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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 $NaBH_4$. 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), CuK_α 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 20°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 $NaBH_4$ (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: $MgCO_3$ above 600°C and $CaCO_3$ 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-

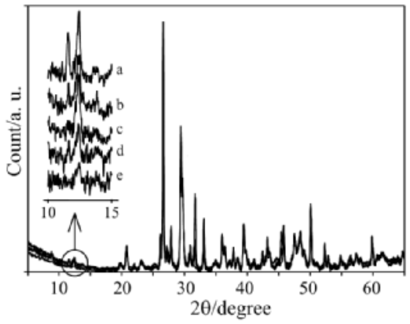

Fig. 1 X-ray powder diffraction patterns of natural sample NaRC1. The changes in the clay reflections are shown in the insert. Samples were a – untreated and treated in AGO-2 for b – 30 s, c – 1, d – 4 and e – 8 min

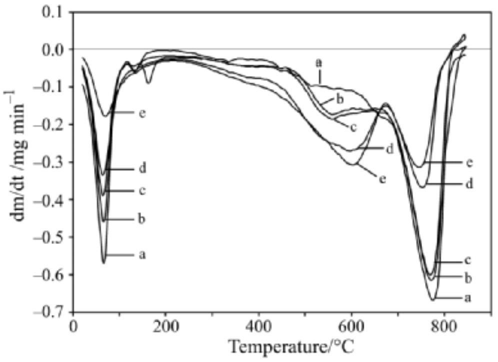

Fig. 2 DTG results of natural sample NaRC1. Samples were a – untreated and treated in AGO-2 for b – 30 s, c – 1, d – 4 and e – 8 min

flection at 20.8° (superposition of quartz and illite) decreases significantly. Reflections at 26.15° (aragonite) and 29.4° (calcite and dolomite) also vanished. Very strong reflections of CaO appeared at 37.3 and 53.8°. This fact is very interesting, for the samples were heated up to 850°C, but the oxides remain in a form of a pure crystalline phase, not reacting with amorphous phase formed after dehydroxylation of clay minerals. The starting composition (clays, quartz, carbonates) of the samples investigated in this work is similar to that of the clay paste used for the production of ancient ceramics, except of high content of carbonates. The problem of lime in fired ancient ceramics was discussed recently in [17].

Two new reflections at 32.65 and 33.75° are interesting because of the changes in their intensities: the longer is the mechanical activation of the samples before heating, the stronger are the reflections.

Comparison between DSC and TG

In our TA experiments we were able to compare the results after TG and DSC measurements for the purpose of our problem. The comparison is carried out for the experiments with model artificial mixture NaAC2 with an admixture of dechlorination agent $NaBH_4$ in the amount of 2.5 mass%. The first half of TG curve (T<450°C) is shown in Fig. 4a, because this is the range of our DSC experiments. Besides, for the artificial mixtures, high-temperature part of the TG curves has no peaks of mass loss. Like the natural samples (Fig. 2), the mass loss at dehydration decreases with the increase in the mechanical activation. DTG peak of the mass loss at 60°C becomes lower and broader, the second one appears near 120°C. Weak and smooth peak near 250–260°C is probably formed by the evaporation of PCB-containing oil, an analogue of pollutants.

DSC results are shown in Fig. 4b. All the samples have only one endothermic peak. All the peaks resolved on the DTG curve are merged into single broad peak on the DSC curve.

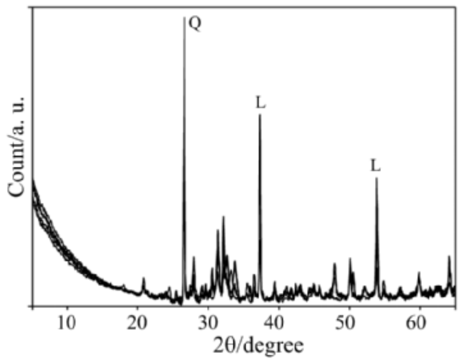

Fig. 3 X-ray powder diffraction patterns of natural sample NaRC1 after TG experiments. The strongest reflections are those of quartz (Q) and lime (L)

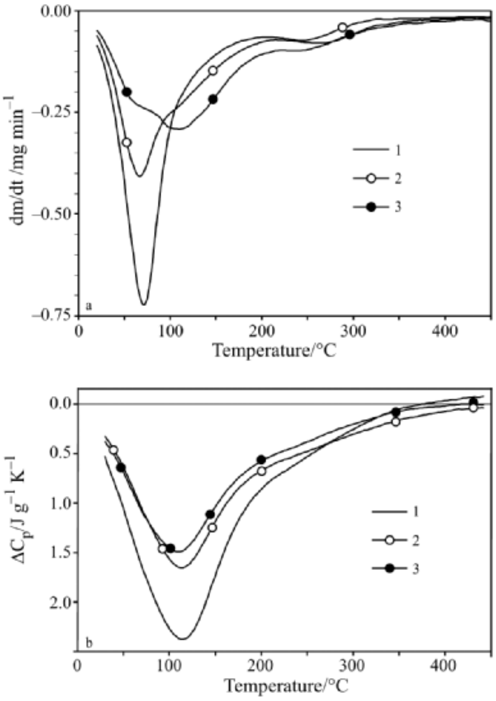

Fig. 4 a – Thermogravimetric and b – calorimetric results for model artificial mixture NaAC2. Samples were treated in SPEX 8000 for 1 – 8, 2 – 30 min and 3 – 2 h

Why mechanical activation improves the dechlorination of pollutants

It was shown above that the mechanical activation of natural samples results in three effects: (*i*) destruction of clay minerals; (*ii*) decrease of the peak attributed to the decomposition or evaporation of pollutants; (*iii*) transformation of carbonates. The last effect is the evident consequence of mechanical activation. It is clear that the milling leads to the decrease in the temperature of decomposition of carbonates, but it is not quite evident how it relates to the pollutants. More clear is the relation between pollutants and clays.

Clay minerals are good sorbents for large organic molecules. Wide distance between aluminosilicate layers allows them to absorb readily both ions and neutral species. Sorption of organic solvents, dyes and pigments is the theme of large number of papers, including those in thermal analysis [18–23]. Moreover, the difference in the interlayer distances between various species of clay minerals is the base for the identification of the species [24]. Mechanical activation of contaminated natural samples results evidently in the destruction of crystal structure of clay minerals. It is seen from significant decrease in the amplitude of dehydration peak near 70°C, its broadening (Fig. 2), and from the vanishing of clay minerals reflections on XRPD patterns (Fig. 1).

The low-content pollutants (like PCB of 0.004%) do not form usually bulk phases of their own, but disperse as impurities in other crystalline phases or concentrate in sorbents, for example in clays. When the sorbent is destructed, its contents are released and become accessible to a dechlorination agent.

Conclusions

Thermogravimetry and X-ray powder diffraction of natural samples and model artificial mixtures showed that the mechanical treatment affects the clay content and thermal properties of carbonates (calcite and dolomite). The destruction of crystalline structure of clay minerals is favorable factor for the dechlorination of PCB, for low-content pollutants are concentrated and stored in clays as natural sorbents.

Changes in carbonates are mainly in the decreasing of decomposition temperature. This factor is considered not to affect significantly on the dechlorination of PCB.

Calorimetric results show that the interaction between water and sample increases with the grade of mechanical activation. DSC curves do not show the details in decomposition of low-content impurities due to the ‘smoothing’ of calorimetric signal.

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