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A novel method for recovery of acidic sludge of used-motor oil reprocessing industries to bitumen using bentonite and SBS

Ahmad Jonidi Jafari[1], Malek Hassanpour[2], Mitra Gholam[1], Mehdi Farzadkia[1]

1- Department of Environmental Health Engineering, School of public health, Iran University of Medical Science, Tehran, Iran
2- MSc Student of Environmental Health Engineering, School of Health, Tehran University of Medical Science

** Author for Correspondence: malek.hassanpour@yahoo.com*

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ABSTRACT

Acidic sludge is a by-product from used motor oil reprocessing industries, which thousand tons of this sludge are disposed into the environment as a hazardous waste material daily .The acidic sludge contains unsaturated compounds that are polar and asphaltene. The bitumen under certain conditions is produced from mixing of bentonite, polymer styrene – butadiene – styrene (SBS), and acidic sludge.

Context and purpose: The objective of this study was the recovery of acidic sludge to bitumen using additives such as bentonite and SBS. Also, the effect of additives with different weight percentages (wt%)on the performance parameters of bitumen was evaluated. At first, spilled oil was separated from the acidic sludge by a centrifugal concentrator. Then, concentrated acidic sludge and additives were mixed in together. Finally, the performance tests were carried out to compare the quality of acidic sludge with the obtained products.The results indicated that performance parameters such as softening point (SP), weight loss, penetration degree, PI, Frass breaking point, and temperature susceptibility (TS) were promoted from 37°C, 1.3%, 230 dmm, -0.07854, -5°C and 0.0451 to 54°C, 1%, 130 dmm, 2.7094, -11°C , 0.02721, respectively. According to the paired sample t-test analysis, a significant difference was found between the bentonite dosage and the improved performance parameters from concentrated acidic sludge and obtained products ($p_{value} \leq .001$). The bentonite and SBS with 2 and 4 wt%, respectively were determined as the suitable additives in the recovery of acidic sludge to bitumen.

Key words: Acidic sludge- Bitumen- SBS polymer- Used motor oil

INTRODUCTION

According to the database of Iranian industry organization, there are more than two hundred recycling units of used motor oil currently. The recovery method for used motor oil in Iran companies is an acid / clay process [1, 2]. Acidic sludge is a by-product of this process. Unfortunately, in this process, from one hundred barrels of used motor oil, just fifteen barrels of acidic sludge are obtained as refuse. There are many methods so that disposal of acidic sludge such as incineration, landfill, refuse and recovery. Acidic sludge composition is very complex and it is not known well [2, 3].The acidic sludge contains unsaturated compounds, which are polar and asphaltene. Acidic sludge composition is similar to bitumen. Bitumen contains hydrocarbons with high molecular weight including oil, resin and asphaltene [4].In the other words, the chemical composition of the petroleum bitumen is organic hydrocarbons, while the colloidal structure are asphaltene and maltene. Asphaltene forms the suspended and dispersed colloidal system, whereas maltene forms the continuous part [6, 5]. The study of Jumoke *et al.* (2008), showed that the acidic sludge, as a by-product (industrial waste), could be converted to the valuable products and raw materials of other processes, such as manufacturing processes, including organic fertilization, explosive materials, paint, ink, chemical fiber and industrial detergent [6,7]. Processing of acidic sludge produces different commercial products such as surfactants, sulfuric acid, light hydrocarbons, coke, activated carbon, furnaces fuel and boilers, types of bitumen and asphalt and thermal insulation, etc. Also acidic sludge can be used as the amending of bitumen materials and preparation of carbon rods [8-10]. Based on the studies of technical and economical view-point that have been conducted by the Iranian industries organization, the bitumen materials as a raw material or the additives for cycle of production are used in different industries such as wool fibers, booklet, laminated paper envelopes, asphalt heat insulation, plastic bags, automotive fan belt, PVC flooring, proof insulated pipe covers, blown bitumen, emulsion bitumen, polymer bitumen, complementary of bitumen refinery, motorcycle battery, paint, ink, printing ink and liquid bitumen, etc.

