

Types of natural bitumens, composite properties and their classification

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Abstract. Asphaltites are hard, brittle and form a rough and uneven surface due to their physical properties. They have a glassy luster, can be ground to a powder state and melt at relatively high temperatures above 1000°C. Classification of the main deposits of bitumen and bituminous rocks of Azerbaijan.

Keywords: bitumens, petroleum, shale, coal tar, bituminous rocks

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1. Introduction. Natural bitumen, due to its chemical properties, is highly stable, durable, flexible, water-resistant, convertible, etc. That is why in ancient times people used bitumen as a waterproofing and binding material. Bitumen was used to cover water and grain storage facilities, the walls and floors of palaces, and to cement stone-paved city streets.

Aristotle and Hippocrates, who lived four centuries BC, wrote about bitumen deposits. Historical documents from the 8th century contain information about the existence of solid bitumen deposits in Baku and its environs.

In the Middle Ages, travellers and naturalists reported on Absheron's oil deposits, as well as bitumen deposits. In his notes, Marco Polo noted the occurrence of bitumen on Absheron, and its use for burning and treating animals. Later, oil began to be produced from bitumen [12].

Bitumen is a natural raw material consisting primarily of a mixture of carbon and hydrogen with a small amount of oxygen and sulfur-nitrogen substances, a small amount of metals and a significant amount of asphaltene-resinous substances.

2. Methodological part. Easily soluble in sulfur dioxide, chloroform and other organic solvents. Oil, shale, and coal bitumen are widely distributed in nature. Azerbaijan has abundant petroleum bitumen. The elemental composition of bitumen is approximately as follows: carbon 80-85%, hydrogen 8.0-11.5%, oxygen 0.2-4.0%, sulfur 0.5-7.0%, nitrogen 0.2-0.5%. The amounts of sulfur and nitrogen in petroleum bitumen vary greatly.

Absheron bitumen contains the lowest amount of sulfur (on average 0.8%) and a minimal amount of nitrogen [2].

Bitumens are divided into solid (sticky) and solid petroleum bitumens, solid and solid shale bitumens, and coal tar. According to R.B. Gun, Table 1 presents the range of petroleum bitumens produced for sale in the territory of the former USSR [3].

As can be seen from this table, bitumen is mainly used as a paint and insulating material when laying asphalt on roads and in various construction works [13].

Table 1. Assortment of bitumens released for sale in the territory of the former USSR, according to R.B. Gun [13].

Group	Semi-group	Brand	Standard
Solid petroleum bitumen (viscous, sticky, plastering) for roads	for roads	BND-200/300, BND-30/200, BND -90/130, BND-40/60, BND-200/300, BND-30/200, BN-90/130, BN-60/90	GOST-22245-76
	for construction	BN -50/50, BN -70/30, BN -90/10, BHCK-5	GOST-6617-76 THAT 38101397-73
	for the production of ceiling coverings or roofing and waterproofing	BNK -45/180 BNK -90/40, BNK -90/30	GOST- 9548-74
			THAT-38101566-75
	special	for color: batteries, special volumes	GOST -8871-76
		with signs B, V, G in the field of paints and varnishes, tires, electrical engineering	GOST -21822-76
		In the rubber and tire manufacturing industry. Brands A and B	GOST - 781-68
		For pipeline insulation. Brand BNI-IV, BNI-V.	GOST 9812-74
		for obtaining the metal paint color AB-2	THAT -39-013-73
	Dry petroleum bitumen	road	BK-25/40, BK -40/70, BK -70/130, SKB-40/70, SKB -70/130, SKB -130/200, MK-25/40, MK-70/130, MQ-130/200
Coal tar	for roads	Д-1, Д-2, Д-3, Д-4, Д-5, Д-6	GOST-4641-74
	special	for painting firewood Du-7, Du-8 (sharban)	THAT -6-16-1163-67
Hard (viscous, sticky) shale bitumens	for roads and sidewalks	BS-0, BS -1, BS -2, BS -3, BS -4, BS -5, BS -6	THAT -6-08-304-74
	For painting and insulation	BS -1, BS -II, BS -III	THAT -38 10941-75
Pure shale bitumens	for roads and sidewalks	S-1, S-2, S-3	THAT -6-08-304-74

Until recent years, bituminous rocks in Azerbaijan were studied for two purposes: 1) as an exploration factor in predicting oil deposits formed at depth, and 2) for the extraction of high-viscosity oil from bitumen using mine and quarry methods.

