

Study of Usage Areas of Clay Samples of Asphaltite Quarries in Sirnak, Turkey

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Abstract. The asphaltite of Sirnak, Turkey are in the form of 12 veins and their total reserves are anticipated to be approximately 200 million tons in a field of 25.000 hectares. The asphaltites at the Sirnak region are in the form of fault and crack fillings and take place together with clay minerals at their side rock. The main raw materials used in the production of cement are limestone, clay and marn known as sedimentary rocks. Limestone for CaO and clay minerals for SiO₂, Al₂O₃, and Fe₂O₃, which are the main compounds of clinker production, are the main raw materials. Other materials containing these four oxides like marn are also used as cement raw material. Conformity levels of the raw materials to be used in cement production vary according to their chemical compounds. The rocks to be used as clay mineral are evaluated by taking the rate of silicate and alumina into consideration. The soils suitable for brick-tile productions are named as sandy clay. Their difference from the ceramic clays is that they are richer in terms of iron, silica and carbonate. These soils are also known under the names such as clay, arid, alluvium, silt, loam and argil. Inside these soils, minerals such as quartz, montmorillonite, kaolinite, calcite, limonite, hidromika, sericite, illite, and chlorite are available. Some parts of the soils consist of clays in amorphous structure. Limestone parts, gypsums, organic substances and bulky rock residuals spoil the quality. The soils suitable for brick production may not be suitable for tile production. In this case, their sandy soils should be mixed up with the clays with fine granule structure which is high in plasticity. During asphaltite mining in Sirnak region, clays forming side rock are gathered at dump sites. In this study; SQX analyses of the clay samples taken from Avgamasya, Seridahli and Segürük asphaltite veins run in Sirnak region are carried out and their usage areas are searched.

1. Introduction

The main raw materials that are used for the production of cement are the limestone, clay and marly, all of which are known as the sediment rocks. The limestone is the main component for CaO as is clay for SiO₂, Al₂O₃, and Fe₂O₃; which are the main components for clinker production. Other materials that contain those four oxides in their contents such as the clay, are also used as the raw material in cement production. The suitability and the fidelity rate of the raw materials to be used in cement production are proportional with their respective chemical composition. For the limestone component, the lime is used as criteria. The value of this component presents information regarding the components such as SiO₂, Al₂O₃, Fe₂O₃ and the CaO content. The rocks to be used as the clay mineral; the analysis is made based on the silicate and alumina ratio [1].

The homogeneity is also crucial for the clay to be utilized as a raw material for cement in addition to the mineralogical and chemical properties during the chemical analysis of clay; the percentages of



Al_2O_3 , SiO_2 , Fe_2O_3 , CaO , MgO , K_2O , Na_2O , SO_3 as well as the rate of loss of ignition should be determined. In the mineralogical analysis, the elements that form impurities on the external surface of the clay minerals and their ratio (in%) should be determined. It is expected that the $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio in the chemical composition of the clay to be used for cement production is 2/1, the % ratio of the SiO_2 remains at a certain upper limit and the amount of the alkali oxides remain below %1. The kaolin, used to manufacture white cement is also important in the cement industry as a clay mineral. Clay usually contain elements that are plastic and non-plastic in terms of the mineralogy. The plasticity related properties of the clay is one of the most distinguishing feature within the minerals and thus it defines the property of formability with water. This feature is directly linked to the colloid percentage within the structure of the clay minerals and the particle fineness of the clay. The plasticity count of the clay that is used in Cement Industry should vary between 15 – 20 %. In addition, sintering is preferred to occur at 900 – 1050 °C for the clay to be used in cement industry [1].

Apart from the main raw materials, the additives that are required for clinker production are materials with Fe, SiO_2 or Al_2O_3 with an effect to smooth down the chemical composition of the raw composition. The fired pyrite, low grade iron ore, laterite, quartz sand or the quartz materials that are formed by the degradation of the di-metamorphic rocks and bauxites. In Turkey, a large amount of kaolin is used for the production of white cement. As the hard and alunite containing kaolin types can be used for this purpose the cement, kaolin is exported as well. In addition, the gypsum, natural and artificial pozzolanic materials high furnace sinter, siliceous and calcareous ash, silica fume and lime with different amounts in recent years, which are obtained during the crushing and milling of the clinker, are used as additives in the production of different types of cement.

