Deicing and Corrosive Performances of Calcium Acetate Deicer Made from Bamboo-Vinegar*

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Abstract—Calcium magnesium acetate (CMA) is environmentally benign deicing chemicals that can replace sodium chloride that is widely used on roads and highways at present for snow and ice control to provide safe driving conditions during winter. The price of CMA from petroleum-derived acetic acid is quite expensive. The bamboo vinegar is the by-product from bamboo charcoal production. The bamboo vinegar was used to prepare calcium acetate as raw materials, and its deicing and corrosive performances were studied in this paper. The results show that the freezing temperature of calcium acetate is lower than that of sodium chloride when they have same molar concentration, the deicing performance of calcium acetate is better than that of sodium chloride when they have same moles, while the deicing performance of sodium chloride is better than that of calcium acetate. The corrosion of sodium chloride on iron-nail and steel-nail is larger than that of calcium acetate whether they have same mass concentration or same molar concentration, and the corrosion of sodium chloride and calcium acetate on iron-nail is larger than that on steel-nail, and calcium acetate almost hasn't corrosion on steel-nail.

Keywords—bamboo vinegar, calcium acetate, corrosion, deicer, deicing performance

I. INTRODUCTION

Bamboo is a kind of the important renewable resources, and it is usually called the second forestry resource except the wood in China. Bamboo or the bamboo processing residues can be used to produce bamboo-charcoal and bamboo-vinegar liquor by pyrolysis besides its traditional uses such as everyday commodities, art works, paper pulping, artificial bamboo board, plybamboo, et al [1], [2]. At present bamboo charcoals have been widely produced and applied in China, Japan and other countries to be adsorbent in chemical industries, environmental protection, medical and food industries, et al. At the same time large amount of bamboo vinegar as byproduct from bamboo pyrolysis has been produced every year in China. There are many kinds of organic components in bamboo vinegar through determining the bamboo vinegar by using GC-MS, and the water is 80%~90% of the total bamboo vinegar, and the main organic components are organic acids and phenols, and others little components includes aldehydes, ketones, alcohols and esters, et al, and the total organic acids and phenols are 7%~11% of the total bamboo vinegar, whereas the acetic acid is about 6% of the bamboo vinegar, that is to say the acetic acid is the main component of organic acids in bamboo vinegar, the other little organic acids include formic acid, propionic acid, butyric acid and et al, and the total phenols are 6%~8% of the total bamboo vinegar [3]. Bamboo vinegar can be used to be soil bactericide, soil modifier, fertilizer synergist, plant growth accelerator, food additive, deodorant and skin-protection and cosmetology additive, et al, but at present its effective development and application was limited for its complicated components [4].

Deicer is a kind of chemical namely deicing salt which can be used to lower the freezing point of water, reduce and control ice and snow on roads along with sand [5]. At present the deicer in the world can mainly divided into two kinds of species, one kind includes sodium chloride, calcium chloride, magnesium chloride and potassium chloride, et al, and this kind is usually called deicing salt which is cheap but harmful to the growth of crops, urban flowers and plants [6], [7], at the same time it has heavy corrosion to the iron, steel, specially to concrete road and bridge [8], [9]. At present for the main components of deicers used in northern of China are sodium chloride, calcium chloride and magnesium chloride, the deicers have made great damage to the concrete roads and bridges, plants and flowers along the roads in the cities [10]. Another kind of deicer consisting of calcium acetate and magnesium acetate is regarded as green and environmentally benign chemicals in the world, and has little corrosion on steel-bridge and iron-bridge, and little damage to concrete road, highways and bridge, plants and flowers, so it can prolong the using life of road, highways and bridge, also has little effect on the growth of plants and flowers, at the same time has lower deicing limit temperature than chlorides [7], [11]. But the price of calcium acetate and magnesium acetate from petroleum-derived acetic acid is quite expensive, which limits their application only in environmentally sensitive areas now, e.g. airport, how to low their cost is the key of wide application [12], [13]. The environmentally benign deicer calcium acetate was prepared from the bamboo vinegar which is the by-product of bamboo charcoal production, and its deicing and corrosive performances were studied in this paper.
II. MATERIALS AND METHODS

A. Instruments and Reagents

Instruments: Charring furnace; Rotating Evapori meter; PHS-2 pH-Meter; UV-1201 Ultraviolet visible Spectrophotometer; DLSB10L/20 Low Temperature Cooling Fluid Circulating Pump.

