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Preparation of Sustained-release and Salt Containing Anticoagulation

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Abstract. Sustained-release and salt containing anticoagulation is a kind of admixture which can take the initiative to melt snow on the road. However, currently most of products on the market are foreign products, and few domestic products do not have a long-term effect. To enhance sustained-release and long-term effect of anticoagulation, this paper chooses different carriers, preparation methods, surfactants, the concentration ratio of saline content carriers to surfactant, surfactant modification temperature. Studies determine that the modified volcanic powder is used as a carrier, that samples which possess well sustained release character, that using Span-80 and Span-60 as surfactants to have the package on carriers, that the proportion of surfactants and saline content carriers for 1:5 is the best, that surfactant modified temperature is 80°C.

Introduction

Sustained-release and Salt Containing anticoagulation is a kind of admixture which can take the initiative to melt snow on the road. Being added with asphalt mixture, salts from admixture release slowly from capillary spaces to lower the freezing point of ice when vehicles loading. Compared with traditional deicing salts, sustained-release anticoagulant admixture in asphalt pavements can reduce the cost of winter road maintenance and the damage to the environment. Anticoagulant pavements originated in Europe in 1960s. At present it has been used on the road in more than 300 cities around the world [1]. Switzerland firstly developed it. They mixed calcium chloride with asphalt pavement, namely, V-260 [2]. In the late 1970s, Japan introduced admixtures of V-260 and applied them to road surface. In the early 1990, Japan developed Mafilon, or MFL [3]. MFL is a surfactant that help salt adsorb on carriers through special preparation.

Based on the latest advances in recent ten years, some universities in China begin to study on salt snow-melting asphalt pavement. Zhang LiJuan [4] researched on performance and workability of snow-melting asphalt pavement of Mafilon and admixtures. Cui Longxi [5] made a research on asphalt roads mixed up with V-260 to find out the way that salt can be mixed up in the mixture.

Currently most products in domestic markets are foreign technology, with the problem of a lack of variety and high price. And the only two domestic products are unstable and cannot be used in a long term. So the study uses surfactants to have the package processing on saline content carriers to improve the performance of sustained-release in case to guarantee long life.

Experimental

Materials

NaCl, volcanic rocks, diatomaceous earth, zeolite, fly ash, Span-60, Span-80, OP-10, Tween 80, Tween 20, sodium dodecyl benzene sulfonate etc.

Instruments

3H-2000 the specific surface area BET Tester, S-4800 SEM, TJ270-30A infrared spectrometer, magnetic stirrer 85-2C, DDS-11A digital conductivity meter etc.

Preparation of Anticoagulation

Modification of Volcanic Rocks

Volcanic rocks were ground and calcined at 800~900℃. Modification volcanic powder with specific surface areas≥ 350m2/kg was prepared.

Preparation of Saline Content Carriers

According to the ratio, separately added modification volcanic powder, volcanic powder, diatomaceous earth, zeolite and fly ash in saturated brine at 20~30℃, mixed 4~5h then dried to constant weight at 105~120℃. Saline content carriers were prepared.

Preparation of Sustained-release of Surfactant Solution

According to mass ratio of organic solvents and surfactants as (1~10): 1, mixed them up, heated to 60~70℃, stirred 25~30min. Sustained release of surfactant solution was prepared.

Preparation of Anticoagulation

According to the ratio, saline content carriers were added to sustained-release of surfactant solution, mixed 4~5h, dried to constant weight at 130~140℃. Anticoagulant ice agents were prepared.

Methods

Determination of Electric Conductivity

DDS-11A digital conductivity meter was used to test conductivity of samples and changes of chloride to evaluate absorption and release properties of the sample [1].

Water Penetration Test

a. Stab the bottom of a transparent plastic cup to observe and record the test.
b. 10g sample was added, then vibrated to make the sample in the bottom of the transparent plastic cup compact.
c. 50ml distilled water was poured down the side of the plastic glass, then observed its permeability and recorded penetration time and infiltration time.

Results and Discussion

Choice of Carriers

Adsorption property of sustained-release salt containing anticoagulation is influenced by porous carriers. The larger the specific surface area of carriers is, the stronger the adsorption of chloride is. To enhance the performance in removing ice and snow of anticoagulation on asphalt pavement and extend the life of anticoagulation, this paper should choose a porous and large specific surface area material as carriers.