In order to use of acidic sludge as a raw material for the production of the bitumen, some amendments should be done about it [11]. In the physical modification, materials such as bentonite, polyethylene, ethylene vinyl, ethylene vinyl acetate, SBS and other forms of these polymers are used [12]. Bentonite has also been found to be as one of the most effective additives that is categorized as one of the montmorillonite group. It is used as fillers, stabilizers, and agent concentration in the bitumen materials [13]. SBS has thermoplastic and elastic properties. The viscosity of SBS at the mixture temperature is close to the viscosity of bitumen. Also, with decrease the temperature to below 100 °C is formed a rubber network in bitumen and it takes the form of a rubber material. However, it is dependent on the percentage and type of the polymer [14]. SBS has a strong interaction with bitumen. Bitumen/polymer interaction, polymer structure and phase continuity are the necessary conditions for a polymer to be successful and effective in bitumen modification. SBS is blended with bitumen by mixing at 170 °C [15]. Worldwide, more than 7 types of bitumen are used, depending on the climatic zones. But in Iran due to the high cost of bitumen production, two types of bitumen 85/100 with high penetration and 60/70 with lower penetration are used. According to the classification, which is based on the degree of penetration and SP, the bitumen 85/100 is used in colder environments, while the latter is used in the tropical climates. In the southern regions of Iran, bitumen 40/50 and 20/30 should be used but it is not commercially available [16,17]. The objective of this study was the recovery of acidic sludge to bitumen by additives such as bentonite and SBS polymer. In the present work, the performance tests on acidic sludge and obtained products were carried out. The effects of SBS polymer and bentonite contents on the performance parameters were also studied. To the best of our knowledge, this is for the first time that the acidic sludge of used motor oil reprocessing industries was used for recovery to bitumen.

MATERIALS AND METHODS

In this study the acidic sludge was supplied from Baharan Shimi factory, Isfahan, Iran. Linear-like SBS polymer and bentonite were purchased from Petrochemical Company of Tehran and the Mining of Bentonite Company, Isfahan, Iran, respectively. The properties of SBS polymer and bentonite are shown in Tables 1 and 2, respectively.

Table 1: The XRF analysis of bentonite

LoI a)	CaO	MgO	K_2O	Na_2O	Fe_2O_3	Al_2O_3	SiO_2
5.32	1.68	2.4	0.39	2.17	3.04	14.22	70.06

a). Loss of ignition at 1000 °C.

Table2: The properties of SBS Polymer

Polymer properties	Values	Test method
Toluene solution viscosity 25% pa.s	5	MA 04-3-064
Volatile matter, %	0.4	ASTM D-5668
Hunterlab color	2	ASTM D-1925-70
Total styrene (on polymer) %	31	ASTM D-5775
Hardness, shore A	76	ASTM D-2240
Ashes %	<0.35	ASTM D-5669

This experimental study was performed in the laboratory conditions. Acidic sludge samples were mixed with duplex high-shear mixing system composed from a Polytron 6100 connected to a high-shear aggregate PT-DA 3020/2 along with a low-shear propeller mixer Polymix (Figure.1), (Kinematika Co, Switzerland) for 30min. After concentrating by centrifugal concentrator, with retention time of one day, the spilled oil was separated from acidic sludge due to the difference in density between two phases. Afterwards, bitumen performance tests were carried out on the concentrated acidic sludge (without spilling oil). To accomplish the tests each beaker containing 50 g of acidic sludge was heated to 180°C in an electrical heater. Then, the SBS polymer and bentonite (modifiers) were added to the samples with 2 to 4 wt% and 1,2,4,6,8, and 10 wt%, respectively. Standard tests including ASTM-D5, ASTM-D6, ASTM-D36, and IP ASTM 2000: Part 80; EN 12593 , were used to measure the penetration degree, weight loss, softening and Frass breaking point respectively. Finally results were analyzed using Excel Microsoft 2007 and SPSS version 18 software (The paired sample t-test analysis).