Reagents: Calcium oxide(CP), Sodium chloride(AR), Sodium hydroxide(AR), Phenolphthalein(AR), Methylene blue(AR), et al.

B. Distillation and refinement of bamboo vinegar

Distillation is a kind of method to separate the components with different boiling point in raw bamboo vinegar. Ordinary pressure distillation is used at temperature about 100 to separate the raw bamboo vinegar produced by bamboo carbonization and putting aside for 4 months in advance.

C. Determination of the amount of organic acid and pH in bamboo vinegar

0.1mol/L sodium hydroxide solution was prepared and calibrated by using potassium hydrogen phthalate (M=204.2g/mol). The organic acid content of bamboo vinegar is determined through acid -base titration by using 0.1mol/L sodium hydroxide solution calibrated above and by using phenolphthalein as indicator.

pH value of bamboo vinegar is determined with PHS-2 pH-Meter which was calibrated by potassium hydrogen phthalate buffering solution with pH 4.00 and phosphate buffering solution with pH 6.86.

D. Preparation and performances measurement of calcium acetate deicer

1) Preparation of calcium acetate deicer

Calcium hydroxide powder was put in distilled bamboo vinegar with known organic acid concentration, then stirred evenly, and reacted 30-50 minutes under the room temperature by controlling the pH value at about 7.5. Yellow filtrate can get from the solution by filtering the insoluble solid, and then is decolorized by adding little activated carbon powder to be colorless or light yellow filtrate namely calcium acetate solution from which solid calcium acetate can be obtained by evaporating and crystallizing or spray drying.

2) Measurement of deicing performance of deicers

The deicer solution was prepared and put in DLSB10L/20 Low Temperature Cooling Liquid Circulating Pump, then the temperature of deicer solution was lowered gradually, at every chosen temperature point, the temperature was maintained 1h to make sure the equilibrium between the solid and liquid in deicer solution, and the freezing data of deicer solution at different temperature was recorded until the lowest freezing temperature.

Solid deicer powders with same mass or moles of were scattered uniformly on the surface of ices made from water in the container respectively, then the volume of water melted in every container was measured at some time interval to evaluate the deicing efficiency of deicer, the larger the volume of water melted within same time was, the higher the deicing efficiency of deicer was.

3) Corrosive comparison of deicers on steel and iron

Environmentally benign deicer must not only make sure its deicing efficiency, but also has little negative influence on surrounding environment such as iron, steel, concrete roads, bridges, flowers and plants, et al. The corrosion of deicer solution with different mass concentration and molar concentration on iron-nail and steel-nail chosen to represent the iron and steel was investigated in this paper. The iron-nail or the steel-nail was fixed with thread and then soaked in the deicer solution with certain mass or molar concentration, and taken out after some time, then cleaned, dried and weighed, finally the mass loss rate namely corrosive rate of iron-nail or the steel-nail was calculated by (1). Higher the mass loss rate of iron-nail or the steel-nail was, higher the corrosion of deicer on iron-nail or steel-nail was.

\[ R = \frac{W_1 - W_2}{W_1} \times 100\% \]  

\[ R - \text{rate of corrosion, \%; } W_1 - \text{mass of raw iron-nail or steel-nail, g; } W_2 - \text{mass of iron-nail or steel-nail after being corroded, g} \]

III. RESULTS AND DISCUSSION

A. Determination of total amount of organic acids and pH value of bamboo vinegar

The acetic acid content of bamboo vinegar must be determined before it being used to produce deicer calcium acetate, and the acetic acid content is difficult to determine individually for the organic acid components in bamboo vinegar are complicated, for the main component of organic acids is acetic acid, so the total organic acids content of bamboo vinegar can usually represent the acetic acid content. The total organic acids content of bamboo vinegar was measured by acid-base titration, and the pH value was analyzed by pH-Meter in this paper, and the results were presented in Table I.

