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BENTONITE AND RELATED DEPOSITS WORLD ECONOMIC SIGNIFICANCE AND SITUATION IN GREECE

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ABSTRACT

Within the group of mineral resources, the industrial minerals have surpassed the metallics in world production value since 1950 and today achieve twice the value of the metallics. In the statistics on amounts of all resources, bentonite (along with attapulgite) ranks 20th (before copper and zinc), in the statistics on value, it ranks 37th. The bentonite group covers about 200 areas of application with prices between 100 and over 1.000 US $/t.

Greece is one of the leading producers of bentonite, whereby almost all of the bentonite comes from the Cyclade Islands Milos and Kimolos. There we know of about 10 different technical varieties, of which the best are autochthonous types originating by hydrothermal alteration but altered halmyrolytically by Quaternary marine transgressions.

ON THE CHARACTERISTICS OF BENTONITE MINERALS

The name bentonite stands for argillaceous industrial rocks of varying mineralogical composition but with similar properties. Basically, this is a commercial name. Its two main groups are

-- "smectite", of which the main mineral is montmorillonite, a lamellary built up sheet silicate with a capacity for swelling greatly,
-- "hormite", of which the main mineral is attapulgite (or palygorskite), a sheet silicate, built up like a bundle of straw and with a great capacity for adsorption.

Related to attapulgite are sepiolite and its corresponding rock meerschaum; related to montmorillonite are beidellite, nontronite, etc. In a closer sense the name bentonite refers to montmorillonite, to the smectite group.

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Bentonites are active clay mineral rocks with the following characteristic properties: In dry condition they can be relatively hard and even porous so that they can absorb considerable amounts of liquids. Starting at a certain limit, however, and when the solid substance and a liquid are mixed mechanically, they take on the character of a putty, later a paste, and with even more water a jelly or a gel. Finally, with an evident thixotropic behavior, they change into a dispersion in which they can bind and exchange dissolved materials. Technical use is gladly made of this adsorptive capacity.

From this property which also extends to the removal of grease, fat, oil and dirt from wool, the original English term "fuller's earth" (from the Latin "fullo = I clean") and the German expression "Walkerde" are derived. Later with the development of the American West especially in Wyoming, similar but not completely comparable active clays were found, which were first called gumbo, but then later bentonite after Fort Benton, Montana (KNIGHT 1898). Only later and after a period of confusion as to the name, which has not been completely eliminated today, and with the discovery of the mineral montmorillonite (from Montmorillon in France), it became clear that this really did not correspond to attapulgite (named after Attapulgus in Georgia), the real "fuller's earth". Thus, it is recommended to use both names separately.

The bentonite clay minerals greatly fluctuate mineralogically from location to location and numerous local varieties and their mineralogical names were not very helpful for the nomenclature. In general, one should differentiate between

-- the montmorillonite type (i. e. bentonites in the real sense) and the
-- attapulgite type (= palygorskite).

Among the montmorillonites there are two subtypes,

-- sodium montmorillonite (the main mineral of Na-bentonite) and
-- calcium montmorillonite (the main mineral of Ca-bentonite).

The montmorillonite from the type locality Montmorillon is a predominantly Ca-montmorillonite, which structural formula is calculated by GRIM & GÜVEN (1978) as

$\{(Si_{3.80}Al_{0.20})(Al_{1.76}Fe^{3+}_{0.02}Mg_{0.23})O_{10}(OH)_2\}M^{+}_{0.43}$.

In addition, there are special varieties such as hectorite, which is rich in lithium, saponite, and varieties called organoclay, in which organic complexes are bound to the montmorillonite. The term "fuller's earth" is also used in a few Anglo-Saxon publications (e. g. JONES 1972, ROBERTSON 1986) for calcium bentonite. This has caused additional confusion.

It is recommended that the expression "fuller's earth" be eradicated as well as the German expression "Bleicherde", which is used for attapulgite as well as for activated bentonite. In the countries of Eastern Europe the term is even used for vermiculite (SCHOMBURG et al. 1988).

Bentonite is, seen stratigraphically, a relatively young material, usually not older than Cretaceous, but with a clear point of emphasis in the Palaeogene. There are also deposits known in the Upper Palaeozoic and in the Pleistocene. The formation environment is primarily marine, but also limnic. The inclusion of predominantly rhyolitic volcanic glass in a water body and insitu bentonitization (with hydrothermal processes) are favorable preconditions for the formation of bentonite.

