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The Improvement of the Mechanical Stability of Bituminized Waste Form

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Abstract

Bituminization exhibits a volume reduction and bituminized waste forms have a high leach resistance in comparison to cement-based wastes, however their mechanical stability is unacceptable. This paper reports a method of producing bituminized waste forms, having dimensional and mechanical stability like cement-based waste forms, as well as maintaining their own merits. The bitumen used in sample preparation is straight-run distillation bitumen of penetration 60/70. The waste used for the experiment was bottom ash generated from a hazardous wastes incinerator. An addition 1~5 wt% of sulfur was unable to increase the mechanical stability. Bitumen waste forms with ash contents of 40, 50, and 60 wt%, adding of spent PE(spent agricultural polyethylene film) by 5, 4, 3 wt% or more, respectively, resulted in maintaining dimensional and mechanical stability. The compressive strength of waste forms containing ash content of 40 wt% and waste PE 20 wt% exhibited compressive strength of 3447 kPa (500 psi), and softening point of 135 ^{o}C.

1. Introduction

Cement and bitumen are generally used as the matrix material for the solidification of hazardous and radioactive wastes. These materials have been used to deal with radioactive waste from the beginning of nuclear industry, because their characteristics are well defined by civil engineering researchers. Currently, their applications have been extended to mixed wastes.[1,2)]

The process to make cement-based waste form(cementation) is very simple, and it can be conducted at room temperature. However, the waste form produced reveals some demerits such as a very low leach resistance and a volume increment. In addition, quality control of the waste forms is difficult due to their high sensitivity in changing the chemistry and pH of waste.[3,4)] Whereas, bitumen does not react visibly with the substances which they contact. Quality control of these waste forms can be done easily even in the case of changing the waste stream composition and pH. Also, bitumen-based waste form exhibits very low leaching of contaminants because the matrix is impervious. Bituminization which is accompanied by both mixing and evaporation processes can lead to high volume reduction.[5,6]

Bituminized waste forms, however, are deficient in mechanical and dimensional stability.[7] This stability is closely related to the long-term stability of waste forms at landfills. As the mechanical and dimensional stability of bituminized waste forms primarily depend on containers, engineering reinforcements at landfills are required for long-term stability.

The objectives of this study were to develop a bitumen-based waste forms, maintaining their own merits and having mechanical and dimensional stability like the cement-based waste forms. Bottom ash generated from a hazardous wastes incinerator was bituminized using straight-run distillation asphalt without and with additives, respectively. Sulfur and polyethylene which is spent agricultural polyethylene film were chosen as additives.

2. Equipment and Material

<u>Equipment Description</u>

In this study the pot type equipment was employed in a bituminization and bituminization was carried out by batch operations. The pot type mixer is the simplest equipment currently used in the bituminization process and it allows easy maintenance. As the reactor was heated by using heating oil, the local over heating can be avoided. The temperature of the heating oil was adjusted by an electrical heater. The temperature ranged between 25 ^{o}C and 240 ^{o}C. A mixer with three mixing blades was operated by a DC motor with speeds from 70 to 550 r.p.m. The temperature of the mixture in the pot measured by temperature sensors and fed back to heater controller for precise temperature control.

<u>Bitumen</u>

The bitumen used for the sample preparation was a straight-run distillation asphalt, a penetration 60/70 paving asphalt. Table 1 shows physical properties of the bitumen 60/70 used.

Table 1 Physical Properties of Bitumen 60/70

Property	Test Condition	Unit	Value
Penetration	25℃, 100g, 5s	1/10 mm	63
Softening Point	Ring and Ball	℃	48.8
Flash Point	Cleveland Open Cup	℃	328
Ductility	25℃, 5 cm/min	cm	150
Solubility in trichloroethylene		%	99.8

Bottom ash

The ash used in this experiment was the bottom ash generated from an industrial hazardous waste incinerator. Bottom ash was crushed smaller than 120 mesh (0.125 mm) and dried for 24 hours at 110°C before bituminization.