The soil that is suitable for the production of bricks and tiles can be dubbed as arenaceous clay. The difference of those from the ceramic clay is that their richer in iron, silica and carbonate. This type of soil is also known as clay, arid, mil, silt, loam and argil. This type of soil contains minerals such as quartz, montmorillonite, kaolinite, calcite, limonite, hydro-mica, sericite, illite and chlorite. A part of this soil is comprised of amorphous clay. Limestone particulates, gypsum, organic materials and the residues of large rocks are the factors that disrupt the purity. The soil that is suitable for the production of bricks may not be suitable for the manufacturing of tiles. In such a case, the loam should be mixed with fine grain clay with higher levels of plasticity. In some cases, soils with high oil content, which are sensitive to drying, should be mixed with lower plasticity and higher mil. Being able to be used both as brick and the tile and requiring no more process are the primal qualifications of the soil.

It is also desirable that the organic humus acids that increase the plasticity and processability of the soil are present in the raw materials of bricks and tiles. On the other hand, containing higher levels of pyrite is not favourable for the soil. The gases that may be emitted during the degradation of the pyrite may crack the product or may form soluble salts depending on the sintering. Bricks and tiles that are covered with such salts have less resistance against the pressure and the frost. Soluble salts would have an effect on the mortar, which is applied between the bricks and thus the salts may lead to the risks such as the collapse of the construction. Since the clay that contains excessive amount of mica increases the rate of permeability, they are considered as harmful substances. Coal shards within the soil is also unacceptable because they may cause the regional cracks and swelling on the product during the sintering. The main standards that are desired in the soil for brick – tile production is as following; CaCO_3 content should be below 35%; the amount of the particles that are larger than 3mm should not exceed 1%, the plasticity juice should be between 25 - 35%, the hardness should be above % (in MOHS scale) when sintered at 100 °C, the shrinkage after drying (creeping) should be less than 10% as the water absorption should be more than 80% (for brick) and less than 18% (for tile) The soil for bricks and tiles should be sintered at 800 – 1000°C without any blow out's and cracks with tile colour. The amount of the coarse grains above 0.2 mm (in %), in the soil the type of the coarse grains in it, the mouldability of the soil and their dry tension strength should also be determined [1].

2. Mining Potential of Sirnak Region

While a part of the western regions of Sirnak Province is located in Dicle Area of the Southeastern Anatolian Region, the rest remains within the Eastern Anatolian Region. The city is surrounded with Mardin in West, Siirt in North, Hakkari in Northeast as it is neighbored by Iraq and Syria in the East. Except of some plains in the western and southern sides of Sirnak Province, most of the region is covered with plateaus, which are split by rivers. In its mountainous regions, high attitude masses that are linked to Southeast Taurus system are present. With the exception of the regions in the east of the city, close to the Syrian and Iraqi borders, the city is almost entirely covered with mountains. The Northeastern Region, in which Sirnak is located, falls into the line that is called the geological edge fold. The Alpine orogenesis had an impact in the area. As the result of the studies, conducted by our Directorate General, formations to be utilized as raw materials for the Industry and energy were found. They include phosphate, raw materials for cement and asphaltite. Phosphate formations are located in Uludere County while Merkez and Cizre Counties host clay and limestone that is suitable as raw material for cement production. The Cement materials in Merkez County have been found at Balveren town and the villages of Cakirsogut and Toptepe. A possible limestone reserve with the potential varying between 33.750.000 and 78.750.000 m³ in Balveren Town and between 79.734.000 and 186.012.000 m³ in Çakirsogut village have already been determined. The Toptepe village calcareous marl site is determined to hold a possible clay deposit of 29.063.500 - 67.811.500 m³ for raw materials for cement. Another site within the Province that is suitable to be used as a raw material in cement production is the clay deposit at Cizre Cudiyet neighborhood. The possible reserve here is estimated to be 33.750.000 m³. Gerür and Silerut-Senoba phosphate formations at Uludere site were formed as phosphorite and glauconite. The P₂O₅ % grades of the pits are 1.34% and 1.5% respectively. Due to their limited and low grades and reserve size, they are not deemed economically feasible. The most important known asphalt deposits are located in Merkez and Silopi counties of Sirnak province and a thermal power plant that will utilize the asphaltite reserve as the fuel is being planned to be built [2].

