorb CSC), using bi-channel aspirators LAT ASP 3 II. The flow rate was ca. $60 \text{ dm}^3/\text{h}$ and corresponded to $4.7\text{--}5.1 \text{ dm}^3$ of process gases aspired to the bed with active carbon in particular phases of the process.

Before each test series, ambient temperature and humidity were measured using a thermohygrometer Hanna Instruments HI 9564. Due to high level of dust in air samples, after each measurement ducts were blown through with clean air to remove accumulated residues of gases and dusts.

Vapors of volatile organic compounds adsorbed on activated carbon were analyzed using a gas chromatograph Varian 450-GC and a column Varian VF-WAXms ($30 \text{ m} \times 0.25 \text{ mm ID DF: } 0.25 \text{ }\mu\text{m}$). Activated carbon from the absorbing pipe was placed in 5 cm^3 flasks, then 2 cm^3 carbon disulphide (CS_2) were added, flasks were tightly closed and left for 20 min, shaking its content from time to time. Solution from above activated carbon layer was then taken into 2 cm^3 vial and placed in an autosampler of the chromatograph. Desorption coefficient of the method was 80%. Temperature of the oven (column) was $110 \text{ }^\circ\text{C}$, maintained for 10 min, temperature of the batchmeter – $225 \text{ }^\circ\text{C}$, split – 1/20, temperature of the detector – $250 \text{ }^\circ\text{C}$, carrier gas was helium, the flow rate of the carrier gas – $1 \text{ cm}^3/\text{min}$, injection volume – $5 \text{ }\mu\text{l}$.

3. RESULTS AND DISCUSSION

Every process of neutralizing waste contaminated with volatile organic compounds (VOC) is characterized by technical parameters that can influence the volume of their emission during processing. In the case of stabilization/solidification processes, as activities that cause releasing of volatile or semi-volatile compounds, the following should be taken into account: (i) mixing waste with binding components, (ii) diluting mixture with water that can displace volatile organic compounds from adsorption sites, (iii) increase in the temperature of reacting mixture during hydration of binding factors (e.g. cement and lime mixture) [7]. Knowledge of the characteristics of emission of gaseous contaminants in real time enables evaluation of the dynamics of the process, as well as the effectiveness of operations that stabilize releasing of VOCs vapors.

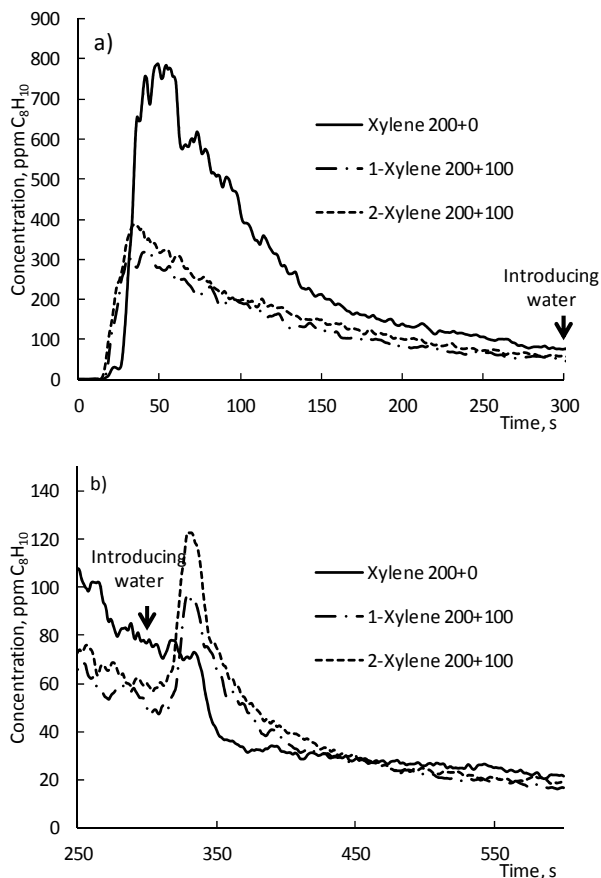


Fig. 1. Characteristics of xylene emissions during the processes of stabilization/solidification of soils using 100 g of cement in homogenization (a) and hydration (b) phases

Figures 1–3 present changes in momentary concentrations of xylene in the reactor during particular phases of the neutralization. Results of continuous measurements showed that its emission was strongly dynamic in the first stage of the homogenization phase.