The use of bituminous rocks in road construction continues to be successful to this day. Bitumen is also used in other applications. In recent years, a number of countries have focused on extracting various metals from natural bitumen.

3. Results and discussion. It is known from geological literature that in some cases, bitumen contains high concentrations of metals such as vanadium, nickel, scandium, rhenium, molybdenum,

titanium, etc. Thus, the concentration of these useful components in bitumen is 5-10 times higher than in the surrounding rocks.

High amounts of vanadium have been found in bitumen deposits in Venezuela and the CIS in Tatarstan, Emba, and Ukhta. Shales and viscous bitumens sometimes form unique uranium-bitumen deposits, which also contain very large reserves: for example, the Ambrosia Lake deposit in New Mexico, USA.

Figure 1 shows the composition and sequence of formation of natural petroleum bitumens.

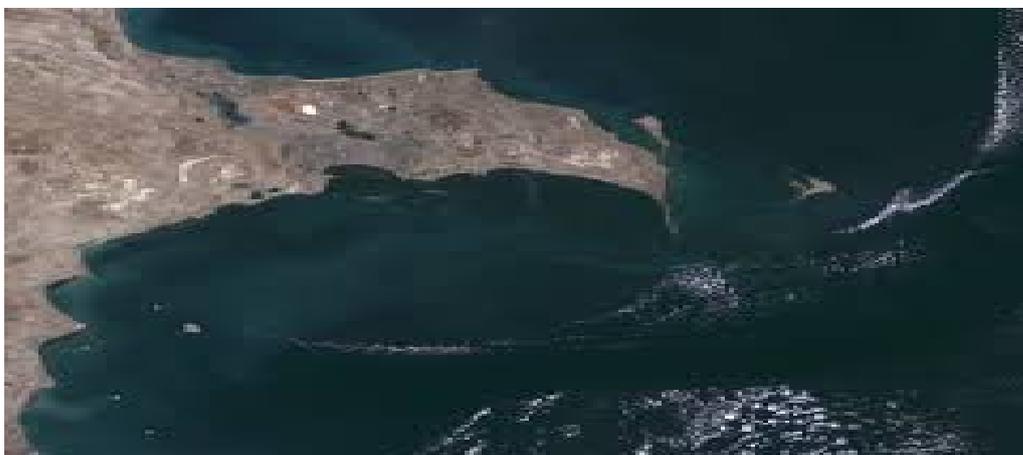


Figure 1. Formation of natural petroleum bitumen

As can be seen from the figure, on the one hand, bitumen is successively formed from naphthenic-methane and naphthenic oils in the form of malts, asphalts, asphaltites, kerites and anthroxolites, and on the other hand, waste is formed from methane and methane-naphthenic products.

Table 2 presents the classification of the main deposits of bitumen and bituminous rocks in Azerbaijan.

According to the classification, the main deposits of bitumen and bituminous rocks of the republic are located in Absheron, Shamakhi-Gobustan and the Lower Kuryansk oil and gas region.

In this table, in the composition of bitumen, along with oils, at the Kirmaki deposit, polyesters and resins make up 50.1-78.5%, at the Ziyilpiri deposit 21.0-47.91%, at the Binagadi deposit 3.65-19.5%, at the Shubani deposit 6.43-11.68%.

This shows that oils and polyester resins are distributed differently in bitumen at oil fields. There is no difference in the distribution of benzene resins (6.4-16.20%), alcohol-benzene resins (85-32%), and asphaltenes (13-43%) in bitumen.

The carbon content of these bitumens is typically 75-85%, the hydrogen content is approximately 9-12%, and the oxygen, nitrogen, and sulfur content is approximately 2-4%. The bitumens in all of these deposits are of the solution and asphalt types.