Phosphate (P): Uludere-Ortabag phosphate reserve sites. Grade: Low grade glauconite phosphate. (1.34%-1.5% P₂O₅) Reserve : Small Scale. **Raw Materials for Cement Production:** (Cmh) Cizre-Cudiyet Neighborhood. Grade: Undetermined. Reserve: 33.750 000 – 78.750.000 m³ Possible Clay Reserve: Merkez-Toptepe Village. Grade: Undetermined. Reserve: 29.063.500-67.811.500 m³ Possible Clay Reserve. Çakirsogut Village Grade: Undetermined. Reserve: 79.734.000-186.012.000 m³. Possible limestone reserve. Balveren Town Grade: Undetermined Reserve: 33.750.000 m³ possible limestone reserve [2]. **Asphaltite:** Data from 2011 shows that Sirnak Province hold an estimated (known + possible) 72.90 million tons of asphaltite reserve while the data from the end of 2012 indicated that the reserves, with the newly discovered sites, has increased to 104.6 million tons [3].

The asphaltite mines that had been idle for decades due to the presence of terrorist activities in the region have been re-activated at the end of the 8th Development plan. They contribute to the regional economy as well as the energy balance of the state [4]. The total asphaltite production in Turkey was registered as 1293ktons [5-6].

3. Geological Properties of the Areas in Sirnak Region and Mining Activities

The oldest geological rock formation in the region is the old and out cropping Devonian Süke formation, located east of Harbul. This formation is mainly comprised of calcareous shale and schist. On the upper layer, the harbul formation, made of the permo-carboniferous limestone quartzite, greenish chalk and fine layered quartzite is present. The Harbul formation contains four quartziferous brownstone belts. Harbul formation is followed by the Goyan formation (upper layer) from Triassic (Verfenian) period. This formation is comprised of fine layered limestone, calcareous schist, red - purple and red schist and to the upper layers, various types of schist added with fine dolomite layers, ranging from grey to dark grey. On top of the Goyan formation, the old Cudi group from Jura - cretaceous period is found. It is estimated that the bottom of this group, which reaches up to a 1.000

meters in thickness, is dominated by Middle Triassic are while the ceiling is comprised of middle and upper cretaceous period. This group is mainly made of dark colored petit chalk and dolomite and it is the place of the rock formations for Southeastern Anatolian Oil beds. In the middle of this group, a black colored bituminous schist interlayer with a thickness reaching up to 10 meters is found. This horizon plays a crucial role for the formation of asphaltite compound cores. On top of the Cudi Group, the old Germav formation from Campanian and Maastrichtian periods with a thickness of 1600 - 2000 meter is located. The Germav formation branches out upwards to the following sections; Lower Sirnak Formation: intercalation of the limestone with highly hard marn and softer marn (Campanian), Middle Sirnak Formation: the intercalation of the cherty marn and softer marn (Maastrichtian), Upper Sirnak Formation: the intercalation of the limestone with hard, compact marn and softer blue - grey marn, Lower Germav Formation: Soft, greenish marn, upper Germav formation: Well layered marn containing dark grey and hard brownstone banks. On top of the Germav Formation, the old, bluish grey colored Baricman chalk from Paleocene period can be found in patches. This limestone layer, which varies between 20 - 200 meters in thickness and which is not found around Harbon, is covered by the red coloured terrestrious Gergüş formation (dated back to Paleocene - Lower Eocene) that is comprised of thick layered conglomerate, limestone, shale and marn. This last formation is 800 - 1000 meters thick.