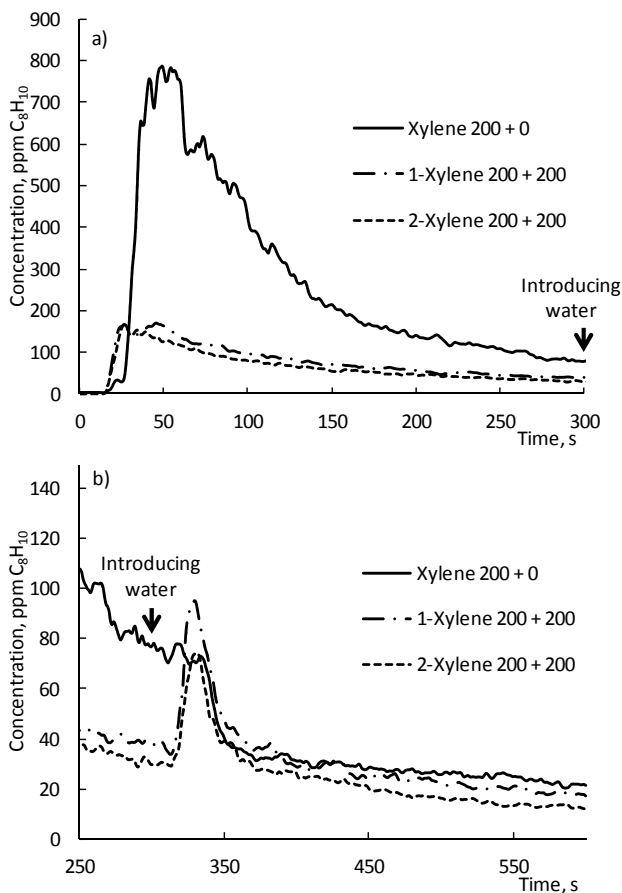


Fig. 2. Characteristics of xylene emissions during the processes of stabilization/solidification of soils using 200 g of cement in homogenization (a) and hydration (b) phases

The research confirmed beneficial effect of waste hermetization using Portland cement CEM II 32,5 R. As a result of introduction of fine-grained binder, a decrease in maximum momentary concentration of C_8H_{10} in the first phase of the process by 59.5/50.7; 78.5/78.6; 96.5/96.5 mass rates (for each repetition) was observed, in respect to the zero sample (Table 2). Suppression of rapid vaporization was a result of (among others) sealing soil with fine-grained binding materials. The experiments also showed high repeatability of measurements.

Table 2

Maximum temporary concentrations of xylene in the reactor and their values after introducing cement [ppm]

Sample	Homogenization phase	Hydration phase
Xylene 200 + 0	785	77.8
1-Xylene 200 + 100	318	96.4
2-Xylene 200 + 100	387	123
1-Xylene 200 + 200	169	95.5
2-Xylene 200 + 200	168	74.5
1-Xylene 200 + 400	27.4	41.3
2-Xylene 200 + 400	27.8	39.7

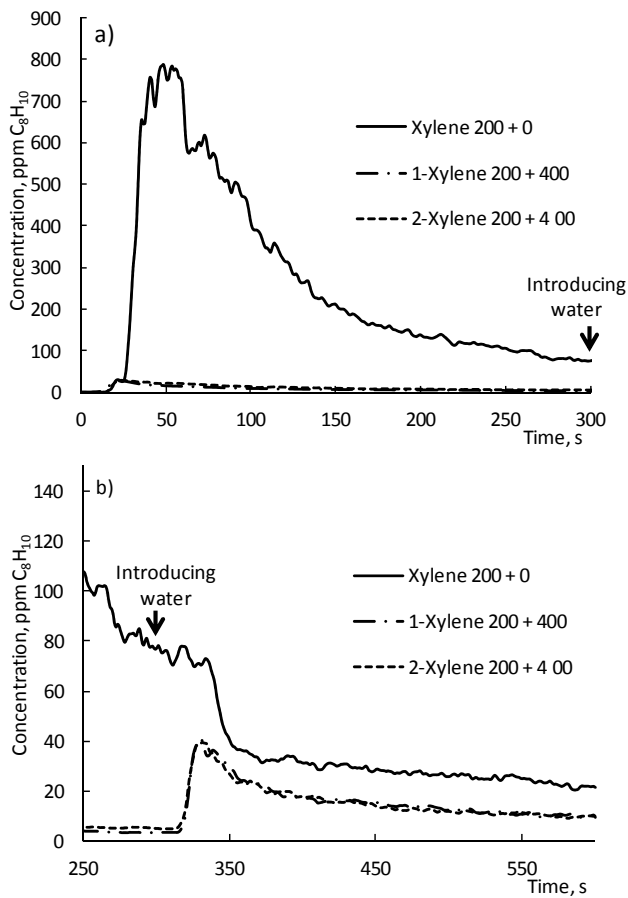


Fig. 3. Characteristics of xylene emissions during the processes of stabilization/solidification of soils using 400 g of cement in homogenization (a) and hydration (b) phases

In order to initialize the hydration of components of Portland cement, introducing water is necessary. Adding water to soil contaminated with xylene (that is characterized by very low solubility and significant volatility) may cause rapid release of xylene from pores and soil cracks. An increase in concentration of xylene was observed in all tests of samples stabilized with Portland cement. In other research on cementation of soil contaminated with benzene such increase was only observed for the dose of binder at the level of 200% of the mass of soil being neutralized [10].