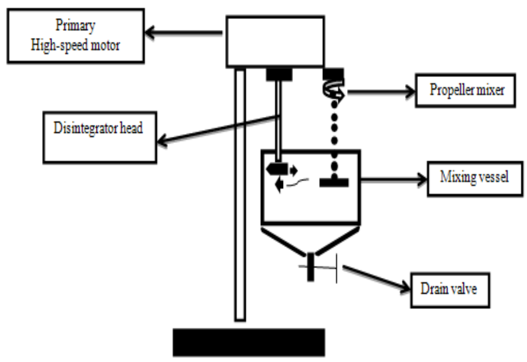

Fig 1: High-speed and high shear double –mixer set

Penetration Index (PI) Estimation

The index was calculated using the empirical equations 1 and 2. PI represents the susceptibility of bitumen against temperature. Temperature susceptibility decreases with increase of temperature.

$$PI = \frac{20 - 500A}{1 + 50A} \qquad (1)$$

$$A = \frac{\log 800 - \log P}{T - 25} \qquad (2)$$

In these equations, A, P, and T are TS, penetration degree and SP, respectively.

Temperature susceptibility (TS) Estimation

TS was also calculated using the empirical equation 2. In general, changes in the concentration of bitumen (penetration degree or viscosity), which comes from changes on the temperature conditions, are called TS. Thus, the lower value of TS represents the improvement in bitumen properties.

Performance Grade (PG) Estimation

PG was estimated using semi-empirical equations 3 to 5. PG is determined based on the properties of the used bitumen in situations such as climatic conditions and aging of bitumen.

$$PG = H,-L \quad (3)$$

$$H = T_{R\&B} + 20 \quad (4)$$

$$L = 2T_{FRASS} \quad (5)$$

In equations 3 to 5, H, L, T_{FRASS} and $T_{R\&B}$, are the maximum and minimum of tolerable temperature, Frass breaking point and SP, respectively [18].

RESULTS AND DISCUSSION

At first, the performance tests were carried out on the acidic sludge. Then, spilled oil was separated from acidic sludge. Table 3 and 4 show the performance parameters of acidic sludge and concentrated acidic sludge, respectively.

Table 3: The performance parameters of acidic sludge

Properties	Values
SP (^{o}C)	25
Weight loss %	3
Penetration degree (dmm)	*
PI	*
Frass breaking point (^{o}C)	*
PG	*
TS	*

*These parameters were not measurable

Table 4: The performance parameters of concentrated acidic sludge

Properties	Values
SP	**37 ^{o}C**
Weight loss %	**1.38**
Penetration degree	**230 dmm**
PI	**-0.07854**
Frass breaking point	**-5 ^{o}C**
PG	**(-10,57)**
TS	**0.0451**

Due to the poor quality of the used motor oil for reprocessing operation, to improve the quality, the fresh motor oil is added to the used motor oil with defined ratio in the factory. This process increases the amount of spilled oil into the acidic sludge. Therefore, because of the high fluidity limit, the performance parameters of acidic sludge in Table 3, could not be measurable, except both SP and weight loss. It can be seen from Table 4 that after the separation of the spilled oil from acidic sludge, both viscosity and performance parameters were improved. Therefore, the bitumen was obtained with a SP/penetration degree of 37/230 and the PG [-10, 57]. According to the research of Rasoulzadeh *et al.*(2010), due to adding of heavy vacuum slopes from 1 to 5 wt% into the vacuum bottom residue (VB), the value of SP was reduced from 41 to 32 ^{o}C . This phenomenon can be related to the change in the asphaltene/ maltene ratio in the VB and fluidity limit. Therefore, the penetration degree and Frass breaking point were increased from 202 to 280 dmm (deci-millimetre) and -19 to -27 ^{o}C, respectively [19,20]. It can be concluded that the separation of spilled oil could improve the performance parameters.

