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ABOUT THE INCLUSION OF AN INSECTICIDE IN ZEOLITIC MATERIALS

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Abstract

The commercial product Supercypermetrin (3-phenoxy-α-cyanobenzyl-3-(2,2-dichlorovinyl)-2-(2,2-dimetyl)-cyclopropanecarboxylate) [SCM] in the liquid form was included in the zeolitic host. A natural zeolitic material of clinoptilolite type [CT] from a Slovakian deposit was used. The chemical control of the guest desorption was used for checking the existence of a new inclusion compound. The desorption of the insecticide under relatively drastic conditions (12 g of product in 200 ml H_2O) showed a hindered and regulated release of the insecticide. Thermal curves obtained by means of a derivatograph and IR spectra were used for the study of the insecticide [SCM] enclosed (10%) in the zeolitic host and its desorption.

Keywords: clinoliptilolite, inclusion compounds, insecticide Supercypermetrin, zeolites

Introduction

By sorption of the insecticide SCM on zeolites a new compound was obtained [1, 2] for agrochemical purposes. It represents a new inclusion compound whose host is a zeolitic material and the insecticide is the guest component.

Inclusion compounds belong in a lately studied group of chemical compounds. The number of papers dealing with them has increased extremely rapidly since 1983. Their structure has been described if prepared in the form of single crystals or only indirect proofs of their existence have been provided created [3].

The rate of desorption of the enclosed guest may be used to study the interactions between the two components of the formed inclusion compound. Both components may be [4, 5] inorganic or organic compounds.

Crystalline inclusion compounds have an ordered host lattice with empty areas, but not all space must be filled by the guest. The static disorder is coming from the free voids, the dynamic one is resulting from the relatively high am-

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plitudes of the guest motion [4]. There are three possibilities for the migration of the guest molecules [6, 1] in zeolites:

a) all channels are parallel, and no joint in one-dimensional system (mordenite, laumontite...)

b) the parallel or differently oriented channels are joint and form a two-dimensional system; the guest molecules may thus migrate in plane (heulandite, levynite, stilbite...)

c) migration of the guest molecules is allowed in three-dimensional areas, formed by the combination of all ways for motion (chabazite, erionite, faujasite, ZSM-5, ...)

Zeolitic material from east Slovakia is of clinoptilolite type. The structure of the main mineral (>57%) is similar to that of mordenite. It belongs in the group of heulandite [7, 8] and it is formed by monoclinic plates (length: about 10 μm, width: 1–2 μm) situated in different ways in space and thus forming free areas. Some voids are created and limited by the side position of two broader plates. If the size of pores in the crystals were estimated from the volume of sorbed water (in some cases 265 ml H_2O/1 g), which may be distilled off, it could be assumed that about 50% of the volume of each crystal is accessible to the water and other guest molecules, provided that their volume is compatible with the size of the pores. Zeolitic products containing different compounds (useful for the pharmacy [5, 9, 10], perfumery [5], agrochemical: fertilizers or growth stimulation agents [5] and others [5, 11] have been prepared in our laboratory. In all cases the compounds were stabilised by enclosing them into the zeolitic host with pore sizes of 0.76×0.35 and 0.46×0.33 nm [5]. By the sorption of the insecticide on the zeolitic host a new solid insecticide [6] was formed. This is ecologically less harmful because its excess is not released into the environment.

Insecticides of the group of synthetic pyrethroides are replacing organophosphates, chloroderivatives and carbamates [12]. They are readily soluble in water and may be destroyed by photolysis. These properties are improved by synthesis of the esters of 2-dichlorovinyl (resp. 3-bromodivinyl-2,3-dimethylcyclopropanecarboxylic acid with 3-phenoxy-α-cyanobenzyl. One member of this group, Supercypermetrine (SCM) – 3-phenoxy-α-cyanobenzyl-3(2,2-dichlorovinyl)-2-(2,2-dimethyl)-cyclopropanecarboxylate is the subject of this paper.

By sorption of SCM in liquid form on CT-type zeolites a new product can be prepared [1, 2] which may be in the solid form and less toxic for the environment, because its excess is not released into the soil and waters.

Chemicals

The natural zeolitic material from the deposit Nižny Hrabovec lying in the Eastern part of Slovakia is proposed for use. Grain size: max. 0.2 mm–2%; min. 0.09 mm–10%.

