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COMBINATIONS OF NATURAL AND SYNTHETIC INCLUSION COMPOUNDS AND THEIR THERMAL STABILITY

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Abstract

Inclusion compounds do not belong to the group of simple compounds. They consist of molecules of the host and guest components. Some of them form supermolecules and exhibit supermolecular properties.

Combinations of inclusion compounds as even more complicated systems need more methods to be used for their identification. Thermoanalytical study enables to study the sorption during their formation and the progressive liberation of their individual components and parts. Many layered silicates, phosphates and other similar synthetic and natural compounds enclosing or adsorbing cyclodextrins, pharmaceuticals, aromatics, various agrochemicals and inorganics are analysed from the view of their formation and properties.

Keywords: combined inclusion compounds, combined hosts, combined guests, cyclodextrins, cyanocomplexes, guest, host, inclusion compounds, strength of bonding, zeolites

Introduction

Combinations of inclusion compounds (each formed by a host structure *H* and guest component *G*) make the original starting inclusion compounds more stable. Liberation of their guest component is in most cases in some way hindered and in contrary the host component may be sometimes also stabilized. Only indirect proofs of existence of such products can be found and it is only a special literature dealing with the inclusion phenomena, edited since 1983 – starting Vol. 1 of the Journal of Inclusion Phenomena and later in other similar periodicals and monographies. Inspite of this fact the combinations of inclusion compounds are known and useful. For example in the human and animal bones and teeth the apatitic layered $Ca_8(HPO_4)_2(PO_4)_4{\cdot}5H_2O$ forming the host and the dicarboxylates sorbed as guest components exist [1]. Otherwise the dicarboxylates are known host components of inclusion compounds [2, 3]. The role of one part of water molecules present in the phosphates was described and checked [4] already in 1977 as zeolitic (two from four water molecules in the phosphate may be thus exchangeable).

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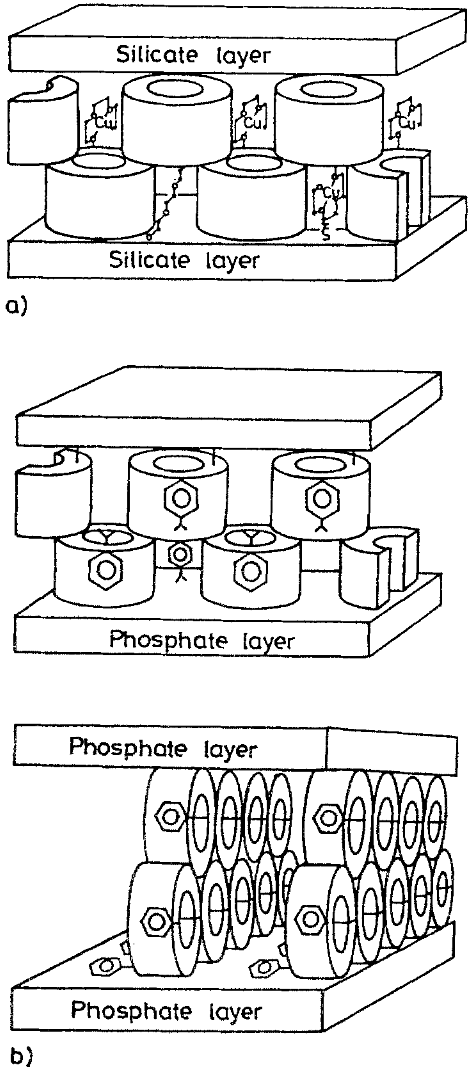

Fig. 1 a) Situation of β-CD trien molecules (triethylene cyclodextrin derivative) in the interlayer space of the Cu exchanged montmorillonite. b) Benzoic acid enclosed in the cyclodextrins and interlayered in zirconium phosphate

Equally other natural or synthetic clays and clay-like minerals are known as containing a whole inclusion compound in the form of new guest or at least their hosts structure are in some way combined in a more complex host. Kijima *et al.* referred about one of their products, where the modified cyclodextrin (CDen) is intercalated in copper(II)-montmorillonite [5] or in its other form [6]. In this case – similarly as in others – the original clay host compound alone becomes combined and therefore more inner spaces are created for the guest components. Some complexation of two or more host components of various kinds occurs differing from general single component host structures, exhibiting three dimensional cages, channels, layers [6–10].

