

# Combined decontamination processes for wastes containing PCBs

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## Abstract

This project has focused on the development of a complex assembly of mutually corresponding technological units:

- a low temperature thermal process for the desorption of PCBs and other organics from soils and other contaminated solid wastes;
- the extraction of PCBs from soils by an ecological friendly aqueous solution of selected surfactants;
- the chemical decontamination of PCBs in oils and in oil-in-water emulsions by metallic sodium and potassium in polyethylene glycols in the presence of aluminum powder;
- the modified alkaline catalyzed chemical decontamination of PCBs in oils and in oil-in-water dispersions in a solid-state reactor (in a film of reacting emulsion on solid carriers); and
- the breakdown of PCBs in aqueous emulsions with activated hydroxyl radicals enhanced by UV radiation. The processes operate in a closed loop configuration with effluents circulating among the process unit. These technologies have been verified at laboratory and pilot-plant scales.

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## 1. Introduction

Polychlorinated biphenyls (PCBs) were produced in relatively large volumes in the former Czechoslovakia (approximately 25,000 tonnes were produced). Their excellent stability and thermal properties make PCBs suitable as a heat transfer medium and dielectric liquids in electrical transformers and capacitors [1]. Because of their widely publicized biological effects, the manufacture of PCBs ceased in Czechoslovakia in 1984. However, because of their persistence, a large proportion of the total PCBs (some PCBs were imported as well as exported) are still present in the environment. At present, an inventory of the remaining PCBs is in progress in the Czech Republic. Actually, the rough esti-

mates indicate that there are units of thousands of tonnes of capacitors, transformers and contaminated oils and approximately 100,000–200,000 tonnes of PCB-contaminated soils in the Czech Republic. The principal contaminant PCBs in the Czech Republic are in a commercial product Delor 103 (over 90% of PCB contamination has its origin in this mixture). Delor 103 is a mixture of PCB congeners with a prevailing content of tri- and tetra-chlorinated congeners (Cl-1: 2 congeners, 0.3%; Cl-2: 4 congeners, 10.5%; Cl-3: 11 congeners, 64.0%; Cl-4: 12 congeners, 24.1%; Cl-5: 7 congeners, 1.1%).

Until now, no waste decontamination technology was available in the Czech Republic. At present, one incineration unit has started operation. However, alternative decontamination technologies are desirable, mainly focused on the decontamination of selected types of wastes like contaminated soils and/or adsorbents, transformer oils, parts of

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electrical capacitors, where the possibility of recycling is promising.

PCBs are principally being destroyed by incineration [2–7]. Incineration, however, often emits more toxic compounds if is not carefully controlled. Polychlorinated dibenzodioxins and dibenzofurans have both been observed in the combustion of PCBs [8–11]. The technology of cleaning the combustion gas to the severe environmental demands currently happens during a sensitive stage of the incineration method. Incineration as a destructive method is irreplaceable in many cases (especially for pure PCBs). However, some other alternative techniques seem viable, environmentally friendly and cost-competitive for reducing of PCB concentration in many selected wastes.

Different methods for the destruction of PCBs have been proposed and include wet-air oxidation [12,36], super- or supra-critical oxidation [7,21], bioremediation [13–15], sodium metal-promoted dehalogenation [16–20,40–51] reductive dehalogenation with a strong reductant (including ECOLOGIC [39] and Commodore Solution Na/NH<sub>3</sub> Technology [40] processes), photolysis in the presence of hydrogen donors and oxidants [28,29], base-catalyzed dehalogenation (BCD [33], KPEG (NaPEG) process [30–32,60,61]), electrolytic reduction [34], zero-valent iron-promoted dechlorination [35,36], catalytic dehalogenation with noble metals [37,38], extraction with solvents [52–56], and a number of other chemical methods, obviously based on laboratory experiments only [22–27].

Other emerging methods for the separation of PCBs from a solid matrix have been published (low temperature thermal desorption, extraction, vitrification) and some of them have been widely adopted [33].

The evaluation of source materials indicates that the priority in waste to be treated in the Czech Republic is likely to be PCB liquid, then PCB soil. This is the reason why we will focus on evaluating the following treatment technologies: thermal desorption, chemical dehalogenation and extraction. The objective of the present work was to experimentally verify the efficiency of decontamination of PCBs in wastes like contaminated soil, oils and water by these technologies at pilot-plant conditions where the individual processes operate in a closed-loop configuration.

The technological objectives of a complete remediation system are:

- to obtain clean decontaminated soils which could be recycled to the environment;
- to obtain decontaminated oils which could be used as fuel (for heating of a thermal desorption unit) and/or recycled (in the case of decontamination of transformer dielectric liquids); and
- to recycle decontaminated product waste-water back to the extraction step.

The pilot-plant experiments were carried out at the IDOS Prague Inc., Waste Treatment Facility, near Pribram, Czech Republic.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Soil

Three types of contaminated soils (see Table 1) were used for thermal desorption and extraction experiments. They were excavated from localities previously contaminated: Milovice (contaminated as a consequence of the repeated escape of heat-transfer liquids), Milevsko I (contamination resulting from the release of heat-transfer liquids) and Milevsko II (soil transferred from the factory ZEZ in Žamberk, Czech Republic, where the production of electrical capacitors took place). The dominant commercial PCB mixture used has the commercial name Delor 103 (it is a mixture of congeners with mainly three and four atoms of chlorine).

#### 2.1.2. Chemicals used

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Sodium hydroxide: Ilirida Ltd., Prague 9  
 Potassium hydroxide: Degussa A.G., Werk Luilsdorf  
 Polyethylene glycol 300 (PEG 300): Dow Benelux N.V., Terneuzen  
 Sodium: Dr. Bilger Umweltconsulting GmbH, Hanau  
 Praestol 600 (polyacrylamid): Stockhausen GmbH, Krefeld  
 Sodium carbonate: Solvay-Chem, Prague 4  
 Aluminium powder: ALBO Schilenk a.s., Bojkovice, CZ  
 FeCl<sub>3</sub>: HCl Chemicals, Prague  
 Novanik 1047(aloxylates of fatty alcohols): Chemical Plants A.G., Nováky, Slovakia (HCl Chemicals, Prague)  
 Cyclodextrine(hydroxypropyl-beta-cyclodextrine): Sigma–Aldrich  
 DDAB (didodecyl dimethyl ammonium bromide): LONZA, Prague  
 BARDAC-22 (didecyl dimethyl ammonium chloride): Sigma–Aldrich  
 Hydrogen peroxide: Chemical plants A.G., Sokolov, Czech Republic  
 AC-SILCARBON: HCl Chemicals, Prague

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### 2.2. Methods

#### 2.2.1. Analytical procedure

A standard procedure was used to determine the congeners of Table 2.

*2.2.1.1. Principles of the method.* The samples of soil were mixed with the solvent (acetone/*n*-hexane, 1/1, v/v) and submitted to extraction by sonication. Partially concentrated extracts after cleaning-up the extract solution were analyzed by gas chromatography (HRGC) with electron capture detector.

Table 1  
Characteristics of soils

Locality	Cox (%)	Distribution of sizes of particles (mm) (%)					
		0.001	0.002	0.01	0.01–0.05	0.05–0.25	0.25–2.0
Milovice	1.01	7.9	8.6	14.8	9.3	22.2	53.7
Milevsko I	1.41	15.0	17.0	24.3	15.3	21.0	39.4
Milevsko II	1.01	9.6	11.0	18.9	17.2	16.0	47.9
“Termidos”	0.93	5.2	6.6	12.8	12.	23.9	50.5
	pH	Exchangeable ions (mmol/100 g)					
		H <sup>+</sup>	Ca	Mg	K		
Milovice	7.71	4.5	6.57	0.24	0.18		
Milevsko I	7.48	4.0	12.85	1.69	0.71		
Milevsko II	7.17	2.5	10.69	1.46	0.32		
“Termidos”	8.03	–4.5	16.58	1.46	1.1		

Types of soils: Milovice and Milevsko II: loamy-sand type of soil; Milevsko I: sandy-loam type of soil; Sample Milevsko I after the treatment in thermal desorption has been declared in Table 1 as “Termidos”. PCBs were dominantly sorbed at soils with higher content of clay (Milevsko I). The content of humic compounds (as Cox) before and after the thermal desorption process did not differ significantly. This fact could indicate, that agricultural value of a treated soil remained almost preserved.

Table 2  
Aqueous extracts, content of individual congeners in mg (in 150 ml of extraction solution)

Sample	Congener no.							
	28	52	101	118	153	138	180	Sum
Winsor I (o/w)	0.060	0.014	0.005	0.004	0.010	0.005	0.001	0.100
Microemulsion a	0.003	0.004	0.001	–	0.001	0.001	0.001	0.011
Microemulsion b	0.210	0.078	0.015	0.010	0.010	0.012	0.001	0.336
Novanik	0.056	0.009	0.002	0.002	0.001	0.001	0.001	0.072
Cyclodextrine	0.041	0.005	0.001	0.001	0.001	0.001	0.001	0.051
DDAB-Bardac	0.185	0.046	0.010	0.007	0.009	0.012	0.001	0.270

Type of soil: Milevsko I: size fraction bellow 2.5 mm. Original concentration of congeners of PCB (in mg/kg dry): PCB-28 = 78, PCB-52 = 24.7, PCB-101 = 4.1, PCB-118 = 4.0, PCB-153 = 3.2, PCB-138 = 3.9, PCB-180 = 1.3. Total sum, 119.2 mg/kg dry. Coincidence in mass balance of the sum of congeners between original composition in the soil and in the soil and extracts after treatment did not exceed on average 34% in absolute value.

Quantification of the congeners was carried out by using external standards (10 ppm samples in 2,2,4-trimethylpentane, Reference Materials for Residue Analysis, dr. Ehrenstofer comp.).

