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THE IMPACT OF ROAD MAINTENANCE SUBSTANCES ON METALS SURFACE CORROSION

Jolita Petkuvienė[1], Dainius Paliulis[2]
Vilnius Gediminas Technical Univeristy
E-mail: [1]jolita.kairyte@gmail.com; [2]dainius@ap.vgtu.lt

Abstract. The purpose of research is to assess changes in the visual metal surface due to the exposure of road maintenance salts and molasses ('Safecote'). Chlorides of deicing salts (NaCl, $CaCl_2$) are the main agents affecting soil and water resources as well as causing the corrosion of roadside metallic elements. Molasses ('Safecote') is offered as an alternative to deice road pavement by minimizing the corrosion of metal elements near the road. A laboratory experiment was carried out to immerse and spray metals with NaCl, $CaCl_2$, NaCl:$CaCl_2$ and NaCl:Safecote solutions. The obtained results showed that NaCl:Safecote solution had the lowest coating with corrosion products (the average 17±4 % of the surface). The solutions of NaCl, $CaCl_2$ and NaCl:$CaCl_2$ had the highest percentage rate of the corrosion product on the metal surface reaching an average of 33±5 %.

Keywords: road maintenance salts, sodium chloride, calcium chloride, Safecote, metals, corrosion.

Introduction

Corrosion is a destructive attack on metal containing a chemical or electrochemical reaction to the environment (Ahmad 2006). Corrosion is the result of the interaction between metals and aggressive surrounding environments such as temperature, relative humidity, pH and the deposition rate of pollutants (chlorides, sulphides, carbonates, etc.) (Almarshad, Syed 2008). Additionally, the corrosion process itself affects the environment toxically by releasing heavy metals (Belghazi *et al.* 2002) on the soil or into water resources by contaminating them. The contamination of soil and water resources can cause bigger problems especially when metals get into the food chain. Metals can move through the food chain into plants, animals and the human body by causing various damages.

Salts are one of aggressive environments inducing corrosion. During winter time, salts are the main problem in countries where snow and ice cover the pavement. They are widely applied as road maintenance substances to deice road pavement in Lithuania. Salts are applied worldwide as a good dicer for its quite simple and easy use and low cost (Vosylienė *et al.* 2006). However, salts have two main disadvantages. The first one is that salts negatively affect natural roadside environment and its components (Vosylienė *et al.* 2006) such as vegetation (Zaveckytė, Ščuupakas 2005; Baltrėnas *et al*. 2006; Kazlauskienė, Baltrėnas 2007), soil (Hääl, Sürje 2006; Jelisejevs, Urbanovuchs 2007) and water quality (Sanzo, Hecanr 2006). The second disadvantage is that the corrosion of metal is also caused by salts. It is known that metals are the component of road elements. For example road signs, fences, bridges and cars are made of the same kind of metal. The corrosion of road elements causes the deterioration of bridges, decreased safety and high economic costs.

Scientists suggest using NaCl with the product 'Safecote'. It is based on molasses which is a by-product of sugar production. In this case, environmental damage caused by salts would be minimized. 'Safecote' is a good alternative especially at minimizing damage to vehicles and metallic infrastructures. The use of 'Safecote' with salts (NaCl) reduces application rates of salts from 30 % to 50 % (Burtwell, Wilson 2004). At the same time, the mixture reduces corrosion about 40 % comparing with NaCl solution (Wilson *et al.* 2002).

The purpose of this article is to assess changes in the visual metal surface due to the exposure of road maintenance salts and molasses ('Safecote').

Methodology of the Experiment

Experimental research was carried out in the chemical laboratory of the Department of Environmental Protection at Vilnius Gediminas Technical University (VGTU). The duration of experimental research was 100 days due to the reason that Lithuania has a winter season that lasts for three months which is roughly about 100 days. Experimental research was conducted under normal laboratory conditions (19–20°C temperature, 38–40 % relative humidity).

