J. Indian Chem. Soc.,
Vol. 97, May 2020, pp. 791-798

Evaluating the surface free energy and moisture susceptibility of modified asphalt mixtures with nano hydrated lime under saturated conditions with deicer materials and distilled water

Hamid Behbahani*[a], Gholam Hossein Hamedi[b] and Vahid Najafi Moghaddam Gilani[a]

[a]School of Civil Engineering, Iran University of Science and Technology (IUST), Tehran, Iran

E-mail: behbahani@IUST.ac.ir

[b]Department of Civil Engineering, University of Guilan, Rasht, Guilan

Manuscript received online 30 December 2019, revised 03 January 2020, accepted 19 January 2020

Pavement freezing in the snow and frost season has been causing a lot of trouble for road travelers every year in many countries. One of the strategies for winter maintenance of roads is the use of deicer materials that have been studied by many researchers for their effective factors. In this study, the effect of additives used as asphalt binder modifier on the moisture susceptibility of hot mix asphalt (HMA) under saturated conditions with deicing materials has been investigated. In order to evaluate the moisture susceptibility caused by deicing materials including sodium chloride (NaCl), calcium magnesium acetate (CMA), calcium formate (CaF) and potassium chloride (KCl) in addition to distilled water (DW), indirect tensile strength (ITS) test and the surface free energy (SFE) method have been used. The results show that the use of nano hydrated lime (NHL) increases the ITS and tensile strength ratio (TSR) values of samples saturated with deicing materials.

Keywords: Deicing materials, indirect tensile strength, surface free energy, asphalt binder modifier, moisture susceptibility.

Introduction

Moisture penetration into pavement layers as a result of rain water and deicing materials used in roads is one of the main reasons for early destruction of asphalt mixtures and eliminates adhesion at the contact surface of asphalt binder and aggregate, which results in moisture susceptibility. Its coincidence with the load of passing traffic can also intensify the destruction[1,2]. In order to preserve a high level of roadways service which translates to mobility and safety in cold seasons, deicers for controlling of ice and snow are often used. Nevertheless, widespread utilizing of these materials has many consequences, for instance, damage within the asphalt pavement structure[3], or loss of skid resistance[4]. Damage to the asphalt mixture in the presence of deicers is greater than when only water exists[5]. Moreover, it has been reported by researchers that when pavement underwent freeze-thaw cycles, that effects attributable to deicers appeared[6].

Penetration of deicing materials into the structure of asphalt mixtures eliminates adhesion at the contact surface of asphalt binder and aggregate and causes moisture damage. One of the methods to increase the resistance of asphalt mixtures against moisture susceptibility is to use additives to improve the properties of the asphalt binder. Several studies have been conducted to improve the performance of asphalt mixtures by using anti-stripping additives added to asphalt binder[7–19] or aggregates[20–26].

Problems and purposes:

Many studies have been carried out on the effects of deicing materials on asphalt mixtures, but in this study, the effect of three new deicers (calcium magnesium acetate (CMA), calcium formate (CaF) and potassium chloride (KCl)) with NaCl on the moisture susceptibility of asphalt mixtures in the different freeze-thaw cycles has been investigated. Also, another novelty of this study is to investigate the adhesion and cohesion of asphalt binder and aggregates and their detachment energy in the presence of various deicers using with the surface free energy method. In order to reduce the damaging effect of deicing materials, a mineral nanomaterial (nano hydrated lime (NHL)) has been used to modify the asphalt binder properties, which has improved the surface free energy of asphalt binder and aggregates under the impact of the penetration of deicing materials. The main goals of the study are as follows:

Investigating the effect of using various deicer materials on the moisture susceptibility of asphalt mixes through mechanical methods (ITS test).

Investigating the effect of various deicer materials on surface free energy parameters of asphalt binder and asphalt mixes.

Studying the effect of anti-stripping additives in adhesion free energy of base and modified asphalt binder and aggregates.

Evaluating of freeze-thaw cycles on the performance of asphalt mixtures under the influence of deicer materials.

