PROPERTIES AND APPLICATIONS OF PALYGORSKITE-SEPIOLITE CLAYS

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ABSTRACT: The palygorskite-sepiolite group of clay minerals has a wide range of industrial applications derived mainly from its sorptive, rheological and catalytic properties which are based on the fabric, surface area, porosity, crystal morphology, structure and composition of these minerals. For assessing potential industrial uses, the mineralogical and chemical composition of the clay and its basic physical and physico-chemical parameters must be determined. Then some particular properties of commercial interest can be modified and improved by appropriate thermal, mechanical and acid treatments, surface active agents, organo-mineral derivatives formation, etc. In this paper, a revision of the principal characteristics of commercial palygorskite-sepiolite clays is presented, and potential uses are suggested according to these data. New products and applications are being investigated and those concerning environmental protection in particular, are noted. Finally, possible health effects of these elongate clay minerals are discussed.

While commercial deposits of palygorskite and sepiolite are rare, these two clay minerals occur relatively frequently in sediments and soils.

Both palygorskite and sepiolite clays are so-called 'special clays'. The annual production in the western world for the former is estimated to be around two million tonnes; production comes mainly from the southeastern USA (Miocene deposits in Florida and Georgia), about 1.8 million tonnes in 1989 (Ampian, 1991), and from Senegal, Spain, Australia, India, Turkey, South Africa and France to a much smaller extent. Sepiolite is less abundant than palygorskite. The former is a typically Spanish mineral; in fact, over 90% of sepiolitic clays are produced in Spain (also from Miocene deposits). Other small operations are in Nevada (USA), Turkey and China. The annual production of sepiolite in Spain is close to 800,000 tonnes (O'Driscoll, 1992).

The interest in these minerals lies in their special sorptive, colloidal-rheological, and catalytic properties which are the basis for many technological applications.

STRUCTURAL FEATURES AND PHYSICO-CHEMICAL BEHAVIOUR

Palygorskite and sepiolite are phyllosilicates inasmuch as they contain a continuous two-dimensional tetrahedral sheet; however, they differ from other layer silicates in that they lack continuous octahedral sheets. Their structure can be considered to contain ribbons of a 2:1 phyllosilicate structure, each ribbon being linked to the next by inversion of SiO_4 tetrahedra along a set of $Si-O-Si$ bonds. Ribbons extend parallel to the X-axis and have an average width along Y of three linked pyroxene-like single chains in sepiolite and two linked chains in palygorskite (Fig. 1); in this framework, rectangular channels run parallel to the X-axis between opposing 2:1 ribbons. As the octahedral sheet is discontinuous at each inversion of tetrahedra, oxygen atoms in the octahedra at the edge of the ribbons are coordinated to cations on the ribbon side only, and coordination and charge balance are completed along the channel by protons, coordinated water and a small number of exchangeable cations. Also, a variable amount of zeolitic water is contained in channels.
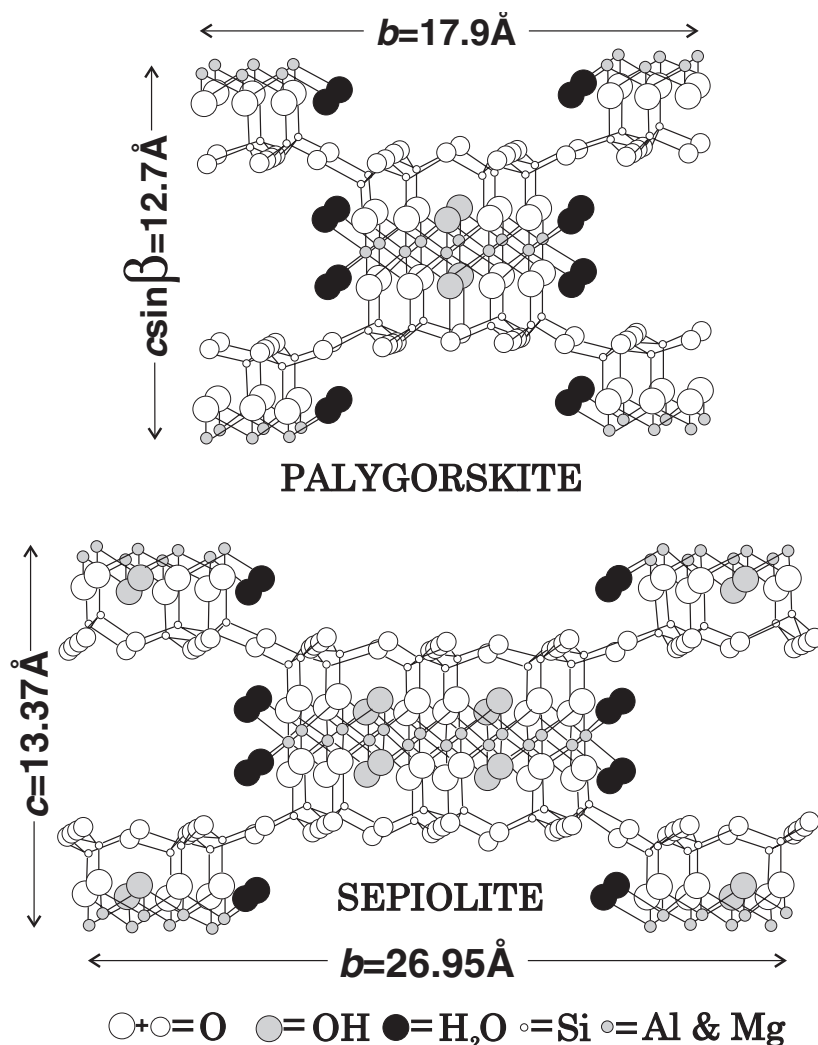
FIG. 1. Schematic structure of palygorskite (after Bradley, 1940) and sepiolite (after Brauner & Preisinger, 1956). (Jones & Galán, 1988).