Table 3 shows the chemical composition of natural bitumen from the Beridash deposit of the Shemakha-Gobustan oil and gas region.

Table 2. Classification of the main bitumen and bituminous rock deposits in Azerbaijan

Oil-gas-tuminous region (NGBR)	Bituminous rocks		Deposits
	Geochronological age	Lithological composition	

Absheron	Balakhany (Productive Layer) Stage (N ² ₁ b ₁) Balakhany (Productive layer) stage (N ² ₁ b ₁)	Sandy, siltstone, clayey, limestone deposits, sandstones, limestones, siltstones	Fatmai, Sianshor, Dighah, Pirallahi, Kirmaki, Binagadi, Ziyilpiri, Shubani, Puta
	Sarmatian N ₁ ³ , Chokrak N ₁ ² , Diatom and Maykop, Chokrak N ₁ ² bases	Sandy, siltstone, clayey deposits	Shorbulag
Shamakhi-Gobustan	Chokraksky N ₁ ² stage	Sand, sandstone, siltstone, clay	Girgyshlak, Nardaran, Akhtarma, Cheildag
	Absheron (Q ¹ ab), Agchagil (N ² ₂ ak) and Lower Caspian (Q ¹¹ hz ¹) stages and substages	Medium and fine-grained sands, detrital limestones, gray clays	Rakhim, Gylych, Barydash, Solohai, Ayrantokan, Girdag
Near the Kura Depression	Balakhany (Productive layer) stage (N ₂ ¹ b ₁)	Granular sands, siltstones, clays	Kirlykh, Akhtarma, Gyrrykh, Babazenen, Pashaly, Merkezi, Akhtarma

Table 3. Chemical composition of natural bitumen from the Beridash deposit

Layer	Bitumen content, %	Group composition of bitumen				Elemental composition of bitumen		
		Oils (+PE resins)	Benzene resins	Alcohol-benzene resins	Asphaltenes (+carbenes)	C	H	O+N+S
I	35.82	40.45	9.25	21.34	28.95	78.98	10.13	2.15
II	59.25	36.52	8.63	27.05	26.98	-	-	-
I	2.65	46.42	10.22	19.05	24.31	81.31	11.75	-
II	3.83	19.67	6.03	31.80	42.50	-	-	-
I	18.14	26.8	4.7	24.6	37.6	-	-	-
II	5.41	20.9	9.7	20.3	49.1	-	-	-
III	7.23	26.1	5.3	17.8	48.8	-	-	-
IV	3.45	27.2	8.1	22.8	36.1	-	-	-
V	41.78	20.6	11.3	23.6	38.9	-	-	-
VI	11.99	23.7	9.1	24.5	42.8	-	-	-
VII	11.99	24.7	16.9	15.7	42.8	-	-	-
VIII	4.35	8.0	3.4	6.7	76.6	-	-	-

Layer	Hydrocarbon composition group, %			Low molecular weight	Bitumen grade
	Percentage of fractions				
	Methane-naphthenic	Aromatic			
		Monocyclic	Polycyclic		
I	50.91	35.43	14.05	12.96	Asphalt
II	52.73	10.60	28.19	8.50	
I	65.97	13.04	13.29	2.88	Malta
II	61.42	5.94	27.74	3.76	Asphaltite
I	70.1	17.8	8.1	2.8	Asphalt
II		59.4	31.0	9.3	-
III	60.0	19.5	21.8	9.0	-
IV	37.5	29.1	30.1	9.0	-
V	56.7	19.0	19.8	4.5	-
VI	58.80	18.1	19.0	9.4	-
VII	0.8	57.7	33.4	12.6	-
VIII	68.8	6.7	27.5	7.9	Asphaltite (grehemite)

In these bitumens, along with oil, polyester, benzene, and alcohol-benzene resins and asphaltenes are distributed almost evenly. Only in layer VIII, the very last layer, does the amount of asphaltenes increase sharply, while the other resins, on the contrary, decrease sharply.