A number of special properties of bentonite favorite its usage in the recovery of hazardous waste materials. Regard to the chemical formula of bentonites,

$$X_{0.8}(AL_{0.3}Si_{7.7})(AL_{2.6}Fe_{0.9}Mg_{0.5})O_{20}(OH)_4nH_2O$$

it is used as fillers, stabilizers and the agent concentration. According to Table 1, over seventy percent of bentonite's structure is SiO_2 that plays an important role in both strengthening and hardening of the final products. Greasy and soap-like properties of bentonite and its ability to absorb large quantities of water with an accompanying increase in volume of as much as 12–15 times of its dry bulk, and higher cation exchange capacity are among other interesting properties. In bentonite, the variety of exchangeable cations affects the maximum amount of water uptake and swelling. Its swelling ability makes it as an effective sealant. Hence, when bentonite is mixed with bitumen, the swelling of bentonite within the interstices of bitumen, is resulted in the plugging of the voids in the structure of bitumen [21].

After adding the modifiers (i.e. bentonite and SBS polymer), the performance parameters of concentrated acidic sludge were modified. Figures 1 to 4 show the performance parameters of the obtained products.

Fig. 1 shows that the highest SP and the lowest penetration degree were obtained in the conditions of 2 wt% bentonite, 54^{o}C, and 140 dmm, respectively. By adding more bentonite up to 10 wt%, the value of SP was decreased to 36 ^{o}C. Consequently, the penetration degree was increased to 235 mm. Figure 2 shows that the minimum weight loss and the maximum Frass breaking point were 1% and -10^{o}C, respectively. By adding more bentonite up to 10 wt% bentonite, weight loss was reached to 1.4 %. According to Fig. 1 and 2, both the penetration degree and weight loss in products were significantly reduced, while SP and Frass breaking point were significantly increased. These changes of parameters were considerable between the concentrated and initial acidic sludge.

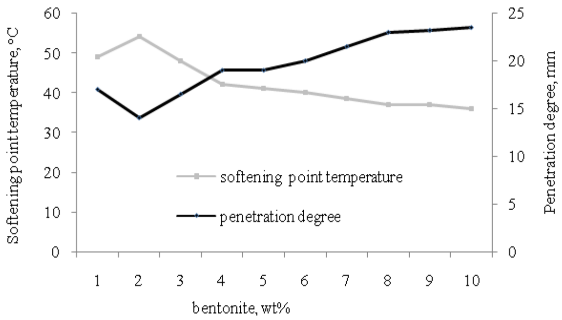

Fig 1: The effect of bentonite wt% variations on both SP and penetration degree (2 wt% SBS)

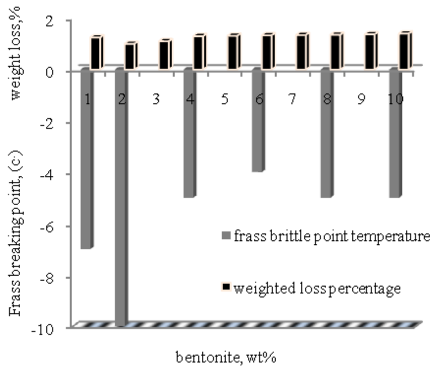

Fig 2: The effect of bentonite wt% variations on both Frass breaking point and weight loss (2 wt% SBS)