Sulfur

Sulfur used in this experiment was a reagent, having a melting point of 112.8 °C and a specific gravity of 2.07 at 20℃.

Spent agricultural polyethylene film(Spent PE)

Polyethylene is saturated aliphatic hydrocarbon polymer as well as thermoplastics being very stable chemically.[8] In Korea, agricultural polyethylene film having 1~2 year life is made from mainly low density polyethylene(LDPE), and generate about 90,000 tons of waste per year. Polyethylene used in this experiment was spent agricultural polyethylene film from waste recycling. Typically, low density polyethylene has density of 0.910~0.925 g/cm^3 and softening point of 105 °C.[8]

3. Methods

Waste form preparation

Cylindrical waste form specimens(diameter of 5 cm and height of 8 cm) were cast into the teflon molds consisting of 3 pieces. The mixed bitumen flowed from the vessel directly into the teflon molds. After cooling for 24 hours at room temperature, the teflon mold was removed. Solidified waste forms were produced from the mold.

Compressive strength

The compressive strength of bitumen and bituminized waste form is measured by the ASTM D 1074-83. The vertical rate of deformation for these tests is set at 0.05 cm/min/cm of specimen height. The Nuclear Regulatory Commission(NRC) has recommended that the unconfined compressive strength should be evaluated at the point where 10 % deformation in specimen height occurs. For radioactive wastes, the U.S. NRC suggests that waste forms exhibit a minimum unconfined compressive strengths of 414 kPa(60 psi).[9]

Softening point

Softening point testing was performed in accordance with the ASTM D 36-70 "Test Method for Softening Point of Asphalts and Tar Pitches(Ring and Ball)".

Form stability in air

Appearance change of waste form was observed as a cylindrical waste form specimen was standing in air for several hours.

4. Results and Discussion

Effect of sulfur

Sulfur is obtained as a by-product from the off gas and petroleum distillation processes or desulfurization at steam power plants. Sulfur is used as a crosslinking agent of vulcanization in rubber industry. Sulfur also serves as a crosslinking agent in bitumen of various molecular weight complexes. As results of the experiment reaction temperature of sulfur and bitumen exhibited 180 ^oC, the experiment was conducted with 150 r.p.m and 180 ^oC. The amount of sulfur added varied from 0, 1, 3, and 5 wt% with respect to ash loading(content) 30, 40, 50, 60, and 67 wt%, respectively. The result revealed that the addition of sulfur in bituminization gives little effect on softening point and penetration of waste form, but no effect on compressive strength of waste form.

Fig. 1 shows an effect of the addition of sulfur 3 wt% on the softening point of the waste form. At ash loading below 50 wt%, little effect of sulfur exists, while no effect above 50 wt%. In contrast, addition of ash loading leads to an exponential increment of softening point. Fig. 2 shows comparison of compressive strengths between waste forms added sulfur of 3 wt% and waste form without sulfur. Sulfur has no effect on compressive strength of waste form, whereas the increase of ash leads to an exponential increment of compressive strength. However, compressive strength of waste form with an ash loading of 67 wt% exhibits only about 462 kPa(67 psi). Maximum limit of amount of ash loading was determined to be 70 wt%, and in the case of ash loading of more than 70 wt% bitumen is unable to act as a binder, so that waste form began to break to pieces.

Effect of spent agricultural polyethylene film(Spent PE)

Fig. 3 shows the scanning electron micrograph of the mixture of bitumen and 10 wt% waste PE. It was found that waste PE existed as net structures in bitumen.

Fig. 4 illustrates an effect of spent PE contents on the softening point of waste form. Adding spent PE to bitumen leads to an increase of the softening point from 48 ^oC to 118 ^oC. However, above a certain loading of PE it has no effect on the softening point. This is due to the effect of softening point of spent PE(about 105 ^oC). For ash loading of 40 wt% the same trend as previous result was obtained. For radioactive waste, the NRC has recommended that waste forms exhibit a minimum softening point of 70 ^oC.