Volcanic rocks, diatomaceous earth, fly ash, zeolite and modified volcanic rocks were prepared for saline content carriers. 36g sodium chloride was weighed to prepare for saturated solution. 20g porous carriers was mixed up with the saturated solution. Stir 4h, filter to remove liquid after soaking 24h, dry to constant weight at 105~120*℃*, namely, mixing → soaking → suction filtration → drying, and recycle for 3 times, then grind it to obtain saline content carriers. A, B, C, D, E, are the five saline content carriers. Respectively weigh same mass of different kinds of saline content carriers, added to the volume of distilled water. Conductivity meter test were conducted to test conductivity within 3h and results are shown in Figure 1.

Figure 1 shows that conductivity of five saline content carriers increase over time, in an order as zeolite > modified volcanic rocks > volcanic > diatomite > fly ash. It shows that the adsorption of chloride decreases gradually. The conductivity zeolite saline content carriers change rapidly over time, while others change very slowly over time.

Different carriers have different adsorption performance. Adsorption capacity is in influence of its structure, not only the cumulative area of desorption, but also accumulation desorption diameter of carriers. Materials with same surface area but different accumulation desorption diameter have different desorption and adsorption capacity. Therefore, five carriers were tested to determine BET specific surface area. Results are shown in table 1.

Table 1 Specific surface test values of five saline content carriers

Carrier	Specific surface area $[m^2 \cdot g^{-1}]$	Accumulation desorption area $[m^2 \cdot g^{-1}]$	Accumulation desorption diameter$[4V \cdot A^{-1}]$
Volcanic rocks	298.8	39.81	54.57
Zeolite	136.7	23.62	83.32
Fly ash	3.32	4.01	41.55
Diatomite	402.4	88.68	98.70
Modified volcanic rocks	360.9	67.2	72.38

Table 1 shows that the order of accumulation desorption area is fly ash < diatomite < volcanic < modified volcanic < zeolite which means adsorption capacity of zeolite to fly ash increases gradually. The order of accumulation desorption diameter is zeolite > diatomite > modified volcanic > volcanic > fly ash. Comparing figure 1 with table 1, it shows as for the strong adsorption capacity of chloride, zeolite is the ideal carrier. But in view of its long-term use, zeolite soon released adsorbed NaCl which has an impact on slow-release.

Modification volcanic rocks were obtained after calcining in 800~900*°C*. Data indicates that accumulation desorption diameter of modification volcanic rocks increased obviously resulting the surface area of the volcanic rocks increases obviously. Therefore, conductivity and adsorption capacity of modification volcanic rocks increase. As for application, the price of zeolite is much higher than volcanic rocks. In all, modification volcanic rocks were chosen as porous carriers for sodium chloride.

Choice of Preparation Method

Under the pressure of porosity osmotic, capillary and vehicle load, sodium chloride adsorbed in modified volcanic rocks pore was slowly released from porous structure of volcanic rocks, which meet the demand for declining condensation point to prevent ice from thawing. But when it comes to water, the internal salt will release, greatly shorten life span. To extend the life of cleaning away snow and ice and slowly release chloride, the study modified volcanic rocks saline content carriers again, that is, cladding a layer of surfactant.

As preparation method 1.3 (2) to obtaining samples E, that is, weigh some quality of surfactant Span-60, mix with ethanol and Span-60 as 5:1 by volume, stir 1h, then prepare surfactant sustained-release solution. Mix samples E with surfactant solution as 5:1 by quality, stir in 80 *°C*, dry to constant heavy in 135*°C*. Sample E with a layer of surfactant was prepared, namely, samples F.

Respectively weigh the same quality sample E and F and added into certain volume of distilled water. Conductivity meter test was used to test the conductivity within 3h. The results were shown in Figure 2.