Due to the addition of bentonite ratio up to10 wt%, the volume of the products was increased. Penetration degree and weight loss were increased because of the trapped air inside the products and swelling. Thus, the both of SP and Frass breaking point were decreased. It should be mentioned that the reduction of penetration degree means the reduction of the fluidity limit[22,23] .In general, the reduction of the penetration degree of polymer bitumen compared to basic bitumen can be related to the high resistance to temperature. However, such a reduction can be result in the reduction of flexibility and britting of bitumen at low temperature[24,25]. The research of Hamidi et al. (2010) showed that with the addition of 1.5 to 6 wt% bentonite, the value of SP was increased from 63 to 67 ^{o}C in rubber bitumen. The least penetration degree was obtained in the 3 wt% bentonite (25 dmm), which is in full agreement with the findings of the current study[26,27]. It should be mentioned that the weight loss for natural bitumen in the best conditions is 1% [27, 28]. The weight loss of the bitumen during the asphalt baking is due to emissions of volatile organic compounds. This condition prevents from the hardening of bitumen of asphalt [28, 29].The results of Frass breaking point test are used to describe the behavior of bitumen at low temperatures or cold climates with long time of freezing. It is worth to mention that low viscosity and hardening of products affect the results of the Frass breaking point test [30,31].

Fig. 3 illustrates that with the addition of more SBS, the value of SP was increased from 50 to 54^{o}C. Therefore, the penetration degree was decreased from 14.3 to 13 mm. Figure 4 shows that with the addition of SBS wt%, weight loss did not change and was constant at 1%. Therefore, Frass breaking point, was decreased to -11^{o}C.

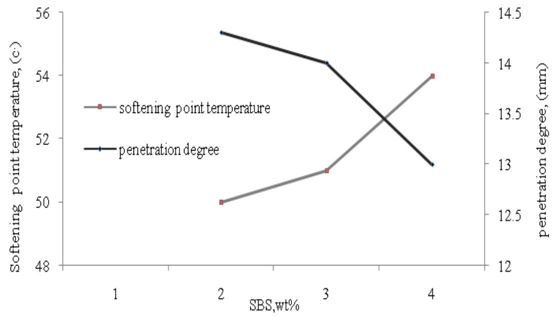

Fig 3. The effect of SBS wt% variations on the SP and the penetration degree (2 wt% bentonite)

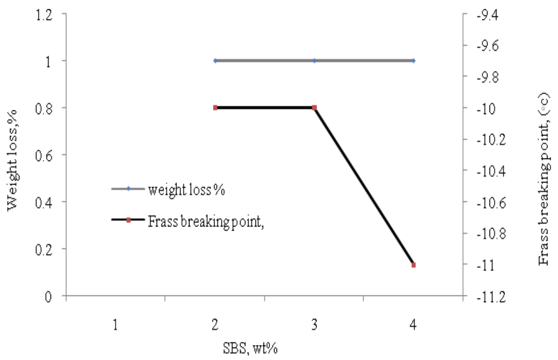

Fig 4: The effect of SBS wt% variations on the Frass breaking point and weight loss (2 wt% bentonite)

Fig. 3 and 4 show that the addition of SBS wt% increases the viscosity of products due to the fillering, stabilizering and concentrating properties of bentonite, and also the rubber and thermoplastic properties of the three-dimensional network polymer. This condition is resulted in an increase of fluidity and decrease of the penetration degree (about 130 dmm). The bitumen with a penetration degree of 30 to 130 dmm is the optimal bitumen for the climatic conditions of Iran [30,31]. The polymer phase forms a continuous network and absorbs the lubricating constituents of bitumen, which is directly resulted in the improvement of SP, penetration (the effect of soft network formation at medium temperatures) and Frass breaking point (the effect of brittleness of bitumen at low temperatures) [31,32]. The modification of bitumen by polymers improves its mechanical properties including increase of the viscosity, allowing the expansion of the range of temperature service and the improvement of the deformational stability and durability of bitumen [33]. The same value of SP for samples obtained from 2 wt% bentonite and 2 wt% fixed SBS (i.e. 54°C) could be because of the interaction between the additives or non-uniform samples of concentrated acidic sludge or due to the non-uniform amount of spilled oil, which has been separated [34,35]. The results of study Chen *et al.* (2003), showed that with addition 1 to 6 wt% SBS on the bitumen samples of 31/93 and 43/62, the value of SP was increased .Based on the study of Casey *et al.* (2008], with addition of SBS from 2 to 4 wt%, the value of SP in the mastic asphalt was increased from 39.8 to 46.5°C [36]. Rasoulzadeh *et al.* (2010) have used the recycled polyethylene to improve the properties of vacuum distillation residuals and have found that the SP was increased from 41 to 117°C. Penetration degree rate was also reduced from 202 to 47 dmm. It is necessary to mention that in the current study the used SBS polymer was contained 20-30% polyethylene. The high value is the SP of bitumen, the less is the susceptibility to temperature changes. SP of bitumen at [20 to 85 °C) 70 °C is an optimal bitumen for climatic conditions of Iran [37]. SP represents the temperature at which bitumen is in the fluidity state under a specific pressure. If the fluidity limit of bitumen occurs at high temperatures, the morphologies resistance of asphalt will be high and, therefore, the permanent or plastic deformation will be delayed.