Materials and methods

Deicing materials:

Usually, all deicers act in the same way. They lower the freezing point and convert snow and ice into slush or water. The deicing materials permeate into snow or ice, dissolve in it and form condensed water, which flows under the ice or heavy snow, and separates them from the surface of the road. Table 1 shows the engineering properties and eutectic point of deicing materials used in this study.

Table 1. Engineering properties of deicing materials used in this study

Deicing chemical	Formula	Eutectic (°C)	Concentration (%)	Molar mass (g/mol)
Sodium chloride	NaCl	–21	23.3	58.44
Calcium and magnesium acetates	CMA	–30	31.0	300.55
Calcium formate	CaF	–11.5	32.6	130.113
Potassium chloride	KCl	–10.5	19.5	74.55

Aggregates:

The aggregates used in this study are of granite type. The physical properties and grading of the aggregates (ASTM standard) are given in Tables 2 and 3, respectively[27–34].

Asphalt binder:

The asphalt binder is a pure type with a penetration grade 60/70 which was supplied from the Jey Oil refinery. The base and modified asphalt binder specifications with 1.0% of the NHL are presented in Table 4. To mix the NHL and asphalt binder, first the asphalt binder should be heated to 150°C and the NHL slowly poured into a mixer bowl with 12000 rpm. The mixing process should continue for 20 min. The SEM test was conducted prior to asphalt experiments to evaluate the distribution of NHL in asphalt binder and guarantee their uniform dispersion. Fig. 1 depicts the distribution of NHL in asphalt binder. It is evident that NHL are scattered in different directions and in all parts of the sample.

Table 2. Physical properties of granite aggregates used in this study

Property	Standard	Granite	Specification limit
Special gravity (coarse grains)			
Bulk	ASTM C127	2.65	–
Effective		2.66	–
Apparent		2.65	–
Specific gravity (fine grains)			
Bulk	ASTM C128	2.65	–
Effective		2.66	–
Apparent		2.65	–
Specific gravity (filler)	ASTM D854	2.54	–
Los Angeles abrasion (%)	ASTM C131	19	Maximum 30
Water absorption (%)	ASTM C127	1.3	Maximum 2
Needle and flake particles	ASTM D4791	10	Maximum 15
Flat and elongated particles (%)	ASTM D5821	96	Minimum 10
Sodium sulphate soundness (%)	ASTM C88	9	Maximum 15

Table 3. Applied grading aggregates in this study

	Sieve size (mm)					
Limits	19.0	12.5	4.75	2.36	0.3	0.075
Lower-upper limits	100	90–100	44–74	28–58	5–21	2–10
Passing percentage	100	95	59	43	13	6

in the fridge at –18°C for 16 h. After that, they were immersed in a hot distilled water (DW) or deicing materials bath with specified concentration, which its temperature was 60°C for 24 h. Finally, the samples were brought to a temperature of 25°C. By using eqs. (1) and (2), the amount of indirect tensile strength (ITS) and indirect tensile strength ratio (TSR) are calculated for each samples, respectively[35,36]:

Table 4. Engineering properties of asphalt binder used in this study

		Asphalt binder	
Test	Standard	60–70	60–70 with 1.0% NHL
Penetration (100 g, 5 s, 25°C), 0.1 mm	ASTM D5-73	69	65
Ductility (cm)	ASTM D113-79	110	120
Softening point (°C)	ASTM D36-76	48	51
Flash point (°C)	ASTM D92-78	267	320
Viscosity at 115°C (mPas)		0.776	0.862
Viscosity at 135°C (mPas)	ASTM D4402	0.289	0.301
Viscosity at 150°C (mPas)		0.156	0.176