Chemical composition [7, 8]; SiO_2 70.90%, Al_2O_3 12.07%, Fe_2O_3 1.38%, TiO_2 0.157%, CaO 2.94%, MgO 0.80%, K_2O 3.29%, Na_2O 0.54%, MnO 0.015%, P_2O_5 0.041%, CO_2 0.25%, SO_3 0.06%, FeO 0.52%.

The broad-spectrum insecticide SCM was used in its commercial form (Chemix, Bratislava) named CYPER 10 EM. It is prepared as an olive-green aqueous microemulsion containing the mixture of isomers (*trans* : *cis* ratio of 65 : 35 to 55 : 45) in a concentration of 100 g l^{-1}.

Methods

Thermal analysis, IR spectra and chemical control were used for the identification of the samples.

TA was carried out with a derivatograph (MOM Budapest); sample mass: 100 mg; heating rate 10°C min^{-1} up to 900°C in air.

IR spectra were recorded with a Specord 80 Spectrophotometer using KBr discs (50/500 mg).

Chemical control was made by means of gravimetric method using 2 g samples, 950°C, 10 min.

Zeolitic materials were used as recommended in preliminary studies [6] and also in an activated form (by Cu(II) ions). A solution of $CuSO_4{\cdot}5H_2O$ (1 mol dm^{-3}) was added (500 ml) to the sample of CT (100 g) and the product was formed by allowing the mixture to stand for 10 days. The activated product (CuCT) was decanted, washed with H_2O, dried (60°C) and used in measurements for comparison with the original sample (CT).

Sorption of the insecticide was effected for both the original and the activated forms of the zeolitic material. To the aqueous suspension of the zeolites (100 g) in 500 ml H_2O was added the commercial product CYPER 10 EM (4 ml). After a ten-day contact the product was filtered off and treated in the same way as the zeolitic material.

Desorption of the guest from the products was controlled after mixing (12 g) with distilled water and allowing to stand for 1 h or 1, 3, 5, 7 or 10 days with occasional mixing. The product was filtered off and dried.

Results and discussion

Amounts of the insecticide known as effective against the individual insects [1, 6, 12] were adsorbed on the zeolitic – CT host. SCM sorption was increased by the use of the activated form: CuCT.

TA measurements were used to check the formation of new products in comparison with the zeolitic mineral alone (CT) and the forms activated with copper ions.

The zeolitic material, in agreement with preliminary work [6, 9, 10 11], starts to decompose at 65°C. The total loss in mass (Fig. 1) in the TG curve (14%) may be ascribed to the loss of the OH groups and of the sorbed H_2O. The highest loss of water (about 8%) is observed, in agreement with [13], at 220°C, when also bound water (the sorbate) is liberated. The water bound in the lattice is liberated at about 550°C and higher. During the dehydration the residual water molecules are split of in a heterolytic way [13] and they are transformed to OH groups. At about 750°C the destruction of the host lattice starts and a new hydrated amorphous phase [13, 5] arises.

The CuCT forms start to decompose at 80°C, in agreement with [9]. A weak endothermic process, missing in the CT alone is indicated by the DTA curve (Fig. 1) between 300–360°C. The total mass loss in the TG curve is 14%. The destruction of the host occurred in the same region as in the CT sample, but the new amorphous phase was not found at this temperature.

The rapid decomposition of the insecticide SCM (Fig. 2) is accompanied by a very strong exothermic processes in the DTA curve. Also, two joint weak endothermic processes are found in the temperature range 200–490°C overlapped with the exothermic process. At 80°C the water loss is accompanied by the loss of the guest insecticide. The total loss indicated by the TG curve is 24%, by 10% exceeding the loss of water for CuCT on Fig. 1.

