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CLAY DEPOSITS IN BULGARIA

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ABSTRACT

In Bulgaria there are explored reserves of kaolin, bentonites, kaolinite and refractory clays, and fine-ceramic clays highly exceeding the volume of production. The kaolin is used in the refractory, porcelain-faience, electro-porcelain, paper-producing, chemical and other branches of industry. Refractory and fine-ceramic clays are widely applied in the production of refractory, porcelain, sanitary-ceramic, electrical insulation and stoneware goods. The bentonite clays are used in foundry, drilling and hydroconstruction, for pelletization, for clarification of mineral oils and wine, in cosmetics and ceramics. The residual kaolinite clays could be used as a raw material for production of coagulants, in ceramic masses for production of stoneware pipes and floor slabs, for non-metallurgical aluminium oxide and salts for coloured paper.

INTRODUCTION

In Bulgaria there are large deposits (more than 5 million tons reserves) of kaolin, bentonite, kaolinite, refractory and fine-ceramic clays. The raw material produced satisfies the demands of domestic customers and is well appreciated on the international market. The high quality of clays allows their direct application in industry; only clays for some special products are subjected to additional treatment and processing. The industrial production of clays in Bulgaria originated in the beginning of the 20th century with the construction of the first ceramic factories. Till 1948, when the systematic and purposeful exploration of clay deposits began, production of clays was 10 kt per year. Detailed geological prospecting, that has been carried out for the last 45 years provide the country with 150 millions of tons of clay reserves. Meanwhile the production of these raw materials increased intensively, reaching its maximum in 1980 - 675 kt (fig. 1). Clay production, during next ten years, was of almost constant volume, which was of sign of production and market stability. In 1992 clay production in Bulgaria was reduced to the volume of 30 years ago.

MINERAGENY

Clay deposits in Bulgaria are distributed specifically in the morpho-tectonic regions and zones (fig. 2). They are allocated mainly in the Moesian Plate, The Rhodopes massif and the Kraishte zone, and locally in the Sakar-Strandja tectonic zone, the Western Balkan tectonic zone, the Srednogorie tectonic zone and the Forebalkan tectonic zone. Clay deposits are mainly primary (residual) and secondary (sedimentogenic). The residual

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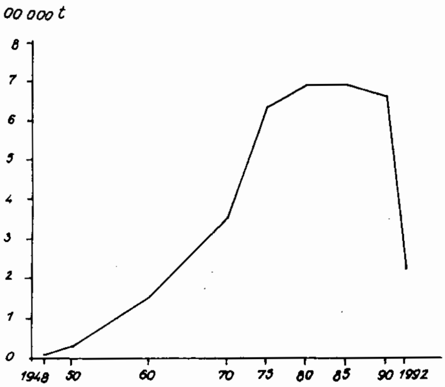


Fig. 1: Production of clays in Bulgaria.

deposits are formed in the both consolidated regions - the Moesian Plate and the Rhodope massif; large deposits of kaolin-quartzic sands being concentrated in the first one and large bentonite deposits - in the second one. Secondary deposits are products of sedimentogenesis, taken place in stabilized and mobile tectonic zones. Deposits of refractory and fine-ceramic clays have been generated in the Moesian Plate (Pleven district), the Kraishte zone, the Western Balkan zone and the Forebalkan zone. Bentonite deposits have been allocated in the Moesian Plate, the Srednogorie tectonic zone and the Sakar-Strandja tectonic zone. The kaolin deposits of the Moesian Plate, the bentonites of the Rhodope massif and the refractory and fine-ceramic clays of the Kraishte and the Moesian Plate are of the greatest economical significance.

CLAY DEPOSITS

1. Kaolin

The kaolin is produced by washing of kaolin-quartzic sands, the economical deposits being positioned in northeastern Bulgaria (fig. 2). The kaolin-quartzic sand deposits (27 deposits) are allocated in the area of 3000 km^2 in the southern part of the Moesian Plate, between the towns of Ruse and Tervel. The kaolin-quartzic sands fill up large karst fields, appearing at different levels of the Lower Cretaceous limestones. The karst has a very irregular and complicated configuration and dimensions from small pits and backsets, of diameter not more than 50m, to large fields with backsets and valleys, of area of $10km^2$. In the section of deposits from bottom up there are: limestones, basal clays (called "mantle" clays), kaolin-quartzic sand and cover (fig. 3).