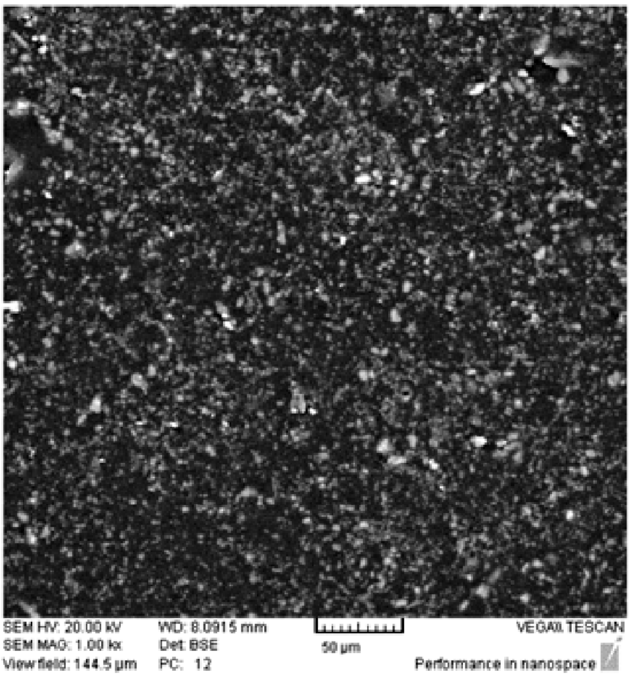

Fig. 1. SEM image of modified asphalt binder with NHL.

Test methods:

Moisture susceptibility test by the AASHTO T283 method:

In order to simulate wet conditions, the samples were first saturated with deicing materials for 5 min. After that, they were kept for 5–10 min in a submerged state under the absence of vacuum conditions. Saturated samples were kept

$$ITS = \frac{2F}{t\pi d} \quad (1)$$

$$TSR = \frac{ITS_{wet}}{ITS_{dry}} \quad (2)$$

where F is the force at the failure moment (KN), t and d are the thickness and diameter of the asphalt sample (cm), respectively. ITS_{wet} and ITS_{dry} are the indirect tensile strength average of the wet and dry samples (KPa), respectively.

Surface free energy method:

The surface free energy (SFE) of base and modified asphalt binder and aggregates were measured using the Sessile Drop test[37] and the Universal Sorption Device[38], respectively. One of the most significant theories used extensively to describe the components of SFE of various materials is the acidic-basic theory[39]. According to this theory, the SFE of each material is divided into three non-polar, acidic, and basic based on the type of surface molecules forces. The total SFE is obtained by combining these components from eq. (3):

$$\Gamma = \Gamma^{LW} + \Gamma^{AB} \quad (3)$$

where Γ is the surface free energy of the whole material, Γ^{LW} is the non-polar component of surface free energy and

Γ^{AB} is the polar component of surface free energy. According to eq. (4), the Lewis acid (Γ^+) and Lewis base (Γ^-) parameters constitute the polar component of surface free energy.

$$\Gamma^{AB} = 2\sqrt{\Gamma^+\Gamma^-} \tag{4}$$

The free energy of adhesion (ΔG_i^a) has two principal components: non-polar component, or Lifshitz Van der Waals, and the polar or acid-basic component. Eq. (5) is applied to determine the adhesion-free energy between the asphalt binder and aggregates.

$$\Delta G_i^a = \Delta G_i^{aLW} + \Delta G_i^{aAB}$$

$$= 2\left[\left(\sqrt{\Gamma_s^{lw}\Gamma_l^{lw}}\right) + \left(\sqrt{\Gamma_s^+\Gamma_l^-}\right) + \left(\sqrt{\Gamma_s^-\Gamma_l^+}\right)\right] \tag{5}$$

where ΔG_i^a is the free energy of adhesion, ΔG_i^{aLW} is the non-polar component of free energy of adhesion, ΔG_i^{aAB} is the polar component of free energy of adhesion, Γ_S^{LW}, Γ_S^+, and Γ_S^- are the aggregate components of surface free energy, Γ_l^{LW}, Γ_l^+, and Γ_l^- are the asphalt binder component of surface free energy. Eq. (5) is used for an HMA when the surface free energy components of the asphalt binder and aggregates have been measured. Eq. (6) is used to calculate asphalt binder and aggregate adhesion in the presence of water and deicing materials. The subscripts 1, 2 and 3 symbolize asphalt binder, aggregates, and water (deicing), respectively.

