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Upgrading Iranian petroleum sludge using polymers

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Abstract

One of the most valuable wastes of the oil industry is oil sludge, found at oil wells, oil pipelines and refineries, and stored in storage units. Oil sludge has many similarities with heavy oil components. This study evaluates the use of oil sludge from the Iranian Oil Pipelines and Telecommunication Company for the manufacture of asphalt. The approximate structure of the oil sludge was analyzed and compared with the structure of conventional bitumen for road construction. Marshall asphalt samples were analyzed according to the American Society for Testing and Materials D1559 0–5–7.5–10–12.5 standard using 15% oil sludge with bitumen and aggregate. To study the physical characteristics of samples of Marshall asphalt, two important tests were performed (1) to determine the pressure resistance, and (2) the relative deformation of examples of all samples. The results showed that asphalt resistance is increased using 25–50% sulfur and 2–7% butadiene styrene polymer. Therefore, Marshall asphalt samples with 30% sulfur were prepared with bitumen and oil sludge. Fifty percent oil sludge in bitumen and a 2% polymer and 15% oil sludge mix with bitumen gave the best results. These mixtures are economically viable.

Keywords Oil sludge · Asphalt · Marshall resistance · Styrene-butadiene-styrene · Polystyrene

Introduction

During drilling, transportation and refining of crude oil, oil sludge is produced. In general, “oil” refers to non-hydrophilic, petroleum-based materials, or vegetable and synthetic oils. During the biological treatment of industrial chemical wastewater, surplus biological sludge is always produced. At oil refineries, both oil sludge and biological sludge are produced on a daily basis. It is estimated that sludge represents between 30 and 40% of the investment cost and 50% of the operating costs of oil refineries (Kim et al. 2009). In general, oil sludge produced in oil refineries contains organic and inorganic substances that are different from other refinery products, and factors such as crude oil composition, size and age of the refinery have an effect on these (Kai et al. 1985). One of the major environmental problems associated with all oil industries, including refineries, petrochemical plants, mines and transportation terminals, is oil sludge containing heavy metals and petroleum compounds at various stages of processing.

Due to its high compatibility, high temperature resistance, and high salt tolerance, oil sludge is also used in the production of asphalt concrete (Qinga et al. 2008). Asphalt, or bitumen, must be resistant to harsh conditions over the long term (Lewandowski 1994). Bituminous mixtures are used in Iran in mixes to form asphalt mixed with aggregates. There are different types of asphalt surfacing, e.g., for paved roads and airports. Aggregates are usually natural, synthetic or indirectly produced by factories producing melted metals. In most cases, natural stones have to broken down by crushers to achieve the fine grade required for mixing in with asphalt. Aggregates used to make different types of asphalt should have special characteristics that include different grain, hardness, durability, cleanliness, grain shape and surface quality. Material gradation is one of the main processes used to give the strength and load-bearing capacity to asphalt. Bitumen is a very important component and is used with a number of different coatings for reinforcement. Among these are specific coatings for oil and gas (Haddadi et al. 2007).

Bitumen has a complex chemical structure and is composed of compounds found in crude oil. Petroleum bitumen comprises a large number of different colloidal and

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suspended hydrocarbons. Carbon and hydrogen are the two main elements of bitumen, and their percentage by weight is 70–87 and 10–15%, respectively. In addition to carbon and hydrogen, other elements such as nitrogen, phosphorus, halogens and metals such as nickel, iron, cobalt and vanadium are found in bitumen. Crude oil can be fractionated into asphaltene and Malten. Malten is a group of petroleum aromatic compounds into which polar aromatic (resin) and saturated (paraffin) compounds are classified. The physical and chemical properties of bitumen are the determining factors for its use, and are affected by the quantity and quality of its ingredients and the process of refining hydrocarbons. Additives used to change the characteristics of asphalt, especially for concrete pavement, have lead to improved technical specifications. The first examples of asphalt sulfur were created in America and Canada in the mid-seventies (Bissada 1985). Increasing the sulfur content improves the properties of bitumen, including enhanced permeability, reduced viscosity and improved adhesion of the bitumen for aggregation, and has been used to produce asphalt concrete with higher mechanical resistance (Kandhal 1982). The pavement performance of sulfur-extended asphalt in different parts of the world indicates consistency of performance in most regions, equal to or better than that of conventional asphalt (Filippis 1998). Economic factors, such as increased lifespan and durability compared to conventional asphalt promote the use of asphalt after sulfur has been added, and increases savings due to energy expenditure by reducing the temperature necessary for the production of the asphalt mix (Miller 1981) and to make it resistant to oil-based solvents.