Among the kaolin-quartzic sands there are mainly kaolin lense-like bodies of dimensions not more than 5 m, and sand and clay/kaolin sand lenses of length from 1 m to 20 30 m. The kaolin-quartzic sand is composed of variable quantities pelite (kaolin), aleurite, psammite and gravel. The last three fractions are monomineralic, quartzic. The kaolin-quartzic sands are of white to dark-red colour. Sands of white , light-pink and light-cream colour, of more than 12 % kaolin and chemical composition Al_2O_3 + TiO_2 more than 29,5 %, Fe_2O_3 less than 1,7 % are of economical interest. The mineral resource has been outlined as bodies of length from 20 m to 1500 m and thickness from 2m to 70m, average 30m [Georgieva, 1988]. Only the kaolin (fraction less than 10 m), the quartzic sand and the gravel are used, while the aleurolite has no application.

The deposits are concentrated in two districts: Kaolinovo town and Senovo town. Kaolin quantity is higher in the deposits of the Kaolinovo district (deposits: "Izgrev" - 28%; "Balabana" - 26,4%; "Sekulovo" - 25,4%; "Saragiol" - 25,1%; "Doirantzi" - 25,1% etc.) while kaolin quantity is lower in the deposits of Senovo district (deposits: "Viatovo" - 17,5%; "Esennitzite" - 22%; "Zlaten Dol" - 21,5%.

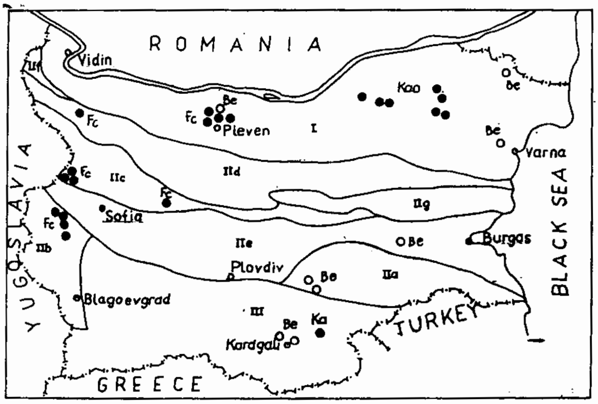


Fig. 2: Map showing the principal deposits of clays in Bulgaria. I. Moesian Plate, II. Alpine Folded System, a-Sakar-Strandja tectonic zone, b-Kraishte tectonic zone, c-West Balkan tectonic zone, d-Fore-Balkan tectonic zone, e-Srednogorie tectonic zone, f-Kula Folded zone (South Carpathians), g-East Balkan Tectonic zone, III. Rhodope massif. Be - Bentonite; Ka - Kaolinite clays; KaO - Kaolin; Fc - Fireproof and ceramic clays.

The kaolin is composed of Kaolinite (75-83%), hydromica (4-7%), orthoclase (3-4%), albite (1-4%). Dickrite, nacrite and chaluasite are established locally. The kaolinite is observed in hexagonal, trigonal and pseudohexagonal individuals.

The kaolin has different average values of the chemical composition and whiteness in the deposits of the both districts (table 1).

The variation in kaolin chemical composition and whiteness has been determined by the coefficient of variation, showing that the material is characterized with rather even content of Al_2O_3 and even distribution of the whiteness, with even distribution of the Fe_2O_3 and uneven quantity of TiO_2.

The kaolin is mined from 3 deposits but there 27 deposits explored. It is used in the refractory, porcelain-faience, electrical porcelain , cellulose-paper, chemical and other branches of industry and is exported.

Table 1: Composition and whiteness of the kaolin from the Kaolinovo and Senovo district.

Components, % Characteristics,%	District			
	Kaolinovo		Senovo	
	from	to	from	to
Al_2O_3	34,3	36,3	32,1	34,4
Fe_2O_3	0,62	0,98	0,7	1,15
TiO_2	0,21	0,65	0,2	0,4
whiteness 110^{o}C,	80,2	86,8	73,1	81,5
whiteness 1350^{o}C,	90,8	95,8	89,7	92,2

2. Kaolinite clays

The kaolonite clays are part of the residual complex formed over Oligocene andesites and andesite tuffs in the Eastern Rhodopes [Todorova, 1966]. They are explored in the "Glavanak" deposit, Haskovo district. The "Glavanak" deposit is composed of three formations: volcanogenic, residual and sedimentogenic [Petrov, 1991].