$$\Delta G_{132}^a = \Gamma_{12} - \Gamma_{13} - \Gamma_{23}$$

$$\begin{bmatrix} \left(2\Gamma_3^{LW}\right) + \left(4\sqrt{\Gamma_3^+\Gamma_3^-}\right) - \left(2\sqrt{\Gamma_1^{LW}\Gamma_3^{LW}}\right) \\ -\left(2\sqrt{\Gamma_3^+\Gamma_1^-}\right) - \left(2\sqrt{\Gamma_1^+\Gamma_3^-}\right) - \left(2\sqrt{\Gamma_2^{LW}\Gamma_3^{LW}}\right) \\ -\left(2\sqrt{\Gamma_3^+\Gamma_2^-}\right) - \left(2\sqrt{\Gamma_2^+\Gamma_3^-}\right) + \left(2\sqrt{\Gamma_1^{LW}\Gamma_2^{LW}}\right) \\ +\left(2\sqrt{\Gamma_1^+\Gamma_2^-}\right) + \left(2\sqrt{\Gamma_2^+\Gamma_2^-}\right) \end{bmatrix} \tag{6}$$

Results and discussion

ITS:

The ITS results of the samples in 1, 3 and 5 cycles, and in conditions of saturation with DW and deicing materials are presented in Fig. 2. The use of deicing materials in the initial cycles will increase the resistance of the HMA against moisture susceptibility. But after several cycles, due to the penetration of these materials into the asphalt and their acidic properties, the ITS values are reduced[40–43], which can be attributed to the loss of the mixture adhesion or asphalt binder cohesion due to the more presence of samples in the deicing material. The use of 1.0% of the NHL as an asphalt modi-

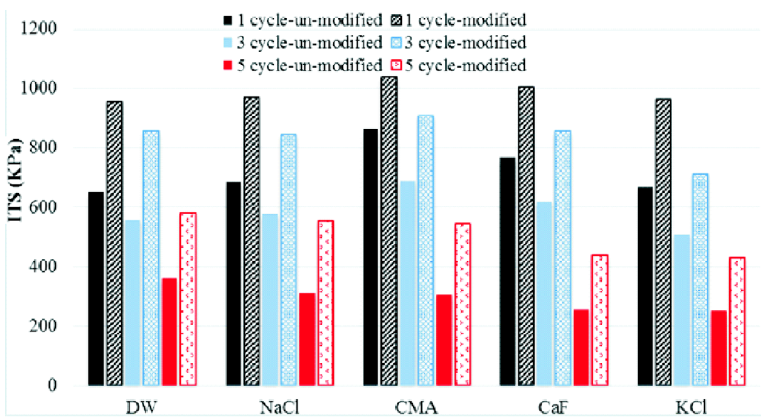

Fig. 2. The ITS test results under saturated conditions with DW and deicing materials.

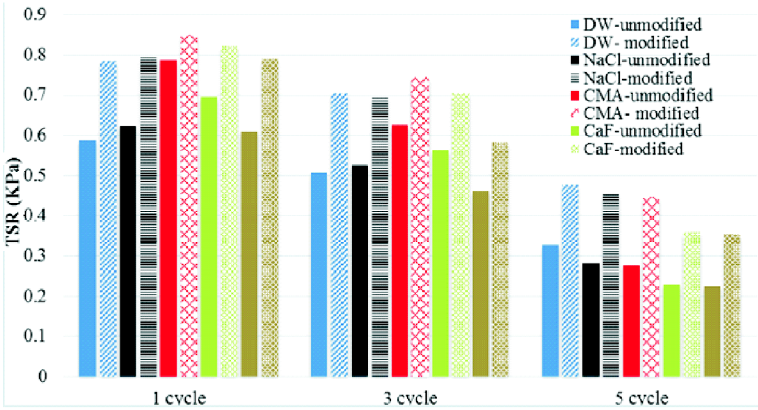

Fig. 3. TSR results under saturated conditions with DW and deicing materials.

fier increases adhesion and cohesion in the mixture and cause those HMA to have more resistance to deicing materials in higher freeze-thaw cycles than non-additive samples. It should be considered that the use of deicing materials on the surface of the asphalt is unavoidable in winter.