During bituminization, adding more than 25 wt% of spent PE increases viscosity of mixture so much that pot type mixer can not discharge the mixture. The maximum limit of addition of spent PE in a pot type mixer was observed to be 25 wt%.

Fig. 5 shows the effects of the addition of waste PE on compressive strength of waste forms. In the Fig. 5, the bottom line depicts a mixture of bitumen and spent PE, the top line indicates a mixture containing additional loading of 40 wt% ash. In the case of a waste form without spent PE, compressive strengths of bitumen itself and bituminized waste forms with 40 wt% ash are similar. It results from their poor mechanical and dimensional stability. The more amount of addition of spent PE is increased, the more the gap between two lines enlarges. This is due to fact that a slope of a line of compressive strength for ash loading of 40 wt% increases remarkably.

In the case of the ash loading of 40 wt% leads to high viscosity of mixture, since spent PE is uniformly distributed into waste form. The density of spent PE exhibits ranges between 0.910 and 0.925 g/cm^3, and bitumen of 1.03 g/cm^3. In the case of the mixture of bitumen and waste PE, partial phase separation occurred at a mixing temperature above 170 ^{o}C. Increase of addition of spent PE and loading of ash leads to high viscosity of mixture when mixing, so that partial phase separation can be avoided.

Comparison of Effect

Fig. 6 shows the effects of additives on the softening point and compressive strength of waste form containing ash loading of 40 wt%. Function of sulfur as crosslinking agent was estimated to be unsatisfactory to significantly increase softening point and compressive strength, whereas waste PE afford to increase them. The addition of spent PE of 20 wt% elevates softening point to 135 ^{o}C and compressive strength to 3447 kPa(500 psi) that is 8.3 times of that suggested by NRC.

Fig. 7 illustrates the appearances of waste forms after being exposed at room temperature in air for 90 days. As shown in Fig. 7(A), the waste forms with ash contents of 40 and 50 wt% and sulfur of 3 wt% collapsed entirely after exposed for 20 days, and the shape of waste forms with ash contents of 60 wt% deformed after 90 days. Waste forms containing spent PE are illustrated in Fig. 7(B). Even after 90 days, waste forms keep their original shapes. As results of experiments, it is investigated that addition of spent PE of 5, 4, 3 wt% or more with respect to ash contents of 40, 50, 60 wt%, respectively, is able to maintain dimensional and mechanical stability of final waste form. However, sulfur as a crosslinking agent has no effect on the dimensional and mechanical stability of waste forms.

4. Conclusion

1. Maximum loading of ash in bitumen is determined to be 70 wt%.
2. Sulfur as a chemical crosslinking agent has no effect on the softening point, the compressive strength, and the dimensional and mechanical stability of the waste form.
3. The addition of spent PE can afford to not only maintain dimensional and mechanical stability of waste forms, but also improve in softening point and compressive strength of them, by adding 5, 4, 3 wt% or more with respect to ash contents of 40, 50, 60 wt% respectively.
4. Complete mixing between spent PE and bitumen accomplished at temperature above 170 ^{o}C. Partial phase separation occurred by density difference between waste PE and bitumen can be avoided by increasing viscosity of mixture by loading ash in bitumen. When addition of 25 or more wt% spent PE, however, a pot type mixer is

unable to discharge mixtures due to high viscosity of mixtures.

5. Therefore, by addition of spent PE in bituminization of ash waste, the dual effects are obtainable; which is (1) to make the very stable bituminized waste form, (2) to recycle the spent PE.

