DECHLORINATION OF CONTAMINATED SEDIMENTS OF IONIAN SEA
Thermoanalytical investigations

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Natural dredged sediments contaminated by PCBs from the heavy industrialized harbor of Taranto (S. Italy) on the Ionian Sea, previously dechlorinated by mechanical activation in different ball mills (SPEX and AGO-2), together with synthetic mixtures emulating the contaminated sediments, were submitted to thermogravimetric and calorimetric measurements as well as to X-ray powder diffraction in order to clarify the dechlorination reaction mechanism.

Both major sediment components, i.e., carbonates and clay minerals, were found to be affected by the mechanical activation. As trace pollutants like PCBs are concentrated in clays, the mechanical activation of sediments increases the release of pollutants yielding a more active decontamination.

DSC results were less informative as calorimetric peaks from different thermal events were found to overlap.

Keywords: clays, decontamination, DSC, mechanical activation, TG, X-ray powder diffraction

Introduction

Marine sediments are rich in heavy metals and organic pollutants, e.g. polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, and so on, especially in basins with high industrial activity [1]. Sediment acts as a potential sink for many hazardous chemicals. Since the industrial revolution, human-made chemicals have been emitted to surface waters [2]. Due to their properties, many of these chemicals stick to sediment. In particular PCBs have been extensively used for long time as liquid insulators for their physical stability and chemical inertness and despite the fact that they have banned since the ’70 are considered as one of the most ubiquitous and persistent pollutants that jeopardize the global ecosystem [3]. The development of efficient technology for the degradation of PCBs has attracted a great interest. Mechanical treatment has been recently applied with success to solve environmental problems [4–9] and, more recently, specifically for PCBs degradation by the present authors [10]. To develop the decontamination technology, it is necessary to know the detail information about all operating steps (reagents, concentrations, reactions, etc.). Thermal analysis allows one to receive the information of this kind [11–13], including the changes in the reactivity of a substance after mechanical activation [14, 15].

This work describes the results of thermoanalytical (DSC and TG) investigations of natural samples and model artificial mixtures after mechanical activation. The results allowed us to identify those changes in the samples that govern the reaction of dechlorination. Technical details of the decontamination technology are out of the scope of this report.

Experimental

The samples for the experiments are the air-dried dredged material of the ‘Piccolo Sea’ (Ionian Sea, Taranto). These consist of fine-powder mixture of carbonates, clay minerals, quartz, and halite. Bulk chemical composition of the samples ranges due to the different places of the sea bottom where they were taken off. The most attention was given to the amount of several pollutants: polychlorinated biphenyls, polycyclic aromatic hydrocarbons, heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn). Their content, usually small enough, was analyzed according to special procedures. For example, the PCB content was found to be about 0.004% [16]. Such a small amount of a phase cannot be controlled by conventional thermoanalytical techniques. The changes in the PCB–soil system during the mechanical activation can be considered only after indirect analysis of the changes in the properties of the bulk soil sample.

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To magnify the effects of PCB–soil interaction and to make visible the changes in the system, artificial mixtures of silica gel and PCB-contaminated oil were prepared. The mixture models the mechanical and thermal properties of the natural contaminated soils. The PCB content of these samples was 0.227%.

The dechlorination of the sediments and artificial model mixtures was proceeded by means of the reaction with NaBH₄. The reagent was added to the sediments and artificial mixtures in an amount of 2.5 mass%.

The mechanical activation was performed using planetary ball mill AGO-2 (Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia) and ball mill SPEX 8000 (Spex Industries, USA). To prevent the samples from wetting or drying, just after the treatment these were placed into a closed container.

X-ray powder diffraction was used for the analysis of the samples before and after thermoanalytical experiments. The measurements were carried out using diffractometer D8 GADDS (Bruker), CuKα radiation, with 2θ ranging from 5 to 65°.

Calorimetric measurements were carried out using DSC 204 Netzsch with standard aluminum crucibles in a flow of high-purity Ar (24 mL min⁻¹). Sample mass ranged within the limits of 7.51–7.55 mg. Each sample was heated twice, two runs immediately one by one, from room temperature to 450°C at a heating rate of 15°C min⁻¹. Dehydration and evaporation (decomposition) of organic components took place during the first heating, producing endothermic effects, together with conventional heat capacity. During the second heating, only heat capacity acted. The results after the second run were subtracted from those after the first run, yielding the pure effect of the dehydration and decomposition.

Thermogravimetric measurements were carried out using TG 209 Netzsch with a gold crucible in a flow of high-purity Ar (30 mL min⁻¹). Sample mass ranged within the limits of 20.1–20.0 mg. The samples were heated from room temperature to 850°C at a heating rate of 15°C min⁻¹. The results were corrected for blank experiments. The reproducibility of the results in the blank measurements was better than ±0.015 mg.

**Results and discussion**

In this section we report the results of X-ray powder diffraction and thermogravimetry for only one sample, NaRC1. This is a natural sample of the ‘Piccolo Sea’ with an admixture of dechlorination agent NaBH₄ (2.5 mass%). X-ray powder diffraction patterns of rest natural samples were very similar to that of sample NaRC1, differing only in the intensity of the reflections. Artificial mixtures were not analyzed by X-ray diffraction. DSC measurements were found to be not quite informative for our purposes.

X-ray powder diffraction patterns (XRPD) of sample NaRC1 after various durations of mechanical activation are shown in Fig. 1. These contain the reflections of calcite, dolomite, aragonite, illite, kaolinite, quartz, and halite in the starting sample. New reflections do not appear after the activation, and the mechanical treatment should be considered not forming new phases in an amount quite large to be detected by X-ray powder diffraction. Contrary, the reflections of clay minerals (8.8, 11.55 and 12.4°) decrease with increasing time of the treatment.

The derivatives of TG (DTG) for the samples NaRC1, initial and after mechanical treatment, are shown in Fig. 2. Peak near 70°C is the dehydration of clay minerals. Weak peaks in the range 100–200°C are probably the result of the evaporation or decomposition of organic admixtures. The greater the time of mechanical activation, the less the peak. Mass loss at these peaks is about 0.5%. Such a small amount of a phase makes it impossible to detect the X-ray diffraction from the phase, and we may only suppose what it could be. All the phases detected in X-ray patterns are in amount much greater than 1% and do not form the peaks of mass loss in this temperature range.

The next peak on the DTG curve of the starting sample is near 600°C. This is the decomposition of hydroxyls in clay minerals. Carbonates start to decompose at more higher temperatures. According to XRPD, the starting sample contains the mixture of carbonates. These are to be decomposed at different temperatures: MgCO₃ above 600°C and CaCO₃ above 700°C. This appears in the sample after mechanical treatment: peak at 780°C decreases but new one at 600°C increases. Total mass loss above 500°C remains constant, about 20%, that is equal to about 40–45 mass% of carbonates in a sample.

XRPD patterns of the samples after TG measurements are shown in Fig. 3. The reflections of clay minerals (8.8, 11.55, 12.4, 19.8°) vanished. The re-