The TSR results in different freeze-thaw cycles in saturated conditions with DW and deicing materials are presented in Fig. 3. Among the deicing materials, the samples saturated with CMA and KCl have the highest and lowest resistance to moisture susceptibility, respectively. Although the samples saturated with deicing materials in the first and third cycles had higher TSR values than those saturated with DW, with the continuation of the process until the fifth freeze-thaw cycle, the resistance of the mixtures decreased, and the damage process of the samples accelerated and the aggregates detached from asphalt binder and no longer had a good adhesion for load bearing. Use of 1.0% NHL had a significant effect on the increase and return of tensile strength of samples saturated in deicing materials. The most obvious effect of using asphalt binder modifiers is in CMA-saturated samples. NaCl is the other recommended substances for use as deicing materials in asphalt samples modified with the NHL.

Surface free energy (SFE):

The measurement results of the SFE components of as-

Table 5. Surface free energy components of aggregates used (ergs/cm^2)

Solutions	Γ^+	Γ^-	Γ^{AB}	Γ^L	Total SFE, Γ
DW	26.12	534.25	236.26	57.23	293.49
CMA	75.21	492.31	384.85	48.20	433.05
NaCl	56.15	524.70	343.29	56.80	400.09
CaF	94.57	481.03	426.57	43.10	469.67
KCl	68.35	502.40	370.62	53.10	423.72

Table 6. Surface free energy components of asphalt binder used (ergs/cm^2)

Solutions	Mixture type	Γ^+	Γ^-	Γ^{AB}	Γ^{LW}	Total SFE, Γ
DW	AC 60-70	3.27	1.18	3.93	14.11	18.04
	AC modified	3.15	1.49	4.33	20.54	24.87
CMA	AC 60-70	3.57	1.10	3.96	13.58	17.54
	AC modified	3.52	1.48	4.56	19.67	24.23
NaCl	AC 60-70	3.38	1.15	3.94	14.01	17.95
	AC modified	3.35	1.57	4.59	20.12	24.71
CaF	AC 60-70	3.69	1.07	3.97	13.74	17.71
	AC modified	3.67	1.32	4.40	18.87	23.27
KCl	AC 60-70	3.44	1.13	3.94	13.92	17.86
	AC modified	3.43	1.52	4.57	19.86	24.43

Table 7. Free energy of adhesion result (erg/cm^2)

Mixture type	Solutions	Asphalt binder-aggregate	Asphalt-water (deicing)	Asphalt-binder in presence of water (deicing)
AC 60-70	DW	151.53	64.31	–122.88
	CMA		64.09	–141.79
	NaCl		64.35	–139.43
	CaF		64.46	–146.84
	KCl		64.31	–141.53
AC modified	DW	163.09	72.57	–119.57,
	CMA		72.75	–137.62
	NaCl		73.03	–134.58
	CaF		72.62	–143.53
	KCl		72.77	–136.73

phalt binder and the aggregates in the presence of the deicing materials and DW are presented in Tables 5 and 6. As is clear from Tables (5 and 6), the acidic and polar SFE components of the aggregates and un-modified asphalt binder in the presence of the deicing materials are larger than those of the same DW components. This indicates that most of the bonds formed between asphalt binder-aggregate in the presence of the deicing material are easily broken and asphalt binder stripping occurs on the aggregate surface. The application of the NHL as an asphalt binder modifier has led to a decrease and increase in the acidic and basic properties of HMA in the presence of deicing materials, which means reducing the risk of moisture susceptibility in the HMA.

The results of Table 7 indicates that under dry conditions (the absence of DW or deicing materials), the modified asphalt binder separation from the aggregate surface area unit is difficult and requires more energy. In fact, the application of the NHL has increased the free energy of adhesion. Also, the adhesion free energy of asphalt binder-water has increased due to the deicing materials, which indicates an increase in the tendency for the combination of asphalt binder-deicing materials, and for the increase of spontaneous emulsification which is one of the mechanisms of the moisture susceptibility.

According to column (asphalt-binder in presence of water in Table 7), deicing materials have more negative detachment energy than DW. In other words, when the three materials of asphalt binder, deicer, and aggregate are in contact, the deicer changes the energy of the system to reach the state with the lowest energy level, which results in stripping. The detachment energy of sample in the presence of deicing materials is closer to zero due to the modification of the asphalt binder properties with NHL. The detachment energy of the samples in presence NaCl, KCl, and CMA are approximately equal, which means that the NHL improved their performance of adhesive behavior of asphalt binder and aggregate similarly.