Kijima [5] showed that the layered montmorillonite clay mineral forms a combined host lattice (from one layered component and from one single channel-like). Cyclodextrins (CD) as cyclic polysaccharides exhibit a cylindrical cavity [2, 8, 9, 11–13] capable to include different further molecules (Fig. 1). Therefore the CDs alone are useful as stabilizators for various guest: volatile, odoriferous or also toxic compounds [11, 12], pharmaceuticals [12, 13] or models or enzymes [7]. Kijima in further papers supposes on the other hand that polar, but unchargeable CDs others than β-cyclodextrin may be taken up by montmorillonite as the guest.

The results of Kijima syntheses [5, 6] depended – equally as later and also in the case of other products in our laboratories [14–19] – upon the cationic form of the mineral host.

In some cases of inclusion compounds only a rather spatious [10], even also often polymeric guest component G_2 or G_3 [10] subtitutes [16] the original smaller guest component G_1 (often water molecules) in the polymeric host H_1 or in their combination of $H_1 . H_2$ type [14, 19]. Some of such new products and some heteromolecular complexes will be treated in this review, too, because they represent some combinations of the single component host or guests [19–23]. In all here treated cases weak supramolecular interactions may be found and utilized. They represent an important approach to develop [3] the analytical, topochemical and material properties. The principles, that govern these interactions are essential in making possible predictions [3, 24] and in definite mode then affect the thermal behaviour of new products arisen by combinations of inclusion compounds or at least their hosts [16] or part.

Presence of metals

Sorbed metallic cations present in various host structures are also decisive [8, 17, 25–28] for the enclosure of a further new guest or for their chemical properties. Some aliquot of metals is not only substituting the cations present in the host of clays or mineral compounds [25–29]. But the ions or atoms [15, 25–28] are in structural way dispersed [30 –32], sometimes whole halides [16, 32–34] are enclosed in the host layer.

Yariv with coworkers [33] described caesium chloride enclosed together with the water molecules in the kaolinite. Other alkali halides are described as sorbed in the synthetic zeolites [32], too. The natural potassium chloride in the natural clinoptilolite zeolite represents [16] a slow releasing fertilizer. The Ca, Mg, Ni, Ag, La, Ce or Rb exchanged X and Y zeolites are studied in [36] for their inter and intra crystalline diffusion. For silver–zeolite systems the ^{129}Xe

NMR spectra helped to elucidate [26, 27, 37] the Ag(I) cations after oxidation as AgO_x aggregates formed and dissolved in the zeolite.

In montmorillonites the interlayer space is the principal active site of the mineral. The surface activity is primarily determined by exchangeable metallic cations and their hydratation spheres [38]. Attention is therefore focused on the behaviour or exchangeable cations. Yariv studied the effects of temperature on surface acidity and on thermal acid base reactions inside the interlayer space. They found benzidine not evolved at 200°C from the clay. Strong coordination (between metals and benzidine) affects the reactions, which occur during the thermal treatment of the organic compound sorbed by Mn, Co, Ni, Cd, Zn and Hg exchanged montmorillonites.

The surface activity of the clay mineral is a problem in various areas, where the clays may be useful (agriculture, technologies, water, ecology, beverages and oil clarification etc.). The most of coloidal properties (mainly clay dispersion in various media or absorption of different molecules or ions) are affected and depend upon the present metals.

In the preparative chromatographic columns for the study of clay-organic monomer interactions the role of exchangeable cation was found important in the case of montmorillonites [39]. Thermal treatment (heating at 520°C) helped to create binding at points of contact between the clay plates. Only some loss of hydrated water below 110°C was found. In the use of Slovak natural clinoptilolite (CT) zeolite similar positive separative effects [14] were found in our gas chromatographic experiments [40].