In a typical experiment, the samples that had been pre-dried for 48 h at 35 °C (alternatively by anhydrous sodium sulphate) were crushed and extracted (5 g of the sample + 40 ml of the solvent mixture) by sonication for 20 min. A volume (400 µl) of surrogate standard (PCB congener no. 209) was added to the extract. The solution was concentrated by evaporation (in a Kuderna-Danish concentrator). Co-elutants were removed by extraction with mercury and sulphuric acid. Clean-up of the extract was carried out on a Florisil column using a mixture of 6% diethylether in *n*-hexane as the elutant. The clean extracts were concentrated to 3 ml by bubbling nitrogen through the solution and then analyzed by HRGC. Calibration of the ECD response was carried out by measurement of the calibration solution at seven concentration levels (using CRM 481 certificated stock solution of respective congeners in non-polar solvents). A DB-5 capillary column (60 m × 0.25 mm × 0.25 µm) was used. The column conditions for HRGC were as follows: temperature of the feed 250 °C, initial hold at 60 °C for 2.5 min, increased from 60–220 °C at the rate 30 °C/min, increased to 280 °C at

the rate 1 °C/min, hold at the 280 °C for 10 min. ECD-grade nitrogen as a carrier gas was used and the temperature of the detector was 310 °C.

2.2.1.2. *Determination of PCBs in contaminated waste water.* This standard procedure covers determination of the selected congeners (Table 2):

Extraction of PCBs from aqueous-phase was carried out by *n*-hexane. After clean-up and concentration, the extracts were analyzed by the method of HRGC with ECD (see above mentioned procedure).

Method detection limit: 3.8 ng/L (sum of 7 congeners)

Method reporting limit: 7.7 ng/L (sum of 7 congeners)

RSD: 10% (for concentration level 2100 ng/L)

Recovery: 100% (for concentration level 2100 ng/L)

2.2.1.3. *Determination of PCBs in an oil-phase.* The analysis of the sum of seven indicative congeners applies to a European (Czech) Standard ČSN EN 61619, based on extraction with *n*-hexane and HRGC with ECD. This procedure is

recommended by Czech Waste Law, Edict of Ministry of Environment of Czech Republic No. 384 (the capillary column gas chromatography method was slightly modified).

The collection of samples and analytical procedures have been performed by laboratories ANECLAB Inc., Ceske Budejovice, CZ and EcoChem Inc., Prague, CZ.

### 2.2.2. Extraction of PCBs from contaminated soils with aqueous solutions

In line with our previous screening experiments, the mobilization components were a non-ionic surfactant (Novanic 1047 A-aloxyates of fatty alcohols) and a quaternary salt, both in the form of individual components and/or in micro-emulsions [56]. Mixtures of organic solvents (higher hydrocarbons and alcohols) in the form of micro-emulsions have been selected as solubilization components. Non-ionic surfactants have been selected due to their relatively high efficiency of mobilizing PCBs in different types of soils, and their commercial availability at a low price. These economic aspects seem to be dominant for a potential future decontamination application. Cyclodextrine was selected as a solubilization component of a natural origin. The capability of cyclodextrine to increase the apparent solubility of non-polar organic compounds has been demonstrated recently [57]. The quaternary salt BARDAC-22 manifests suitable characteristics both as efficient biocide and surfactant.

The following extractants have been used:

- (1) Winsor I  
The selection of proper surfactant and co-surfactant has been carried out from the point of view to obtain a system with low viscosity and in a stable one-phase liquid. Particularly, Novanic 1047 A of 3.5% wt., and *n*-pentanol of 2.5% wt. in water have been tested.
- (2) Micro-emulsions
  - (a) micro-emulsion I  
Mixture of quaternary salt DDAB (didodecyl dimethyl ammonium bromide) + decene-1 + water in mass ratio 21/57/22.
  - (b) micro-emulsion II  
Mixture of DDAB + dodecane + water, in mass ratio 21/57/22.
- (3) Non-ionic surfactant (Novanic 1047A, 1% wt.) in water.
- (4) Cyclodextrine (hydroxypropyl-beta-cyclodextrine, 1% wt.) + water.
- (5) Quaternary salt BARDAC-22 (didecyl dimethyl ammonium chloride, 1% wt.) in water.

The selection of extraction agents was a compromise between extraction efficiency of individual agents and their ability to be used as cost-acceptable compounds in the case of potential industrial application of extraction technology. Other surfactants were also used, such as Tween 40, Tween 80, Brij 58, Brij 92, Hyonic NP-90: all manifested a comparable extraction efficiency as the inexpensive Novanic 1047 A.

The experimental conditions were as follows:

- (a) Laboratory experiments:  
The sample of soil Milevsko I was selected. In a typical experiment a 100 g sample of soil was introduced in a glass beaker (500 ml) and 200 ml of extraction solution was added. The beaker was shaken for 24 h at the intensity of 1 shake/sec, at ambient temperature (18–22 °C). Each experiment was repeated 5 times. The liquid-phase was cautiously sucked off after sedimentation and potentially presented solid micro particles were separated by centrifugation. The sample of liquid was collected and analyzed.
- (b) Extraction of PCBs from contaminated soil at pilot-plant scale:  
Since laboratory tests demonstrated only a weak extraction of PCBs, insufficient for potential industrial application at a comparable hydrodynamic arrangement; it seems evident that a pre-treatment operation liberating the strongly-linked organics from soil particles would be necessary. In a previous paper [58], the authors have published a method of enhanced reductive dechlorination. The soil was treated in two phases: in the first phase, the soil was sprayed with some selected nutrients with the aim of activating the growth of natural soil bacteria. We believed that in the course of this activation phase the release of adsorbed organic compounds would be enhanced as a consequence of the lowering of interfacial tension. This phenomena was verified experimentally. As a result, enhancement of leaching of the part of weakly adsorbed PCBs was noticed.

Application of ammonium sulfate and N and P nutrients resulted in an increased amount of organics being extracted in aqueous leachates during this period. On the basis of this finding we have proposed a procedure for enhancement of extraction of PCBs from soils with aqueous solvents. The proposed technique can be applied on a moving as well as on a static bed of soil. The reasons why we have used the static bed arrangement were lower investment and operation costs, although the efficiency of extraction in a moving bed would certainly be higher.

**2.2.2.1. Pilot-plant characteristics.** Pilot-plant consists from 3 concrete rectangular boxes, with a total ground plan area 110 m<sup>2</sup> and side walls 1.6 m high. The surface of walls and the floor were covered by water- and acid-proof coatings, and all boxes were drained to a common reservoir of aqueous extracts. The capacities of treated soil in the individual boxes were 16, 40 and 27 tonnes, respectively. The height of soil layer in the boxes was approximately 1 m.

**2.2.2.2. Procedure. Activation period:** The indigenous bacteria were activated by spraying the layer of contaminated soil with an aqueous solution of nutrients: 1% wt. of ammonium sulfate and 0.3% wt. of ammonium phosphate.

The soil was mechanically homogenized before being introduced to the boxes. During the experiments, soil samples for analysis were taken from six different positions in individual boxes and were homogenized. With the exception of the time of spraying, the upper level of soil was covered with a plastic sheet to avoid direct contact with air. The intensity of spraying was  $0.2 \text{ m}^3/\text{m}^2$  of the area of surface of soil. Application was repeated four times a week for a total of 8 weeks.

The extraction was performed by spraying the surface of soil with aqueous solution of 1% wt. of non-ionic surfactant (Novanik 1047 A) at an intensity of about  $0.25 \text{ m}^3/\text{m}^2$  each week, during a 16 weeks period.

Contaminated percolates from both the activation and extraction steps were collected in a stock reservoir and were continuously treated in a attached decontamination unit, as described below.

### 2.2.3. Clean-up of contaminated extraction waters-destruction of PCBs with hydroxyl radicals

It is well known that  $\text{H}_2\text{O}_2$ , in the presence of compounds of Fe(II) can very effectively oxidize numerous organic substances (so called Fenton reaction, [28,29]). This agent seems also to be a potential oxidant of many xenobiotic compounds. We have studied its potential for the decomposition of PCBs. Two sets of experiments were carried out, i.e. at laboratory and pilot scale.

#### (a) Laboratory experiments

*Course of the typical experiments:* Tube silicon photo-reactor with a high pressure Hg-lamp was used (manufacturer is UV-Systeme GmbH, Heidelberg, Germany). Real electric input power in the experiments was 150 W. Flow of contaminated water through the reactor was continuous. Water was pumped from the storage tank of the volume of 2 L through the reactor in the loop back to the tank at a rate of 25 L/h. Time of the experiment was 90 min. (These preliminary experiments were performed at the UV-Systeme Laboratories in Heidelberg).

*Radiation in the absence of ferrous catalyst:* Concentration of hydrogen peroxide (35%, v/v) was 1 mL in 2 L of water. Temperature of reaction was  $25^\circ\text{C}$ . Initial acidity of water was pH 7.8 and in the course of reaction decreased to the value of pH 6.8. Redox potential (indicator of the course of reaction) increased after the injection of hydrogen peroxide to a value of 500 mV and gradually decreased in line with the consumption of peroxide to the initial redox potential value of raw water.

*Radiation at the presence of ferrous catalyst:* The initial pH of the contaminated water was corrected to 2.8 by addition of sulfuric acid. 1 mL of hydrogen peroxide (35%, v/v) and 2 g of Fe(II) catalyst were added to a storage tank of a volume of 2 L. The original value of the redox potential increased to 500 mV and gradually decreased over the course of 40 min to the initial level of raw water. Another portion of peroxide (1 mL) was added and the experiment continued for another 50 min. At the end of the operation the redox potential stabilized at 390 mV. The final concentration of hydrogen peroxide was  $10 \text{ ug/L}$ , and the pH value of the water was pH 2.4.