For the samples Xylene 200 + 400, higher concentrations of xylene were observed in the phase of hydration than in the homogenization phase. Sealing the mixture with a high dose of fine grained binder effectively lowered its emission during homogenization. However, after diluting the mixture with water release of gaseous contaminants from intergranular spaces was observed. Simultaneously during neutralizing soils contaminated with liquid compounds of low solubility in water, addition of excess diluting water may cause their elution.

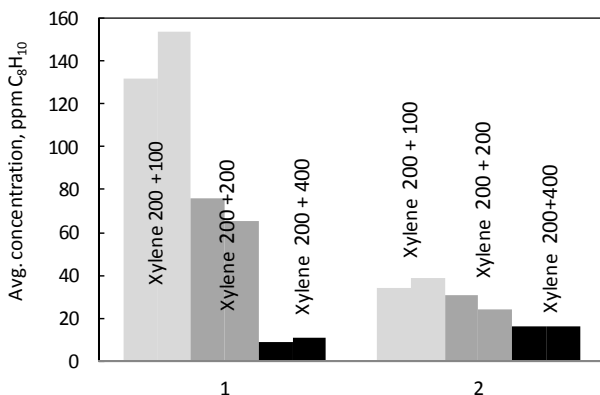


Fig. 4. Average concentration of xylene over the reacting mixture during the process of stabilization/solidification (on-line measurements):
1 – waste homogenization stage, 2 – hydration stage

Quantitative and qualitative analyses of gaseous contaminants adsorbed on activated carbon during waste homogenization (phase 1 of the experiment) confirmed the direct effect of binder dose on the level of xylene emission (Fig. 4). Characteristics of changes in average concentration of analyzed solvent calculated based on continuous measurements and the mass of xylene adsorbed on activated carbon agreed (Figs. 4 and 5, homogenization phase). In the hydration phase (after diluting the mixture with water), some differences were observed. For the sample xylene 200 + 200, the average xylene concentrations above the surface of reacting mixture (for two repetitions) in the phases of homogenization and hydration were 1986 and 1952 mg C₈H₁₀/m³, 1414 and 1416 mg C₈H₁₀/m³, respectively (Fig. 5).

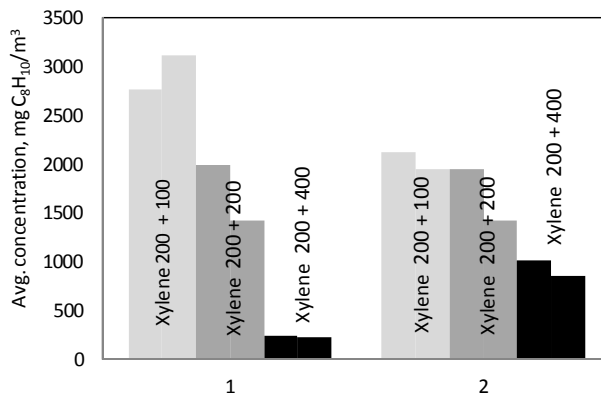


Fig. 5. Average concentration of xylene over the reacting mixture during the process of stabilization/solidification:
1 – waste homogenization stage, 2 – hydration stage

The observed deviations might be a result of measurement errors, caused (among others) by clogging the flow of inducted air by some solid impurities (dusts). During homogenization of soil with stabilizing components (phase 1), a significant fluffing of binder being introduced was observed. Emitted solid contaminants were sucked in together with the air from the reactor bowl. Assembling an additional dust filter on the inducting channel of the MicroFID detector might be insufficient. In addition, differences in flow rates of process gases inducted by measuring instruments should be taken into account. The volume of the air sample taken by the flame-ionization detector was $0.6 \text{ dm}^3/\text{min}$, whereas the flow rate of the air running through pipes with activated carbon was ca. $1 \text{ dm}^3/\text{min}$. The total volume of analyzed air inside the reactor for each phase of the process was, respectively: ca. $4.7\text{--}4.8 \text{ dm}^3$ (GC), ca. 3 dm^3 (FID).

4. CONCLUSIONS

The process of stabilization/solidification can be an effective method of processing soils contaminated with small or medium amounts of aromatic hydrocarbons, both in situ and ex situ, eg. in a waste processing plant.

Introducing of Portland cement CEM II 32,5 R resulted in reduction of maximum momentary xylene concentration recorded in the homogenization phase.

High doses of stabilizing components caused increase in the mass and volume of waste, as well as affect the quality of measurements. Measurement errors may be caused by excessive dust and clogging antidust filters.

The cement proportion in waste-based composites can be lowered using additional components sorbing organic contaminants, e.g. powdery activated carbon, powdery

clay or shredded rubber. Their application in the process of waste neutralization will be the subject of further research.

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