Table 4 presents the characteristic properties of some bituminous rocks of the Absheron Peninsula. The table shows that, for individual deposits and samples, the bitumen content in the rock ranges from 3.65% to 19.5%.

However, in most cases it is 7–10%. Bitumen has a density of mainly 1.08–1.11 g/cm³ and foams at a heating temperature above 1500 °C [11].

Table 4. Characteristic properties of some bituminous rocks of the Absheron Peninsula

Deposit	Extracted bitumen	Results of various tests					
Kirmaki	Bitumen content in rock -%	7.26	9.17	10.12			
	Bitumen density – g/cm^3 , at 250 ⁰ S	1.081	1.095	1.11			
	Permeability at - 25 ⁰ S	0	0	0			
	Duntillik-25 ⁰ S temperaturda	0	0	0			
	Lower temperature	Foams when heated above 150 ⁰ C					
Ziilpiri	Bitumen content in rock -%	7.09	8.83	12.38			
	Bitumen density – g/cm^3 , at 25 ⁰ S	1.09	1.11	1.129			
	Regeneration at -25 ⁰ S	0	0	0			
	Duntillik at temperature -25 ⁰ S	0	0	0			
	Low temperature	Foams when heated above 150 ⁰ C					
Binagadi	Bitumen content in rock -%	19.5	9.30	14.36	9.68	6.48	3.65
	Density of bitumen, g/cm^3	1.084	-			1.91	
Shubany	Bitumen content in rock -%	8.13	11.68		6.43		
	Lower bitumen temperature	Foams when heated above - 150 ⁰ C					

In classifications, the term "asphalt" refers to types of bitumen that are readily soluble and have a solid resinous content and occupy a transitional position between solutions and asphaltites, and also melt at high temperatures.

The oil content of asphalt ranges from 25–40%. Physically, asphalt is a brittle, glassy, and sometimes opaque mass. It softens with gentle heating. The softening point of asphalt ranges from 20–300°C to 80–1000°C. This depends on the amount of asphaltenes it contains (Fig. 2).

Depending on the asphaltene content (10-15%-40-45%), asphalts are classified into different types. The amount of coke in asphalts is small (10-20%). The elemental composition of asphalt consists of 80-85% carbon and 9-10% hydrogen. The sulfur content varies widely: from 7 to 10%. The oxygen content is 2–3% and depends on the intensity of oxidation. Changes in nitrogen content are caused by oxidation. Typical asphalts are bitumens, which contain equal amounts of oil, resin, and asphaltenes.

Asphaltic asphalts are solid bitumens containing less than 25% of the oil component and, accordingly, more than 75% of asphalt-resinous substances completely soluble in chloroform.

Asphaltites are hard and brittle in their physical properties, producing a rough and uneven surface. They have a vitreous luster, can be ground to a powder, and melt at relatively high temperatures (over 1000°C). Asphaltites are divided into two large groups: clay-sonite and greimite. Academician Sh.F. Mekhtiyev (1957) distinguished the following types of natural bitumen in Azerbaijan: asphalt, asphaltite, kir, wet kir, and bituminous sands. Here, asphalt and asphaltite are understood as indicated above [5, 6, 7].

The term "shale" refers to bituminous rocks composed of dark, uniform clays. The bitumen content of oil deposits ranges from 2% to 30%, sometimes much higher.

4. Conclusions. Bituminous sands are sandy rocks impregnated with bitumen, are classified as natural petroleum asphalts and are considered a product of oil weathering.



Figure 2. Laying asphalt pavement

Malta is a type of bitumen, a cross between petroleum and asphalt. Its specific gravity is close to 1.0. According to V.A. Uspensky's classification, the oil content in malt ranges from 40% to 65%. Its elemental composition is 80-87% C, 10-12% H, and the S and O² content varies widely. Malta solutions differ from asphalts and asphaltites in their viscosity and stickiness.

Natural genetic types of bitumen, such as malta, asphalt, and asphaltite, are widespread in the deposits of the Absheron Peninsula. Among the natural bitumens, greite and even anthroxolite are sometimes found, which are considered products of high-grade metamorphism of bitumen [10].

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research.

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