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Four different types of solution with special concentrations were chosen for experimental research (NaCl, $CaCl_2$, NaCl:$CaCl_2$ and NaCl:Safecote). These concentrations are actually used for winter road maintenance in Lithuania. Sodium chloride (NaCl) is mixed with deionized water to prepare 23 % concentration of NaCl solution which has 7,6 pH. When the temperature of the environment increases up to – 4°C, it is recommended to mix NaCl with $CaCl_2$ in mixing ratio 7,3:1 which is the solution of 8,0 pH. $CaCl_2$ solution with 8,5 pH is rarely used as a deicer though this opportunity is possible. The concentration of Calcium chloride ($CaCl_2$) solution is 30 %. The last substance is 'Safecote' which is a new deicer in Lithuania. Actually, it has not been used on roads yet because this product is at the initial stage of experimentation in Lithuania. 'Safecote' can be characterized as having good anticorrosion properties, is perfect ice and snow melter, not harmful to the environment and has the binding of particle properties. 'Safecote' is mixed with NaCl solution at ratio 9:1 (NaCl:Safecote) where 900 ml of 23 % NaCl solution was mixed with 100 ml of pure 'Safecote'. This mixing ratio is recommended to be applied in Lithuania due to the dominated condition. This solution has 5,6 pH.

To conduct investigation, three types of metals were used and included carbon steel (S235JRG2), stainless steel (No. 1.4541) and galvanized steel (DX51D). The chemical composition of metals (wt, %) is presented in Table 1. All metals used in experimental research are applied to produce road metallic elements such as bridges, crash barriers, road signs and some parts of the car body.

During experimental research, two types of methods embracing immersion and spraying were performed. Each metal was immersed into each solution as shown in Fig. 1A during the investigation period applying the first immersion experimental method. The second method was called spraying because each metal was sprayed with each solution every week during experimentation (Fig. 1B). About 5 ml of experimental solution on metal surface was sprayed each time.

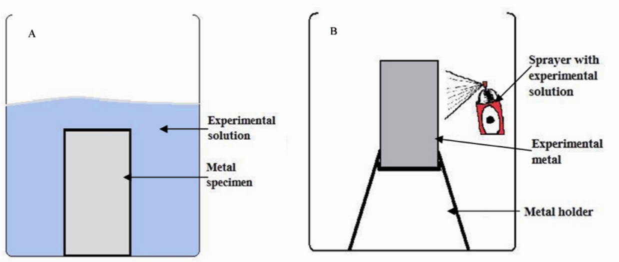

Fig. 1. Laboratory experiments. A – Immersion method; B – Spraying method

Every metal sample was cut into the size of 55×30 mm. Each metal has different thickness, for instance, galvanized steel - 1.5 mm, stainless steel - 4 mm and carbon steel - 5 mm. The samples were mechanically polished with 400, 500 and 600 emery papers and lubricated using deionized water before exposure. The polished samples were cleaned with acetone, washed using deionized water (Rosliza *et al.* 2008; Cho *et al.* 2008) and dried. After preparation, experimental metals were immersed and sprayed with test solutions for 100 days after cleaning. The picture of every metal after experiment was taken in order to assess changes in metal surface. The assessment was performed using a standard picture (Fig. 2).

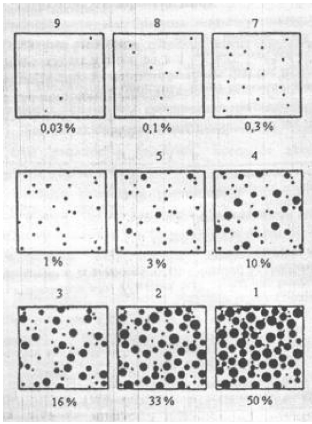

Fig. 2. The visual metal specimen's assessment by using a standard picture (Šulčius 2006)

Table 1. Chemical composition of experimental metals (wt, %)

Composition Metal type	Carbon (C)	Silicon (Si)	Manganese (Mn)	Sulphur (S)	Phosphorus (P)	Chromium (Cr)	Nickel (Ni)	Aluminium (Al)	Titanium (Ti)	Nitrogen (N)	Iron (Fe)
Carbon steel	0.12	0.02	0.42	0.14	0.09	-	-	0.06	-		99.15
Stainless steel	0.08	0.75	2.00	0.015	0.045	18	10	-	0.7	0.1	68.31
Galvanized steel	0.25	-	-	0.04	0.1	-	-	-	-		99.61

Five independent people participated in the visual metal surface assessment in order to avoid inaccuracy. From the obtained data an average value and confidence interval were calculated.

Results of the Performed Assessment

The performed investigation revealed that the cover of the corrosion product on metal surfaces depends not only on metal but also on a method used in research. The spraying method had a bigger impact on metal comparing with the immersion method. The cover of corrosion products on metals was from none to extensive.