Electrical properties

The behaviour of inorganic compounds or clays affected by the enclosure or at least intercalation is known [8–10, 41] (Fig. 2). Several possible phenomena in more simple or complex cases – during the intercalation and in the arisen superstructures are described. Already the thickness of crystals during the intercalation of water molecules alone, thermomechanical properties during heating, cooling and intercalation – all changed are to be seen even in the simple vanadylphosphates [42].

The electrical properties as consequence of the metal-ion contribution to the conductivity in α-zirconium phosphate [43] is strongly enhanced by the surface hydration (at relative humidities 5–90% the conductivity increases at 20°C from 8^{-8} to 10^{-5} S cm^{-1}).

The presence of metals is utilized also in solid electrolyte galvanic cells (as heart pacemakers, memories) like Lithium-iodine [44] or these using iodine adducts of poly-(2-vinyl pyridine) and its copolymers [45].

The quantity of metal ions exchanging the original metal present in the starting compounds depends on the preparation conditions [17, 18, 29, 38, 39].

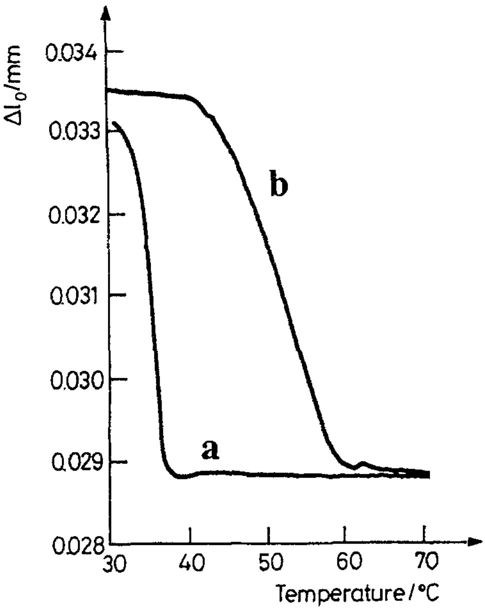

Fig. 2 Thermochemical study of $VOPO_4{\cdot}2H_2O$: a) heated, b) cooled. Rate of heating: 0.5 K min^{-1} [42]

The silver exchanged clinoptilolite zeolite (CTAg) shows changing conductivities [28]. But the water is still present and its residual molecules would enhance the sorption of other compounds (iodine e.g.) [35, 46, 47].

The increasing tin content in the zeolites of mordenite type is responsible for the increasing conductivity [29]. The highest measured value was: $\sigma = 0.6{\cdot}10^{-1}$ S cm^{-1} at 120°C in a water saturated atmosphere.

The zeolitic CT material doped with iodine or iodides (KI or AgI) was also studied [35, 46, 47] and the presence of enclosed species positively affected the measured σ values.

The doping by iodine [48] served us in the first research, where we used the tetracyanonickelate $Ni(NH_3)_2Ni(CN)_4{\cdot}nH_2O$ clathrates and the $Ni(en)_3Ni(CN)_4{\cdot}nH_2O$ [17, 19, 49] after doping them by I_2/KI solution. The achieved σ value was 10^{-6} S cm^{-1}. Also reactions of some parts of clathrates (dioxane or NH_3) with iodine increased the measured values [49].

In the case of other compounds the electrical properties are often studied in connection with the intercalation of neutral molecules into the phosphates of different types [4, 50, 51]. Even the intercalation of cyclodextrins [21] or aminoacids [20] or cations [42, 53] and bases [52] was studied. Naturally the interlayer water represents always a responsible factor.

Zeolites

The presence of potassium has a determinative function for the thermal stability of the zeolites of CT type [54]. The structural data of japanese natural CT zeolite were used for other study [55]. The name clinoptilolite was introduced to characterize the alkali and silicium rich members of zeolites of the heulandite group.