At the upper sections, the old Lutetian Midyat formation that is comprised of marine based limestone and is spread widely. The Neogenic terrestrial or marine brown stone is represented by the, clay, conglomerate and basalt. The Plio-Quaternary formations on the other hand, are comprised of the terrace sets, solely made of sandy – soiled pebbles. There are very large landslide areas in the region. Crushed brownstone, marn and large blocks that were broken off from Becirman chalk can be found in such sites and areas [7].

4. Material and Method

The asphalt mining in Sirnak Region is generally carried out by open cast mining method and the manufactured asphaltite are minced at Crushing – Screening facilities before putting on sale. On the other hand, the wall rock clay, produced during the manufacturing process is collected from dump sites in various sizes. In this study, whether the general purpose wall rock clay samples, obtained from the Avgamasya, Seridahli and Segürük asphaltite mines, which are some of the important asphaltite veins, active in Sirnak Region, have any area of utilization in Cement Industry or not was analyzed. General samples were collected from the aforementioned mining pits in compliance with the Sample Collection Methods and the SQX analysis was conducted in Anatolian University Ceramic Research Center Eskisehir.



Figure 1 Sirnak open cast mining and obtaining clay samples



Figure 2. Dump stock sites for wall rock clay in Sirnak

Pictures from the open cast mining activities in Sirnak Region can be seen in figure 1 while the figure 2 shows the dump sites for wall rock clay in Sirnak.

4.1 The Clay Analysis of the Wall Rock Sample from Sirnak Avgamasya Asphaltite Vein

The Avgamasya asphaltite vein lies towards southwest – northeast direction in the east of Sirnak Province. The works on the asphaltite vein were carried out on and off between 1964 – 1983. During those years, a total of 208 drilling were performed. 137 of the drilling works (1.677.85 m) were shallow drilling thus were conducted for the purposes such as preliminary asphaltite exploration, mining etc. The remaining 71 drilling works (vertical, inclined, deep > 11.060.95 m) were conducted for exploration and reserve purposes. Its reserve is 8.154.000 tons and its known length is 2600 meters. Its width varies between 8-50 meters (averaging 17 meters) The thickness was measured as 80 meters at its widest point. It has a cone shape and its inclination is close to perpendicular. Slope of the vein is towards northern west. The asphaltite material is almost always hard and fragmented towards the pockets of the vein. On the other hand, the material becomes highly fragile inside the wide parts of the vein. Therefore the material turns to dust during the processes. Its quality is as follows; Water 1%, Ash 38.81%, sulphur 6.70%, original lower heating value 4620 Kcal/kg. [6; 8-10].

Table 1 The results of the analysis of the wall rock sample from Avgamasya asphaltite pit

Avgamasya sample, SQX Calculation Result, Flux: $\text{Li}_2\text{B}_4\text{O}_7$						
Component	Result	Unit	Det.limit	El.line	Intensity	w/o normal
Na_2O	0.28	mass%	0.06	Na-KA	0.06	0.23
MgO	3.60	mass%	0.06	Mg-KA	1.72	2.90
Al_2O_3	3.72	mass%	0.06	Al-KA	5.71	3.00
SiO_2	11.81	mass%	0.03	Si-KA	17.40	9.52
P_2O_5	0.38	mass%	0.01	P-KA	1.82	0.31
SO_3	1.23	mass%	0.01	S-KA	4.14	0.99
K_2O	1.71	mass%	0.01	K-KA	16.81	1.37
CaO	17.77	mass%	0.02	Ca-KA	138.34	14.32
TiO_2	0.34	mass%	0.03	Ti-KA	1.19	0.27
V_2O_5	0.35	mass%	0.02	V-KA	1.84	0.29
Cr_2O_3	0.17	mass%	0.01	Cr-KA	1.93	0.14
Fe_2O_3	2.57	mass%	0.01	Fe-KA	63.83	2.07
NiO	0.12	mass%	0.01	Ni-KB1	6.19	0.10
ZnO	0.19	mass%	0.01	Zn-KA	17.45	0.16
A.Z.	55.75	mass%				55.75

The results of the analysis of the wall rock sample from Avgamasya asphaltite pit are indicated in Table 1. It is not useful for the production of bricks, tiles. When the results are reviewed, it is clear that the % Al_2O_3 and % SiO_2 values are not at the desired levels. Therefore, the clay sample, obtained from the vein is not suitable for the manufacturing of bricks and tiles.