The results of study Nazarbegay *et al.* (1993), showed that with addition 1 to 6 wt% polyethylene, the value of SP was increased but,the penetration degree was decreased. Airey *et al.* (2004] have reported that with addition of 3 to 7wt% SBS, the penetration degree and SP were changed from 73 to 49 mm and 47 to 88 °C, respectively. In the research of Sadeghipour *et al.* (2007), with addition of 4 wt% SBS, the amount of SP was increased while, the penetration degree was decreased. The results of study Sengoz *et al.* (2009), showed that with addition 2 to 6 wt% SBS on the bitumen sample of 50/70, the value of SP was increased from 49 to 69°C while,the penetration degree was decreased from 63 dmm to 48 [38,37]. These results are in good agreement with the findings of the present study.

The weight loss of obtained products, as shown in Figure 4, was equal to the determined standard for bitumen. The Frass breaking point was also decreased from -10 to -11°C. It should be mentioned that of -12°C is an optimum point for climatic conditions of Iran [39]. It is worth to mention that the higher negatives values of Frass breaking point is translated to the higher degree of elasticity of the bitumen and asphalt. Mixing of products at high temperatures is led to the stripping of some volatile organic compounds in bituminous materials and also some restructuring happen. Therefore, the weight loss is increased .In the other words, Frass breaking point could be increases and subsequently thermal cracks of asphalt coating decreases at low temperatures, which in turn leads to the increase of pavement durability [39, 40]. The study of Abtahi *et al*.(2007) showed that with addition of 2 to 5 wt% SBS, the values of SP, penetration degree, weight loss and Frass breaking point were changed from 51°C to 61 , 66 to 36 mm, 1.36 to .04% and -8 to -14°C, respectively for the sample of bitumen 60/70, Isfahan Refinery. Based on the investigation of Isacsson et al.(2003), with addition of 3,6 and 9 wt% SBS, on the bitumen samples of 60/70, 60/120, 160/220, obtained from Venezuela and Mexico, both penetration degree and Frass breaking point were decreased, whereas SP increased. In the study of Behbahani *et al.*(2007) with addition of 2,3,4,5 and 6 wt% styrene – butadiene – rubber (SBR) polymer, both SP and penetration degree were increased for the sample of bitumen 60/70, Tehran Refinery [40,41]. Airey *et al.* have reported that with addition of SBS wt%, the value of Frass breaking point was changed from -12 to -28°C .These results are consistent with the findings of the present study. Table 5 shows the values of TS, PI and PG after the addition of modifiers to the concentrated acidic sludge.

According to the Table 5, the sample 2 was achieved the highest PI and PG and the lowest TS. The addition of bentonite up to 10 wt% was increased the value of TS. After addition of SBS from 2 to 4 wt%, the value of PI was increased and the value of PG was equal to the sample 2.