This structure of chain phyllosilicate results in a fibrous habit (Fig. 2) with channels running parallel to the fibre length. Channels are 3.7 × 10.6 Å in sepiolite and 3.7 × 6.4 Å in palygorskite. Fibre sizes vary widely but generally range from *c*. 100 Å to 4−5 μm in length, *c*. 100 Å to *c*. 300 Å in width, and *c*. 50 Å to *c*. 100 Å in thickness.

Sepiolite is a Mg silicate close to trioctahedral phyllosilicates, while palygorskite appears to lie midway between dioctahedral and trioctahedral phyllosilicates (Fig. 3), with 1.1−2.5 octahedral positions occupied by Al + Fe^{3+} and 1.1−2.8 by Mg at the five octahedral sites (Paquet *et al*., 1987; Galán & Carretero, unpublished results). Four H_2O molecules per half unit-cell are present in the channels (zeolitic water) and four others are bound to octahedral cations. The cation exchange capacity of both minerals is quite low; it ranges from 4 to 40 mEq/100 g, but the higher values are probably related to impurities.
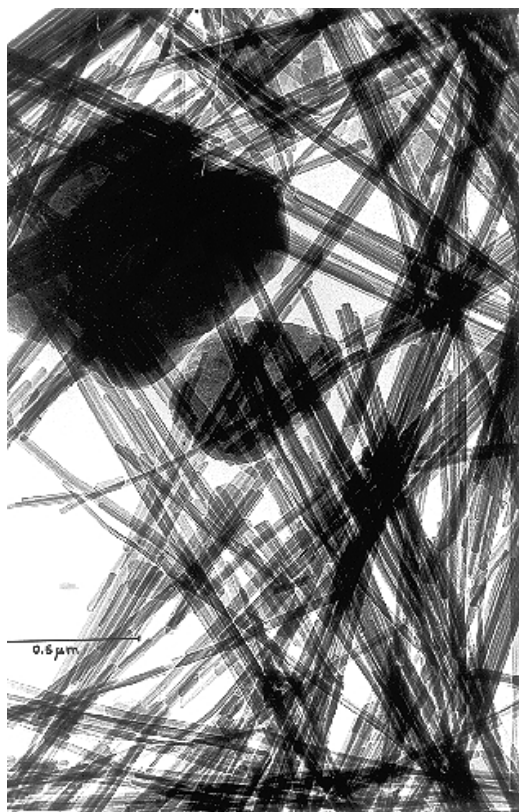
FIG. 2. TEM of Torrejón palygorskite (Spain) with some illite crystals.