As a rule, the exchangeable ions of sodium or potassium influence bentonite properties favorably, exspecially the swelling capacity, the latter primarily for the sodium bentonites. Calcium bentonites do not swell as well but they are exceptionally suitable for bleaching clay purposes. The best montmorillonite properties are, apart from the intercrystalline swelling capacity, extremely fine cystals, lamellar structure, large surface and negative excess charge, which leads to the incorporation of exchangeable ions. Because of this, such bentonites are highly reactive.

Bentonite activation is used for bentonites of low swelling capacity, in which sodium is replaced, e. g. by soda, or alkali is activated in the presence of plenty of water. In addition, there is acid activation in which the bentonites are corroded with the addition of acids in order to improve the adsorption properties.

AREAS OF APPLICATION

Bentonite minerals find application in about 200 areas. Here the mineralogical origin of the products found on the market under the most varied trade names is unclear in some cases.

Classical areas of application are in pharmacy and cosmetics (base and filler material for creams, powder, especially baby powder, and for face masks). Bentonite is a biochemical catalyst, for instance in the production of certain enzymes.

The production of soap and detergents from natural bentonite by many groups of people has been known for a long time; it is presently undergoing a rejuvenation as a substitute for detergents containing phosphates.

The purification and bleaching of animal, vegetable and mineral oils is also a long known field of application for attapulgite and bentonite in calcinated form.

In refining and stabilizing sugar, wine, beer, and fruit juices, montmorillonite is also used, also as a catalyst for organic chemistry processes, e. g. the cracking of paraffin oil and for removing strong smelling components in mineral oils, waxes, fats, and grease.

In the paper industry activated bentonite removes impurities and improves the effect of the printing ink and the distribution of the fibers in the paper.

In a small amount bentonite is used as a mild abrasive, as a binder for pencil graphite, as a filter in dry cleaning. A large area of application is the processing of foods (mustard, ketchup, cornflakes, flour), also its pelletization (the most suitable are acid activated sodium bentonites).

In the foundry industry bentonite supports the forming of molds and their resistance at high temperatures. It is also used for pelletization in ore smelting (e. g. for iron ore) and for the production of granulated fertilizers as well as pet food substitutes, for liquid manure disposal and as cat litter.

Bentonite can be used exceptionally in the drilling industry as a suspending agent, in which the largest amounts of bentonite were used for decades as an additive to the drilling flush. Here the thixotropic effect is the decisive, physical characteristic. Additives are used in the production of paints and emulsions (e. g. fingernail polish).

Finally, the use of bentonite should be mentioned in engineering; e. g. in sealing of ditches for foundations, dam flanks, disposal sites, and for the production of thixotropic curtains with drilling injection. These areas of application are only the most important ones.

THE SITUATION OF THE WORLD DEPOSITS

In Europe the Federal Republic of Germany should be mentioned as the fourth largest producer of bentonite (Süd-Chemie AG near Freising and Moosburg, Erbslöh Geisenheim).

Important European bentonite countries are France, Spain and Italy, but above all the United Kingdom (Laporte Industries PLC and Steetly PLC) and Greece, the world's third largest producer of bentonite (this will be discussed separately). The other European deposits lie in Poland, Czechoslovakia, Rumania, and Yugoslavia.

In Africa deposits in Algeria, Togo (attapulgite-bentonite) and the South African Union are known. In Asia we know deposits from the USSR, Israel, Cyprus, Turkey, India and Pakistan (fuller's earth). In Australia the most important deposits lie in New South Wales.

In America the oldest deposit giving the name lies in Montana, USA. The largest portion of bentonite is used here in the drilling industry. The state of Wyoming ranks first as to amount. As a whole in the USA, the section of activated bentonite is developing better than that of natural bentonite. The main producers are the companies Dresser, Halliburton, American Colloid Co., Engelhard Co., EEC American Inc., Wyo. Ben. Inc., Milwhite Co. Inc., and Teague Mineral Products and the British firm Laporte. Further important American bentonite countries are Mexico (Quimica Sumex SA.), Brazil, Peru, Chile, and Argentinia.