A pure bitumen (asphalt) mixture used as linker has many shortcomings in terms of its performance. Efforts have been made to eliminate these defects by modifying bitumen. Polymers are the most common class of material used to modify bitumen (Tayfur et al. 2007). Different polymers have their own advantages and disadvantages and they can be used to modify the characteristics of bitumen to reach an ideal (Airey 2004). In general, polymers used in modified bitumen fall into three groups: rubber, thermoplastic polymers and thermoset polymers. These materials increase the strength of bitumen concrete, and also prevent the spread of reflection cracks, extend the operational life, reduce the cost of asphalt pavement and help to solve environmental problems (Shirkavand Hadavand and Aznaveh Yazdi 2011).

Features of sludge in oil tanks differ hugely (Yildim 2007). Annually, about 500 t of oil sludge is produced. Accumulated in oil sludge are additives such as suspension agents, dispersion agents and thickeners, which pose a serious problem for the environment. The use of oil sludge in useful materials such as low molecular weight organic compounds and carbon residues helps to solve the problem of its disposal, as does its use in the manufacture of cement and asphalt (Chang et al. 2000). The recovery of oil from oil sludge is of considerable importance, and finding ways of avoiding wasting this valuable material has been on the agenda of universities and research centers for some time. Sulfur compounds mixed with bitumen can increase its strength, modulus of rigidity, deformability, viscosity, and different methods of safe production have been studied for this. Increasing the sulfur content by 30–50% in bitumen causes the bitumen to have significantly increased resistance. Among a variety of polymers, styrene-butadiene-styrene (SBS) is mostly used in modified asphalt (Chen and Huang 2007). Adding from 3 to 6% of the polymer significantly improves the flexibility, resistance and temperature sensitivity of asphalt (Chen and Huang 2007). The viscosity of bitumen solutions in heptol and heptane above the level causing the onset of asphaltene precipitation has been studied by Mozaffari et al. 2015). Capillary driven flow under Bingham yield stress has also been investigated (Mozaffari et al. 2017).

Materials and methods

Marshall asphalt samples were characterized after homogenization with oil sludge to determine the temperature of combustion for oil bitumen mixes with different proportions of components. Strength, compression and relative deformation tests were performed on the samples.

Substances used

The tested substances are as follows: sludge oil, bitumen (Khalsa 60–70), aggregates, sulfur, polymers.

Tests on pure bitumen

The ash-weight, penetration grade, softening point, stretch, viscosity, and weight loss, were the technical characteristics of bitumen determined according to standard American Society for Testing and Materials (ASTM) methods (Table 1; bitumen base 60–70).

Test to determined the temperature of combustion of oil sludge

The temperature of combustion of bitumen was determined according to ASTM D92. The ignition temperature was 326 °C, but oil sludge containing volatile and lighter components had a lower ignition temperature.

Table 1 General results of bitumen base 60–70

Sample number	ASTM		Test method	Property	Results
	Minimum	Maximum	ASTM		
1	232	–	D 92	Temperature of combustion	326
2	–	–	D 70	Special weight	1.016
3	60	70	D 5	Degree of influence	63
4	49	56	D 36	Softening point	50
5	100	–	D 113	Hoist	115
6	–	–	D 2170	Kndrvany	244
7	–	0.8	D 1754	Weight loss	0

ASTM American Society for Testing and Materials

Table 2 The temperature of combustion of bitumen mixed with different percentages of oil sludge

Sample number	Temperature of combustion	Bitumen weight (g)	Weight of oil sludge (g)	Percentage of oil sludge
1	326	83.4	0	0
2	308	79.23	4.17	5
3	278	77.15	6.25	7.5
4	240	75.06	8.34	10
5	204	73	10.42	12.5
6	165	70.89	12.51	15

Test to determine the temperature of combustion of bitumen mixed with oil sludge

Various percentages of oil sludge were added to the bitumen and then the temperature of combustion determined for all samples according to ASTM D92. Table 2 shows that with an increasing percentage of oil sludge the temperature of combustion of bitumen decreases. With increasing temperature, gases released from the bitumen surface ignited when they reached the flame.