#### (b) Decontamination of PCBs in aqueous extracts in a pilot-plant unit

The method is based on the oxidation reaction with hydroxyl radicals. The device consists of a continuously operated vertical tube reactor provided with a UV-radiation emitting high pressure Hg lamp (UV-Oxidationanlage, UX-2, input power 2 kW, capacity up to  $5 \text{ m}^3/\text{h}$ , manufacturer of the reactor is UV-Systeme GmbH, Heidelberg, Germany). Contaminated extract-waters collected from the unit of extraction of soil extraction in two storage tanks (each with volume of  $2 \text{ m}^3$ ) were pumped in a closed circuit through the UV-reactor and through a filter with activated carbon (AC) back to one of the operating storage tanks (see Fig. 1). The experimentally determined flow of water was 100–800 L/h. The number of passages through the loop depended on the initial concentration of PCBs in the aqueous extracts. The evolution of the reaction was controlled by the measurement of the redox

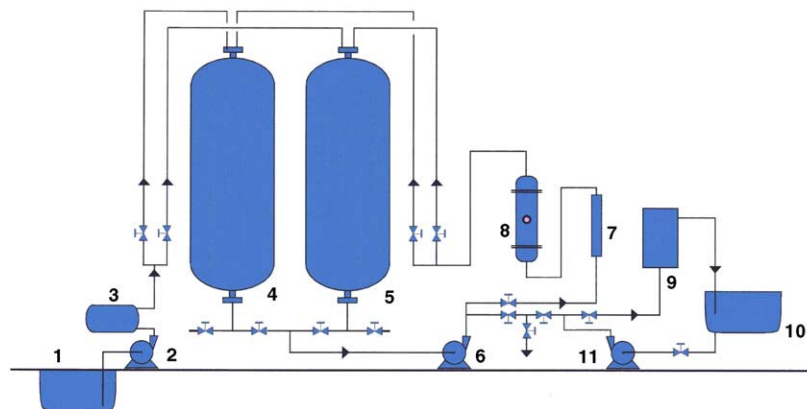


Fig. 1. Scheme of pilot-plant unit of decontamination of water contaminated by PCBs. 1, Tank for contaminated water; 2, pump; 3, sand filter; 4 and 5, storage tanks; 6, circulation pump; 7, rotameter; 8, reactor with UV lamp; 9, activated carbon filter; 10, tank for solution preparation; 11, pump for circulation of water through active carbon filter.



potential of the reaction mixture. The AC filter volume was 200 L, filter was packed with granulated activated carbon SILCARBON. The superficial velocity of liquid in the filter was 0.7 mm/s. The volume of treated liquid in a typical batch experiment was 2000 L, flow of liquid through the reactor was 100 L/h. In the course of the experiment the total volume of hydrogen peroxide (35%, v/v) added was 2000 mL. The experiment was performed at the absence of Fe(II) catalyst. Redox potential was continuously maintained at the level approximately 500 mV, pH was accommodated at pH 7.5 and the temperature was maintained between 18 and 20 °C. Times of reaction were from 96 to 240 h.

#### 2.2.4. Clean-up of highly contaminated waste water

Aqueous condensates both from thermal desorption and fixed-bed reactor (see below) contained a high level of intact PCBs and/or organic compounds, including products of the partially decomposed oil fraction in the case where oil-in-water emulsions were treated by chemical dehalogenation in fixed-bed reactor. Two methods of decontamination of waste water were applied:

- Waste water containing fewer than tens of micrograms of PCBs and below approximately 1% of wt. of both solid non-sediment impurities and an oil fraction was treated by chemical destruction with UV/OX in the loop with AC filter (see above).
- Decontamination of waste water containing PCBs in the order of units or tens of milligrams per liter and over 1% of weight of oils and solid impurities by adsorption on inorganic adsorbent and AC.

These types of waste waters (condensates) were treated as follows:

The separation of the oil-phase was performed by using column-type separators. Aqueous-phase was subsequently intensively mixed with activated bentonite (bentonite was activated by its treating with the saturated aqueous solution of  $\text{Fe}_2(\text{SO}_4)_3$ ), in the proportion of approximately 1 kg of bentonite to 1000 L of water. The procedure continued by neutralization of this slurry with lime to pH 7 at a gentle mixing in the presence of flocculating agent (polyelectrolyte, commercial product Praestol 600, in the ratio 50 mg/1000 L). The precipitating flocks were settled and filtered. The transparent but usually still “brown” waters were filtered with activated carbon and treated in the UV/OX reactor. The partially decontaminated waters were used for preparation of aqueous solvents to be used in the soil extraction. The remaining concentration of PCBs in treated waters was in the range of 50–200 ng/L. Contaminated sorbents were treated in a fixed-bed reactor.

#### 2.2.5. Chemical dehalogenation of liquid PCBs wastes

**2.2.5.1. Sodium process.** The process uses reductive dehalogenation to destroy PCBs by exchanging the chlorine on the biphenyl molecule with hydrogen, forming biphenyl and NaCl. The process uses activated elemental sodium in fine dispersion in paraffinic oil as the electron donor required for the reaction. Sodium dihydrido bis(2-methoxyethoxy) aluminate (commercial name Synhydrid), and/or ethanol are used as activators [59]. The batch process consists of two agitated reactor vessels, each with a volume of 1000 L (see Fig. 2). The PCB-contaminated oil is placed in the first reactor vessel, which is then purged of air with nitrogen. Particulate sodium

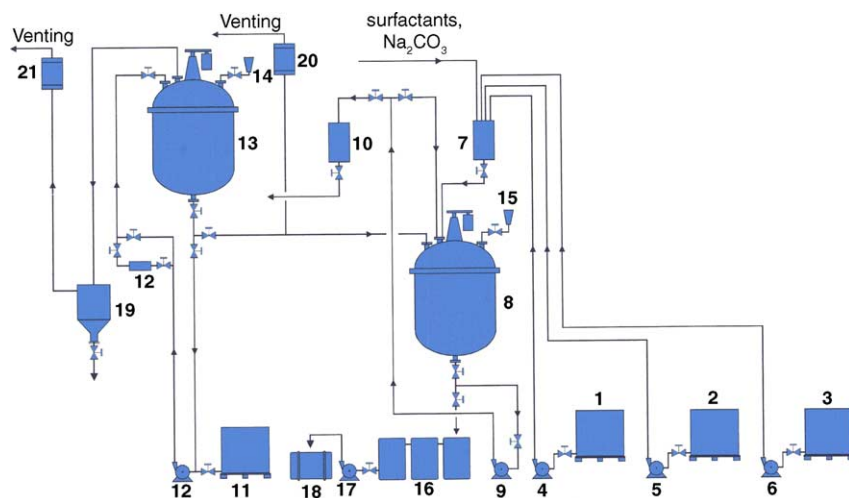


Fig. 2. Chemical decontamination of liquid PCBs wastes, pilot-plant unit. 1, Storage tank for oil-condensate generated in the thermal desorption chamber; 2, storage tank for the aqueous solution of potassium hydroxide; 3, storage tank for polyethylene glycol; 4–6, pumps; 7, graduator of the individual liquid components of the reactive emulsion; 8, mixed vessel for preparation of the reactive emulsion and/or for neutralization of the surplus of sodium in the decontaminated oil leaving the chemical reactor 13; 9, pump; 10, graduator of the reactive emulsion and the subsequent blending of the emulsion with solid particulate carrier; 11, storage tank for contaminated oils; 12, gear pump; 13, chemical reactor-decontamination of oils with activated sodium dispersion or with KPEG solution; 14, dosing of activated sodium dispersion and/or KPEG solution; 15, dosing of ethanol; 16, separators of the residues and reminders after the chemical decontamination reactions; 17, pump; 18, storage tank for decontaminated oil; 19, condenser of aqueous vapors and demister; 20 and 21, filters with activated carbon.

that meets a maximum size specification of 10  $\mu\text{m}$  was placed in the first reactor at a mass ratio of Na:PCB (sum of seven congeners) between 2 and 33. When the reaction is complete the content of first reactor is transferred to the second vessel where the surplus of ethanol is added to quench the reaction (in the final step the ethanol reacts with the unreacted sodium, forming sodium ethanolate). The process generally results in effluent PCB concentrations of approximately 10 mg/L. At this PCB level, or less, the treated oil is disposed off or might be blended for energy recovery in the burners of a thermal desorption unit. The existing pilot-plant equipment has a batch capacity of 600 L. The cycle time per batch, including the time for preheating of contaminated oil in the first reactor vessel, is about 22 h. Both reactor vessels are equipped with external electrical heating and mixing devices. Mixing is achieved by a turbine-impeller at 1000 rpm. The typical reaction sequence includes heating the oil to 80 °C for 16 h, introduce the reacting agents, stir for approximately 4 h at temperature, heat to 120 °C and stir for 6 h, transfer the contents to the second vessel where ethanol is added. The content of the second vessel is subsequently exhausted, the solid residues are separated in a cascade of settling tanks and they are finally filtered. Suspension of sodium in paraffinic oil (33% of the weight) was activated with Synhydrid and ethanol in the mass ratio of Synhydrid/ethanol/Na = 5/0.5/100. The maximum inlet concentration of PCBs in treated oil in the existing equipment was approximately 4000 mg/kg.

**2.2.5.2. Modification of the KPEG process.** The rate of reaction was measured in a bench-scale reactor with a volume of 50 L and in a pilot-plant reactor (having the same configuration as in the case of sodium technology).

(a) Bench-scale testing

The experiments were performed in a mechanically agitated batch reactor with external heating at intensive agitation of the batch by turbine-like impeller. The speed of agitation was about 3000 rpm. The feed of oil was 35 kg and oil was before the initiation of the reaction contaminated with Delor 103.

In a typical experiment, a corresponding amount of powdered KOH was dissolved at the temperature approximately 80 °C in a liquid PEG 300 and this reaction mixture was added into a reactor containing a preheated amount of contaminated oil. The initial temperature of oil (approximately 90 °C) very rapidly increased to the desired level, without any additional heating of the reaction mixture (the reaction is strongly exothermic). The aluminum powder was added carefully to the reaction mixture during the course of reaction in the form of a suspension in oil (the production of gas is instantaneous and violent).

(b) Pilot-plant experiments

Two mechanically-agitated reactor vessels have been used (Fig. 2). The reaction mixture (mixture of PEG 300 with potassium hydroxide, so-called KPEG phase) was

prepared in the upper reactor vessel and transferred by gravity to the lower reactor vessel containing preheated oil. The system works auto-thermally (the heat of reaction maintained the temperature at the desired level). The space in the reactor above the level of agitated liquid was flushed with nitrogen: the outlet gases containing  $\text{N}_2$ ,  $\text{H}_2$  and water vapor were drawn through the water cooler (condenser) and AC filter to prevent some potential escape of PCBs to the atmosphere. EX-motor and turbine-type impeller rotating at 1000 rpm were used. When the reaction was over, the agitation ceased, and after cooling of the content to approximately 90 °C the heavier KPEG phase was easily separated from the oil-phase and was collected in drums (it is believed, that this phase could be recycled as reaction mixture many times, however, we did not carry out such experiments). At present, this KPEG phase is decomposed in a thermal unit.