Zeolites are of general formula

$$M_xM_y'N_z[T_m,T_n'\ldots O_{2(m+n+\ldots)-\varepsilon}(OH)_{2\varepsilon}](OH)_{br}(aq)_p.qQ \qquad [16],$$

according to Meier. They are of different types, both their natural and synthetic forms. Mumpton [56] made a differentiation in thermal stability between the heulandite and clinoptilolite. The CT structure is stable up to about 700°C, whereas the heulandite structure is upon heating to about 450°C destroyed.

According to Koyama and Takeuchi [54] the potassium atoms are in channels C-running parallel to axis a (channels A and B are parallel to axis c and ten and eight member rings are formed here). In the eight member rings the potassium (coordinated by six oxygen atoms of the rings and three additional water molecules) prevents the collapse is some extent, even if most of water molecules are removed.

The CT type of Slovak zeolitic material used in our papers [14–19, 34, 35, 46, 47] is capable to exchange the M(I) or M(II) metals in its cationic part by other cations, sometimes as included in intrazeolitic way [15, 30, 31]. It is capable to exchange the original guest (water) for various organic or inorganic compounds [16]. The liberation of the first aliquot of the sorbate (guest G_1, G_2 ...) is in dependence on the kind of the sorbate between 150–400°C. In all products up to date [16, 55, 60–62] the sorbed compounds (pharmaceuticals, fertilizers, insecticides (Fig. 3), odoriferous essences e. g.) are stabilized and they can be released in a regulated way.

The potassium content of this CT material [57, 58] is similar to the Japanese ones [54] with known structure.

In the case of our Slovak natural material, there are only indirect proofs of their structure [30, 55, 16, 34, 28, 40, 47, 59–62].

Montmorillonites

The presence of metals in montmorillonite represents an important factor in its behaviour. The mineral is made up with negatively charged layers of silicates in general: $(Al,Fe,Mg)_{2-3}(Si,Al)_4O_{10}(OH)_2$ and with cations in silicate interlayers [6, 39]. Therefore it is known, that it sorbs different organic compounds as guests. Some of them are inserted in the interlayers on the basis of a cation ex-

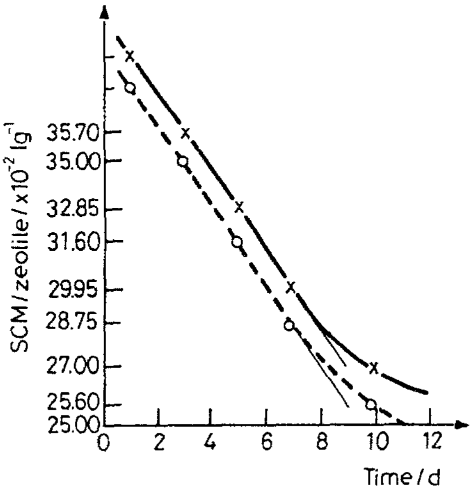

Fig. 3 Desorption of insecticide Supercypermetrin SCM from the product CT – SCM in a time relation

change mechanism. The water molecules are together with the cations in the interlayer space. Some competition between the interlayer water and sorbate persists.

For the amelioration of the sorption in clays the Ca(II), Cu(II) or otherwise exchanged minerals from the original Na(I) form [6, 14, 15, 63, 64] are often used. In the case of the alkylammonium exchanged montmorillonites the thermal stability is decreasing with the increasing length of the alkyl chain.

Cyano complexes

Cyano complexes are a well-known type of inclusion compounds [24, 59, 65–69]. The metallic ions affect very strongly their thermal stability [24, 59, 65–70]. But equally the basis B, the kind of the guest *G*, and their numbers present in the general formula $M(B)_mM(CN)_4\cdot nG$ are decisive for the temperature interval, when the guest is liberated or when the host structure is starting its destruction. In tabullary form an overview was presented [16]. The temperature, where the guest is lost, is determinative for the guest *G* or basis B substitution possibility. The results were checked by gas chromatographic experiments [67–69]. Also the combinations, prepared from the tetracyano complexes $M(B)_mM'(CN)_4\cdot nG$ containing various basis as dioxane, pyridine [59, 66, 68] and also together with CT zeolite [14, 18] were effective in gas chromatography [14, 70].