By increasing the ratio of oil sludge to bitumen a series of chemical reactions between bitumen and petroleum sludge occurred that was followed by decreased stability of bitumen and ignition of gases at lower temperatures. According to standard ASTM D92, the minimum acceptable ignition temperature for pure bitumen is 232 °C. Samples 2 and 3 with, respectively, 5 and 7/5% of oil sludge to bitumen, had acceptable temperatures of combustion at 308 and 278 °C, but samples 4, 5, 6, respectively with 5, 12/10, 15% of oil sludge to bitumen, did not. The temperatures of combustion of bitumen were lower than the minimum acceptable ignition temperature.

Results and discussion

Pressure resistance and relative deformation test

Pressure resistance and relative deformation tests were conducted on all samples, and the results are shown in Table 3.

The pressure resistance and relative deformation (soft) of asphalt made with a mixture of bitumen and oil sludge decreased as the percentage of oil sludge increased. This was due to the reduced adhesion properties of the bitumen molecules, which lead to the formation of Marshall asphalt with less physical resistance. Marshall asphalt samples with at least 800 kilogram force (kgf) resistance, and 2–3/5 mm softness are acceptable, as seen for sample 1, with 963/9 kgf resistance and 3/5 mm softness, and sample 2 with 907/2 kgf resistance and 3/4 mm softness.

Table 3 The pressure resistance and relative deformation results

Sample number	Softness (mm)	Resistance (kgf)	Gauge degree	Weight of oil sludge (g)	Bitumen weight (g)	Percentage of oil sludge
1	3.5	963.9	255	0	83.4	0
2	3.4	907.2	240	4.17	79.23	5
3	3.3	756	200	6.25	77.15	7.5
4	3	699.3	185	8.34	75.06	10
5	2.9	642.6	170	10.42	73	12.5
6	2.7	623.7	165	12.51	70.89	15

Asphalt sulfur

Asphalt sulfur can be produced by: (1) the mixing of hot bitumen and sulfur, (2) injecting sulfur by weight (solid or liquid) directly into an asphalt mix. Both methods are straightforward and reduce pollution caused by the production of hydrogen sulfide. The resistance of Marshall asphalt (bitumen, oil sludge) in comparison with sample 1 with 963/9 kgf resistance was not satisfactory (Table 4). The amount of sulfur compared to oil sludge (weight of bitumen = 73 g, weight of sludge = 10/42 g) was calculated for bitumen, oil sludge, bitumen and old sludge. Some of the bitumen properties were altered by the presence of sulfur atoms in the chemical structure, which increase the resistance of asphalt, and the formation of polysulfides, which soften bitumen, giving it more elasticity and increased resistance.

Sulfur generally increases the resistance of samples, but according to our results the addition of 30% sulfur to three samples, A, B, C, reduced the resistance compared to a sample with 12/5% of oil sludge. The reason for this may be the oil sludge acting as a factor that inhibits the reaction between sulfur and bitumen molecules (i.e., that prevents the formation of polysulfides), as has been previously shown. In samples A and C only the softness, respectively, of 2, 2/1 mm was acceptable.

Polymer bitumen

For the production of Marshall mix asphalt with compressive strength and softness, SBS polymer was added to a mixture of bitumen and oil sludge. The components were prepared in separate containers. Then each of the containers containing bitumen and oil sludge was placed in an oven at temperatures of up to 180 °C. The polymer was then added to the bitumen and oil sludge. To mix bitumen, oil sludge and the polymer at 180 °C, a dispersant device was used. Materials were mixed for 30 min at around 7500 r.p.m. to create the asphalt samples. The compressive strength and relative deformation (soft-physical) were then determined for all the samples. The modified bitumen samples were examined in two stages.

Stage 1: production of samples of Marshall asphalt (bitumen plus oil sludge plus polymer)

SBS polymer, as the best additive to bitumen, was applied in two stages. Marshall asphalt samples were prepared as a mix of bitumen with 5% of oil sludge. The percentages of polymer for the different samples are shown in Table 5.