ECONOMIC PREREQUISITES AND TRENDS

As a result of overcapacities in Europe and America and the strong decrease in the oil prices since 1986, the bentonite industry has been hit by a clear drop in prices in the last few years. A change is taking place in the oil producing areas of the Gulf of Mexico and the North Sea, characterized by an increase in production which, however, still cannot make good the total losses in the oil bentonite market. Due to the rapid development of new areas of application, this market fluctuates to a great extent, and for a few varieties good prices can be achieved at present, such as for foundry-bentonite, bleaching earth, engineering bentonite, special bentonite for the catalyst industry, food processing industry, the manufacturing of detergents, and for pharmaceutical and cosmetic purposes.

In the production of cat litter, bentonite has overtaken the traditional resources of attapulgite, sepiolite and diatomite. This is due to better adsorptive properties of montmorillonite and its lower health risk (from sepiolite).

Exact statistics of the amount of production or their classification into individual mineralogical varieties is very difficult due to the existing taxonomic and statistical confusion. The world production of bentonites and attapulgites lies in the order of magnitude of 12 - 15 million tons. The most important production countries are the USA, the USSR, Greece and the Federal Republic of Germany (in this order).

It is a generally unknown fact that all the bentonite products available in Greece originate from the Cyclade islands of Milos and Kimolos. Both islands are part of the island arc of the Southern Aegean Sea, a volcanic belt active since the Neogene and extending from the Gulf of Corinth via Milos and Thera to the peninsula of Bodrum.

Smaller deposits also exist on Chios and Lesbos, the bentonite of which was used as healing earth in the ancient world. This is also true of the bentonite of Milos and Kimolos. In particular, Cimolian earth was made famous by PLINY THE YOUNGER.

The Melian earth of PLINY cannot be clearly equated with bentonite. This was probably a mixture of kaolin and silica or even baryte, which its application as a white paint implies, mentioned by VITRUVIUS. The more likely suspicion is that bentonite, which also has an astringend effect because of its alunite contents, was tradet partially like *alumen* just like alunite. According to PLINY the Melian *alumen* was, in addition to the Egyptian one, the best in world at that time. PITTINGER (1975) calls it the "aspirin of the ancient world".

But above all Milos was the island of wealthy Dorian shepherds; the ram's head was the emblem of Melian coins. The availability of native bentonite for degreasing and cleaning ("fulling") wool probably favored the production of high quality textiles considerably. PLINY reports that Cimolian earth was also used by the Greeks themselves as a type of soap for personal grooming. The production of so-called washing soap from olive seed oil and bentonite was the most important industrial use of Melian bentonite even up to the 2nd World War. Even in 1950 23,000 tonnes of washing soap were produced in Greece (HAMBURGER KREDITBANK 1951).

One year earlier, 1949, the suitability of Melian kaolin was discovered for the production of porcelain. With this a new prospection period began on Milos, where the mining of manganese and silver ore had come to a stop during the world economic crisis. In connection with the mining of baryte for the drilling industry, there was an increased interest in bentonite. Even in 1972 Greece ranked 3rd after the USA and Italy among the 24 bentonite producing countries (CALLOT 1976) with an output of 357,413 tonnes of crude bentonite (FELDHAUS 1984). Thus, bentonite ranked third (NOTHOLD 1982) among the Greek resources in yield after bauxite (2.9 million tonnes) and magnesite (1.1 million tonnes). After a drop at the beginning of the 1980s in connection with the oil crisis, bentonite production was able to recover again by 1983.

The largest bentonite producer on Milos is the Silver & Baryt Ores Mining Co., followed by the Mykobar Mining Co. SA. Both companies dry and activate bentonite with soda in their own plants on the island. The Mediterranean Bentonite Co., a subsidiary of the Italian company Laviosa Spa., ships the bentonite to a treatment plant in Livorno. In addition, there are other medium-sized businesses which primarily mine bentonite for foreign importers.

Melian oil well drilling bentonite is exported within Europe and to Nigeria and to the Middle East. Even more important is its use in ore pelletization, especially of iron ores in Canada (in competition with US-bentonites), Liberia and in the Netherlands. Melian bentonite is even valued as a foundry bentonite. The high-grade qualities will probably gain in importance in the future for special applications requiring special purity (e. g. in the area of catalysts). The bentonite reserves of Milos can be estimated at about 50 million tonnes as a result of the discovery of some new deposits.