Table I shows that the color of distillate from bamboo vinegar was lighter than that of raw bamboo vinegar, and the raw bamboo vinegar A was deep brown, whereas the bamboo vinegar distillate A was yellow, and the raw bamboo vinegar B was yellow, whereas the bamboo vinegar distillate B was light yellow. The pH value of distillate from raw bamboo vinegar was lower than that of raw bamboo vinegar, and the organic acids content of distillate from raw bamboo vinegar was larger than that of raw bamboo vinegar, which indicates the organic acids content of distillate from raw bamboo vinegar was richened and increased after bamboo vinegar being distilled. The pH value and organic acids content of raw bamboo vinegar A was 2.8 and 0.111 mol/L respectively, whereas that of from bamboo vinegar distillate A was 2.5 and 0.478 mol/L.
B. Deicing performances of deicers

1) Lowest freezing temperature Comparison of of NaCl and Ca(Ac)_2

As the lowest freezing temperature of DLSB10L/20 Low Temperature Cooling Liquid Circulating Pump used in this paper can only decrease to -20℃, so 0.05mol/L NaCl solution, 0.1mol/L NaCl solution and 0.1mol/L Ca(Ac)_2 solution were prepared to put in the plastic bottles placed in the DLSB10L/20 Low Temperature Cooling Liquid Circulating Pump by using glycerol as cooling liquid, and then the temperature of cooling liquid in the pump decreased gradually, at every chosen measuring temperature, the temperature was maintained 1h to make sure the ice-liquid equilibrium, the freezing results of above three deicer solutions at different temperature were presented in Table II.

Table II shows that 0.05mol/L NaCl solution was more easily to freeze than 0.1mol/L NaCl solution at the same temperature, which indicated that lower the concentration of same deicer solution was, higher its deicing temperature was, while higher the concentration of deicer solution was, lower its deicing temperature was, that is to say lower the freezing point of deicer solution was, higher its deicing capability was [14].

0.1mol/L Ca(Ac)_2 solution has lower freezing point than 0.1mol/L NaCl solution, for example at -11.0±0.1℃, 0.1mol/L Ca(Ac)_2 solution didn’t freeze, whereas the 0.1mol/L NaCl solution had frozen partially, so Ca(Ac)_2 had higher deicing capability than NaCl at same molar concentration.

2) Deicing efficiency comparison of NaCl and Ca(Ac)_2

Eight plastic bottles of distilled water with volume 100 ml respectively were frozen at 0℃ in DLSB10L/20 Low Temperature Cooling Liquid Circulating Pump, then the solid deicers NaCl and Ca(Ac)_2 were scattered uniformly on the surface of ices respectively according to same masses or moles of deicer, and the volume of water melted was written down at 1h interval. The results were presented at Table III and Table IV.

Table III shows that to the same of deicer with different masses, larger the mass of deicer was, more the volume of water melted was, the volume of water melted by 2gNaCl was 84.7 ml in 4 h, whereas the volume of water melted by 4gNaCl was 97.9 ml in 4 h, and the volume of water melted by 2g Ca(Ac)_2 was 63.1 ml in 4 h, and, whereas the volume of water melted by 4g Ca(Ac)_2 was 81.7 ml in 4 h. The volume of water melted by deicer increased gradually with the increasing of time, the volume of water melted by 2gNaCl was 45.5ml, whereas that was 84.7ml in 4 h, and the volume of water melted by 2g Ca(Ac)_2 was 28.1 ml, whereas that was 63.1 ml in 4 h. The results above indicated that the deicing capability of NaCl was better than that of Ca(Ac)_2 when the mass of deicer used was same and on same volume of ice.

Table IV shows that to the same kind of deicer, larger the moles of deicer were, more the volume of water melted by deicer was, and the volume of water melted by 0.025mol and 0.05mol Ca(Ac)_2 was 86.9ml and 97.7ml in 4h respectively, and that by 0.025mol and 0.05mol NaCl was 84.5ml and 94.8ml in 4h. The volume of water melted by deicer Ca(Ac)_2 and NaCl respectively increased gradually with the increasing of time, the volume of water melted by 0.025mol Ca (Ac)_2 was 41.5ml and 86.9ml in 1h and 4h respectively, and the volume of water melted by 0.025mol NaCl was 37.0ml and 84.5ml in 1h and 4h respectively. The results above indicated that the deicing capability of Ca(Ac)_2 was better than that of NaCl at same moles used and same time.

