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Laser decontamination and decomposition of PCB-containing paint ☆

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ABSTRACT

Decontamination of concrete surfaces contaminated with paint containing polychlorinated biphenyls is an elaborate and complex task that must be performed within the scope of nuclear power plant dismantling as well as conventional pollutant cleanup in buildings. The state of the art is mechanical decontamination, which generates dust as well as secondary waste and is both dangerous and physically demanding. Moreover, the ablated PCB-containing paint has to be treated in a separate process step.

Laser technology offers a multitude of possibilities for contactless surface treatment with no restoring forces and a high potential for automation.

An advanced experimental setup was developed for performing standard laser decontamination investigations on PCB-painted concrete surfaces. As tested with epoxy paints, a high-power diode laser with a laser power of 10 kW in continuous wave (CW) mode was implemented and resulted in decontamination of the concrete surfaces as well as significant PCB decomposition.

The experimental results showed PCB removal of 96.8% from the concrete surface and PCB decomposition of 88.8% in the laser decontamination process. Significant PCDD/F formation was thereby avoided. A surface ablation rate of approx. 7.2 m^2/h was realized.

1. Introduction

Concrete structures in nuclear plants are usually provided with protective coatings to minimize the penetration of radioactive nuclides into the concrete matrix [2]. Until the 1980s these paints contained polychlorinated biphenyls (PCBs) as plasticizers. Because of the carcinogenic properties of PCBs, production and use of them have been prohibited in the Federal Republic of Germany since 1989 [3]. In the dismantling of nuclear facilities, these PCB-containing paint layers must be treated separately, as specified in the German *PCBAbfallV* (PCB/PCT Waste Ordinance) [3]. The Karlsruhe fuel-reprocessing plant (WAK) represents a special example of PCB decontamination. In an investigation of PCB concentrations in floors and walls at the plant, 67% of the samples [4] significantly exceeded the German legal limit for toxic contamination of 50 mg/kg PCBs [5]. Nuclear power plants have approximately 20,000–200,000 m^2 [2] of PCB paint-coated concrete surfaces that have to be analyzed and subsequently decontaminated. The same mechanical methods (cutting, chiseling, and hammering) used for decontamination of radioactively contaminated surfaces are used for removal of PCB-containing layers. The removed paint must be treated in a secondary step in a hazardous waste incinerator at temperatures higher than 1,000 °C for decomposition of the toxic chemical substances [6]. The modus operandi is inefficient, produces secondary waste, and poses a high risk to operators. The growing number of nuclear power plants scheduled for decommissioning in the near future provided the impetus for investigation of alternative decontamination technologies with higher overall efficiencies and lower operator exposure levels and incorporation risk by Bayliss et al. [7].

When a high-power diode laser with a laser power of 10 kW is used in continuous wave (CW) mode, PCB-containing paints can be removed from the concrete surface and decomposed directly on the surface by high-energy laser radiation, thereby avoiding direct formation of toxic products. The basic technology involves melting of the contaminated concrete surface by laser radiation and fixing of the radioactive particles in the molten concrete [8–10]. This application generally requires a high amount of energy to melt the concrete and results in an ablation rate of 1.2 m^2/h [11]. Burning only the paint, however, requires less energy, enabling much higher ablation rates of more than 6 m^2/h to be achieved, as has been demonstrated in laser decontamination of epoxy paints [1]. Moreover, in contrast to conventional combustion or even mechanical decontamination technologies, laser radiation allows fast,

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localized generation of very high temperatures with no restrictions on geometry.

The high-power diode laser generates temperatures of more than 1,000 °C at the PCB-painted concrete surface. These temperatures lead to the direct decomposition of PCB [6]. Thermal quenching of the flue gas to temperatures of less than 250 °C prevents the formation of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [12]. The ablation process, the decomposition of PCB, and the decontamination of the concrete surface can be evaluated with an integral measurement system for temperature measurement and certified PCB and PCDD/F sampling. In comparison with mechanical removal processes, this process generates very little dust. Other advantages of the laser technology are the extremely low mass of the laser device and the lack of counteracting forces generated during processing. This allows for a very compact and lightweight carrier design, minimizing the setup time required onsite. Furthermore, the process can easily be remotely controlled. The investigations into laser decontamination of PCB-containing paint layers presented in this article provided the proof that laser technology is able to decontaminate and decompose PCBs on concrete surfaces with low emissions and offers great potential for optimization of the overall dismantling process.