Table 5: The values of TS, PI and PG after the addition of modifiers to the concentrated acidic sludge

sample	wt% bentonite	wt% SBS	TS	PI	[1]$T_{R\&B}$+20°C	L	PG	
1	1	2	0.0280	-1.918	69	-14	69	-14
2	2	2	0.0261	3.0147	70	-20	69	-20
3	2	3	0.02911	2.217	71	-20	69	-20
4	2	4	0.02721	2.7094	74	-22	69	-20
5	4	2	0.03672	0.5774	62	-10	62	-8
6	6	2	0.0401	-0.0228	60	-8	55	-8
7	8	2	0.04511	-0.7854	57	-10	55	-8
8	10	2	0.04836	-1.225	56	-10	55	-8

1 - The maximum acceptable temperature of bitumen (softening point temperature plus twenty degrees celsius).

Table 6: The performance parameters of optimal for climatic condition of Iran country

The properties of bitumen	The optimal properties of bitumen for climatic condition of Iran	The best obtained values in the current study
SP (°C)	20 to 85	54
Weight loss%	1	1
Penetration degree(dmm)	30 to130	130
PI	-2 to +2	0.5774
Frass breaking point	-12	-11
PG	Different	Different

The high values of TS are not appropriate for bitumen from the service-life point of view. The cause of this fact is that bitumen is composed of some solids (asphaltenes) and glass-forming materials (oils and resins, maltenes) [42].The PI is used as a good indicator for classifying bitumen rheological behavior. If the value of PI be close to +1(the ideal state), the bitumen will present the best performance. The optimal range of PI for paving is +2 to -2. PI >2 being indicative of a gel type bitumen, whereas PI <0 being typical of a sol [43].With addition bentonite wt%, PI showed some fluctuations, which can be due to the scattering of the obtained values for SP and penetration degree [44,45]. With Addition SBS wt%, PI was inclined towards +1.The numerical values of PI greater than +1 indicate the lower TS of bitumen. This suggests that in areas with high differences in temperature, the type of bitumen can show favorable properties. Bentonite increases TS, while SBS enhances the continuity. Thus, the range of temperature tolerance can be improved. The research of Isacsson *et al.* showed that with addition SBS wt% on the bitumen samples of 60/70, 60/120, 160/220, TS was decreased. In another research by Behbahani *et al.* the addition SBR wt%, for the sample of bitumen 60/70, PI was also increased. Airey *et al.* have reported that with the addition of SBS wt%, PI was changed from -0.09 to 5.29. The results of study Sengoz *et al.* showed that with addition SBS wt% on the bitumen sample of 50/70, the value of PI was increased from -0.92 to 2.46 .The study of Abtahi *et al.* showed that with addition SBS wt%, PI was increased from -0. 2716 to +0.45, which is full agreement with findings of present study [46-48].

The result of PG has some utilities such as deciding about the use of bitumen in a given climatic condition, obtaining the engineering properties and as well as grading of bitumen. In the grading system, the physical properties are constant for all of the performance degrees, but the temperature at which the physical properties was obtained could be changed, depending on the atmospheric conditions of usage [49,50]. Traffic conditions has also critical role in the selection of the type of bitumen. If the traffic rate at the equivalent standard axles (80KN) is exceeded from 10^7, the designer has to select the bitumen with one degree more than available PG. For instance the bitumen with 70-16 PG would be used instead of 64-16 [50,51]. In the current study, four types of improved PG were found as 69-20, 69-14, 62-8, 55-8.The results suggest that these types of bitumen would be used in different regions of Iran.

Table 6 summarizes the best obtained values for products in the current study together with the optimal properties of bitumen for climatic conditions of Iran.

CONCLUSIONS

In this study a new method was applied to recovery of acidic sludge to bitumen. Bentonite and SBS were used as additives in different wt% to obtain the optimal values of bitumen's properties. The results showed that the separation of spilled oil from the acidic sludge was promoted the performance parameters. It was found that the bitumen of 54/130 in the best conditions based on the values of SP and penetration degree. The other parameters of bitumen such as weight loss, PI, Frass breaking point, and TS were as the same as the typical bitumen (petroleum bitumen). Based on the results of PG test, obtained products would be used in the construction and building applications in the different regions of Iran.

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