C. Corrosion comparison of deicers on metal

1) Corrosion comparison of deicers with same molar concentration on metal

Eight clean plastic bottles with covers were divided into A group and B group and each group had four bottles. 0.1 mol/L Ca(Ac)_2, 0.3 mol/L Ca(Ac)_2, 0.1 mol/L NaCl and 0.3 mol/L NaCl solution with same volume was put into four bottles of A...
group respectively, and the same solution to four bottles of B group. Four iron-nails fixed with thread were dipped into the solution in four bottles of A group respectively at same depth, and four steel-nails fixed with thread were dipped into the solution in four bottles of B group respectively at same depth, then the iron-nails and steel-nails were taken out to clean, dry and weigh at 3 days interval for measuring and comparing the corrosion of iron-nails and steel-nails corroded by above deicer solutions. The corrosion results of deicer solutions with same molar concentration on iron-nails were shown in Table V, and the corrosion results of deicer solutions with same molar concentration on steel-nails were presented in Table VI.

Table V shows that when the molar concentration of Ca(Ac)₂ and NaCl solution was same, either 0.1 mol/L or 0.3 mol/L, the corrosive impact of NaCl solution on iron-nail was much larger than Ca(Ac)₂ solution at same time. The corrosion rate iron-nail corroded by 0.1 mol/L Ca(Ac)₂ solution and 0.1 mol/L NaCl solution was 1.920‰ and 5.780‰ respectively, and the corrosion rate of iron-nail corroded by 0.3 mol/L Ca(Ac)₂ solution and 0.3 mol/L NaCl solution was 0.893‰ and 4.581‰ respectively after 12 days.

Table V shows that the corrosive impact by NaCl solution on iron than Ca(Ac)₂ solution at same time. The corrosion rate of iron-nail corroded with increased with the increasing of time, but that by Ca(Ac)₂ solution changed hardly with the increasing of time. The corrosion rate of iron-nail corroded by deicer solution with low molar concentration was larger than that with high molar concentration. The corrosion rate of iron-nail corroded by 0.1 mol/L NaCl solution and 0.3 mol/L NaCl solution was 5.780‰ and 4.581‰ respectively, and the corrosion rate of iron-nail corroded by 0.1 mol/L Ca(Ac)₂ solution and 0.3 mol/L Ca(Ac)₂ solution was 1.920‰ and 0.893‰ respectively after 12 days.

Table V shows that the corrosive impact by NaCl solution on iron than Ca(Ac)₂ solution at same time. The corrosion rate of iron-nail corroded with increased with the increasing of time, but that by Ca(Ac)₂ solution changed hardly with the increasing of time. The corrosion rate of iron-nail corroded by deicer solution with low molar concentration was larger than that with high molar concentration. The corrosion rate of iron-nail corroded by 0.1 mol/L NaCl solution and 0.3 mol/L NaCl solution was 5.780‰ and 4.581‰ respectively, and the corrosion rate of iron-nail corroded by 0.1 mol/L Ca(Ac)₂ solution and 0.3 mol/L Ca(Ac)₂ solution was 1.920‰ and 0.893‰ respectively after 12 days.
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Table VI shows that the corrosive impact by NaCl solution on steel-nail increased with the increasing of time, but that by Ca(Ac)2 solution changed hardly with the increasing of time. The corrosion rate of steel-nail corroded by 0.1 mol/L NaCl solution, whereas the corrosion rate of steel-nail corroded by 0.1 mol/L Ca(Ac)2 solution was almost the same as that by 0.3 mol/L Ca(Ac)2 solution after same days. The corrosion rate of steel-nail corroded by 0.1 mol/L NaCl solution and 0.3 mol/L NaCl solution was 3.554‰ and 2.577‰ respectively, and the corrosion rate of steel-nail corroded by 0.1 mol/L Ca(Ac)2 solution and 0.3 mol/L Ca(Ac)2 solution was 0.458‰ and 0.227‰ respectively after 12 days.

Table VI shows that the molar concentration of Ca(Ac)2 and NaCl solution was same, either 0.1 mol/L or 0.3 mol/L, the corrosive impact of NaCl solution on steel-nail was much larger than that of Ca(Ac)2 solution at same time. The corrosion rate of steel-nail corroded by 0.1 mol/L NaCl solution and 0.3 mol/L NaCl solution was 3.554‰ and 2.577‰ respectively, and the corrosion rate of steel-nail corroded by 0.1 mol/L Ca(Ac)2 solution and 0.3 mol/L Ca(Ac)2 solution was 0.458‰ and 0.227‰ respectively after 12 days.