Carbon steel as conventional construction material is widely used in road elements. According to Mobin (2008), low concentration of copper (Cu) and nickel (Ni) increases the corrosion of carbon steel. Carbon steel used in this research does not contain any concentration of Cu and Ni as they are very poor to corrosion resistance metal. The percentage rate of the Carbon steel corrosion product covered by the immersion method is presented in Fig. 3. $CaCl_2$ solution made the highest impact on metal surface by covering with corrosion products about 92±5 % of all surface. When carbon steel was immersed into NaCl and NaCl:$CaCl_2$ solutions, the surface of this experimental metal was covered on average by 50±4 %. NaCl solution mixed with 'Safecote' made zero damage to carbon steel, covered metal surface with black coat and protected from corrosion.

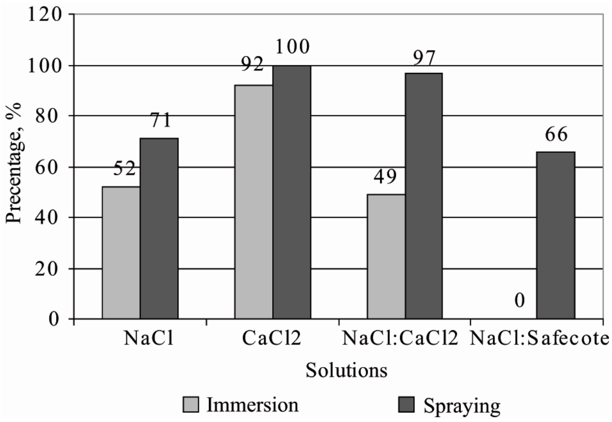

Fig. 3. Percentage rate of carbon steel corrosion product cover by immersion and spraying methods

100±1 % cover with corrosion products was made on carbon steel by spraying with $CaCl_2$ solution (Fig. 3). The received results showed that the mixed solution of NaCl and $CaCl_2$ induced 97±5 % of cover to the corrosion product on carbon steel. When experimental metal was sprayed with NaCl solution, the surface was covered by 71±4 % of the corrosion product. 66±4 % of cover with the corrosion product was made using NaCl:Safecote solution.

Stainless steel is the most popular type of steel used on road elements because of its resistance to corrosion and high strength. Qiao *et al.* (2009) investigated that the high concentration of chromium (Cr) gives stable corrosion potential to metal. Nitrogen (N) increases stainless steel strength and improves resistance by pitting and crevice corrosion in chloride ions containing solutions. Stainless steel used in research contains 18 % of Cr, 10 % of nickel (Ni) and 0,1 % of N. Ni also gives resistance to corrosion (Mobin 2008).

The composition of stainless steel informs that this experimental metal has the highest resistance to corrosion which is proven by the results of the performed research. NaCl:$CaCl_2$ solution covered about 10±2 % with the corrosion products of the stainless steel surface by performing the immersion method (Fig. 4). The other solutions used did not change the experimental metal surface at all (0 %).

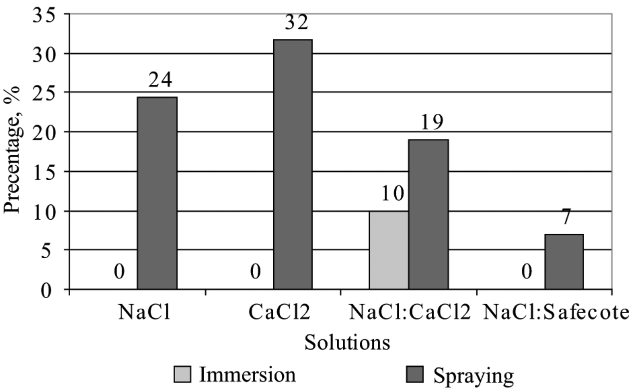

Fig. 4. Percentage rate of stainless steel corrosion product cover by immersion and spraying methods

However, the spraying method showed that stainless steel is still attackable to salt exposure (Fig. 4). $CaCl_2$ covered about 32±5 % with the corrosion products of the stainless steel surface and NaCl solution covered 24±2 % of the surface. When stainless steel was sprayed with NaCl:$CaCl_2$ solution, the surface was covered about 19±4 % of corrosion products. NaCl:Safecote solution made minimal surface changes (7±2 %) which was 4,5 times lower changes comparing to $CaCl_2$.