The residual formation is composed of kaolinite clays, kaolinitized tuffs and kaolinitized andesites (fig. 4). The kaolinitized clays are composed mainly of kaolinites, as second-order minerals there are hydromica

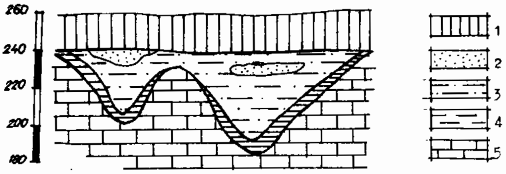


Fig. 3: Geological cross section of the deposit of kaolin-quartzic sands. 1 - mantle: soil, loess, clay and gravel; Quaternary; 2 - sands, 3 - kaolin-quartzic sand, 4 - basic clays, 5 - limestone - Lower Cretaceous.

and montmorillonite, and as a specific mineral there is chalousite. They are refractory. The mineral resource is of thickness to 40 m, average 20 m. It contains (in % of hardened mass): Al_2O_3 - 30 -37 %, average 33 %; CaO - 0,5 - 2,9 %, average 0,7 %, MgO -0,2 -0,9 %, average -0,4, Fe_2O_3 - 1,0 19, average 8,6%, As - less than 0,01 %.

The kaolinite clays of "Glavanak" deposit can be used as coagulants [Parvanov et al.,1985, Cholakov, Petrov, 1988] and as a material in ceramic masses for production of stoneware pipes and floor slabs [Petrov et al., 1990]. They are interesting as a resource for production of non-metallurgical dialuminium oxide and salts for coloured paper. The deposit is in a process of exploitation.

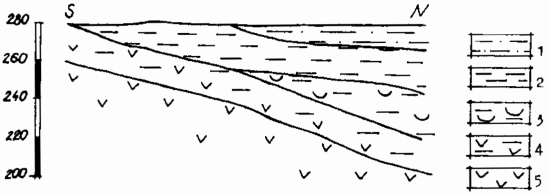


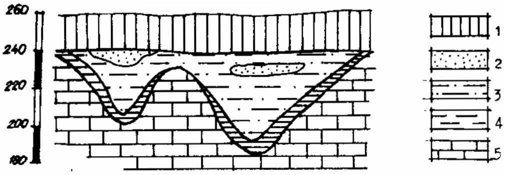
Fig. 4: Geological cross section of the deposit "Glavanak". 1 -Sedimentary (sand-clay) packet, 2 - Kaolinite clays, 3 - kaolinization tuffs, 4 - kaolonization andesites, 5 - andesite.

3. Refractory and fine-ceramic clays

The refractory and fine-ceramic clays are sedimentogenic continental: Hettangian and Plensbachian lake-marshial clays and Lower Sarmatian alluvial lake-marsh. Deposits of Lower Jurassic clays are allocated in the Kraishte district (5 deposits), Zabardeto district (13 deposits), Etropole district (2 deposits) and Western Forebalkan (1 deposit). There are from 1 to 11 layers of thickness from 1 m to 10 m, locally to 20 m [Trashliev and Atanasov, 1989]. Only 3 of the 21 explored deposits are in a process of exploitation: "Zhabliano" (Kraishte), "Garmishte" (Zabardeto district) and Klisurishte (Western Forebalkan). The reserves of the "Zhabliano" deposit, where there are seven clay layers of hydromica-kaolinitic type, are of the greatest quantity and the best quality. The clays from the "Zhabliano" deposit are finely dispersed (fraction below 0,01 m - more than 86 %), refractory (1680ø C^0) and highly plastic (30 % after Pfedgerkorn). The main mineral in them is kaolinite - 1T, and the second-order minerals are hydromica - 1M, muscovite, quartz, orthoclase

Table 2: Chemical composition (in % of hardened mass) of the clay of the 7th layer of the "Zhabliano" deposit.