Lately also tetracyano complexes of other kind enclosed in polymeric matrices as polystyrene (0.28% w/w) were described by Flamini *et al.* [71] as new dyes with inherent thermal (>200°C) and photo stability and lately others [72], too.

Cyclodextrins in combinations

The individual modified forms of cyclodextrins are also sensible to the presence of individual metals [12, 15, 18, 75]. Even more when the cyclodextrins were combined with montmorillonites [5, 6], clinoptilolitic or other natural [15, 18, 30] or synthetic [72] zeolites. Natural zeolite in cationic forms of Ca(II) and Cu(II) was used for the reaction with the derivatives of cyclodextrin [15, 75]. A better coordination of Cu(II) ions with OH and H_2O present in the clinoptilolite was found. This fact had an influence on the sorption of cyclodextrin. The results showed, that products prepared from the Cu(II) form of zeolite were more stable than that prepared from the Ca(II) form.

Thermal behaviour

Synthetic zeolites – and equally natural are used [72] as host components in the combinations of inclusion compounds. Often the synthetic ones serve as model compounds [31, 72–74]. Strongly energetic water adsorption sites (60–120 kJ mol^{-1}) were stated. After the occupation of these sites by water, further amounts of water molecules forming already clusters [73] may be sorbed, but only into a swelled structure (at higher pressures) of the synthetic zeolites. Encapsulation of more spatious molecules – like phthalocyanine [23] – is possible. Some supercages formed.

The thermoanalytical study helped to check the existence of a serie of new compounds prepared from natural zeolitic material of clinoptilolite (CT) type. A higher thermal stability was achieved in every case. The results of thermal analysis showed, that desorption of enclosed or 'anchored' guest was performed in a regulated way. As guests were sorbed fertilizers (K, N-P and N-P-K) [16, 60–62], insecticides of pyrethroide group [16, 76], veterinary pharmaceuticals – iodine [55], salicylic acid [16, 30], cyclodextrin derivatives [15, 18, 30, 75], spironolactone [30, 74]. Slow releasing fertilizers, agrochemicals, perfumery, pharmaceuticals were gained and proposed to an industrial utilization.

From the results of ac and dc conductivity measurements [28, 35] the indirect proofs of their existence were obtained, too (Fig. 4).

Desorption tests [16, 18, 55] were made besides the analytical methods also in field experiments [60, 62]. Some products because of their adsorption in physiologically harmless mineral are very useful for ecology. Moreover also toxic ions: cadmium, lead, chromium and mercury were effectively removed from wastes, row materials and intermediate products of the fertilizers producting industry [77, 78]. A characteristic phenomena of the change of smooth original crystals surface to an amorphous – in some way impregnated surface [16] – was found, similarly as it was found in the case of borates and other inorganic compounds [79].

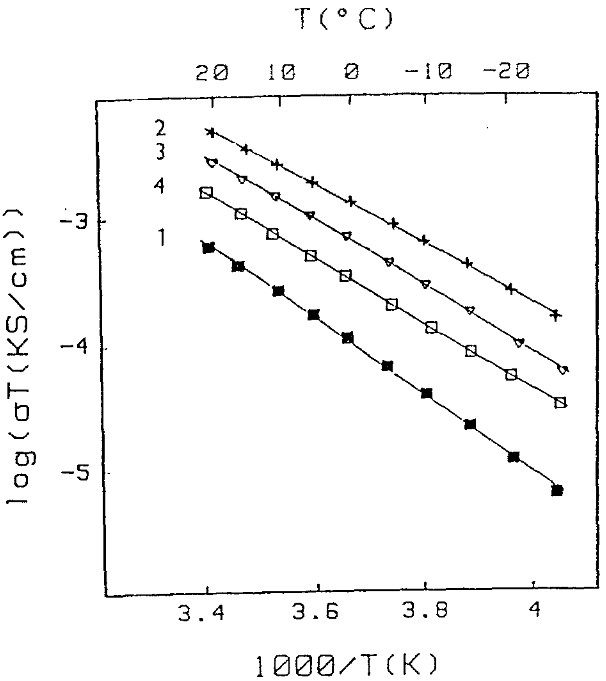

Fig. 4 Arrhenius plot of a pellet of natural clinoptilolite CT (1), its forms with different contents of iodine (2, 3) and silver (4)