Acknowledgement

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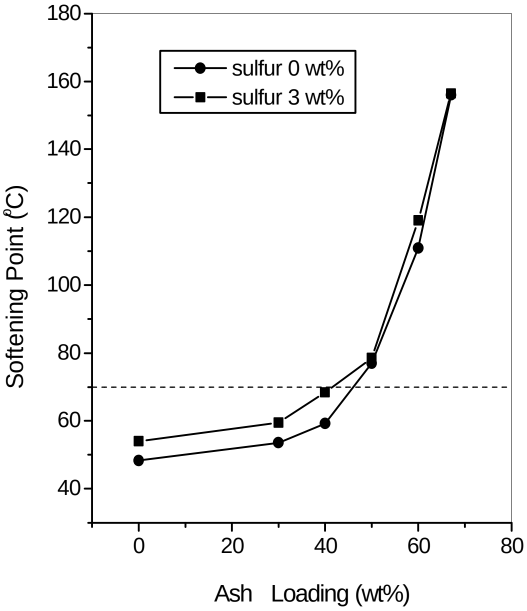


Fig. 1 Influence of sulfur on the softening point of waste forms

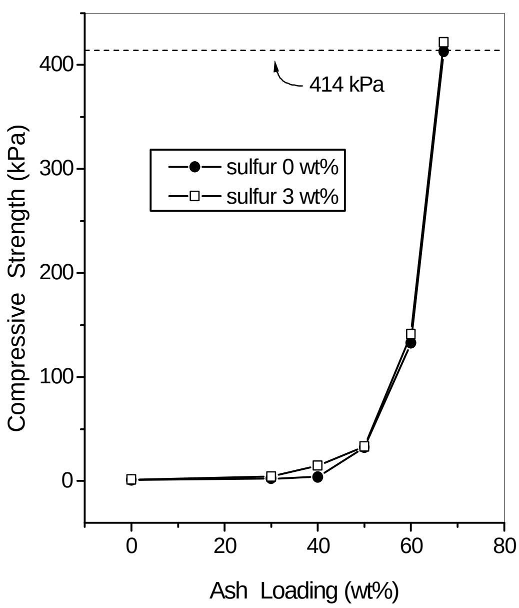


Fig. 2 Influence of sulfur on the compressive strength of waste forms (deformation 10%)

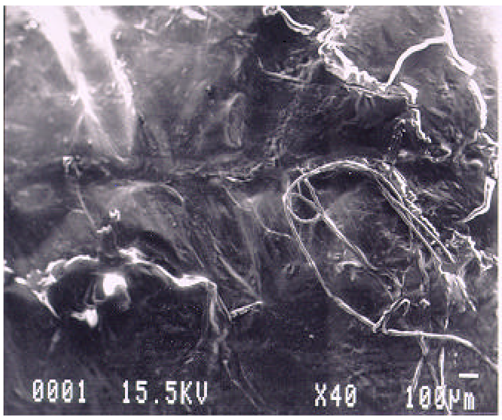


Fig. 3 Scanning electron micrograph of the matrix (bitumen + waste PE)

