

CYANIDE-FREE AND BIODEGRADABLE ANTI-CAKING AGENT FOR DE-ICING SALT

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ABSTRACT

The caking of de-icing salt is an important issue. Caking causes the aggregation of salt particles, which ultimately results in salt that can't be spread over road surfaces. Different anti-caking agents have been identified over the previous decades, among which ferrocyanide (also known as hexacyanoferrate or YPS) is the most commonly used. As a result, considerable amounts of ferrocyanide enter the environment each year. Proper salt management and the application of best practices should result in avoiding harm to the environment. Nevertheless a comprehensive monitoring study of the environmental fate and potential effects on water quality caused by ferrocyanide is lacking. Although the data available does indicate that soil and water contamination occurs in some specific situations, such as in the vicinity of salt storage and also in the runoff water. Replacing ferrocyanide with a proven environmentally safe anti-caking agent would eliminate this concern. An aqueous solution of complexation products of stereoisomers of tartrates with Fe(III)chloride is an alternative to ferrocyanide. This anti-caking agent is readily biodegradable and as such does not pose any risk to the environment. The anti-caking properties of iron tartrates have been tested with different kinds of salt at both a pilot and industrial levels. This paper presents the results of these tests and compares the two anti-caking agents.

1 INTRODUCTION

The use of salt (sodium chloride) to keep roads clear of ice and snow is a widespread practice. De-icing salt often has to be transported from production to storage locations, from where it is distributed. Salt must be kept free of lumps during storage, transportation and spreading over the road surfaces. This function is performed by the small addition of chemicals called anti-caking agents. In practice it is principally ferrocyanide (or hexacyanoferrate or $\text{Fe}(\text{CN})_6^{4-}$) salts that are added as anti-caking agents to the de-icing salt. This results in considerable amounts of ferrocyanide entering the environment each year. Cyanides and metal cyanide complexes are strong inhibitors of cellular metabolism and are not readily biodegradable. Therefore the concentration of these salts in the environment must be kept as low as possible. This is reflected by the very low concentrations allowed in soil and water by legislation.

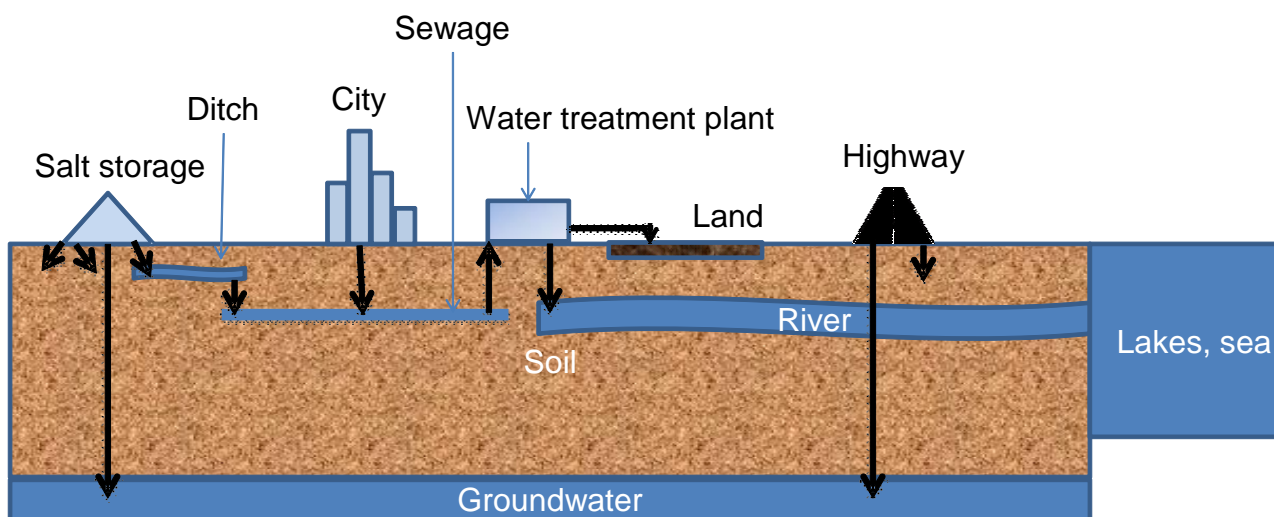


Figure 1 – Salt additives can enter the soil or water in different ways, including runoff from nearby salt storage, or via snow-melt containing the de-icing salt. Snow-melt, which is processed in water treatment plants, can also be the origin of solid or liquid effluents containing salt additives. The black arrows in the illustration above indicate the streams that can contain salt derivatives.