The presence of micropores and channels in these minerals together with the fine particle size and fibrous habit account for their high surface area. The average external and internal surface areas have been estimated to be 400 and 500 m^2/g, respectively, in Vallecas sepiolite, and 300 and 600 m^2/g in Attapulgus palygorskite (Serna & van Scoyoc, 1979). Nevertheless, the BET surface area of sepiolite is only $\sim$300 m^2/g compared to 150 m^2/g for palygorskite.

The surface area can be modified by heating and by acid treatment (Fernández Alvarez, 1970, 1972, 1978; González *et al*., 1984; Jiménez López *et al*., 1978; Bonilla *et al*., 1981; López González *et al*., 1981; Cornejo & Hermosín, 1986, 1988; Suárez, 1992; Vicente Rodriguez *et al*., 1994). The area for sepiolite is maximal after heating at 150°C, at which $\sim$10% of hygroscopic water is lost, and decreases after thermal treatment between 200 and 400°C due to micropore destruction and structure folding. Acid treatment increases the surface area because it virtually destroys the minerals and produces amorphous silica products preserving the fibrous morphology. Dry grinding for a short time ($\leqslant$15 min) causes thinning of fibrous particles and hence an increase in the surface area without structural alteration.

The structure of these minerals includes three types of active sorption sites: (a) oxygen ions on the tetrahedral sheet of the ribbons; (b) water molecules coordinated to Mg ions at the edges of structural ribbons (two H$_2$O molecules per Mg^{2+} ion); and (c) SiOH groups along the fibre axis (Serratosa, 1979). Silanol groups are formed as a result of broken Si$-$O$-$Si bonds at external surfaces balancing their residual charge by accepting either proton or a hydroxyl group to form Si$-$OH groups. The relative abundance of these groups can be related to fibre dimensions and crystal defects, and increases with acid treatment.

Clays consisting mainly of one of these minerals are of commercial interest. These clays usually contain impurities of quartz, feldspars, carbonates, gypsum, cristobalite, smectite, illite, kaolinite, chlorite and iron oxides. Some of these minerals (quartz, feldspars, Al-smectites, illite, kaolinite, chlorite) are detrital in origin, while others (carbonates, opal, gypsum, Mg-smectites) are formed paragenetically with the fibrous clay minerals.

Palygorskite and sepiolite clays usually occur with a compact earthy or fibrous fabric, of a bulk density <1 g/cm^3 (0.4$-$0.7); they are white, yellowish-white, greenish, grey or pink in colour. Minerals occur as bundles of agglomerate needle-like structures which disperse in water and other polar solvents to yield a randomly intermeshed network of fibres in the solvent (Fig. 4).