2. Selection criteria

2.1. Polychlorinated biphenyls in nuclear plants

Polychlorinated biphenyls (PCBs) are a group of carcinogenic chemicals with the chemical structure shown in Fig. 1A. The toxic impact depends on the number of chlorine substituents and their positions. Moreover, depending on the positions of the chlorine atoms, 209 different congeners can be formed [13]. PCB consists of two phenol rings with hydrogen or chlorine substituents in positions 2–6 and 2′–6′. Fig. 1B and C show the chemical formulae of PCDD and PCDF, respectively, which may be toxic products of PCB combustion. Direct formation of PCDD/F occurs at combustion temperatures between 600 °C and 800 °C, and indirect formation by recombination by de novo synthesis occurs between 250 °C and 500 °C [6].

Fig. 2 shows some representative PCB-analyses of some drill cores of different rooms (within different walls and floors) of WAK. PCB concentrations were analyzed at different depths in concrete walls at WAK in increments of 0.25 mm by means of drilled cores. The PCB concentrations at the wall surfaces were found to exceed the threshold for hazardous substances of 50 mg/kg for PCBs. The PCB concentrations were found to vary at different points on the same surface and in the same room. The PCB concentration fluctuated by several orders of magnitude between various surfaces as well as between various points on the same surface. It was suspected that the PCB content of the protective coating was not kept constant in the construction or renovation of the corresponding structures. The PCB-analyses shown in Fig. 2 are qualitative and quantitative representative for WAK. The PCB concentrations of seven representative concrete cores are shown in Fig. 2.

Association of German Cement Industry (Verein Deutscher Zementwerke) [14] and Verein Deutscher Zementwerke) [14] say, that the penetration of PCBs into concrete structures depends on the compressive strength of the concrete and functions by the existence of water-filled pores at a given time, the temperature of the concrete, and the presence of heat sources or heat sinks [15]. The chloride concentration decreases exponentially with increasing concrete depth. In the real case, as described by the example of WAK in Fig. 2, the change in PCB concentration follows an exponential curve. Deviations from the exponential progression of the PCB concentration in relation to depth result from additives, cracks, and voids in the concrete structure that act as diffusion barriers and cause the concentration peaks. There is no information in the WAK data about the influence of heat or environmental conditions.

2.2. Selection criteria for Concrete Samples

The property class for concrete for nuclear facilities is defined in DIN 1045. Based on the kind of additives used, the concrete can be quartzite or calcite concrete. The concrete samples were produced according to DIN 1045 as calcite concrete samples containing, in percent by mass, 49% CaO, 9% Na_2O, 5% MgO, 3% SiO_2, 4% Al_2O_3, and 2.5% Fe_2O_3 and as quartzite concrete samples with 49% SiO_2, 21.4% CaO, 6.7% Al_2O_3, and 2% Fe_2O_3 (by mass), as well as in the form of calcite-quartzite samples with a 1:1 mixing ratio. The dimensions of the concrete samples were $150 \times 150 \times 75\ mm^3$ for ease of analysis. For the purposes of simulating realistic behavior, especially at high temperatures, the samples were aged in a CO_2 atmosphere at 35 °C with 3% CO_2 by volume and a relative humidity of 65% for 28 days. The equivalent age of the samples corresponded to 30 years according to Sisophon [16] and Castellote [17].

To avoid damage to the concrete structure by thermal stress or melting during laser treatment, it is important to have knowledge of the behavior of the concrete samples at high temperatures. Table 1 presents the thermal reactions observed to occur in quartzite and calcite concrete during experiments performed in a melting furnace in a previous project. Surface scans of the unpainted concrete samples revealed an average surface roughness

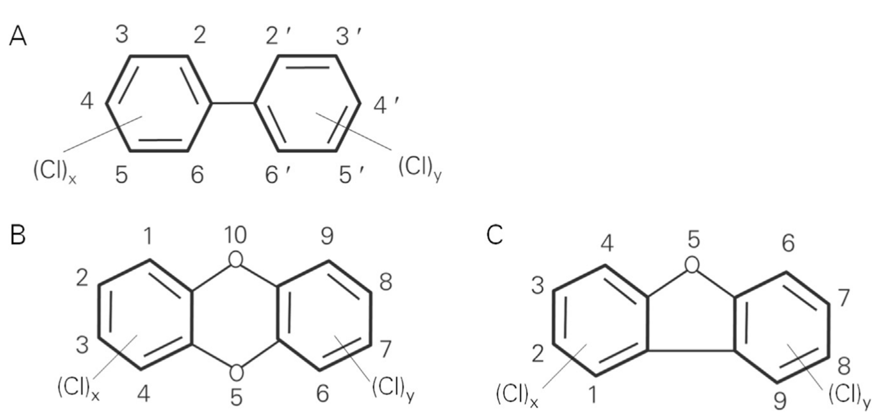

Fig. 1. Chemical structures of PCB and PCDD/F A: Chemical structure of polychlorinated biphenyls (PCB) B: chemical structure of polychlorinated dibenzodioxins (PCDD) C: Chemical structure of polychlorinated dibenzofurans (PCDF).