4.2 The Analysis of the Wall Rock Sample from Sirnak - Seridahli Asphaltite Vein

The Seridahli asphaltite vein is located in the east of the Şilerut settlement towards Geffane in Southwest – North-western direction. The works on the vein were conducted between 1972 – 1986. During that period, a total of 23 prospection and 9 inclined drilling works (totally to 1.453.80 meters) were conducted. Its reserve is 6.067.000 tons. Its inclination was measured to be 74-88 degrees towards southeast direction. Its known length is 2520 meters. Its width, which is 5 meters in average, may decrease down to 0.40 meters in places. Its widest point was measured to be 14.30 meters. It is in a single crevasse fill form. It contains water %27.55, ash %27.53 and sulphur %3.07. Its original lower heating value is 2600 Kcal/kg. It is located at the ceiling of the Cudi cliff [6; 8-10].

Table 2 General analysis results of the upper clay, wall rock sample from Seridahli asphaltite pit

Seridahli sample, SQX Calculation Result, e Flux:Li ₂ B ₄ O ₇						
Component	Result	Unit	Det.limit	El.line	Intensity	w/o,normal
MgO	1.21	mass%	0.06	Mg-KA	0.65	1.12
Al ₂ O ₃	9.21	mass%	0.10	Al-KA	15.78	8.49
SiO ₂	30.04	mass%	0.05	Si-KA	48.88	27.69
P ₂ O ₅	1.08	mass%	0.01	P-KA	5.53	1.00
SO ₃	0.50	mass%	0.01	S-KA	1.82	0.46
K ₂ O	4.38	mass%	0.01	K-KA	45.91	4.03
CaO	10.03	mass%	0.01	Ca-KA	82.54	9.24
TiO ₂	0.72	mass%	0.03	Ti-KA	2.82	0.67
V ₂ O ₅	0.74	mass%	0.02	V-KA	4.46	0.68
Cr ₂ O ₃	0.16	mass%	0.01	Cr-KA	2.15	0.15
Fe ₂ O ₃	6.31	mass%	0.01	Fe-KA	171.87	5.82
NiO	0.16	mass%	0.04	Ni-KB1	1.76	0.15
ZnO	0.33	mass%	0.01	Zn-KA	31.58	0.31
MoO ₃	0.12	mass%	0.01	Mo-KA	40.94	0.11
A.Z.	35.01	mass%				35.01

The general analysis results of the wall rock sample from Seridahli asphaltite pit are indicated in Table 2. It is useful for the production of bricks, tiles. The results show that the SiO₂ % value is around 30 %. This suggests that the sample is a clay that can be used in cement industry.

Table 3 General analysis of the wall rock samples from Segürük asphaltite vein pit no:1 (+4mm.)

Segürük 1 sample, SQX Calculation Result, Flux:Li ₂ B ₄ O ₇						
Component	Result	Unit	Det.limit	El.line	Intensity	w/o normal
Na ₂ O	0.51	mass%	0.08	Na-KA	0.11	0.55
MgO	16.39	mass%	0.07	Mg-KA	10.02	17.61
Al ₂ O ₃	10.25	mass%	0.09	Al-KA	19.53	11.01
SiO ₂	45.63	mass%	0.05	Si-KA	82.15	49.03
SO ₃	0.28	mass%	0.01	S-KA	1.09	0.30
K ₂ O	1.03	mass%	0.01	K-KA	11.76	1.11
CaO	3.66	mass%	0.01	Ca-KA	33.86	3.93
TiO ₂	0.55	mass%	0.02	Ti-KA	2.54	0.60
Cr ₂ O ₃	0.21	mass%	0.01	Cr-KA	2.83	0.23
MnO	0.09	mass%	0.01	Mn-KA	2.11	0.10
Fe ₂ O ₃	9.45	mass%	0.05	Fe-KB1	60.05	10.15
NiO	0.11	mass%	0.01	Ni-KA	6.57	0.12
A.Z.	11.85	mass%				11.85

Its composition 42%-64% SiO₂ , 15% -20% Al₂O₃, 8 % CaO includes the necessary ratios for the production of bricks and tiles. 1%- 2% MgO ve CaO are required for the production of ceramic. Its approximate content of 25% SiO₂ is used in cement production. The General analysis results of the wall rock samples from Segürük Asphaltite Vein Pit No 1 and 2 are indicated in Table 3 and 4. They are suitable for the production of bricks and tiles. The results of the analyses suggest that both samples have the clay properties that are suitable for the production of bricks and tiles.