APPLICATIONS OF PALYGORSKITE AND SEPIOLITE CLAYS

Sorptive uses

Absorption and adsorption are two properties related to the surface area of clay minerals. Absorption is the penetration of fluid molecules into the bulk of an absorbing solid, whereas adsorption implies some interaction between the fluid molecules and the solid surface. Both types of phenomena are encompassed by the term sorption.
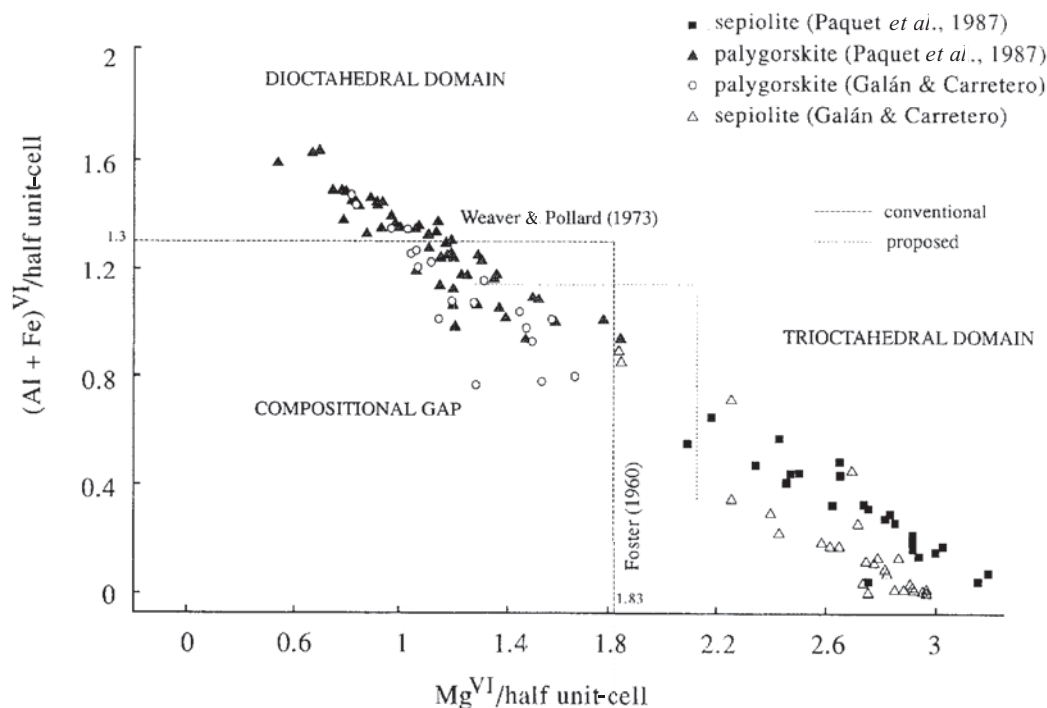
FIG. 3. Chemical composition for sepiolite and palygorskite (Galán & Carretero, unpublished).

According to Santaren (1993), absorption processes involve contact of a free fluid phase with a solid phase that is able to take and hold the fluid. The solid must be porous and permeable, and possess a high surface area and porosity in order to exhibit a high sorption capacity. Absorption usually takes place through capillary action. On the other hand, adsorption involves some interaction between the sorbate-solid surface. Attractive forces between the fluid molecules and the solid surface are less specific and weaker than in a real chemical bond. Some absorption processes also involve adsorption.

Particle-size distribution, microporosity, a capillary structure and the active surface of the solid play major roles in these sorptive processes. The grain size of absorbent granules is also very important because small granules give rise to more extensive and faster absorption due to the increased overall external surface.

In devising sorptive applications, one must consider such clay characteristics as microporosity, capillary structure, surface area and active sorption sites (especially silanol groups), as well as grain size and mechanical strength of granules, and the

features of the liquid to be absorbed. Absorption is dependent on liquid density, viscosity, and surface tension, which determine capillary suction by clay granules; adsorption is even more markedly influenced by the size, shape, and polarity of the molecules involved. Large molecules or small molecules of low polarity cannot penetrate into
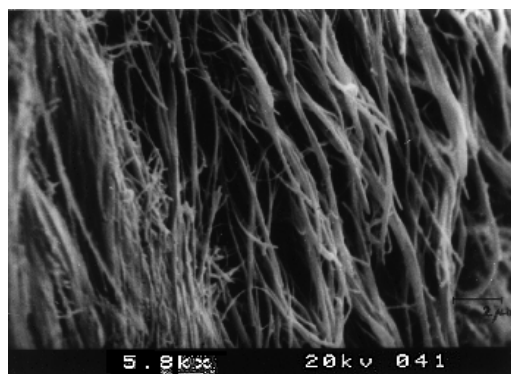

FIG. 4. SEM of Vicalvaro sepiolite (Spain).