The comparison between Table V and Table VI shows that the corrosion rate of Ca(Ac)2 as deicer on steel-nail was lower slightly than that on iron-nail at same molar concentration, and the corrosion rate of NaCl as deicer on steel-nail was almost the same as that on iron-nail at same molar concentration.

2) Corrosive comparison of deicers with same mass concentration on metal

The solutions in III A.1) were exchanged by 24g/L Ca(Ac)2, 24g/L NaCl, 40g/L Ca(Ac)2 and 40g/L NaCl solution respectively, and then the iron-nails and steel-nails were soaked in according to the method II.D.3), and the iron-nails and steel-nails were taken out to clean, dry, finally weigh at 3 days interval, the corrosive impact of deicers with different mass concentration was evaluated and compared, and the corrosion rate results on iron-nails and steel-nails were presented in Table VII and Table VIII respectively.

Table VII shows that the corrosive rate of NaCl solution on iron-nail was larger than that of Ca(Ac)2 solution when the mass concentration of Ca(Ac)2 and NaCl solution was same after same time. The corrosion rate of 24g/L NaCl solution and 24g/L Ca(Ac)2 solution was 5.420‰ and 0.411‰ respectively, whereas the corrosion rate of 40g/L NaCl solution and 40g/L Ca(Ac)2 solution was 4.562‰ and 0.000‰ respectively after 12 days.

Table VII shows that the corrosive impact by NaCl solution on iron-nail increased with the increasing of time, but that by Ca(Ac)2 solution changed hardly with the increasing of time. The corrosion rate of iron-nail corroded by 24g/L NaCl solution and 24g/L Ca(Ac)2 solution was 5.420‰ and 0.411‰ respectively, whereas the corrosion rate of iron-nail corroded by 40g/L NaCl solution and 40g/L Ca(Ac)2 solution was 4.562‰ and 0.000‰ respectively after 12 days.

Table VII shows that when the mass concentration of Ca(Ac)2 and NaCl solution is same, either 24 g/L or 40 g/L, the corrosive rate of NaCl solution on steel-nail was much larger than that of...
Ca(Ac)₂ solution, moreover the corrosive rate of Ca(Ac)₂ solution on steel-nail was little. The corrosion rate of NaCl solution on steel-nail increased with the increasing of time, but that of Ca(Ac)₂ solution on steel-nail hardly increased with the increasing of time. Corrosion rate of steel-nail corroded by 24 g/L NaCl solution was larger than that corroded by 40 g/L NaCl solution, and the corrosive rate of steel-nail corroded by 24 g/L Ca(Ac)₂ solution was larger slightly than that corroded by 40 g/L Ca(Ac)₂ solution at same time. Corrosion rate of steel-nail corroded by 24 g/L NaCl solution and 40 g/L NaCl solution was 3.965‰ and 2.279‰ respectively after 12 days, and that of steel-nail corroded by 24 g/L Ca(Ac)₂ solution and 40 g/L Ca(Ac)₂ solution was 0.674‰ and 0.226‰ respectively after 12 days.

The comparison between Table VII and Table VIII show that the corrosion rate of Ca(Ac)₂ as deicer on steel-nail was much lower than that on iron-nail at same mass concentration, and the corrosion rate of NaCl as deicer on steel-nail was lower slightly than that on iron-nail at same mass concentration.

IV. CONCLUSIONS

The conclusions drawn from the data presented above can be summarized as follows:

1) The freezing temperature of Ca(Ac)₂ solution was lower than that of NaCl solution at same molar concentration. The deicing capability of Ca(Ac)₂ was better than that of NaCl at same moles, whereas the deicing capability of NaCl was better than that of Ca(Ac)₂ at same masses.

2) The corrosive rate of NaCl solution on iron-nail and steel-nail was much larger than that of Ca(Ac)₂ solution either at same mass concentration or molar concentration. The corrosive rate of Ca(Ac)₂ solution on iron-nail and steel-iron was very little, and that of NaCl solution on iron-nail was larger slightly than that on steel-nail at same concentration. So that the Ca(Ac)₂ can be regarded as green and environmentally benign deicer.

3) Until now there is no successful products made from bamboo vinegar, and the research above shows that it is feasible to use bamboo vinegar, by-product of bamboo charcoal production, to produce environmentally benign Ca(Ac)₂ deicer.

REFERENCES