Montmorillonites are well characterized minerals concerning their behaviour during heating [63, 64]. In the literature a lot of products prepared on their basis was found. In the work of Kijima [5, 6, 80] various derivatives of cyclodextrins were enclosed in the clays. Besides others the enclosure of pesticides [81, 82], rodenticide [83] Warfarin (hydroxy coumarine derivative) and griseofulvin [84] in montmorillonite are known. In all cited papers thermal analysis results were used to a theoretical explanations of the bonding in new compounds.

Very well known inclusion compound – cyclodextrin – is used in combination with montmorillonites [5, 6, 80], phosphates [21] and synthetic and natural zeolites [15, 30, 74, 75]. Montmorillonite-cyclodextrin combinations were proposed as encapsulating products or as stationary phases [5, 6].

Products of CT–CD combination are protecting the adsorbed cyclodextrin as guest [15, 18] from the view of their thermal stability and dissolution. In the products CT–CD enclosing further pharmaceuticals [30, 75] we see the double role of CD in the products. It functions as a guest component in relation to the zeolite and as a guest component in relation to the salicylic acid, iodine, spironolactone, resp. water (Fig. 5). Here the use of the formula [16, 30] $H_1.G_1.G_2$ or $H_1.H_2.G_2$ (H_1: zeolite, G_1 and H_2: cyclodextrin, G_2: used pharmaceutical) is

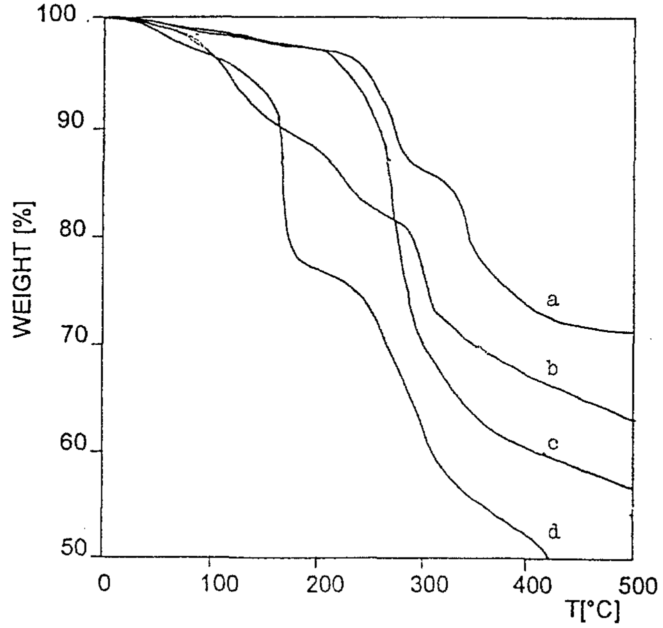

Fig. 5 TG curves of: a) (CTCu – DMβ-CD) – SP and b) its physical mixture; c) CT – (β-CD – SP) and d) its physical mixture

justified. The role of individual components, evaluated by thermal analysis [30, 75] helped to elucidate the role of individual components in the formula.

Cyclodextrin is also reported [21] as enclosed in the phosphates, capable to enclose a row of various organic compounds [20, 50, 51].

The double role of dicarboxylates is interesting, too [1, 3]. Their liberation process from the phosphates shows their role of the guest and the DMSO liberation checked the dicarboxylates as host components.

Combinations of crown ethers and cryptands complexes with montmorillonites are also reported [85].

Specific colour changes are joint with the combinations prepared from various smectite clays and organic photochromic compounds [22].