Proper salt management and the application of best practices should result in neither harm to the environment nor exceeding the maximum levels of cyanides permitted. Nevertheless, there are some specific situations where the risk of contamination is present, as illustrated in the Dutch example.

A complexation product of stereoisomers of tartrates with iron chloride has been developed as a cyanide-free alternative to ferrocyanide. This paper compares the two additives as anti-caking agents in de-icing salts and also their impact on the environment.

2 IRON CYANIDES AND IRON TARTRATES AND THEIR POLLUTING CHARACTER IN THE ENVIRONMENT

2.1 Iron cyanides

Ferrocyanide is thermodynamically unstable; in conditions normally encountered in the environment, thermodynamics can predict the decomposition of ferrocyanide and the formation of cyanide as shown in the following illustration [1]. However, decomposition in the absence of light is slow, with a half-life ranging from years to hundreds of years, depending on the pH and redox potential. Therefore once this chemical enters the environment it can remain there for decades as demonstrated by the fact that former gasworks, which are usually polluted with ferrocyanide, remain contaminated to this day, even when production activities stopped back in the 1960's [1,2].

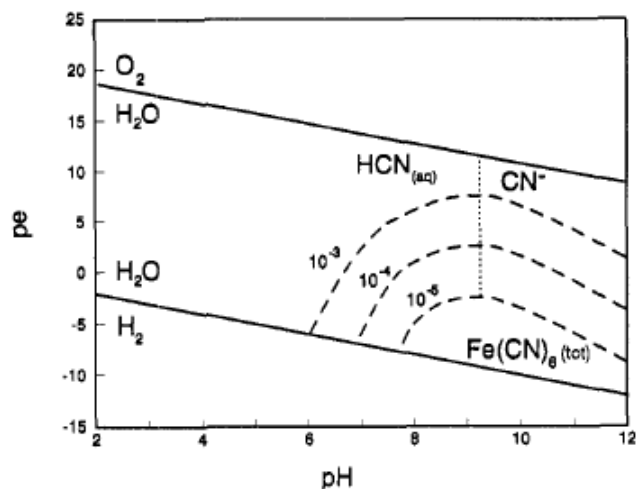


Figure 2 – Predominance of cyanide species in solution as a function of pH, pe, and total cyanide concentration (10^{-3} , 10^{-4} , 10^{-5} M) in equilibrium with solid $\text{Fe}(\text{OH})_3$, as calculated with the equations listed in Table 1. In the area indicated with $\text{Fe}(\text{CN})_6$, cyanide is predominantly present in one or more of the complexed species; in the remaining area it is predominantly present in free forms. $\text{Ca}(\text{t})$, 5 mM; $\text{K}(\text{t})$, 1 mM; ionic strength, 0.01 M [1]

reaction	$\log K^\circ$
(1) $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	13.0
(2) $\text{H}^+ + \text{CN}^- \rightleftharpoons \text{HCN}_{(\text{aq})}$	9.2
(3) $\text{Fe}^{3+} + 6\text{CN}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}$	43.9
(4) $\text{Fe}^{3+} + 6\text{CN}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaFe}(\text{CN})_6^-$	46.5
(5) $\text{Fe}^{3+} + 6\text{CN}^- + \text{K}^+ \rightleftharpoons \text{KFe}(\text{CN})_6^{2-}$	45.4
(6) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	49.9
(7) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{H}^+ \rightleftharpoons \text{HFe}(\text{CN})_6^{3-}$	54.3
(8) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{Fe}(\text{CN})_6^{2-}$	56.7
(9) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaFe}(\text{CN})_6^{2-}$	54.0
(10) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + 2\text{Ca}^{2+} \rightleftharpoons \text{Ca}_2\text{Fe}(\text{CN})_6^0$	55.3
(11) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{Ca}^{2+} + \text{H}^+ \rightleftharpoons \text{CaHFe}(\text{CN})_6^-$	57.0
(12) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{K}^+ \rightleftharpoons \text{KFe}(\text{CN})_6^{3-}$	52.4
(13) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + 2\text{K}^+ \rightleftharpoons \text{K}_2\text{Fe}(\text{CN})_6^{2-}$	53.3
(14) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{K}^+ + \text{H}^+ \rightleftharpoons \text{KHFe}(\text{CN})_6^{2-}$	55.7
(15) $\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightleftharpoons \text{Fe}^{3+}$	2.7

Table 1 – Chemical Equilibrium Reactions and Formation Constants ($\log K^\circ$) used to calculate cyanide speciation [1].