In the desorption control studies (thermogravimetric and gravimetric analysis) it was found that 0.4145 g of SCM was enclosed in 100 g of the CuCT.SCM

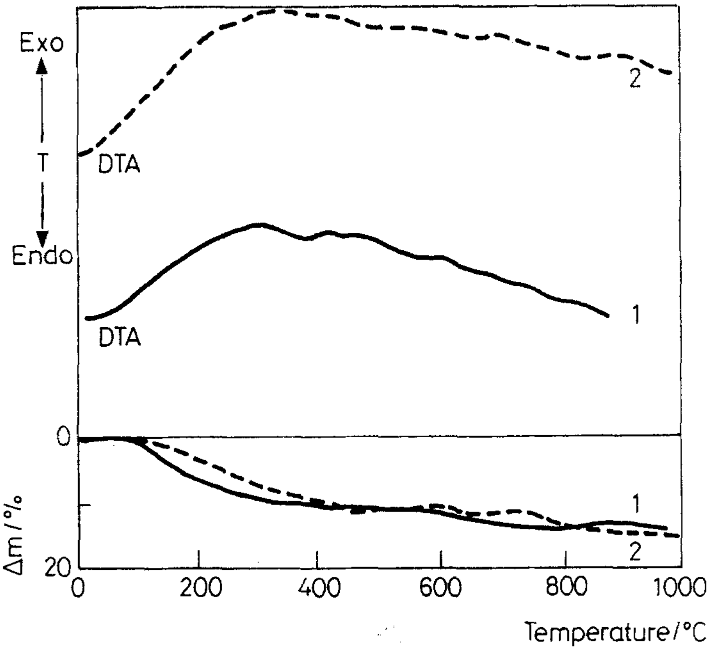

Fig. 1 TG, DTG and DTA curves of zeolitic material CT,(2): of its copper form CuCT,(1)

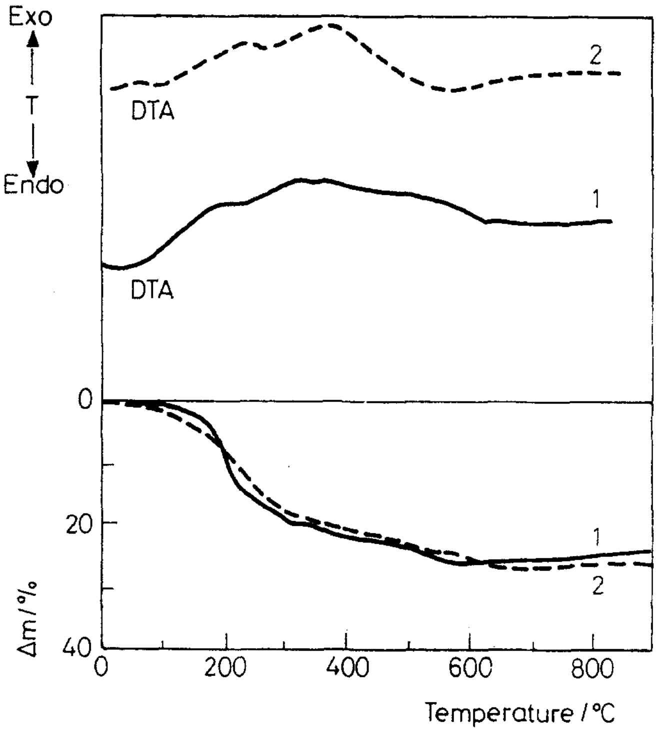

Fig. 2 TG, DTG and DTA curves. 1 – zeolitic copper form (CuCT) – containing SCM; 2 – zeolitic (CT) product containing enclosed the SCM

product and only 0.4095 g in the CT.SCM product. These data agree with the quantities of SCM used during the preparation.

We may consider the DTA curves of CTCu–SCM and CT–SCM samples to be analogous, although during the desorption a different mode of binding could be observed.

The course of the insecticide desorption was followed as a function of the temperature (Fig. 3). The products were in constant (2 g·10^{-1}) contact with water. The total bound quantity of SCM was found to be lost completely after the 28th day of desorption. For the activated zeolite total desorption can be presumed after 30 days. The difference (0.012 g) indicated by Fig. 3 may be explained as being due to weighing error or we can presume that desorption of SCM from the lattice is hindered by an ion-ion interaction (with the copper(II) form of the zeolite), since the insecticide Cyper 10 EM is in the propanecarboxylate anionic form.