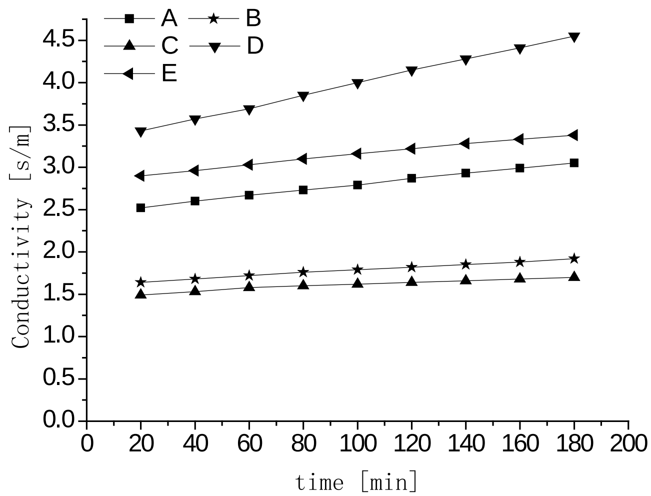

Fig.1 Conductivity change curve of five saline content carriers

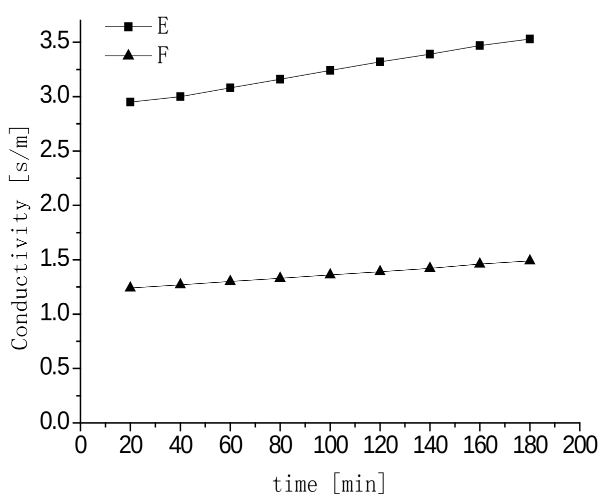

Fig.2 Conductivity change curve of sample E, F

Water permeability test was used on sodium chloride, sample E and sample F as water penetration test. Results were shown in table 2.

Table 2 Result of Water Permeability Test

Type	Permeation time	Running out time	PH
NaCl	3s	52s	7
Sample E	37s	3d	7
Sample F	4d	—	7

Figure 2 shows that, conductivity of sample E without surfactant-coated is greater than surfactant-coated sample F and conductivity changes relatively fast. Sample F slowly release salt.

Table 2 shows that water permeates samples in a short time when NaCl encounters water. Sample E takes a short time to permeate while sample F spends a longer time to permeate and drain. Sample E was obtained by wet modification method, that is, through stirring and soaking to make salt adsorb on porous carriers as much as possible. Because adsorption of sample E modification volcanic powder on NaCl obviously reduced its water penetration but improved the sustained-release property of anticoagulation to a certain extent. Sample F was a sample that sample E was evenly cladded with a layer of waterproofing agent. Sample F had a hydrophobic effect. It cannot be easily dissolved when facing water and its water penetration and drain time are longer, which indicates that water resistant of powder after hydrophobic hydration process on its surface has been greatly improved. Snow-melting substances were able to slowly release from saline content carriers so as to enhance its sustained-release and long-term performance.

Therefore, this study added hydrophobic hydration process to preparation of sustained-release salt containing anticoagulation and cladded surfactants on modification salt. Through combining hydrophilic polar with the substrate, non-polar in polar groups emerges outside so as to achieve hydrophobic effect [6].

Choice of Surfactant

Non-ionic surfactants Span-60, Span-80, OP-10, anionic surfactants sodium dodecyl benzene sulfonate, Span-80 and sodium dodecyl benzene sulfonate which mass ratio is 5:1, OP-10 and sodium dodecyl benzene sulfonate which mass ratio is 5:1 were selected. Ethanol was mixed respectively with the surfactant by 5:1 according to volume for one hour when surfactant was fully dissolved. Sample E was mixed up with different types of surfactant solutions by 5:1 according to mass, stirring in 80℃ for 6 hours and dried to constant weight in 135℃. Sample F, G, H, M, N, and X were obtained.

Respectively weigh the same quality sample, add them into a volume of distilled water and conduct the conductivity meter test within 3h. Test results were shown in Figure 3.

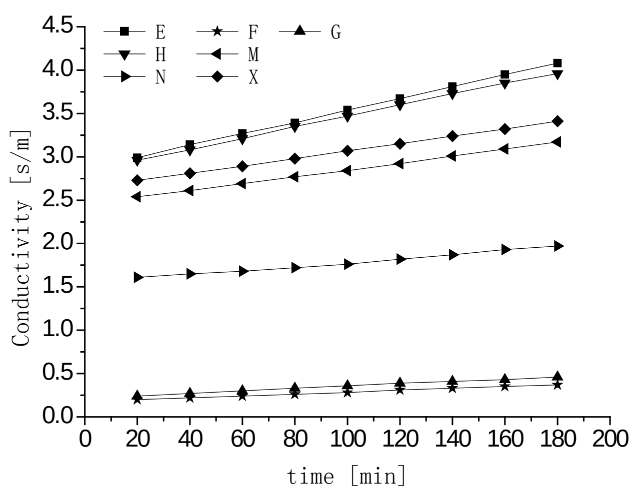

Fig.3 Conductivity Change Curve of Different Samples

Figure 3 shows that the chloride release rate of sample H coating OP-10 and sample E without surfactant is quite the same. There is slow-release effect in sample M and sample X. The chloride release rate of sample N is obvious. The chloride release rate of sample F, G is lower than sample E.