In daylight the complete decomposition of ferrocyanide to cyanides occurs in hours [3]. The biodegradability of (metal) cyanides has been described by R. Roshan and others [4] and by A. Dursun [5]. As Roshan and others conclude: *the ease with which the metal cyanide complexes are degraded generally follows their order of chemical stability with free cyanide being the most readily degradable and iron cyanide the least*. Iron-cyanide complexes are biodegradable but not readily biodegradable. The mobility of ferrocyanide in soil depends on its chemical form for example, as described by de Vries [6]. Iron is a widespread metal in soil and therefore the formation of Prussian blue ($\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$) is likely. The solubility of Prussian blue and its mobility, depend strongly on the pH of the soil and its redox potential. Adsorption on soil particles and therefore the charge, also has a substantial influence on the mobility of ferrocyanide in soil.

2.2 Iron tartrates

The degradation of tartrates is catalysed by the presence of metals such as iron and also light. The photoreaction involves reduction of Fe(III) to Fe(II) and concomitant oxidation of tartaric acid and finally transformation into water and carbon dioxide, as described by Balzani and Carassiti [7]. Iron tartrates are readily biodegradable as described by J. Zhang [8]. Ready biodegradable substances are biodegradable in all aerobic ecosystems including soil. The half-life of tartrates in soils is considered to be 10 days at most [9]. This short half-life and mineralization of tartrates complexed with iron in soil is in line with its ready biodegradability and evidence of its conversion into carbon dioxide and water by microorganisms. Microorganisms are also able to degrade in anaerobic conditions.

2.3 Ecotoxicity classification

Ecological information about the ecotoxicity of the two additives can be found in the Material Safety Data Sheets [10, 11].

Ferrocyanide is classified as harmful to aquatic organisms and possibly causing long-term adverse effects in the aquatic environment. Complexation products of sodium tartrate with iron chloride is not classified as persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB).

	Freshwater Algae	Freshwater fish	Microtox	Water Flea
Ferrate(4), hexakis(cyano-C)-, tetrapotassium, (OC-6-11)-	Not listed	100 mg/L LC50 96 h 19 mg/L LC50 96 h	Not listed	23 mg/L EC50 = 96 h
Complexation products of sodium tartrate With iron chloride	ErC50: > 391 mg/l 72 h Species: Pseudokirchneriella subcapitata (green algae) OECD Test Guideline 201 NOEC: 391 mg/l 72 h Species: Pseudokirchneriella subcapitata (green algae) OECD Test Guideline 201	> 1,000 mg/l LC50 96 h Species: Danio rerio (zebra fish) OECD Test Guideline 203	Toxicity to bacteria : EC50: > 1.08 mg/l 3 h Species: activated sludge Respiration inhibition Method: OECD Test Guideline 209	> 980 mg/L EC50= 48 h Species: Daphnia magna (Water flea)

Table 2 – Ecotoxicity of ferrate(4) hexakis (cyano-C)-, tetrapotassium, (OC-6-11)-

	Persistence and degradability	Bioaccumulative potential	Mobility in soil
Ferrate(4), hexakis(cyano-C)-, tetrapotassium, (OC-6-11)-	Not readily biodegradable	No information available	No information available
Complexation products of sodium tartrate With iron chloride	Closed Bottle test Readily biodegradable. >70% BOD, 28 days, Closed Bottle Test (OECD 301D).	No bioaccumulation	Adsorption to the solid soil particles is not expected

Table 3 - Persistence, degradability, bioaccumulation and mobility in soil

2.4 Comparison between the polluting character of ferrocyanide and iron-tartrate

After ferrocyanide enters the soil it can remain there for decades. However, in the presence of light it can dissociate and form cyanide. Ferrocyanide is classified in water as being harmful to aquatic organisms with the possibility of causing long-term adverse effects. If tartrates complexed with iron enter the soil they become part of the natural low molecular weight organic acid pool naturally present in soil. They quickly decompose in carbon dioxide and water. Tartrates complexed with iron are not classified as persistent, bioaccumulative and toxic.

3 CYANIDE CONTAMINATION IN SOIL AND GROUNDWATER IN THE VICINITY OF DE-ICING SALT STORAGE LOCATIONS

Best practices with de-icing salt help prevent unnecessary burdening of the environment with cyanide complexes. Nevertheless, there are some specific situations where the risk of soil or water contamination with cyanide and its derivatives is higher. These include the areas around storage locations. Contamination is only discovered where monitoring of the soil and water is carried out. Storage sites in the Netherlands are investigated in specific situations, such as sites that are no longer in use, or where ownership changes, or for expansion or renovation activities, or where the designated use of the site changes (e.g. from an industrial to an urban area). Therefore soil and groundwater contamination could occur more frequently than has been investigated to date.