**2.2.6. Medium temperature thermal desorption (MTTD)**

MTTD process uses a batch chamber reactor where soils are placed in trays (flat containers) and indirectly heated from 480–550 °C for approximately 2 (bench-scale) to 5 (pilot-plant) days. The moisture and organics are swept from the chamber using a nitrogen purge and condensate in a condenser.

During several hours of heating, the moisture in the soil is converted to a steam and ships out negligible amount of the PCB originally contained in the soil (of the order about  $10^{-3}$  %). This moisture is condensed and routed to an activated carbon-filtration water-treatment process. After the first several hours of heating there is supposed to be no moisture in the soil and relatively pure PCB and high boiling organics (if any) evaporates from the soil. The organic phase, which represents almost 100% of the total removal from the soil, is condensed and decontaminated in chemical dehalogenation process. The separation of the early aqueous PCB phase from the late organic PCB phase is necessary, because water would react violently with sodium in the sodium process. The KPEG process is unaffected by the presence of water in condensates.

(a) Bench-scale MTTD

This process consists of an insulated electrically heated desorption chamber (adapted glass-work furnace). Interior dimensions: 600 mm wide, 450 mm high, 950 mm long. Treated soils were placed in open sheet-metal tanks of different volumes, and the maximum height of the layer of soil was 300 mm. Water and organics adsorbed to the soil were swept from the chamber using nitrogen and condensed in a condenser and cooler. Aerosols formed were captured in a demister. Gas leaving the demister flows through the AC filter and oxygen is removed in an absorber. A fan circulates nitrogen back to the chamber head-space. The flow of nitrogen was measured and controlled in the range of 100–500 L/h.

(b) Pilot-plant MTTD (Termidos process)

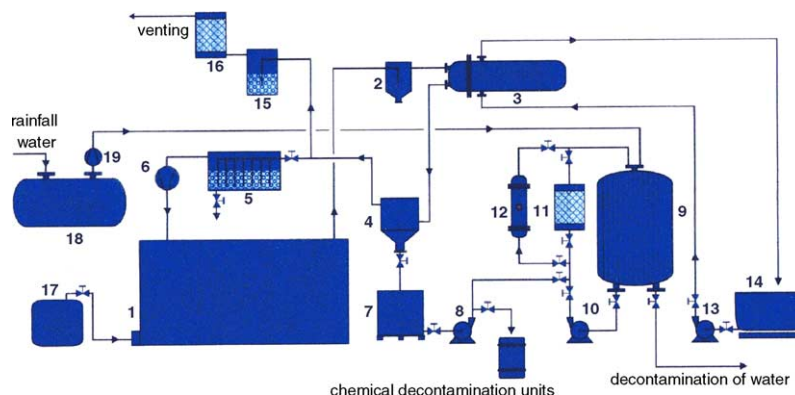


Fig. 3. Scheme of pilot-plant low temperature thermal desorption unit. 1, thermal desorption chamber; 2, separator of solid particles; 3, condenser; 4, demister; 5, scrubber of circulating inert gas and vapors; 6, blower; 7, container of condensates; 8, pump of condensates; 9, reservoir tank for contaminated aqueous condensate; 10, pump; 11, filter with activated carbon; 12, UV lamp; 13, pump for cooling water; 14, reservoir tank for cooling water; 15, siphon trap; 16, filter with activated carbon; 17, storage tank for fuel oil; 18, reservoir for rainfall water; 19, rainfall water pump.

In principle, the pilot-plant unit is an identical copy of above mentioned bench unit. Scheme of unit is given in Fig. 3.

The existing unit occupies an area of about 15 m<sup>2</sup> and has a batch capacity of about 17 metric tonnes soil (placed in 24 flat containers with capacity of approximately 700 kg each, the maximum layer of the soil in the container is 400 mm). The containers are situated in the chamber at two levels. There is sufficient space between individual containers for vapor evaporation and gas circulation to be maintained. The temperature is measured by thermocouples inserted in soil. The chamber is indirectly heated. Heat is supplied by incineration of light heating oil in two burners situated in the side-wall of the chamber (opposite to the entrance gates). The off-gases enter the heat exchanger, which is situated at the bottom of the chamber. The cooling of the head-space of the chamber is performed by a heat exchanger situated at the top of the chamber. Vapors and nitrogen flow out of the chamber a cooler (cooling by circulating water) to condensers (one condenser for aqueous condensate, one for high-boiling organics), demister and absorption (absorption of acid gases in a solution of NaOH and traces of oxygen in an aqueous solution of sodium dithionate Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) and nitrogen is drawn back to the chamber by a fan. The whole thermal desorption unit is connected with the atmosphere through an emergency valve and filter with activated carbon (to prevent the free escape of vapors to the environment in the case of an increase of pressure in a chamber above the pre-determined limit).

### 2.2.7. Alkaline catalyzed chemical dehalogenation of PCBs in oil-in-water dispersions in fixed-bed reactor

This process uses a procedure in which contaminated oil-in-water dispersions (in the proportion 15–40% of weight of oil) are emulsified with reacting agents and sprayed on inert solid particulate carrier forming a thin film on the surface of particles of the carrier. Both evaporation of water and

organics and chemical reaction take place in the range of temperature from 100 to 550 °C resulting in partial decomposition of the PCBs present. Potassium hydroxide, sodium carbonate and PEG 300 are used as reacting agents. The reaction is catalyzed by active carbon, which is derived from sucrose at a higher temperature. The reaction agents are dissolved in an aqueous-phase. As a solid particulate carrier different matters can be used (dry loamy-sand soil of proper size fraction, fly-ash, bentonite, zeolite). The optimum mass ratio emulsion/solid carrier = 0.08/1. The droplets of oil containing PCB are surrounded by an aqueous-phase in the reacting emulsion. During the first several hours of heating, the water-phase is converted to a steam and strips out some portion of the PCBs. This vapor is condensed (aqueous condensate). After evaporation of water, the droplets of oil with high surface area remain in very close contact with concentrated reagents and the rate of dehalogenation reactions is so enhanced. In the final step, the oil with remaining content of non-reacted PCBs (and possibly other organic products of partially decomposed oils) evaporates forming an oily condensate. The necessary condition for an effective contact of phases is the durability of the stable reacting emulsion in the course of covering of emulsion on the surface of carrier solid particles in a mixing device and its stability in the broad range of temperatures. The suitable ratios of individual reaction agents were detected under laboratory conditions. As a first approximation, and for the concentration of PCBs in the original oil-on-water dispersion up to 40,000 kg/kg, the mass ratios PCB/KaOH/Na<sub>2</sub>CO<sub>3</sub>/PEG 300 = 1/6/12/8 can be recommended (PCB is considered as a sum of 7 indicative congeners, see Analysis).

In a typical experiment (see Fig. 2) 800 L of two-phase oil-in-water liquid was mixed with 180 L of 50% aqueous solution of KOH and 180 kg of powdered sodium carbonate, 112 kg of PEG 300 and a solution of 72 kg sucrose in 200 L of water. 3.2 kg of non-ionic surfactant (mixture of alkaline soap + ethoxylated nonyl phenol) was added. This mixture was intensively mixed in a tank to form a stable



emulsion. Consequently, the emulsion was gently mixed with dry Milovice soil, size fraction below 12 mm. Total amount of 9750 kg of soil was placed in flat containers (see MTTD). The height of the fixed bed of the soil with emulsion in individual containers was 400 mm approximately. Containers were transferred to the pilot-plant thermal desorption unit. The reaction mixture was indirectly heated in the inert atmosphere. Similarly as for the MTTD procedure, the temperature gradient of 50–100 °C between the temperature in the gas-phase in chamber and in the reaction mixture was maintained during the course of heating. At the temperature range between 400 and 510 °C in the fixed bed, the residence time of reaction mixture in the chamber was kept approximately 15 h. First condensate with the majority of the water-phase (condensate Ia corresponding to the temperature range 60–120 °C), second condensate I (corresponding to the temperature range 120–200 °C) and third condensate II (where oily fraction is prevailing, corresponding to the temperatures above 200 °C) were collected. Both condensates (I, II), however, slowly disintegrated in two liquid layers (aqueous and oily).

### 3. Results and discussion

#### 3.1. Extraction of PCBs from contaminated soils with aqueous solutions

##### 3.1.1. Laboratory experiments

Table 2 summarizes the extraction efficiency of individual extraction solutions:

- in the course of the extraction process, predominantly the low-chlorinated congeners transfer to the liquid-phase (about 85–90% of observed congeners were No.28 and No.52)
- the largest quantity of desorbed PCBs in a single-step operation did not exceed 4% of the original content of selected congeners in the soil.

From these findings it is clear that a multistage process and more intensive contact between phases is needed, and some pretreatment process should be applied to enhance the ability of organics to extraction solvents.

The best results are obtained using a single-phase bicontinuous emulsion with quaternary salt as a surfactant and/or the use of short quaternary salt in water.

Whereas contaminated soils with high contents of silicate components (sand, gravel) prefer the use of non-ionic surfactants, soils with higher content of clays require ionic surfactant to enhance the effect of solubilization.

The selection of extraction composition has to be experimentally defined, taking into account the composition of the soil. However, as a universal and usually non-expensive solution, a non-ionic surfactant could be selected.

#### 3.1.2. Extraction of PCBs from contaminated soils at pilot-plant scale

Since this technology can be applied to weakly contaminated soils only, the proposed method has been used with samples of contaminated soil from Milovice, where the contamination is low. The original concentration of PCBs was 114.9 mg/kg (sum of indicative congeners of PCBs). At the end of the activation period, a good portion of PCBs was released into an activation aqueous solvent, the starting concentration for washing was 91.13 mg/kg. Time dependence of concentration of PCBs (mg/kg dry) in soil: 0 week: 91.1, 4 weeks: 86.9, 8 weeks: 57.6, 12 weeks: 32.0, 16 weeks: 18.0. We were unable to clean up the remainder of the adsorbed PCBs by extraction.