Table 4 General analysis of the wall rock samples from Segürük asphaltite vein pit no:2 (+4mm.)

Segürük 2 sample, SQX Calculation Result, Flux:Li ₂ B ₄ O ₇						
Component	Result	Unit	Det.limit	El.line	Intensity	w/o normal
Na ₂ O	0.33	mass%	0.08	Na-KA	0.07	0.36
MgO	16.82	mass%	0.07	Mg-KA	10.36	18.19
Al ₂ O ₃	8.15	mass%	0.09	Al-KA	15.67	8.82
SiO ₂	40.14	mass%	0.05	Si-KA	73.16	43.42
SO ₃	0.11	mass%	0.01	S-KA	0.44	0.12
K ₂ O	0.81	mass%	0.01	K-KA	9.41	0.87
CaO	9.77	mass%	0.01	Ca-KA	91.58	10.57
TiO ₂	0.47	mass%	0.02	Ti-KA	2.09	0.50
Cr ₂ O ₃	0.19	mass%	0.01	Cr-KA	2.52	0.21
MnO	0.10	mass%	0.01	Mn-KA	2.22	0.11
Fe ₂ O ₃	8.17	mass%	0.05	Fe-KB1	50.29	8.83
NiO	0.11	mass%	0.01	Ni-KA	6.87	0.12
TeO ₂	0.10	mass%	0.03	Te-KA	4.90	0.11
BaO	0.27	mass%	0.03	Ba-KA	4.98	0.29
A.Z.	14.46	mass%	0.05			14.46

5. Conclusions

The mining activities may lead to environmental effects such as water pollution, insensitivity, visual pollution disruption of the ecosystem, increased amount of dust particles and erosion. In addition, during the mining activities, a large amount of waste is generated depending on the waste / product ratio. Mining wastes is comprised of the plantal top soil, seal-excavation (stripping), waste rocks, clay and wastefill. The mining wastes should be collected, transported and recycled or eliminated. In order to prevent the adverse effects of the mining wastes on the environment, the recycling bears utmost importance. There are recycling methods in Turkey that are being developed and are in project phase. For example; the production of clean coal from the waste of clay containing coal preparation facilities and the utilization of the waste clay for the production of bricks are some of such methods.

The main characteristic of the clay minerals is that they contain aluminium oxide (Al₂O₃) in their chemical composition and that they are made of aqueous aluminium silicates. Iron and alkaline is found within the soil in varying amounts. Any clay mineral variety is hydrothermal based. The clays, used in cement industry as raw materials is loamy and calcareous soil that is formed after the alteration based metal oxides are carried out to an accumulation basin or is formed in place as an alteration mantle in Neogene, Quaternary alluvium and under the terrestrial conditions on the upper levels of the Neogene basins. The clay, which is the main component of the calcareous soil that can be found in the nature abundantly, is also one of the most important raw materials of the industry. Most of the products that we use in our daily lives is made of a clay material.

The wall rock clay, produced as the result of the Turkey – Sirnak mining activities is accumulated within the waste storage sites. Using this clay that is deposited to the waste sites in cement industry or in brick – tile production will prevent the visual and environmental pollution and will provide a beneficial contribution to those industries. This study concluded that the clay samples, obtained from Sengürük and Serihdali asphaltite pits contain materials that are suitable for cement and brick – tile industry. However, it has also demonstrated that the samples, obtained from Avgamasya pit cannot be used in those industries. This study is a preliminary analysis and thus should be supported and supplemented by new samples and experiments to a larger extend.

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