TABLE 1. Characteristics of sepiolite and palygorskite absorbent granules.

	1	2
Bulk density (Kg/m^3)	500−715	600−650
Water absorption (%)	75−120	80−100
Oil absorption (%)	60−95	−
Moisture	12 ± 3	−
Colour	white	white

1: Vallecas sepiolite granules (grain size 0.25–6.3mm) (Galán, 1987).
2: Senegal palygorskite granules (grain size 1−6 mm) (O'Driscoll, 1992).

TABLE 2. European market for cat litter ('000 tonnes).

Country	Total	Lightweight	Heavyweight
Germany	230	160	70
France	205	200	5
UK	150	80	70
Netherlands	100	95	5
Italy	85	75	10
Belgium	40	38	2
Switzerland	30	25	5
Sweden	25	10	15
Spain	25	25	0
Austria	24	20	4
Denmark	17	15	2
Finland	10	5	5
Norway	4	3	1
Portugal	3	2	1
Total	948	753	195

Source: Santarén, 1993

channels, so they can only be adsorbed onto external surfaces, which account for only 40−50% of the overall surface area.

These clays have been used for absorbent purposes since the 1930s; however, use did not expand significantly until World War II, when they were used to absorb grease, oil, water, chemicals and other undesirable substances spilled on the floor of factories, stations, aircraft hangars, etc. Granules should possess adequate mechanical strength (hardness, abrasion and compressive strength) and be stable or chemically inactive, incombustible and non-flammable, and exhibit a high liquid absorbing capacity.

One of the most important markets for industrial clay absorbents is cat litter. Clays used for cat litter can be classified into heavyweight clays (HWC) and lightweight clays (LWC); the latter are made of sepiolite and palygorskite at densities in the range 400−700 kg/m^3. Granule size usually varies from 1 to 6 mm, and grains have round surfaces and are dust-free (Tables 1 and 2).

Absorbent granules are also used as pesticide and herbicide carriers; and bleaching agents for mineral and vegetable oils, paraffins, fats, butter and wine.

In general, the selectivity of fibrous clay minerals for sorption of organic compounds can be used for separating mixed components. Such a selectivity plays a prominent role in the decolourization of oils and in separation processes such as refining of crude petroleum oils by selective adsorption of light fractions, or in cigarette filters, where the minerals selectively adsorb nitriles, ketones and other dangerous polar gaseous hydrocarbons preferentially over less polar compounds such as aromatic hydrocarbons, which enhance tobacco flavour.

As decolourizing agents, these minerals physically retain coloured particles during filtration or percolation and adsorb coloured compounds and convert them catalytically into colourless substances. In the process, the clay acts as an absorbent, an adsorbent and a chemisorbent. These clays are particurlaly effective with mineral oils because coloured compounds are more simple molecules (generally naphthenic derivatives) than those in vegetable oils (chlorophyll, carotenes and xanthophyll) and can readily penetrate into the channels and pores of these minerals (Chambers, 1959) and for the removal of colour and turbidimety in sugar juices (Demirci *et al.*, 1995). The decolouring power is enhanced by acid treatment, which increases the specific surface, number of active sites and porosity of the mineral.

Palygorskite has been used as an active ingrdeient in pharmaceuticals and cosmetics because of its adsorptive capacity. It can act as an adsorbent for toxins, bacteria and even viruses in the intestine (Martindale, 1982), and as a protective coating for the stomach and intestine. However, it may favour the loss of enzymes, vitamins and other essential substances. For this reason, use for extended periods is inadvisable.