No	Sample, Fraction	Components, %				
		$Al_2O_3+Ti_2$	Al_2O_3	TiO_2	Fe_2O_3	SiO_2
1	Clay	33.07	31.40	1.68	1.24	60.62
2	Fraction below 0.01 mm	35.60	33.90	1.70	1.16	57.20



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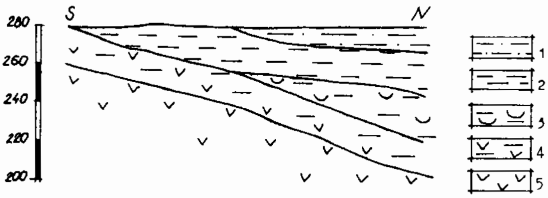

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and albite. The kaolinite is of a crystallization degree after Chinkley - 1 Ch, so it is on the boundary between middle- and highly-crystalline minerals. It has a degree of arrangeness after Clooze - 59,8 i(Cø), so it is among the highly disordered and disordered minerals.

The clay of the 7th layer of the "Zhabliano" deposit is characterized with high content of Al_2O_3 (table 2).

The clays from the "Zhabliano" deposit are high quality resource for refractories and for production of porcelain, sanitary-ceramic and faience goods. They are demanded on the domestic and the international market as well. Their quality can be improved only by classifying on 0,01 mm, and a product of 2,5% higher content of Al_2O_3 and 0,08% lower quantity of Fe_2O_3 (table 2) is produced.

4. Bentonite clays

The deposits of bentonite clays are localized in the volcanogeno-sedimentogenic geocomplexes of the Oligocene and the sedimentary complexes of the Campanian and the Miocene. They are determined as hydrothermal-metasomatic, diagenetic-catagenetic, tectonic-catagenetic and sedimentary ones [Atanasov, Goranov, 1986]. According to their formation, composition and properties Parvanov [1990] differentiated four economical-genetical types of bentonites:

- white - from the acidic pyroclastic horizon of the Oligocene ("Enchetz" deposit", "Zlatna livada" deposit, "Durhana" deposit);
- green - from the mean acidic pyroclastic horizon of the Oligocene ("Propast Dobrovoletz deposit and "Zim-zelen" deposit)
- Miocene redeposited grey-green bentonites ("Goren Bliznak" deposit and "Selska poliana" deposit)
- Sarmatian bentonites ("Suha varbitza" deposit)

The modification of different types bentonites is rather important for the production of some specific expensive goods. It can be realized successfully by a detailed granulometric and mineralogical mapping of the deposits and by technological investigations for an integrated evaluation.

The deposits "Enchetz" and "Propast-Dobrovoletz" are in a process of exploitation. The bentonite clays of "Enchetz" deposit are composed mainly of montmorillonites and second-order minerals kaolinite, crystobalite and bayleyite. After a process of sand liberation and alkaline activation they are used for clarification of mineral oils and wine, as a suspension in cosmetics and as a plastifier in ceramics. The bentonite clays of "Propast-Dobrovoletz" deposit are with yellow-green and grey-blue colour, they are composed mainly of montmorillonites and the secondary minerals - kaolinite, chaluasite, crystobalite, quartz and potassium feldspar. They are used mainly in foundry and for borehole purposes, for pelletization, in the hydroconstruction etc.

The Bulgarian bentonites can be used in the industry, (as a filler in paints, varnishes, caoutchouc etc.), in agriculture (improving the structure of soils) and especially for ecological purposes - for purification of contaminated water and for hydroinsulation of purification equipment.

CONCLUSION

Bulgaria has significant reserves of kaolin, bentonites and refractory clays. The kaolinite is a resource suitable for paper production because of its whiteness, fine dispercity and high degree of crystallization allowing successful delamination. Its production is connected with the production of quartzic sands, used in foundry and for glass-manufacturing. The extension of production is determined by the demands of kaolin and quartzic sand. The bentonite reserves are greater in the deposits near the town of Kardjali, where there is a quarry and an installation for activation of the sodium - potassium bentonite. The raw material is suitable for production of organophille bentonites. There are more opportunities for utilization of clay than the opportunities realized in practice but further mineralogical and technological investigations and an integrated re-evaluation are necessary. The investigations on the explored kaolin deposits carried out in 1993 are very informative in this respect. The newly applied integrated methods allow the realization of a comparison between our kaolin raw material and the material from foreign deposits, which is entirely important in the search of new markets and for the foreign investors. Undoubtedly, this would support the recreation and extension of the production of kaolin, bentonites and refractory clays in Bulgaria.

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