Conclusion

The most important results obtained from the experiments performed on modified asphalt mixtures saturated in distilled water (DW) and deicing materials are:

The use of NHL as asphalt binder modifier increases the ITS and TSR values of deicing-saturated samples compared to similar control samples, and the most obvious impact of the NHL on the increase of ITS value is in higher cycles, especially with CMA deicer.

The penetration of deicing materials into HMA intensifies stripping and causes the detachment of asphalt binder from the aggregate unit surface. Among the deicing materials, CaF has the most negative detachment energy. By using the NHL as asphalt binder modifier, acidic properties due to the presence of deicing materials decline, and the adhesion of modified asphalt binder to aggregates improves. Among the deicing materials, NaCl has the best adhesion performance after the modification of asphalt binder properties.

References

1. S. W. Goh, M. Akin, Z. You and X. Shi, *Construction and Building Materials*, 2011 **25(1)**, 195.
2. Y. Hassan, A. O. Abd El Halim, A. G. Razaqpur, W. Bekheet and M. H. Farha, *Journal of Transportation Engineering*, 2002, **128(4)**, 385.
3. Z. Wang, T. Zhang, M. Shao, T. Ai and P. Zhao, *Construction and Building Materials*, 2002, **142**, 187.
4. S. Ketcham, L. D. Minsk, R. R. Blackburn and E. J. Fleege, "Manual of practice for an effective anti-icing program: a guide for highway winter maintenance personnel (No. FHWA-RD-95-202)", United States, Federal Highway Administration, 1996.
5. X. Shi, M. Akin, T. Pan, L. Fay, Y. Liu and Z. Yang, *Open Civil Engineering Journal*, 2009, **3**, 16.
6. R. Tarefder, H. Faisal and G. Barlas, *Cold Regions Science and Technology*, 2018, **153**, 197.
7. A. H. Albayati, H. M. Al-Mosawe, A. A. Allawi and N. Oukaili, *Advances in Civil Engineering*, 2018.
8. J. Ji, H. Yao, Z. Yuan, Z. Suo, Y. Xu, P. Li and Z. You, *Advances in Civil Engineering*, 2019.
9. K. Mirkoviæ, N. Tošiæ and G. Mladenoviæ, *Advances in Civil Engineering*, 2019.
10. M. R. Kakar, M. O. Hamzah, M. N. Akhtar and J. M. Saleh, *Advances in Civil Engineering*, 2019.
11. H. Al-Mosawe, Z. N. Taki and A. H. Abed, *Advances in Civil Engineering*, 2019.
12. G. H. Hamedi and S. A. Tahami, *International Journal of Adhesion and Adhesives*, 2018, **81**, 90.
13. H. Rahmani, H. Shirmohammadi and G. H. Hamedi, *Journal of Materials in Civil Engineering*, 2018, **30(11)**, 04018278.
14. G. H. Hamedi, A. R. Azarhoosh and M. Khodadadi, *Periodica Polytechnica Civil Engineering*, 2018, **62(4)**, 901.
15. G. H. Hamedi, *Road Materials and Pavement Design*, 2017, **18(6)**, 1375.
16. H. Behbahani, G. H. Hamedi and V. N. M. Gilani, *Petroleum Science and Technology*, 2020.
17. X. Liu, Z. Zhang, X. Yang and Z. Liu, *Petroleum Science and Technology*, 2018, **36(16)**, 1258.
18. A. Julaganti, R. Choudhary and A. Kumar, *Petroleum Science and Technology*, 2017, **35(10)**, 1014.
19. M. J. Ayazi, A. Moniri and P. Barghabany, *Petroleum Science and Technology*, 2017, **35(9)**, 890.
20. F. Moghaddas Nejad, M. Asadi, G. H. Hamedi and M. R. Esmaeeli, *Journal of Materials in Civil Engineering*, 2018, **30(10)**, 04018238.
21. F. Sakanlou, H. Shirmohammadi and G. H. Hamedi, *Materials and Structures*, 2018, **51(2)**, 39.