Catalytic applications

Granules of palygorskite and sepiolite clays are being used increasingly as catalyst carriers on

account of their high surface area, mechanical strength and thermal stability. The catalyst can be impregnated on the surface by treatment with a salt of another metal and can also substitute for some structural Mg cations. Also, Mg^{2+} ions can be exchanged for catalytically significant species such as Ni^{2+}, Pt^{n+}, Pd^{n+}, Zn^{2+}, Co^{2+} and Cu^{2+}.

The catalytic activity of clays is primarily a function of their surface activity (primarily of silanol groups present on the surface, which are slightly acidic and can act as catalysts at reaction sites). Acid treatment of these clays results in the removal of adsorbed cations and impurities, increasing surface area, and altering the pore-size distribution and crystallinity. Heating above 300°C decreases the surface area but increases the strength of granules, which is significant to fluid-bed cracking.

Organo-mineral derivatives

Silanol groups of palygorskite and sepiolite can react directly with organic reagents to form compounds with true covalent bonds between the mineral substrate and the organic reactant.

Grafting reactions have been achieved through Si−O−Si bonds by reacting the mineral with organo-chlorosilanes (Ruiz-Hitzky & Fripiat, 1976), through Si−O−C bonds by addition of alkyl or phenylisocyanates (Fernández Hernández & Ruiz-Hitzky, 1979), by reaction with epoxides (Casal Piga & Ruíz-Hitzky, 1977), and by reaction with diazomethane (Hermosín & Cornejo, 1986).

Rheological applications

The principal applications of palygorskite-sepiolite colloidal grades generally involve thickening, gelling, stabilizing or other modification of their rheological properties. These minerals are used in paints (especially where high thixotropy is advantageous), adhesives, sealants, fertilizer suspensions and cosmetics (e.g. milks, masks), in addition to fluid carriers for pre-germinated seeds.

They are also used in drilling muds. One advantage over other clays such as bentonite is that palygorskite- and sepiolite-based muds are less sensitive to salt (i.e. the desired rheological properties remain relatively constant even at high electrolyte concentrations over a wide pH range below pH 8). At pH>9, peptization causes a sharp decrease in viscosity. Sepiolite has a 'mud yield'

above 150 bbl/ton in saturated salt water (Alvarez, 1984) and palygorskite one of 100−125 bbl/ton (Haden & Schwint, 1967). Additives such as Mg oxide (alone or with lime) and Ba oxide increase the mud yield and inertness to soluble salts.

Unlike palygorskite, sepiolite continues to yield upon working in aqueous suspension through unwinding of its long, flexible crystals, whereas palygorskite breaks across the crystal structure and loses rheology with continued use. Also, sepiolite is the only known clay mineral that is stable at high temperatures; for this reason, it is used in drilling muds for geothermal wells.

Filler applications

After surface modification with an organic compound, sepiolite can be used as a reinforcing filler in rubbers and plastics, as natural rubber and PVC (Ruíz-Hitzky, 1974). González Hernández et al. (1978) compared the behaviour of different sepiolite-filled rubbers with that of kaolin and found the mechanical properties and ageing characteristics of the sepiolite rubbers to be similar or better than those of the kaolin-filled products. Since these studies, sepiolite has been extensively studied as a polymer filler (Acosta et al. 1984, 1986; González Henández et al. 1981, 1982; Xianzhen & Chuyi, 1990).

Palygorskite and sepiolite can also be used in pharmaceutical products (e.g. as excipients in tablets or suspensions) on account of their high active surface, where active products (drugs such as hydrocortisone or dexamethasone) can be retained and subsequently released at an appropriate rate (Hermosín et al., 1981; Forteza et al., 1988).

As fillers, these clays can be used in paints, enamels, detergents, plastics, cements, adhesives, pesticides, etc. Palygorskite in cosmetics acts as a filler with thixotropic properties; however, it also serves as an adhesive and protective agent because it adheres to the skin and forms a protective film. In addition, it adsorbs, or absorbs, grease and other substances. It is therefore used to give the skin opaqueness, to eliminate shine and to cover up imperfections.