Galvanized steel is the third experimental metal used in road element production. When this experimental metal was immersed into NaCl and $CaCl_2$ solutions, corrosion products covered galvanized steel surface on average by 8,5±2 % (Fig. 5). NaCl:$CaCl_2$ and NaCl:Safecote solution made zero cover with corrosion products.

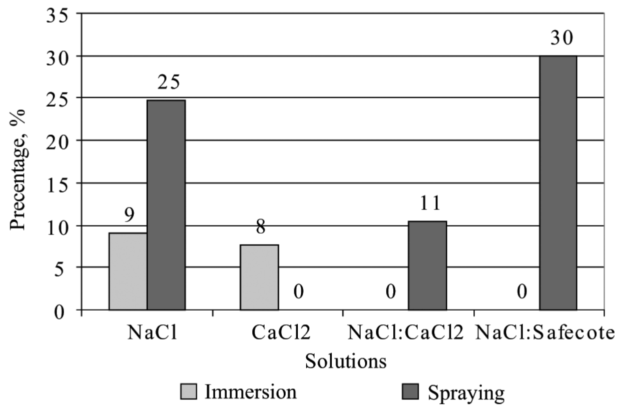

Fig. 5. Percentage rate of galvanized steel corrosion product cover by immersion and spraying methods

The covered part of the galvanized steel surface with the corrosion product is presented in Fig. 5 by performing the spraying method. The biggest cover of the galvanized steel surface was made by spraying with NaCl:Safecote solution (30±4 %). NaCl solution changed about 25±3 % of the experimental metal surface. 11±3 % of corrosion products were covered by spraying with a mixed solution of NaCl:$CaCl_2$. $CaCl_2$ solution made minimal surface cover with corrosion products (0 %).

Discussion

Corrosion resistance mostly depends on the type and composition of metal and the affected solution. According to these properties, metals could be placed by resistance rate after this research. Galvanized steel had lower cover with corrosion products (average 10 %). The average cover with corrosion products on stainless steel was about 12 %. Carbon steel as the most sensitive metal to corrosion had an average of 66 % cover with corrosion products.

An average assessment of the cover of all experimental metals with corrosion products by immersion and spraying methods depending on the used solutions informs about the corrosive properties of experimental substances. The results show that $CaCl_2$ solution had stronger damage to all metals and metal alloys when immersed into the solution. The average cover is 38% of the surface. The mixed solution of sodium and calcium chlorides covered metals on average by 31 % of the surface. NaCl solution made an average 30 % of surface changes. 17 % of cover with corrosion products was due to NaCl:Safecote solution induced corrosion.

Such situation of experimental solutions could be the result of $CaCl_2$ which has good water preservation properties. As it has been mentioned above, humidity increases the corrosion rate to the metals. NaCl:Safecote solution has the lowest impact on the tested metal and metal alloys. Due to good 'Safecote' characteristics, it helps with coating the metal with the anti-corrosion layer.

Conclusions

1. Metals could be classified according to resistance to corrosion by using the spraying method: galvanized steel covered 16 % of the surface, stainless steel – 21 % and carbon steel – 83 %.

2. Metals could be categorized according to resistance to corrosion by using the immersion method: stainless steel had an average 3 % of surface changes, galvanized steel – 4 % and carbon steel – 48 %.

3. The conducted investigation disclosed that considering corrosive impacts on metals, chemical substances used for road maintenance in winter season could be placed in the following way: CaCl2 solution with the highest impact, NaCl:CaCl2, NaCl and the best anti-corrosive properties has NaCl:Safecote solution.

References

Ahmad, Z. 2006. *Principles of Corrosion Engineering and Corrosion Control*. Butterworth-Heinemann. 22 p.

Almarshad, A. I.; Syed, S. 2008. Atmospheric corrosion of galvanized steel and aluminium in marine and marine-industrial environments of Saudi Arabia, *Materials and Corrosion* 59(1): 46–51.

Baltrėnas, P.; Kazlauskienė, A.; Zaveckytė, J. 2006. Experimental investigation into toxic impact of road maintenance salt on grass vegetation, *Journal of Environmental Engineering and Landscape Management* 14(2): 83–88.

Belghazi, A.; Bohm, S.; Sullivan, J. H.; Worsley, D. A. 2002. Zinc runoff from organically coated galvanised architectural steel, *Corrosion Science* 44: 1639–1653.

Burtwell, M.; Wilson, M. 2004. Safecote de-icer in UK winter maintenance, *Safeguarding Winter Travellers* 1–2.