There is a long non-polar group in surfactant OP-10 molecule, resulting in strong hydrophobic performance. Hydrophilic group was caught in the hydrocarbon chain resulting that the hydrophilic capacity is weak. So this study chose OP-10 as one of the hydrophobic agents. OP-10 was dissolved in ethanol to obtain sustained-release surfactant solution. Due to the role of –OH in ethanol molecular, the molecular spatial structure of OP-10 has changed, resulting twist and turn structure [7]. It made hydrophobic of OP-10 molecular was covered by hydrophilic and -OH in ethanol molecular and ether linkage of OP-10 were combined to hydrogen bonds while ethanol molecular was combined with water molecular to hydrogen bonds. A larger of hydrophilic was appeared around OP-10 molecular, resulting in an obvious improvement in hydrophilicity of surfactant and a decline in hydrophobicity of OP-10 surfactant, with the slow-release effect unobvious.

Sodium dodecyl benzene sulfonate is a linear alkylbenzene sulfonate [8]. It is likely that there are not enough alkyl substituents in this study resulting in poor hydrophobic and that the cladding outside salt cannot play a role in hydrophobic. Therefore, it cannot improve the performance of slow-release saline content carriers.

Span-80 is often used as water of non-ionic surfactants in oil [9]. Hydrogen and hydroxyl groups in Span-80 molecular are strongly active in chemical. The dehydration condensation reaction between hydrogen bonding and hydrogen groups were explored, resulting in network structure. Thus it increased the hydrophobicity of Span-80. Span-60 and Span-80 are similar, which are used as water-in-oil surfactants. Sample F, G with Span-60 and Span-80 coated have sustained-release effect.

Scanning surface coating effect of surfactants in salt by electron microscope, the results were shown in Figure 4, Figure 5 and Figure 6.

From Figure 5 and Figure 6, it can be seen that there is a membrane outside modified volcanic saline content carrier, indicating that saline content carrier has been cladded by Span-60 and Span-80. Therefore, Span-60 and Span-80 were explored as surfactants in this study.

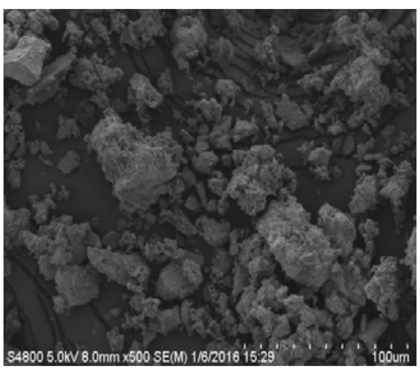

Fig.4 Uncladding modified volcanic saline content carrier

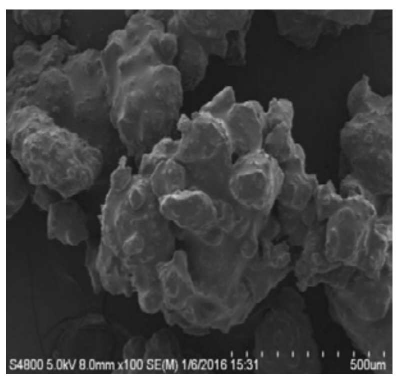

Fig.5 Cladding Span-60 modified volcanic saline content carrier

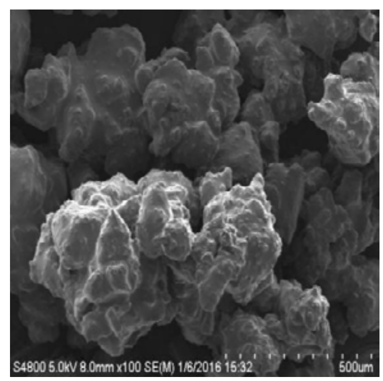

Fig.6 Cladding Span-80 modified volcanic saline content carrier

Choice of Ratio of Surfactant to Saline Content Carrier

Ethanol and Span-60 were mixed up as 5:1 according to volume, stirring for 1h resulting surfactants fully dissolved. Sample E and surfactant solutions were mixed up as ratio of 1:1, 5:1, 10:1 respectively according to mass, stirring for 6h in 80 °C to be fully mixed, dried to constant weight in 135°C. A certain volume of distilled water was respectively added to the same quality samples after drying and weighing. Conductivity were test by conductivity meter test within 3h. Results were shown in Figure 7.