Other uses

Sepiolite has been investigated for animal nutrition applications on the basis of its sorptive, free-flowing, anti-caking, and non-toxic properties,

in addition to its chemical inertness. The principal uses in this field appear to be in formulations for growth promotion, supplement carrying, feed binding and production stimulation. In addition, sepiolite concentrations in animal feeds from 0.5 to 3% in cattle and poultry feed result in increased weight gains of about 7% for pigs and 10% for broiler chickens and rabbits (Alvarez & Pérez Castell, 1982). The improved feed efficiency could be a result of increased protein digestibility through a slower flow of nutrient material along the intestine due to the formation of a sepiolite gel.

According to Alvarez *et al.* (1985), modified sepiolite could also be used to form a stable complex with type-I collagen, thereby allowing monomeric collagen to be isolated for producing biomaterials that can be employed to subtitute wholly or partly organic supporting tissues.

Environmental applications

The properties described make these clays highly suitable for environmental applications. In addition to their use for adsorbing dangerous polar gaseous compounds in cigarette filters, absorbing odour, faeces and urine in cat litter, and as constituents of floor absorbents and cleaning products, these clays can be used to adsorb almost any unpleasant odorant in our environment such as ammonia, isovaleric acid, methylmercaptan, nitrogen dioxide, ozone, pyridine, trimethylamine and methanethiol (Sugiura *et al.*, 1990; Sugiura *et al.*, 1991a; Sugiura, 1993), they control the concentration of ammonia in farm environments (Alvarez, 1984; Sugiura *et al.*, 1991b), and remove pollutants (mainly organics or agrochemicals in soils and metals) from waste water (Helios-Rybicka, 1985; Gutierrez *et al.*, 1995; Mora *et al.*, 1995; Brigatti *et al.*, 1995).

Sepiolite can also be used as a specific carrier for methanogenic bacteria in the production of methane from waste water (Pérez Rodríguez *et al.*, 1989), and, thanks to its rheological properties, for stabilizing coal-liquid mixtures (Alvarez *et al.*, 1985).

PALYGORSKITE AND SEPIOLITE CLAYS AND HEALTH HAZARDS

The health hazards are the potentially harmful effects on humans and animals of the various materials that make up these elongate clays. This is of concern for workers at processing and packaging sites, as well as for consumers using the materials (and also animals, especially cats).

A recent health risk scare occurred in 1988, when the German Consumer Council revealed the presence of microscopic fibres similar to those in asbestos in seven of the European products for cat litter that were analysed; it was suggested that inhaling such fibres contained in the products might lead to the development of lung tumours. The products contained sepiolite and palygorskite.

Previous studies carried out by the Medical Research Council, Pneumoconiosis Unit, at Penarth, UK, in 1978, and subsequently at the Medical and Hygiene Institute of the University of Dusseldorf, concluded that the samples of Spanish sepiolite were outside the risk range. The UK Health and Safety Executive classified sepiolite as a nuisance dust in 1981, but concluded that the material had yet to be demonstrated as harmful. Finally, the former West German Federal Health Office reported that the cat litter product, based on sepiolite, was harmless (O'Driscoll, 1992).

Data on this subject are not conclusive. Oscarson *et al.* (1986) studied the effect of sepiolite and palygorskite on erythrocyte lysis. They found the two minerals to be lysing agents, and structural folding to reduce lysis, thereby suggesting that edge surfaces and silanol groups are important in the process, whereas elongate morphology appears to be irrelevant. They also found that, when mineral surfaces became saturated with cell components (usually after 1 h), the minerals lost their lytic activity. Experiments carried out in Florida and Georgia on men employed in mining and factories led the IARC (International Agency for Research of Cancer, 1987) to conclude that there was inadequate evidence for the cancinogenicity of palygorskite in humans.

Pott *et al.* (1990) and Wagner *et al.* (1987) studied the effects of sepiolite and palygorskite inhalation and injection in rats. The results proved the production of mesotheliomas on exposure to a significant number of fibres greater than 5−6 µm in length.