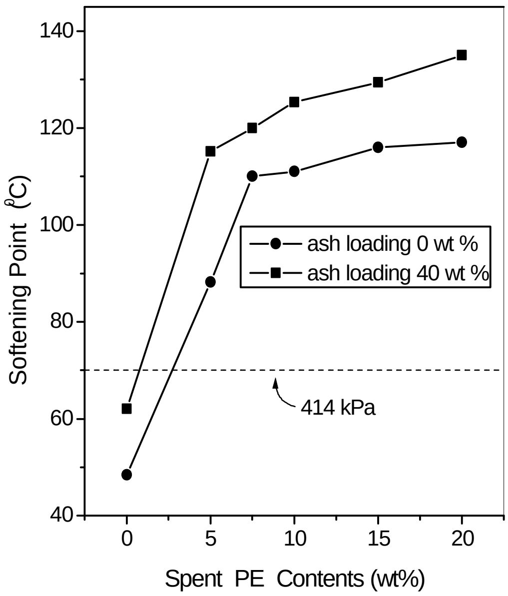


Fig. 4 Influence of spent PE contents on the softening point of waste forms

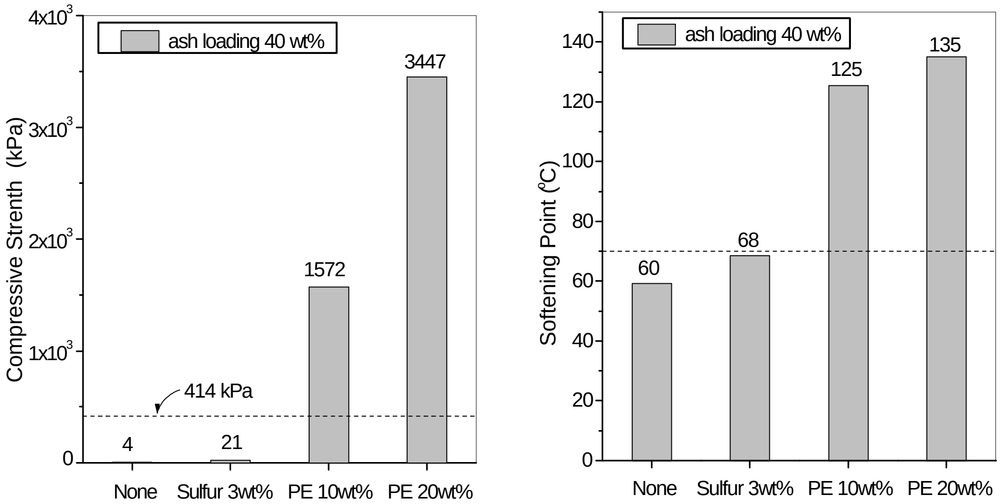


Fig. 6 Influence of the additives on the softening point and compressive strength at ash loading 40wt%

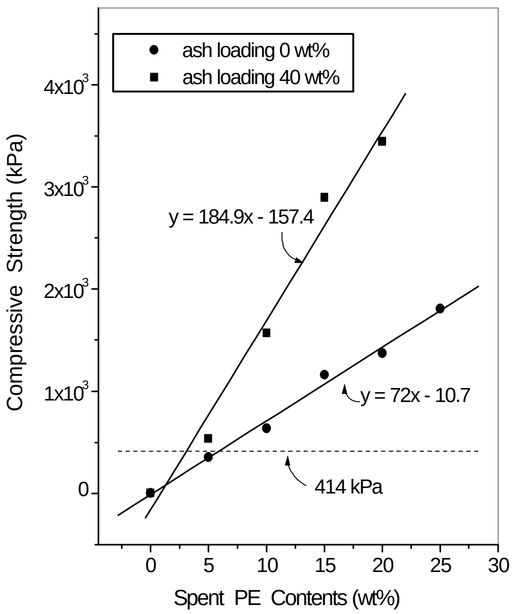
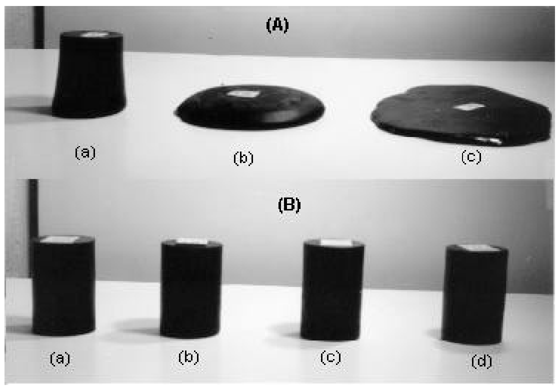


Fig. 5 Influence of spent PE contents on the compressive strength of waste forms (deformation 10%)



(A) (a) sulfur 3 wt% + ash 60 wt%
(b) sulfur 3 wt% + ash 50 wt%
(c) sulfur 3 wt% + ash 40 wt%

(B) (a) spent PE 3 wt% + ash 60 wt%
(b) spent PE 4 wt% + ash 50 wt%
(c) spent PE 5 wt% + ash 40 wt%
(d) spent PE 10 wt%

Fig. 7 The appearance of bituminized waste forms after 90 days