#### 3.2. Clean up of contaminated extraction waters. Destruction of PCBs with hydroxyl radicals

##### 3.2.1. Laboratory experiments

Typical results are summarized in Table 3. A considerable reduction of concentrations of PCBs can be achieved both with or without a catalyst. It is possible to conclude that for relatively low-contaminated waters the role of a catalyst is subsidiary. Some slightly positive role of catalyst is manifested manifests at higher concentrations of PCBs. In the case of higher concentrations of PCBs and/or if containing a portion of other organics or solid impurities (like fine particles of soil, which could settle on the surface of the UV-lamp), it seems necessary to simultaneously apply the separation of these components by sorption.

#### 3.2.2. Decontamination of PCB of aqueous extracts in the pilot-plant unit

Efficiency of destruction of PCBs in the UV/OX system, even in real waste water containing impurities, ions and sur-

Table 3  
Efficiency of decontamination of water, slightly contaminated with PCB, by application of UV/OX radiation

Sample	Congeners of PCB (ng/L)						Sum
	28	52	101 + 118	153	138	180	
Contaminated water	131.1	13.3	43.1	19.5	20.4	6.1	233.5
Water/UV	<1	<1	<1	<1	<1	<1	
Water/UV/ catalyst	<1	<1	<1	<1	<1	<1	
Contaminated water	960.0	95.4	308.6	156.2	143.3	44.6	1714.3
Water/UV/	<1	<1	<1	<1	<1	9.9	
Water/UV/catalyst	<1	<1	<1	<1	<1	2.9	

Influence of the presence of Fe(II)/Fe(III) catalyst.

Table 4  
Decontamination of PCBs from aqueous extracts – effluents from washing soils with selected surfactants

Sample	Time (h)	Sum of seven PCB congeners (ng/L)	Efficiency of dehalogenation (%)
Extract, 1000 ml H <sub>2</sub> O <sub>2</sub>	0	3212.0	
Extract, after 1. Passage through the UV reactor	2.5	863.9	73.1
Extract, after 2. Passage through the UV reactor	5	742.4	76.9
Extract, 1000 ml H <sub>2</sub> O <sub>2</sub> added, after 3. Passage through the UV reactor + AC filter	7.5	62.3	98.0
Extract, after 4. Passage through UV reactor + AC filter	10	27.9	99.1

Volume of treated liquid 2000 L, pH 7.8, UX-2.2 kW. In loop with AC filter (100 kg of granulated SILCARBON, superficial velocity of flow of liquid in the filter 0.7 mm/s). Flow of extract 800 L/h.

factants is significant (see Table 4). However, the combination of UV-technique with adsorption seems to be more effective method of clean-up of contaminated water and reduces the cost of remediation of adsorbent.

The method of UV-radiation was also applied on highly contaminated extraction waters accumulated from the washing of soils (see the Table 5).

The efficiency of decontamination of contaminated waters is high. Due to disproportionate times of reaction, the use of catalyst and/or combination of UV/OX and AC filtration is however inevitable in practice. In any case, optimum reaction conditions have to be determined experimentally.

### 3.3. Chemical dehalogenation of liquid PCB wastes

#### 3.3.1. Sodium process, pilot-plant experiments

Some selected experiments in the pilot-plant unit are summarized in Table 6.

The rate of reaction in pilot-plant equipment at the temperature of about 80 °C substantially differs from the results obtained at laboratory conditions published by other authors [49]. Particularly, the demanded surplus of sodium is not justifiable on the basis of high cost. It has been found that the chemistry of extremely fine sodium particles differs from that of molten fused sodium (melting point 97.7 °C). The rate of reaction was much lower in comparison with laboratory findings. Good destruction efficiency was obtained, however, at the temperature above the melting point of Na and at higher mixing speeds. Because of the decisive temperature dependence of the rate of reaction, the recommended temperature is about 130 °C (the upper limit of the temperature applied depends on the chemical properties (b.p.) of the treated contaminated oil). Reynolds number of impeller  $Re_m$  have to be

at least  $10^6$ , with sufficient cutting ability to maintain the high surface area of metallic sodium in the reactor vessel.

#### 3.3.2. Modification of the KPEG process

The aim was to analyze reaction conditions of a modified KPEG method mainly at pilot-plant conditions, to judge the ability of this method to react with the low-chlorinated PCBs which were the dominant compounds in the Czech commercial mixtures and, at present, represent the principal PCB contamination, to elucidate the role of powdered Al in the KPEG system and finally to compare both sodium and KPEG–Al methods at identical hydrodynamic conditions in pilot-plant reactors, with identical analytical procedures.

3.3.2.1. Bench-scale testing. Some bench-scale experiments are summarized in Table 7.

Our data show a big discrepancy between the previously published data obtained at laboratory conditions with PCB mixtures containing a dominant proportion of highly chlorinated congeners of PCB (Aroclor 1260) [31,32]. The rate of reaction of mixtures of PCBs containing mainly three or four atoms of chlorine is lower. This conclusion corresponds in principle with the laboratory data obtained recently [49], however, the surplus of KOH and PEG as well as the temperature to achieve excellent efficiency has to be much higher in bench reactor conditions. The rate of reaction is strongly dependent on the temperature and relative short periods of reaction temperatures above 100 °C were achieved. To be able to apply this reaction for the decontamination of transformer oils (where the temperature of heating of dielectric oil should be maintained about 100 °C) it is necessary to expect much longer reaction times.

Table 5  
Decontamination of highly contaminated aqueous extracts from washing of soil by UV radiation only (no filtration on AC filter)

Sample	PCB congener no.							Sum
	28	52	101	118	138	153	180	
Raw extract (mg/L)	0.42	0.17	0.04	0.04	0.01	0.01	0.006	0.69
After UV treatment (ng/L)	51.6	8.9	3.9	2.35	0.56	1.65	0.5	69.5
Raw extract (mg/L)	0.12	0.05	0.01	0.01	0.01	0.01	0.01	0.21
After UV treatment (ng/L)	130	35	<5	<5	<5	<5	<5	170

Volume of waters was 2000 L, flow of water 100 L/h, 12 passages of the whole volume of liquid through the reactor. Hydrogen peroxide was continuously added with the aim to maintain the redox potential at the level of 500 mV. No catalyst added. Time of reaction was 240 h.

Table 6

Efficiency of dehalogenation of oil contaminated with PCB by dispersion of metallic sodium, activated with synhydrid (S) and ethanol (E), mass rate S/E/7 cong. of PCB = 5/0.5/100

Time (h)	Temperature (°C)	Conc. PCB (mg/kg) <sup>a</sup>	Mixing conditions	Total amount of Na (in g) added	Mass ratio Na:PCB <sup>a</sup>	Volume of batch (l)
0	80	325.3	Turbine, 250 rpm	4300	33	400
1		294.0				
2		252.5				
3		205.5				
4	Changed to 120	205.5				
4						
10		26.5				
0	80	903.5	Turbine, 250 rpm	5500	15	400
4		700.5				
4	Changed to 120					
12		50.1				
0	100	260.0	Turbine, 1000 rpm	3000	29	400
4		29.0				
6		16.0				
6	Changed to 130					
8		2.2				
0	80	3450.0	Turbine, 1000 rpm	4600	2.2	600
4		2640.0				
4	Changed to 130					
10		<1				

Volume of the batch was 400 (600) L.

<sup>a</sup> Sum of indicative congeners.

The addition of powdered Al has improved the time course of decontamination. The positive influence seems however not decisive, as shown in Fig. 4 (drop in the curve between 210 mg/kg to 140 mg/kg can be attributed to the addition of metallic Al). It is proposed to add Al as an end-step of the process with the goal of lowering the remaining concentration of PCBs to the regulatory limits, if necessary. In comparison with the sodium method, the rate of dehalogenation is quicker, and there are no problems with separation of products of reaction from clean oil.

3.3.2.2. *Pilot-plant experiments.* Indicative results are summarized in Table 8.

The obtained results give evidence to an excellent efficiency of decontamination of PCBs in oils, even in the case of application of the reaction to the low chlorinated mixtures of PCBs. However, abundant amounts of reaction agents are necessary to be able to achieve an efficiency in excess of 99%. The rate of reaction depends on various parameters:

- Between 140 and 160 °C, if the mass ratio KOH/ sum PCBs is approximately 15 and the  $Re_m$  is above  $10^6$  the rate of reaction can be approximated by a first order reaction with a reaction constant of approximately 0.019/min.
- The rate of reaction is low at a temperature below 140 °C and is significantly suppressed in the range of 80–100 °C.
- In line with our experiments, it is supposed that the optimum value of the KOH/PCBs (or PEG 300/PCBs) ratio is approximately 15 (or 30). Higher values of this ratio have

some positive influence on the rate of reaction, but are not acceptable from the economic point of view.

- Special disintegrating mixing devices ensuring great surface area between both liquid-phases are needed.

Despite the results demonstrating a high efficiency of decontamination by this method, there is a drawback. At present, the regulatory levels of PCBs comply with the determination of 6 (or 7) indicative congeners only. When analyzing chromatographs of the oil treated by this method, there is evidence of a pronounced increase of probably di-chlorinated congeners, which were not detected in the original contaminated oil. It seems, that these compounds have emerged probably as a result of chemical changes in the course of contact of congeners having three and four Cl with an alkali environment, with simultaneous substitution reaction. These new congeners are not included in the analytical determination. Therefore, much additional research of the mechanism of this reaction is necessary.

#### 3.4. Medium temperature thermal desorption

##### 3.4.1. Bench-scale

The results of experiments carried out in a bench-scale unit are given in Table 9.