Recently, Santarén & Alvarez (1994) reported epidemiological results for animal experiments involving various administration methods (inhalation, intrapleural injection and intraperitoneal inoculation) and different *in vitro* experiments on the activity of Vallecas sepiolite. The results were consistently negative, showing a low intrinsic biological activity of this mineral and the absence of exposure related diseases. Therefore, Vallecas

TABLE 3. Palygorskite sold or used by US producers, by use.

	1986 s.tons	1987 s.tons	%
Domestic			
Adhesives	6,874	2,723	0.3
Drilling mud	34,720	31,949	3.9
Fertilizers	36,247	35,540	4.3
Filtering, clarifying, decolourizing mineral, oils and greases	13,579	13,795	1.7
Medical, pharmaceutical and cosmetic	379	959	—
Oil and grease absorbents	264,673	163,796	20.0
Paint	19,885	20,303	2.5
Pesticides, etc.	71,314	71,009	8.7
Pet litter	348,710	308,320	37.6
Other	60,519	90,767	11.1
Total	856,900	739,161	90.2
Exports			
Drilling mud	106	102	—
Oil and grease absorbents	23,917	43,309	5.3
Pesticides, etc.	4,937	5,463	0.7
Pet litter	29,505	22,461	2.7
Other	5,407	9,167	1.1
Total	68,872	80,522	9.8
Grand total	920,772	819,683	100.0

Source: Clarke, 1989

sepiolite is not carcinogenic. However, other sepiolites of non-sedimentary origin (with higher crystallinity and longer fibres), such as those from China and Finland, have been shown to have a high intrinsic biological activity in animals.

The carcinogenic activity of these minerals seems to be mostly dependent on their physico-chemical properties (silanol groups), crystallinity and fibre length, which are occasionally related to their genetic environment; however, their potentially hazardous effects should be assessed individually for each deposit and factory on the basis of epidemiological data and the results of sensitive animal tests.

CONCLUSIONS

Sepiolite and palygorskite are currently used in more than a hundred different applications (Tables 3 and 4), most of which are similar to those of the more traditional clays. New commercial products are being investigated, especially those included as organophilic materials in paints, plastics, greases, rubbers, plastisols and cosmetics. The most significant areas for these novel applications are those of catalysis, agriculture and environmental protection. The fundamental properties of these clays are compatible with most known applications but assessment of new potential uses requires further research.

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TABLE 4. Comparison between three industrial palygorskites.

	Torrejón el Rubio (Cáceres, Spain)[a]	Georgia (FL, USA)[b]	Carrión de Calatrava (Ciudad Real, Spain)[c]
Pa (%)	50−70	60−90	50−80
Others	I, Sm, Ch, Q, Ca, Feld	I, Sm, Sp, Q, Ca, Ap	I, Sm, Q
S_{BET} (m^2/g)	146	152	155−170
H_2O abs. (%)	60−110[d]	110−120[e]	170−200[e]
Oil abs. (%)	50−100[d]	80−110[e]	44−54[e]
BD (Kg/m^3)	–	480	560−710
Y (bbl/ton)	–	110[f]	66−69
Primary uses	Drilling muds, fertilizers, pesticides, animal feed	Drilling muds, absorbers, oil industries, catalysts, plastics	

Pa = palygorskite, I = illite, Sm = smectite, Sp = sepiolite, Ch = chlorite, Ca = carbonates, Q = quartz, Feld = feldspars, Ap = apatite, BD = bulk density, Y = mud-yield.
[a] According to Galán *et al*. (1975) and Galán & Castillo (1984).
[b] According to Van Olphen & Fripiat (1979) and "Floridin", Quincy FLA (pers. comm.)
[c] According to Galán *et al*. (1994).
[d] As determined by the Ford method.
[e] As determined by Westinghouse method.
[f] For light and heavy clays.

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