Pressure resistance and relative deformation tests were performed on all samples. Sample 3, despite having higher resistance (1323 kgf) than the other samples, and high softness (4/8 mm), was not acceptable. Samples 4 and 5 were both soft (3 mm), while sample 6 had a resistance and softness, respectively, of 896/4 kgf and 2/5 mm, both of which

Table 4 The results of pressure resistance and relative deformation tests

Sample number	Sulfur weight (g)	Weight of oil sludge (g)	Bitumen weight (g)	Percentage of sulfur	Characterization
1	0	0	83.4	0	–
2	0	10.42	73	0	12.5% of sludge
3	21.9	10.42	51.1	30	A
4	3.126	7.294	73	30	B
5	25.026	7.294	51.1	30	C

A Bitumen, B oil sludge, C bitumen and old sludge

Table 5 Pressure resistance and relative deformation test (stage 1)

Sample number	Softness (mm)	Resistance (kgf)	Gauge degree	Weight of polymer (g)	Weight of oil sludge (g)	Weight of bitumen (g)	Weight of oil sludge (g)	Percentage of oil sludge	Percentage of polymer
1	3.5	963.9	255	0	0	83.4	0	0	0
2	3.4	907.2	240	0	4.17	79.23	4.17	5	0
3	4.8	1323	350	0.834	4.1283	78.4377	4.1283	5	1
4	3	1115.1	295	1.668	4.0866	77.6454	4.0866	5	2
5	3	1096.2	290	4.17	3.9615	75.2685	3.9615	5	5
6	2.5	869.4	230	5.838	3.8781	73.6839	3.8781	5	7

Table 6 The results of the pressure resistance and relative deformation tests (stage 2)

Sample number	Softness (mm)	Resistance (kgf)	Gauge degree	Weight polymer (g)	Weight of oil sludge (g)	Bitumen weight (g)	Percentage of oil sludge	Percentage of polymer
1	3.5	963.9	255	0	0	83.4	0	0
2	2.7	1134	300	1.668	8.1732	73.5588	10	2
3	3	1039.5	275	1.668	12.2598	69.4722	15	2
4	3.8	1077.3	285	4.17	7.923	71.307	10	5
5	5.3	1209.6	320	4.17	11.8845	67.3455	15	5

were acceptable, with 7% of polymer, which compares well with samples with 2 and 5% polymer, which showed less valuable properties. The samples with 4 and 2% polymer were the best, with a resistance of 1115/1 kgf and softness of 3 mm.

Stage 2: production of samples of Marshall asphalt (bitumen plus oil sludge plus polymer)

The results of pressure resistance and relative deformation for these samples are shown in Table 6. The resistance was higher than for the previous samples. However, although samples 2, 4 and 5 showed high resistance they were too soft, hence unsuitable. Only samples with 3 and 2% polymer and 15% of oil sludge had an acceptable resistance of 1039/5 kgf and 3 mm softness. The results in Table 6 show that by increasing the amount of polymer, significant changes to the resistance in comparison with previous samples (samples prepared with bitumen and oil sludge, and samples prepared with sulfur) were obtained. The resistance and softness of samples 1 and 2 increased and then decreased.

Therefore, using the resistance properties of polymers, the softness of the products can be modified.

The pavement resistance of bitumen, due to a reduced penetration grade, can be increased by using SBS. SBS is a flexible long-chain polymer and its thermoplastic properties cause the reduction in the penetration grade of bitumen mixed with it. A three-dimensional network of polystyrene blocks and butadiene middle blocks occur in bitumen with thermoplastic properties (polystyrene blocks), which cause increasing viscosity of the bitumen at high temperatures, and as a result, the penetration grade of the bitumen is reduced, proven by tests of softening point. However, due to the presence of these blocks with elastic properties (butadiene middle blocks) at low temperatures, the bitumen also has good elasticity. Then, by increasing the percentage of polymer, reduced resistance and softness can be achieved, i.e., dominance of the polymer network in the bitumen, which gives morphological discontinuity.

Conclusion

There is currently an increased demand for oil-based resources worldwide. However, the fossil fuel industry and transportation of crude oil, especially in Iran, are associated with the waste of valuable materials due to mismanagement, which is considered one of the biggest problems in this industry. One of the best solutions for this oil waste is the use of oil sludge in various industries including the construction industry. The most important results of the present study, which examined the mixing of oil sludge with bitumen for the manufacture of asphalt, are:

1. Due to a reduction in the stability of the bitumen molecules, the ignition temperature is reduced, but this reduction is not a barrier to the use of Marshall asphalt in construction according to fire hazard tests carried out in the laboratory.
2. By applying oil sludge to bitumen its resistance is reduced because oil sludge reduces the adhesion property of bitumen.
3. The use of sulfur with bitumen and oil sludge did not increase the Marshall strength and caused a reduction in resistance. The oil sludge prevented the formation of polysulfides between the bitumen and sulfur molecules.
4. The use of SBS polymer with bitumen and oil sludge is effective for the production of asphalt, and increased the resistance of samples.

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