Condensates were collected separately in the first phase of heating (up to the volume of 1020 mL, temperature 322 °C), and in the second phase of heating (corresponding to the temperature range in the soil 322–502 °C, 160 ml). The time of heating was sufficient to achieve a quantitative desorp-

Table 7

Modified KPEG process, volume of contaminated oil was 35 L, turbine-like propeller, 3000 rpm

Reaction time (min)	Comments	<i>T</i> (°C)	PCB <sup>a</sup> (mg/kg)	PEG (300 kg)	KOH (kg)	Al (kg)	PCB <sup>a</sup> :PEG:KOH:Al
0	20 kg of oil	115	800	1.5	0.8	0.1	
25	Al powder added	125–130	330			0.05	
68		125–130	140				
	Total		0.016 kg	1.5	0.8	0.15	1:93.7:50:9.4
0		100	600	1.5	0.7	0.1	
40		110	460				
70	Al powder added	115	290			0.07	
130		120	260				
190		120	230				
	Total		0.021 kg	1.5	0.7	1.07	1:85.7:33.3:8.1
0		105	700	1.8	0.7	0.15	
45		105–143	270				
85	Al powder added, increase of <i>T</i> to 140 °C	125	210			0.1	
110		135	140				
380		100	80				
	Total		0.0245 kg	1.8	0.7	0.25	1:73.4:28.6:10.2
0		140	9200	8	3.4	0.1	
60	Reactants added	145–150	580	4	1.7	0.1	
150		150–159	90				
420		150–155	7.4				
	Total		0.325 kg	12	5.1	0.2	1:37.3:15.8:0.62
0		140	15000	8	3.4	0.1	
170	Reactants added	148–157	1700	5	2	0.1	
235		148–149	970				
440		150	250				
	Total		0.525 kg	13	5.4	0.2	1:24.8:10.3:0.38
0		145	810	8	3.4	0.4	
150		150	<1				
	Total		0.0284 kg	8	3.4	0.4	1:282:120:14.1

Paraffinic oil was contaminated by dielectric liquid Delor 103 from electrical condensers. Rate of reaction was enhanced by powdered aluminum.

<sup>a</sup> PCBs were determined as a sum of seven indicative congeners.

tion of both moisture and organics. Samples of treated soil taken from different heights of the heated layer were analyzed separately. Residual concentrations in all levels of soil were identical, below 0.4 mg/kg, which indicated a good heat transfer into the layer of soil. In the first phase of evaporation,

condensates contained insignificant amounts of PCB relative to a total mass of PCBs in the soil (concentration of the sum of PCBs in the condensate was 370 µg/L, or 4.10<sup>-3</sup>%). The fraction corresponding to the organic-phase was diluted in a known volume of *n*-hexane and analyzed. It was found, that

Table 8

Dehalogenation of contaminated oil in pilot-plant reactor by KPEG and at addition of powdered Al

Total time (min)	<i>T</i> (°C)	PCB <sup>a</sup> (mg/kg)	PEG (kg)	KOH (kg)	Al (kg)	PCB:PEG:KOH:Al mass ratios	Efficiency (%)	Comment
0	152	11900	96	48	0			
185	152–165	320			1		97.3	Aluminum added
225	160	150					98.7	
600	80	72				1:30.25:15.12:0.31	99.4	After spontaneous cooling
0	130	17200	48	24	2			
200	152–165	3400	48	24			80.2	
455	154–158	590						
600	140–100	170				1:20.9:10.45:0.43	99.0	Cooling
0	140	95	25	12	0.2			
90	140	13			0.1			
400	140–180	9.1				1:986:473:11.8	90.4	

Agitated reactor vessel and turbine-like impeller at 1000 rpm were used. Batch of contaminated oil was 267 kg.

<sup>a</sup> Sum of indicative congeners.



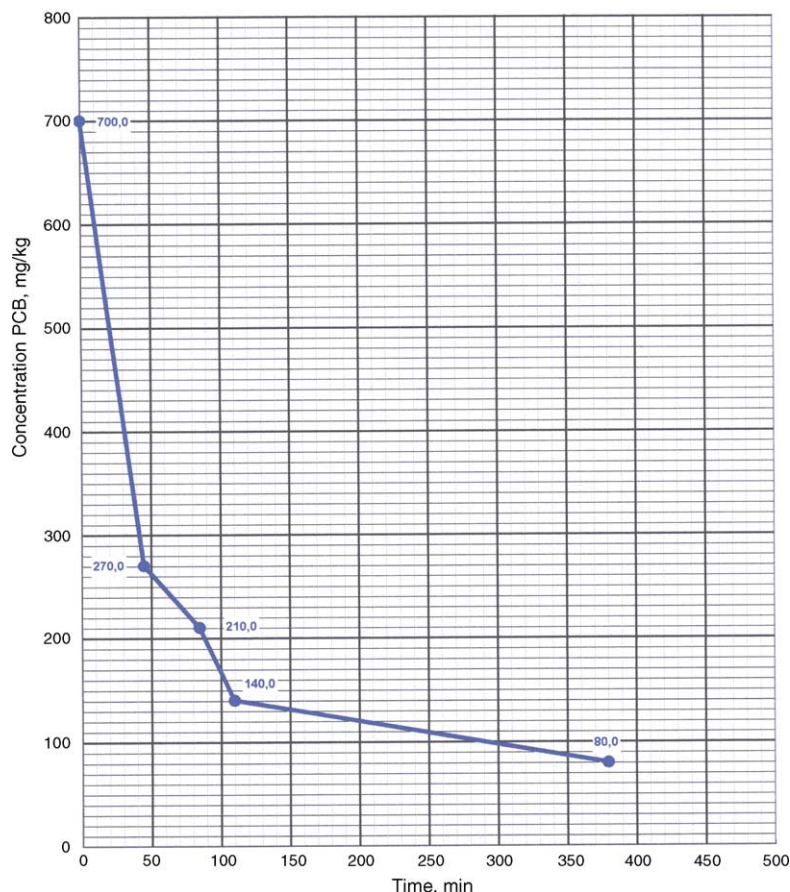


Fig. 4. Time dependence of concentrations of PCBs (mg/kg) in oil treated by modified KPEG method in bench-scale volume of reactor (see procedure no. 3 in Table 7).

the organic-phase (originally 160 ml) represents a very concentrated mixture of PCBs in other non-polar liquids (more than 5% wt. of the total indicative congeners). Surprisingly, it was discovered that the congener No.28 which represented almost 70% of the total mass of indicative congeners in the soil, was only 47% of the congeners in the aqueous condensate. The fate of individual congeners during thermal treatment is

not fully understood and more information is needed. Bench-scale experiments have also shown how firmly moisture (and organics) were adsorbed in the pores of soil particles and subject to a great resistance to transfer of vapors through the layer of soil particles in the static bed.

Some experiments were performed with the addition of powdered sodium hydrogen carbonate. It is evident that the

Table 9  
Rate of desorption of PCB from contaminated soils

Time of experiment (h)	Temperature in the center of layer (A) (°C)	Temperature in the center of layer (B) (°C)	Condensate (A) (ml) sum	Condensate (B) (ml) sum
0	28	29	0	0
1	72	82	0	150
3	80	96	550	500
5	88	98	850	850
7	205	104	960	1050
9	277	191	1010	1100
11	316	227	1020	1100
13	322	320	1020	1100
17	420	349	1130	1130
19	420	410	1180	1230
21	502	428	1180	1230

(A) Contaminated soils, (B) mixture of contaminated soil with 7% wt. of sodium bicarbonate. Type of soil Milevsko II, size of particles below 2.5 mm, sum of indicative congeners 300 mg/kg, content of moisture 3.2% of wt. Height of layer of the treated soil 300 mm, total mass of the soil 32.1 kg, old contamination (more than 20 years). Velocity of nitrogen in the free space above the level of the soil in the chamber: 5.5 cm/min.

Table 10  
Efficiency of separation of PCBs from contaminated soils in pilot-plant batch desorption unit

Type of soil:	Sum of seven indicative congeners (mg/kg dry)		Efficiency of separation (%)
	Before LTTD	After LTTD	
Milevsko I	1163.8	0.425	99.96
Milovice	140	0.1	99.93
Milovice	29	0.1	99.65
Milevsko II	1860	< 0.5	99.97
Milevsko II	3020	< 0.5	99.98
Milevsko II	3810	< 0.5	99.99
Milevsko I	5350	< 0.5	99.99

Capacity 15–18 tonnes a batch, temperature up to 550 °C, nitrogen gas circulation. Soils were contaminated mainly by Czech commerce PCBs products based on the mixture of Delor 103.

decisive phase of desorption takes place at much lower temperatures. This fact can be ascribed to the role of an alkaline additive which enhances the process of reductive dechlorination. The remaining concentration of PCBs in the soil was also very low, below 0.1 mg/kg. A similar procedure has been applied recently in the BCD process [33].

Bench-scale experiments have demonstrated that the method of low temperature desorption is a very effective tool for decontamination of soil contaminated with PCBs and/or other chlorinated organics.

### 3.4.2. Pilot-plan MTTD

Some selected data are summarized in a Table 10.

Table 11 illustrates the fate of individual congeners after the thermal desorption procedure:

The treated soil from batch MTTD process contains a residual concentration below of about 0.5 mg/kg PCB independently on the original concentration in treated contaminated soil and of the type of soil (loamy or sandy). A high efficiency of separation of PCBs from soils (over 99.9%) is demonstrated even in the soil with an original concentration of about 5000 mg/kg PCB.

At present, the regulatory level for unrestricted disposal of treated soil is 0.05 mg PCBs/kg. It is unlikely that lower residual PCB levels can be achieved in the batch MTTD unit because of the fixed-bed configuration. It may be possible to lower the residual levels, however, by incorporating a reductive dechlorination reaction within the LTTD process (by adding caustic soda and/or sodium bicarbonate).

Table 11  
Composition of indicative congeners in the soil treated by thermal desorption in pilot-plant unit

Type of soil	Congeners (mg/kg)							Efficiency of separation (%)
	28	52	101	118	138	153	180	
Milevsko I								
Before LTTD	134	33.1	19.9	23.7	27.6	27.6	23.3	
After LTTD	0.32	0.13	0.05	0.045	0.03	0.035	0.018	99.78
Milevsko II								
Before LTTD	37.5	10.8	4.14	4.24	2.95	3.25	1.72	
After LTTD	0.26	0.074	0.025	0.021	0.021	0.026	0.017	99.31

The possibility of decontaminating contaminated using activated carbon (AC) is also demonstrated: very strong links between PCBs and surface of pores of AC were expected. After the batch MTTD process in the controlled atmosphere (nitrogen with traces of oxygen up to 1% vol.) the specific area of AC has increased by an average of over 20% and AOX (adsorbed chlorinated organics, g/kg dry) decreased by over 90%. Experiments with thermal decontamination of bodies (carcasses) and packages of electrical condensers, after the previous pouring of the dielectric PCB liquid (pure Delor 106), revealed an average composition of scrap from condenser as follows: metallic sheet 0.18 mg/m<sup>2</sup>, Al-foil below 0.001 mg/m<sup>2</sup>, carbon ash 0.16 mg/kg.