The IR spectra of the products show, in agreement with the literature [9, 10, 24], that the intensities of the zeolitic bands (forming the host) are higher than those of the bands assigned to the sorbed insecticide. The parameters of the voids are in agreement with the lengths of the bonds existing in the

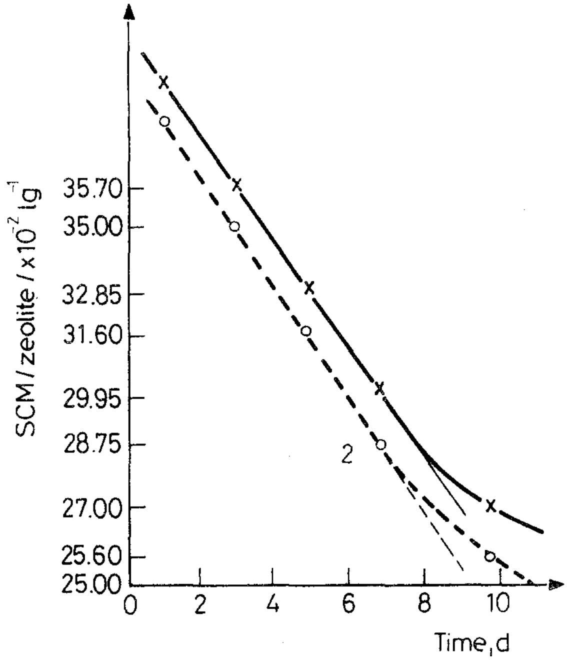

Fig. 3 Nondesorbed amounts of SCM in time relation: 1 – CuCT, 2 – CT

molecule of the insecticide. Therefore some rather strong overlapping of its bands with the intense zeolitic bands occurs. Some discrete bands can also be observed:

1740 cm^{-1}	ν(C=O)	800, 750 cm^{-1}	τ(C–H)
1590, 1500 cm^{-1}	$\nu(C=C)_{arom}$	700 cm^{-1}	ν(C–Cl)
1450, 1400 cm^{-1}	δ(C–H)		

The broad ν_{as}(Al, Si–O) bands have also been found for other zeolitic products [5], but only in the case of the new products; neither for the original zeolitic materials not for the physical mixtures of the starting compounds. According to electron-microscopic observations of the products, some sort of 'impregnation' or 'preparation' of the surface was observed [5, 9, 11] together with the broadening of the ν_{as}(Al, Si–O) band (1200–800 cm^{-1}). Some pits on the surface have been described [5]. The same was found by Galwey [15] for other compounds and the author ascribed this phenomenon to be existence of a foam structure.

On the basis of the IR spectra of the individual samples [1] it can be stated that the content of the (0.4 g) effective compound (sorbed previously on the CT or CuCT zeolitic form (100 g)) decreases linearly with the time of desorption. The $\nu_{1/2as}$(Si, Al–O) values [5] decrease in the case of the CuCT-SCM from

250 cm^{-1} to about 190 cm^{-1} after 10 days of desorption, and in the case of the product CT-SCM from 210 cm^{-1} to 160 cm^{-1}. The narrowing of the band indicates that every day a small portion of SCM is liberated (in laboratory tests: a permanent contact with the surrounding water).

The IR spectra were measured after one hour of desorption, and were found to be identical with those of the original products, presumably because the very small loss of SCM was not detected by the method used. The product was only sparingly soluble in water. Chemical control yielded similar results, the changes in mass loss were observed only in the fourth or fifth decimal position (Sartorius 2004 MP).

The desorption analogues

Even in our drastic desorption tests – 12 g of product in contact with 200 ml H_2O – the desorption was in some way regulated. The effective reagent desorption was hindered, the guest was at least with its one dimension anchored (in some way cutted-in) in the zeolitic host. In agrochemistry, the product will be used in a much higher dilution. Therefore an increased hindrance and thus a stronger regulation of insecticide release into the soil and underground waters can be expected.

Conclusions

The insecticide Supercypermetrin in the liquid form was enclosed in a natural zeolitic material. The amount of the enclosed insecticide was the double of that declared as efficient by the manufacturer. This permits us to suppose that in this manner the time of efficiency of the insecticide against the insects in the crops can be guaranteed.

It is sufficient to use the solid product – SCM included in a calculated amount of zeolite only once, at the beginning of the season. The mechanical losses of the insecticide during the protective works in the fields may be avoided. The excess of the insecticide is not used by the plants. The product represents a slowly releasing insecticide.

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