From figure 7, it shows that when the ratio of surfactants to modified volcanic saline content carrier is 1:1, conductivity is small and conductivity rate changes slowly, that is, chloride is released more slowly because of a large use of surfactants, resulting that too dense the salt-cladded carrier is and chloride is not easily released. When the ratio of surfactant to modified volcanic saline content carrier is 1:10, conductivity rate is a little large and conductivity rate changes more fast, that is, chlorine is released comparably quickly because of a less usage of surfactant, failing to clad saline content carrier completely and chlorine easily released. This ratio is more useful than adding surfactant to asphalt, but a poor long-term effect. Therefore, this paper choose ratio as 1:5.

Choice of Modified Temperature

Modified volcanic saline content carrier was modified in 70°C, 80°C and 90°C and the ratio of Span-80 to saline content carrier is 1:5. Results were shown in Figure 8.

Figure 8 shows that the higher the modified temperature is, the smaller the conductivity changing rate is, that is, an improvement in sustained release performance. Due to there are one or more than one hydroxyl in Span-80 surfactant molecular structure, which can combine with water molecular by hydrogen bonds. With temperature increasing, hydrogen bonds are damaged, the solubility of surfactants and hydrophilic declining. So the trend of adsorbing to solid surface is obvious, which is conducive to improve modified effect. However, adsorption is usually an exothermal process. If temperature is too high, negative impacts on warming will be larger than the beneficial effects of the failure of hydrogen bonds, resulting in a decline in modification, draining and slow-release performance. Therefore, 80 °C is the best.

Conclusions

(1) Adsorption capacity is in the influence of different types of carrier. The adsorption of chloride of modified volcanic powder is better. Modified volcanic rock powder is determined as carrier.
(2) Modified volcanic saline carrier cladding with surfactant explores a good release property, preparation of cladding with surfactant is chosen.
(3) Different types of surfactant affect sustained-release property of anticoagulation. Span-80 and Span-60 are determined as surfactant.
(4) The ratio of surfactant to saline content carrier influences sustained-release capacity of anticoagulation. When the ratio of surfactant to saline content carrier is 1:5, the performance is the best.
(5) Temperature is also an impact of it. 80℃ is selected to be the most suitable temperature.

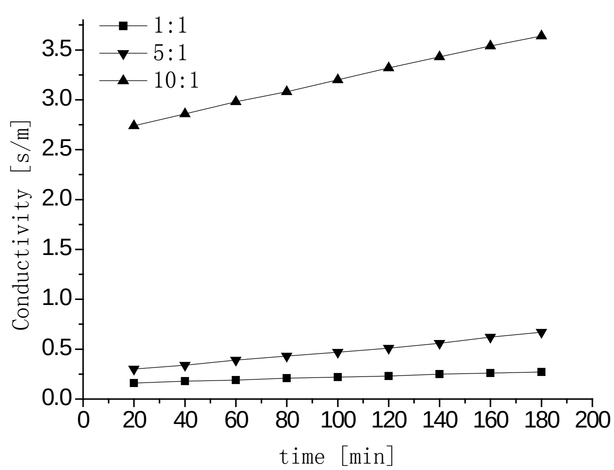

Fig.7 Conductivity in different ratio of Span-60 to carrier

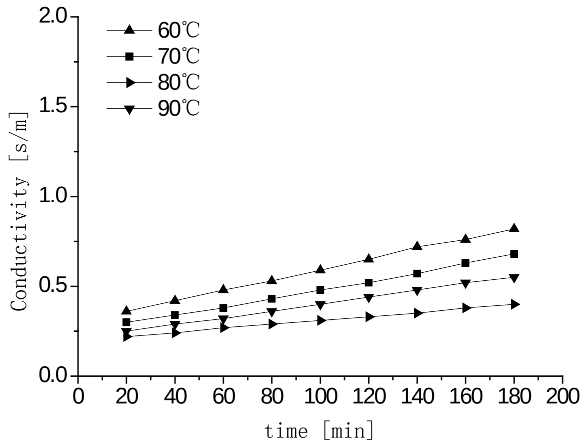

Fig.8 Conductivity in different temperatures

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