The bentonite of Milos and Kimolos originated by the transformation of acidic to intermediate volcanic rocks and their tuffs. The same is true of the smaller bentonite deposits on Chios and Lesbos.

Even SONDER (1925) pointed out that the addition of Mg, which it got from seawater, was necessary for the bentonitization of Melian plagioliparite. WETZENSTEIN (1969) und HAUCK (1984) agree with this. In addition, HAUCK considers an ascendent addition of Mg possible because bloedite (NaMg-sulfate) occurs as an exhalation product. The geophysical exploration of the geothermal field of Milos points to the existence of smaller magma chambers at a depth of 6 to 8 km (FYTIKAS et al. 1989). Since in the Melian magma differentation a residual melt rich in Mg occurs (LEONIS 1983), one cannot exclude an endogenetic addition of Mg. Furthermore, Neogenic dolomites, which are wide spread in West Milos, are possibilities as potential Mg sources, (WIEDENBEIN 1988).

Milos bentonites are essentially Ca-bentonites, which can also contain cristobalite, kaolinite, alunite and opal. A zonation tendency can be observed on Milos, which has the sequence bentonite (+ pyrite) -- kaolininite + alunite + opal -- silica (opal) from bottom to top (WETZENSTEIN 1969). An identical zonation is known from e. g. the rhyolite regions of New Zealand (STEINER 1953, HARVEY 1980, 1981). In the underlaying stratum of the bentonite zone there are futher zones: a zeolite and a feldspar zone. In the meantime MARCOPOULOS & KRANIOTIS (1982) have also been able to prove zeolites (clinoptilolite, mordenite) and analcime by means of radiography in the Melian bentonites.

According to the investigations of HARDER (1972), under basic conditions (pH 10) even 10 p.p.m. Mg in the solution are sufficient for the formation of smectite minerals. There is probably the favorable influence of previous corrosion of the volcanic rocks and tuffs by the impact of fumaroles, possibly only by the addition of heat involved. Indications in this respect have been given by the experiments carried aut by SCHORIN (1972) on tuffs from Thera.

On the whole about 10 different bentonite varieties, which vary greatly as to quality, can be differentiated between on Milos. The undisturbed autochthonous bentonites associated with marine terraces of the Pleistocene are of particulary high quality. Bentonite and kaolin deposits often lie next to each other under such terrace-bodies, whereby the bentonite always points seaward with respect to the kaolin.

On Milos the process of bentonitization probably occured numerous times in alteration with eustatic changes of the sea level. Here the older bentonite was changed again by halmyrolytic processes (WIEDENBEIN 1988). This can be an explanation for the numerous varying smectite types occuring jointly in one single bentonite sample, a particularity of Melian bentonite to which LAGALY & WEISS (1971) have already referred to, as for the general mineralogical variety of varying bentonite samples from Milos and Kimolos as well (FRANZINI et al. 1963, WETZENSTEIN 1969, CAILLÈRE & ECONOMOU 1974, GRIM & GÜVEN 1978).

In the splash zone of the cliffs of Tria Pigadia on the east coast of Milos, even a presumably recent bentonitization of porous, glassy tuffs can be observed. The Mg concentrations necessary for bentonitization are probably created by the same evaporite pumping which leads to early diagenetic dolomitization in supratidal carbonates. An indication of highly basic conditions in the bentonite diagenesis is the occurrence of zeolites mentioned, whose experimental formation from montmorillonite has been known for a long time (NOLL 1936).

CONCLUSION

An increased demand for Milos bentonite can be expectet in the next few years because of the increased demand for high-grade bentonites for special applications. It is important that the high-grade qualities be recognized in the field in order to ensure the selection and to mine them. Here the use of geological expertise is indispensable.

In general, an increased consumption of bentonite can be reckoned with in Europe at a time of increased environmental awareness, since, especially in the areas of new environmental technologies, products based on bentonite show nonpolluting alternatives and prospectives. Even the long-term replacement of potentially hazardous products from sepiolite with those of bentonite could contribute to greater comsumption. In addition, there are completely new areas of application for bentonite, like e. g. the pillared clays (GANGAS et al. 1988) which at present cannot even be predictet yet.

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