Cho, S. H.; Hur, J. M.; Seo, C. S.; Park, S. W. 2008. High temperature corrosion of superalloys in a molten salt under an oxidizing atmosphere, *Journal of Alloys and Compounds* 452: 11–15.

Hääl, M-L.; Sürje, P. 2006. Environmental problems related to winter traffic safety conditions, *The Baltic Journal of Road and Bridge Engineering* I(1): 45–53.

Jelisejevs, B.; Urbanovichs, V. 2007. *Environmental Aspects of Road de-Icing Technologies*. Latvia. 11 p.

Kazlauskienė, A.; Baltrėnas, P. 2007. Trumpalaikiai kelių priežiūros druskos tirpalų ūminio toksiškumo vaivorykštiniam upėtakiui (*Oncorhynchus Mykiss*) tyrimai, iš *Aplinkos apsaugos inžinerija: 10-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis", įvykusios Vilniuje 2007 m. kovo 29 d., pranešimų medžiaga*. Vilnius: Technika, 130–134.

Mobin, M. 2008. Electrochemical studies on the corrosion behaviour of carbon steel in presence of Cu and Ni, *Portugaliae Electrochimica Acta* 26/5: 449–457.

Qiao, Y. X.; Zheng, Y. G.; Okafor, P. C.; Ke, W. 2009. Electrochemical behaviour of high nitrogen bearing stainless steel in acidic chloride solution: Effects of oxygen, acid concentration and surface roughness, *Electrochimica Acta* 54: 2298–2304.

Rosliza, R.; Wan Nik, W. B.; Senin, H. B. 2008. The effect of inhibitor on the corrosion of aluminum alloys in acidic solutions, *Materials Chemistry and Physics* 107: 281–288.

Sanzo, D.; Hecnar, S. J. 2006. Effects of road de-icing salt (NaCl) on larval wood frogs (Rana sylvatica), *Environmental Pollution* 140: 247–254.

Šulčius, A. 2006. *Metalų korozija ir sauga*. Kaunas: Technologija. 298 p.

Zaveckytė, J.; Ščupakas, D. 2005. Druskų, skirtų kelių priežiūrai, poveikio augalijai analizė, iš *Aplinkos apsaugos inžinerija: 8-osios Lietuvos jaunųjų mokslininkų konferencijos „Lietuva be mokslo – Lietuva be ateities“, įvykusios Vilniuje 2005 m. kovo 24 d., pranešimų medžiaga*. Vilnius: Technika, 303–308.

Vosylienė, M. Z.; Baltrėnas, P.; Kazlauskienė, A. 2006. Toxicity of road maintenance salts to rainbow trout Oncorhynchus mykiss, *Ekologija* 2: 15–20.

Wilson, M. I.; Burtwell, M. H.; Zohrabi, A. 2002. *Assessment of Safecote de-icer Product: Phase 2*. PR/IS/13/02. 77 p.

KELIŲ PRIEŽIŪROS MEDŽIAGŲ ĮTAKA METALŲ PAVIRŠIAUS KOROZIJAI

J. Petkuvienė, D. Paliulis

Santrauka

Tyrimų tikslas – įvertinti vizualinį metalų paviršiaus pasikeitimą, paveikiant kelio priežiūrai naudojamomis druskomis ir melasos pagrindu pagaminta medžiaga („Safecote“). Chloridų jonai yra pagrindiniai agentai, kurie neigiamai paveikia dirvožemį, vandens telkinius, taip pat sukelia metalinių kelio elementų koroziją. „Safecote“ kaip alternatyvą siūloma naudoti slidumui ir metalų korozijai sumažinti. Atliekant laboratorinius tyrimus metalai buvo įmerkiami ir purškiami su NaCl, CaCl2, NaCl:CaCl2 ir NaCl:Safecote tirpalais. Eksperimento rezultatai parodė, kad NaCl ir „Safecote“ tirpalas sukėlė mažiausią metalų paviršiaus padengimo korozijos produktais lygį (apytiksliai 17±4 %), o NaCl, $CaCl_2$, NaCl:$CaCl_2$ tirpalai sukėlė didžiausią paviršiaus padengimą korozijos produktais lugį, vidutiniškai 33±5 %.

Reikšminiai žodžiai: kelių priežiūros druskos, natrio chloridas, kalcio chloridas, „Safecote“, metalai, korozija.