Physico-chemical data

Strength of bonding

In the literature of last years we find some studies evaluating the strength of interactions between the compounds forming new – in this paper described – products, further the changes occurring between them and on their surface. Activation energy values for the crystallization, association constants of their formation, phase diagrams, ΔH of interaction, method for studying the rate of intercalation and others are reported.

Lately very deeply studied directions about the cavities and structure probing of zeolites and various new compounds with host-guest interactions are presented in [72].

Morphology

In all our products arisen by combinations of inclusion compounds or at least of their hosts or big molecules [10, 16, 72, 73] we could observe a difference from the starting materials or their physical mixtures concerning the

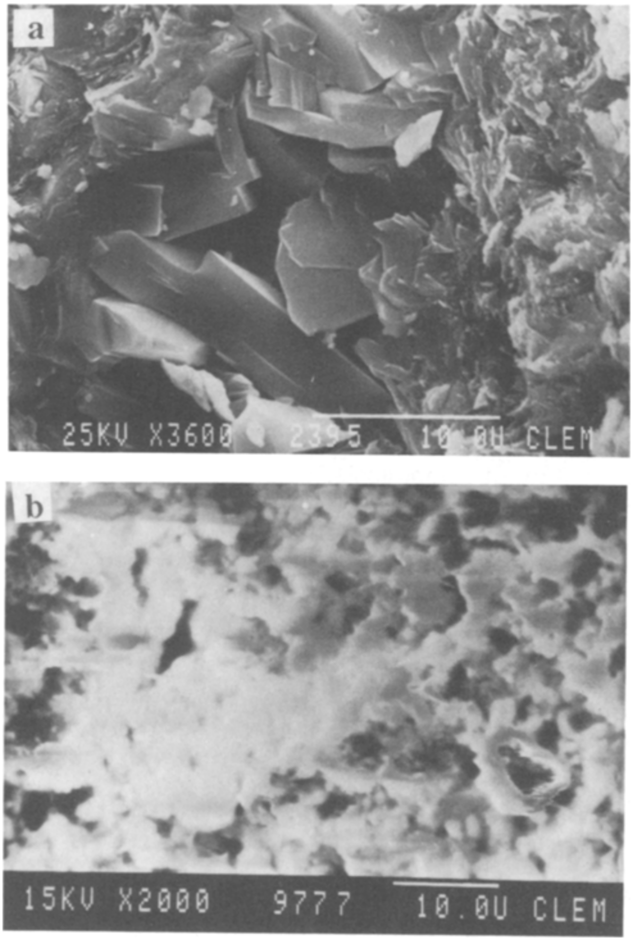

Fig. 6 SEM pictures of: a) clinoptilolite zeolite CT and b) N-P-K fertilizer enclosed in CT

surface. The quite smooth leaflets of CT zeolite disappeared and some quasi little pits appeared [16] or better said some impregnations or preparations were found (Fig. 6) on the surface of the products.

Galwey [86] observed such phenomena in the case of new inorganic products and he held it for some kind of foaming structure.

It is known that inorganic polymers, silicates, borates, phosphates can be transformed into amorphous solids by appropriate heating relatively easily. Otherwise such processes are less known in solid state. Sometimes transformation from the disordered amorphous structure to the ordered crystalline is achieved by the formation of a new compound inside the amorphous matrix, which changed its chemical composition, too. Authors [79] try to use their experiences from the study of borates for the explanation of the amorphisation in the cases of layered silicates, too.

Interesting changes were observed during the thermal degradation of tetracyano complexes [66] in more complicated systems, the resulting oxides forms were [24] also studied and their utility may be predicted from these morphological changes.

Conclusions

The combinations of inclusion compounds, at least of their hosts, equally of the supermolecular structure exhibiting compounds have very interesting properties. But even more as object in thermoanalytical study they may contribute to the theory of the chemistry of inclusion compounds – to the inclusion of one kind of compounds in another one. Thermoanalytical study together with other methods allows to quantify the sorption and equally the desorption of the more or less complicated guest components.

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