### 3.4.3. Chemical dehalogenation of oil-in-water dispersions in solid-state reactor

The efficiency of destruction of aqueous liquid wastes of the type oil-in-water emulsions is demonstrated in Table 12. The efficiency of 83.5% destruction is relatively high. However, the composition of PCBs in both condensates remains at very high levels. Additional treatment of condensation products is necessary and so the costs of decontamination increase.

Much additional research is necessary with the aim to improve the efficiency of destruction of such wastes and lower the quantity of water-phase.

### 3.5. Treatment technology evaluation and ranking

The purpose of this section of the paper is to evaluate and rank the commercial technologies that might be used for the treatment of soils (in general of solid wastes like electric capacitors and/or condensers) and liquids containing polychlorinated biphenyl contamination. We believe that the best treatment technology for treating solid wastes contaminated with PCB is indirect-fired temperature thermal desorption. The evaluation of source materials in the Czech Republic indicates that the priority in wastes to be treated is likely to be PCB solid wastes and PCB liquids in that order. The MTTD process could be duplicated under an amended operating permit until the market in PCB waste and soil matures. The existing modular units could be used for a treatment of contaminated capacitors and/or transformers and could be used onsite for activated carbon treatment or transported off-site for soil treatment at spill location. The existing chemical

Table 12  
Efficiency of destruction of PCBs in contaminated oil-in-water emulsion in solid-state reactor

	Volume, l	Mass, kg	Concentration of PCB, mg/kg	Total amount of PCB, mg
Inlet				
Solid carrier		9750	18	175,500
Emulsion–water	678	678	37	25,086
Emulsion–oil	122	128.1	110,000	14091,000
Inlet total				14,291,586
Outlet				
Solid carrier		9,750	10	97,500
Condensate Ia (taken up to 120 °C)	380	380	7.3	2,774
Condensate I–water	760	760	25	19000
Condensate I–oil	30	31.5	11,000	346,500
Condensate II–water	314	314	32	10,048
Condensate II–oil	56	58.8	32,000	1,881,600
Outlet total				2,357,422

The original oil-in-water emulsion consisted from two immiscible phases: watery-phase (emulsion–water) and oily-phase (emulsion–oil).

processes will require a substantial investment in equipment and technology development to bring it to the level where it can satisfy the needs in of terms of capacity for dehalogenation PCB generated from imported liquids and soil (capacitors) desorption.

The well-known BCD dechlorination process is more realistic from an equipment and cost standpoint, but this process requires a substantial investment for technology rights. We also believe that the need for a liquid dechlorination facility could be substantially reduced or eliminated by dechlorinating PCB in the thermal treatment unit. This technology has been demonstrated at full commercial scale in the U.S.

The existing extraction process can be used for washing oversize and debris screened from the incoming soil feed. Arrangement of individual technologies and flow-sheet of wastes and decontamination products is presented in a Fig. 5.

Comparison of indirect-fired thermal desorption equipment used to treat PCB contaminated soils and dechlorination processes that are available in the United States and rec-

ommendation which designs may be more suitable for our necessities was referred and it is available in the feasibility study for IDOS Waste Treatment Facility [62]. In this study, there are mentioned conventional calciner designs (Astec, RLC, Texas Incinerator), steam strip design (Maxymillian Technologies), hot sand recycle design (SoilTechATP), fluid bed design (RSI), specialized PCB design (ETG) and liquid dechlorination systems (Commodore SET, BCD). Table 13 only summarizes typical small plant commercial indirect-fired design that have been used for the treatment of PCB contaminated soils in the United States, which are as for as capacities similar to our above mentioned unit. Over the years, several other designer of indirect-fired medium temperature thermal desorption system have been tested or used commercially for the treatment of contaminated soils. Most of the designs are no longer in operation for the reason stated. They are reviewed here briefly for background information only.

Information on available PCB-destruction facilities was also incorporated into the United Nations Environment Pro-

Table 13  
Comparison of small plants design used to treat contaminated soil

Supplier	Equipment description and special characteristics [62]
Onsite technologies	OT provides portable calciner designs with the desorber mounted on the trailer, the condensation system on a second trailer The systems have been. used for the treatment oily drill cuttings, but could be used to treat PCB contaminated soils. Soil temperatures of 450 °C are achieved
McLaren Hart	MLH developed a low temperature, batch-charged soil treatment system that is similar to the Termidos process. Heat was supplied by radiation from gas fire heating tubes above the soil bed. A vacuum was drawn on the reactor to enhance contaminant vaporization. The volatilized organics were destroyed in a thermal oxidizer. It seems to be effective for treating soils containing petroleum hydrocarbons only
Shirco	The Shirco unit was a continuous feed version of the soil bed technology that predated the McLaren Hart processor. In this case the bed of soil was placed on a traveling grate and the temperature were higher
LT3	Weston Environmental Services developed and commercially used an indirect-fired processor using hot oil as the heating medium. Hollow screws heated internally by re-circulating hot oil were used to transport the soil through the reactor. Vaporized organics were either condensed or burned in a thermal oxidizer
Bethlehem	Bethlehem Corporation developed a system combining a hot soil recycle with a high efficiency paddle in an attempt to improve heat transfer. The ceiling temperature (315 °C) of the hot oil heating medium limited both the Weston and Bethlehem system. The use of higher temperature oils was considered to constitute a safety hazard

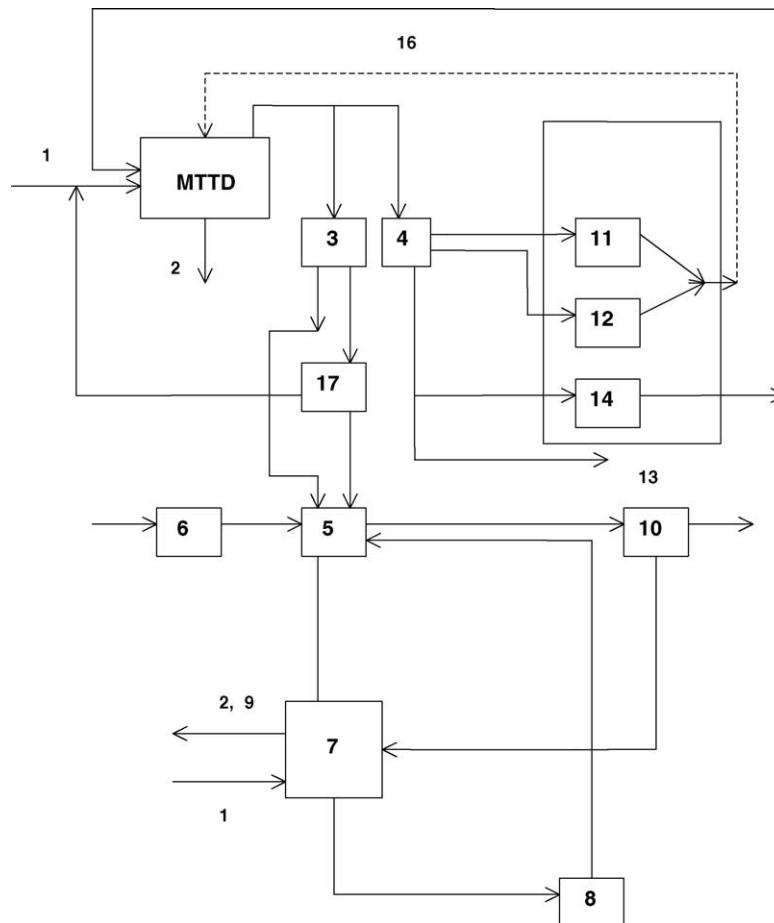


Fig. 5. Arrangement of individual decontamination processes. 1, inlet of the contaminated soil and/or capacitors drained of their liquid and/or contaminated adsorbents; 2, outlet of decontaminated soil; 3, aqueous condensate contaminated with PCBs; 4, oil condensates containing the decisive amount of PCBs; 5, unit of the clean-up of contaminated water (UV-activated carbon system); 6, tanks for waste and/or contaminated underground water; 7, extraction unit (extraction of contaminated soil with aqueous solvents); 8, reservoir of contaminated aqueous extracts; 9, (partially) decontaminated soil; 10, decontaminated water (used for the preparation of the extraction solution); 11, chemical dehalogenation of contaminated oils and water-free oil condensates by sodium dispersion; 12, chemical decontamination of oils and oil-in-water condensate; 13, storage tank of oily residues for incineration; 14, solid-state reactor-destruction of oil–water mixtures by reactive emulsion process; 15, contaminated oil (dielectric liquid); 16, mixing of decontaminated oil (the content of PCBs below 10 ppm) with clean light combustion oil as a fuel for heating MTTD; 17, adsorption of PCB from highly concentrated aqueous condensates and contaminated waste water with high content of solid sediment on activated bentonite.

gramme [63]. The publication responds to request for information on, and to continuing interest in alternatives to incineration and identifies more than 20 vendors who represent that they can treat and destroy PCB oils, transformers, or capacitors, using chemical or physical processes. The survey of currently available non-incineration PCB destruction technologies including the costs is summarized in a Table 14. These technologies realize mainly physical–chemical and chemical methods and do not include incineration. Nevertheless, it must be recognized that some PCB destruction facilities include in this analysis incorporate, or require, an incineration step, generally for the final destruction of the PCBs extracted from electrical equipment.

The reported rate charged to remediate to destroy contaminated transformer oils, waste oils, transformers and capacitors is very variable according to the product but generally lower than the cost of incineration, except in the case of

pure PCBs. Reported rate charged to remediate transformers, capacitors, transformer oils and waste oil contaminated by PCBs varies between 0.35 and 1.78 USD/kg (approximate average is 1.1 USD/kg) for transformers, between 0.14 and 3.3 USD/kg (approximate average rate is 1.42 USD/kg) for capacitors, between 0.15 and 2.63 USD/kg (approximate average rate is 0.88 USD/kg) for transformer oils and between 0.13 and 2.63 USD/kg (approximate average rate is 0.86 USD/kg) for waste oils respectively, see [63].

Rate charged to remediate PCB contaminated soils with thermal desorption was dependent on many factors and ranged from 40 to 500 USD/tonnes [62].