22. F. M. Nejad, M. Arabani, G. H. Hamedi and A. R. Azarhoosh, *Construction and Building Materials*, 2013, **47**, 1523.
23. G. H. Hamedi, *International Journal of Civil Engineering*, 2018, **16(9)**, 1097.
24. G. H. Hamedi, *International Journal of Civil Engineering*, 2018, **16(6)**, 659.
25. G. H. Shafabakhsh, M. Faramarzi and M. Sadeghnejad, *Construction and Building Materials*, 2015, **98**, 456.
26. M. Sohrabi, H. Shirmohammadi and G. H. Hamedi, *Periodica Polytechnica Civil Engineering*, 2019, **63(1)**, 63.
27. ASTM, Standard test method for resistance to degradation of smallsize coarse aggregate by abrasion and impact in the Los Angeles machine, ASTM C131/C131M-14, West Conshohocken, PA, ASTM, 2006.
28. ASTM, Standard test method for flat particles, elongated particles, or flat and elongated particles in coarse aggregate. ASTM D4791, West Conshohocken, PA, ASTM, 2010.
29. ASTM, Standard test method for soundness of aggregates by use of sodium sulfate or magnesium sulfate. ASTM C88, West Conshohocken, PA, ASTM, 2013c.
30. ASTM, Standard test methods for specific gravity of soil solids by water pycnometer, ASTM D854, West Conshohocken, PA, ASTM, 2014b.
31. ASTM, Standard test method for relative density (specific gravity) and absorption of coarse aggregate, ASTM C127, West Conshohocken, PA, ASTM, 2015a.
32. ASTM, Standard test method for relative density (specific gravity) and absorption of fine aggregate, ASTM C128, West Conshohocken, PA, ASTM, 2015b.
33. ASTM, Road and paving materials; vehicle-pavement systems, ASTM D1559, West Conshohocken, PA, ASTM, 2017a.
34. ASTM, Standard test methods for uncompacted void content of fine aggregate (as influenced by particle shape, surface texture, and grading), ASTM C1252-06, 2006.
35. M. Arabani, H. Roshani and G. H. Hamedi, *Journal of Materials in Civil Engineering*, 2011, **24(7)**, 889.
36. N. Bala, M. Napiah and I. Kamaruddin, *Petroleum Science and Technology*, 2018, **36(3)**, 244.
37. H. Rahmani, H. Shirmohammadi and G. H. Hamedi, *Journal of Materials in Civil Engineering*, 2018, **30(11)**, 04018278.
38. A. W. Hefer, A. Bhasin and D. N. Little, *Journal of Materials in Civil Engineering*, 2006, **18(6)**, 759.
39. R. J. Good and C. J. van Oss, "The modern theory of contact angles and the hydrogen bond components of surface energies", in: Modern approaches to wettability, 1992, pp. 1-27.
40. D. Feng, J. Yi, D. Wang and L. Chen, *Cold Regions Science and Technology*, 2010, **62(1)**, 34.
41. Y. Hassan, A. A. El Halim and A. G. Razaqpur, "Laboratory Evaluation and Assessment of the Effect of Runway Deic-

ers on the Mechanical Properties of Asphalt Concrete Mixes Subjected to Freeze-Thaw Cycles", Safety and Security, Civil Aviation, Aerodrome Safety, Technical Evaluation Engineering Division, Transport Canada, Ontario, Canada, 2000.

42. Y. Hassan, A. O. Abd El Halim, A. G. Razaqpur and M. Farha, "Laboratory investigation of effect of deicing chemicals on airfield asphalt concrete pavements materials", Proceedings of the 2nd International Conference on Engineering Materials, San Jose, California, 2001, Vol. I, pp. 299-308.

43. M. H. Farha, Y. Hassan, A. O. Abd El Halim, A. G. Razaqpur, A. El-Desouky and A. Mostafa, "Effects of new deicing alternatives on airfield asphalt concrete pavements", The 2002 Federal Aviation Administration Technology Transfer Conference, 2002.