Our experience with operation of these technologies shows that the disposal of highly concentrated liquids (dielectric liquids from capacitors, oil condensates from MTTD containing more than ca. 5.000 ppm PCB) by chemical methods is not cost-effective and cannot thus compete with the price of



Table 14  
PCB treatment/destruction technologies (transformers, capacitors and oils)

Item	Costs (USD/kg)	Company	Technology
Transformers	0.71–1.78	ABB Service (Germany)	Decontamination with hot solvents
Transformer oils	1.31–2.63	AMEC GeoMelt (Australia, UK, USA)	Vitrification
Transformer oils	0.20–0.75	Aprochim (Brazil, France, Spain)	Casing is treated with solvent vapor. Extraction of oils with solvents
Waste oil	0.13–0.57		
Transformers	0.84–1.42		
Capacitors	0.14–1.25		
Waste oils		Bilger (France, Germany, Netherlands, UK)	The oils are treated with metallic Na
Transformers			
Capacitors	n.a.		
Transformers	2.0	Cintec (Canada)	Solvent washing allowing recycling of metallic parts
Capacitors	5.36		
Transformer oils	0.8	Cleanaway (UK)	Solvent cleaning of transformers and high temperature incineration of residues and oils
Waste oils	0.5		
Transformers	1.0		
Capacitors	1.6		
Electric oils, Waste oils		EcoLogic (Australia, Canada, Japan)	High temperature reduction of organics to methane and HCl in the of hydrogen
Transformers	n.a.		
Capacitors			
Electrical oil		ELF Aprochem (France)	Thermal conversion of PCBs to HCl in the high temperature furnace
Waste oil			
Chlorinated residues	n.a.		
Transformer oils	0.15 USD/L	Fluidex (Australia, South Africa)	Chemical destruction with sodium (at the 100 ppm)
Transformer oils	0.73–1.45	Grosvenor Power (UK)	Catalytic dehalogenation (patented catalyst)
Transformer oils	0.7 USD/L	Manitoba Hydro (Canada, USA)	Dehalogenation with metallic sodium
Transformers, capacitors	n.a.	SD Myers (1), (Brazil, USA)	The components are cleaned with solvent, PCB concentrates are sent away for destruction
Mineral oils, retrofilling	n.a.	SD Myers (2), (Canada, South Africa, UK, USA)	Dechlorination process (KPEG?)
Electrical and waste oil, transformers, capacitors	n.a.	Ontario Power (Canada)	Metallic sodium to destroy PCB, solvent extraction for solid parts
Transformer oils	1.1	Orion BV (Netherlands)	Solvent cleaning associated to an incinerator
Waste oil	1.34		
Transformers	1.34		
Capacitors	1.69		
Waste oil	1.5	Papusha Rocket Technol (Russia)	High temperature chemical destruction (plasma chemical detoxification)
Electrical equipment followed	0.58	Petrochimitekhology (Russia)	Solvent washing of equipment
Oil	0.175		By plasma chemical destruction
Transformer oil	0.6	Powertech (Canada, Japan)	Metallic sodium to destroy PCBs
Transformers	1.65	Safety-Kleen (USA)	Solvent washing of equipment, metallic sodium to destroy PCBs
Capacitors	3.3		
Oils	0.22		
Waste oils	0.44		
Transformers	1.0–1.67	Sanexen (Canada)	Solvent washing of equipment, sodium based reagent to destroy PCBs
Transformer oil	0.34–1.0		

Table 14 (Continued)

Item	Costs (USD/kg)	Company	Technology
Transformer oil	0.95	Shanks (UK)	Solvent washing of equipment, the remaining parts are incinerated
Transformers	1.03		
Capacitors	0.87		
Waste oil	0.63		
Electrical equipment and waste oil	n.a.	Shinco Pantec (Japan)	Solvent washing of equipment, chemical dechlorination of oils with sodium dispersion
Electrical oils	n.a.	TASSCO (Canada)	Removal of Cl from PCB by metallic sodium (with residual content under 2 ppm PCB)
Transformers and possibly capacitors	n.a.	Tredi (Canada, France)	Decontamination of equipment using a non-flammable solvent

their incineration (in CR at present around 1.85 USD/kg). Although up to now there is in CR only one incineration plant equipped with suitable technique, at least two other plants are to be in operation in the not distant future, which could lead to some price cuts. On the basis of the trial operation of the technologies mentioned one can conclude that they are especially applicable to:

- Disposal of condensers
- Lowering of PCB content in transformer oils to ensure their recycling
- Lowering of PCB content in contaminated soils of a limited range (eventually on site) for their re-deposition at the site of the contamination
- Lowering of PCB content in adsorbents to ensure their recycling
- Lowering of PCB content in waste (underground) waters

The best way disposal of capacitors is their disassembling followed by discharge of the dielectric liquid and cleaning of metal parts and solid fillings with MTTD. The evaporated dielectric liquid can be incinerated, and the decontaminated metal parts could be recycled as a secondary raw material. In contrast to the prevailing application of solvent washing of the core and casing of the capacitors (see Table 14) we have found out that the extraction of PCB liquid namely from aluminum-paper rolls is insufficient by this procedure.

In the case of oil condensates from MTTD containing more than approximately 5.000 ppm PCB, their incineration is the preferred cost-effective way. The above presumptions were taken as the basis for the evaluation of operating expenses of the disposal of wastes of different types.

The costs were assessed from data obtained from a limited number of test experiments and should be thus taken as tentative for information purposes. The operating expenses include the costs of energy, chemicals and nitrogen, depreciation of fixed assets, expected transport costs (to 200 km distance), eventually costs of decontaminated soil deposition and waste water disposal as well as operator wages.

- Waste and transformer oils containing up to 5.000 ppm PCB, final concentration below 10 ppm (KPEG method, Na method): 0.85–1.12 USD/kg

- Water, aqueous condensates from MTTD, PCB content up to 30.000 ng/L, final PCB concentration below 100 ng/L: 19.2 USD/m<sup>3</sup>
- Soil with PCB content to 6.000 ppm, MTTD method, final PCB concentration below 0.5 ppm, disposal of waste waters and oil condensates included: to 150 USD/tonnes
- Activated carbon (to ca. 10.000 ppm PCB): maximum 615 USD/tonnes
- Capacitors (costs on disassembling, MTTD treatment and disposal of dielectric liquid are included, the metal parts are used as a secondary raw material): 1.1 USD/kg
- Contaminated solid wastes (debris, pieces) with PCB content to ca. 200 ppm (extraction with aqueous solvents, only PCB lowering below 100 ppm which permits their land filling, the latter costs included): maximum 70 USD/tonnes

As judged from a limited set of data at present available, these costs are essentially in the range as those reported by foreign companies.

#### 4. Conclusions

- (1) The separation efficiency Of the batch low temperature thermal desorption is over 99.9% and by incorporating reductive dechlorination reaction within the MTTD process a regulatory level for unrestricted disposal of treated soil of 0.05 mg/kg can be achieved.

The throughput capacity of the batch MTTD process is low compared to other (continuous) thermal treatment technologies because of the poor heat transfer conditions inherent in the fixed bed. On the other hand, the process has some advantages in that additional treatment capacity can be added on a modularized basis (more chambers for one common condensation unit). The batch process is simple and cost-effective. The inert nitrogen atmosphere in the chamber substantially suppresses the generation of highly toxic intermediates like dibenzodioxins and dibenzofurans during the thermal operation. Preferentially, batch MTTD could be used for carbon regeneration, decontamination of metallic parts of electric condensers and the paper-aluminum rolls. It can also be

shipped offsite for treating suitable quantities of strongly PCB contaminated soil (hundreds tonnes/year/one chamber) at the source of the spill on a very economical basis. The application of batch medium temperature desorption unit is advantageous namely in the case where disintegration of contaminated wastes is inconvenient (big metallic pieces, blocks of concrete). The organic products from thermal desorption, including PCBs, can comfortably be destroyed by chemical methods of dechlorination.

(2) Chemical methods of dehalogenation provide:

- Reductive dechlorination to destroy PCBs in oil which uses hydride-activated elemental sodium as the electron donor forming non toxic compounds of biphenyl and NaCl; and
- Modified KPEG–Al substitution reaction, where one or more atoms of Cl in the molecule of PCB presented in oil are substituted by polyethylene glycol chains and simultaneous reductive dechlorination occurs caused by hydrogen, which is a reaction product of powdered aluminum in an alkaline environment.

The decontamination efficiencies of both chemical methods have been verified in a pilot-plant configuration. The modified sodium process as well as modified KPEG process generally result in an effluent PCB concentration of approximately 10 mg/L. At this PCB level, the oil might be blended for recovery in the burners of the existing batch MTTD unit, or in the case of transformer oils, the treated oil can be recycled. The presence of powdered metals as reacting agents slightly improves the efficiency of dechlorination. Both methods (modified sodium and KPEG–Al methods) are viable procedures for reducing the amount of PCBs in organic solvents and/or oils.

- (3) The extraction of PCBs from soils by aqueous solvent has been proposed and verified the method was based on previous enhancement of the release of sorbed PCBs from soils and subsequent removal of organics by adding environmental friendly surfactants to the washing waters. PCB contamination washed from sandy or gravel type soils is oxidized and destroyed so that the product waters can be re-used in the washing process. The released PCBs are destroyed in the UV/OX process with activated carbon polishing. The efficiency of destruction of PCBs in the aqueous extracts is high (above 99.9% from the inlet PCB content in the treated water approximately 10,000 ng/L). Waste water with higher concentration of PCBs and both inorganic and organic impurities are decontaminated by the sorption on inorganic activated sorbent (bentonite activated with Fe(III) at pH 7.5) and activated carbon.

The efficiency of extraction of PCBs from sandy-loam type soils is in the order of about 87%. The washing process should probably be retained for cleaning screened oversize material and the debris separated from the incoming feed to the thermal desorption unit.

- (4) The products generated by the proposed treatment operations include soils and possibly oil if an indirect-fired

thermal process is used. The soil could be blended for use in a non-agricultural application, especially land reclamation. The oil is treated to a level where it can be used onsite as a fuel supplement in the MTTD or can be recycled.

- (5) These technologies have the particular advantage of being applicable on a smaller scale than is incineration and are, when correctly applied, able to comply with the environmental management regulations.

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