Storage of de-icing salt in general is done either indoors or outdoors and in covered or uncovered piles. In the Netherlands de-icing salt is mainly stored indoors. The most common sources of contamination come from damaged floors, or where the salt is stored temporarily in places where the floor is not leak-proof and is permeable to water or brine.



Figure 3 – Indoor salt storage and situations where water and brine can enter the soil

An examination of contaminated salt storage sites in the Netherlands covering the period 2002-2012 has produced this location overview:



Figure 4 – Cyanide contaminated locations in the Netherlands because of de-icing salt storage in the period 2002 to 2012 (red dots).

City	Soil contamination	Groundwater contamination	year	Reference
Vollenhove	x	o	2009	[12]
Nuenen	x	o	?	[13]
Wageningen	x	x	2004	[14]
Wezep	x	x	2012	[15]
Vriezenveen	x	x	2011	[16]
Ijsselstein	x	x	?	[17]
Den Helder	x	x	?	[18]
Ede	x	x	2008	[19]
Assen	x	x	2011	[20]
Exloo	x	x	2008	[21]
Eijsden	x	x	2010	[22]
Akkrum	x	o	2010	[23]
Tiel	o	x	2006	[24]
Hilversum	x	o	2005	[25]
Raamsdonksveer	x	x	2011	[26]
Oosterhout	x	o	2006	[27]
Maasbommel	x	o	2008	[28]
Zwolle	x	x	2007	[29]
Velp	x	x	2011	[30]
Winschoten	x	x	2004	[31]
Gennep	x	o	2002	[32]
Haaksbergen	x	o	2003	[33]
Wierden	x	x	2010	[34]
Alphen aan de Rijn	o	x	2005 / 2011	[35]
Zwaagdijk	o	x	2009	[36]
Joure	x	x	1993/1998	[37]

Table 4 - Locations in the Netherlands that lie in the vicinity of de-icing salt storage sites where contamination of soil or groundwater has been discovered in the period 2002-2012. X = contamination detected. O= no contamination detected.

All activities causing cyanide pollution must be stopped where cyanide is detected in the soil or groundwater in concentrations above the intervention limit. The pollution must then be removed, isolated or relocated. The storage facilities must be decontaminated where the same area is going to be used for salt storage once again.

Decontamination costs approximately €100 to €110 per ton of soil and approximately €15 per ton of water. By taking into consideration the list of sites shown in the table above and also the average soil and water volumes that must be treated as a result of cyanide contamination, it is possible to derive indicative decontamination costs. As the average amount of soil treated per contaminated site was approximately 1000 m³, the cost of soil decontamination at each storage location averaged €100,000 to €110,000. As the contaminated water volume varied between 100 and 5,400 m³, the average cost for water treatment was in the region of €1,500 to €81,000. These costs do not take into account reconstruction of the storage facilities, nor the surrounding area, nor indeed any other financial costs, such as the consequences of being unable to use the storage facilities during the decontamination and rebuilding activities.

Legislation in the Netherlands states that the best possible technology must be applied in matters of environmental protection. The Soil Protection Act (Wet Bodembescherming Wbb) makes it mandatory to take all the necessary measures to prevent any recurrence of contamination to the environment. Therefore, once soil and water decontamination has occurred, it is necessary that salt storage locations are rebuilt in accordance with strict criteria and that best practices are adopted.



Figure 5 – Reconstruction of a salt storage building after decontamination. The floor is removed and replaced with leak-proof paving - the ground around the storage building is also restructured - a protective coating is applied to the walls inside the storage building - best practice procedures are adopted.

4 QUALITY OF SLUDGE IN URBAN WATER TREATMENT PLANTS

Urban runoff and snow-melt containing de-icing salt and de-icing agents end up in sewage systems and water treatment plants. Water treatment plants produce sludge, which can also be spread over soil, except where sludge contains levels of contaminants high enough to be considered chemical waste. In the Netherlands an investigation into the quality of the water effluent and sludge from water treatment plants was carried out on behalf of the Dutch Ministry of Health [38].

This study was initiated after the discovery that the sludge from an industrial water treatment plant was contaminated by cyanide from de-icing salt. The sludge had to be disposed of as chemical waste.

The authors measured the cyanide content of different types of road salt and sludge from the water treatment plant. All the samples were taken at the end of the February 2006. The month of February had been a relatively warm and dry winter month in 2006 with only limited de-icing activity.

Cyanide was detected in all the samples and in one case it reached 75% of the maximum permitted concentration at which sludge is considered to be chemical waste. The highest cyanide level was found in a region using de-icing salt that had the highest concentration of ferrocyanide. Although this level of concentration did not reach the maximum permitted levels of cyanide, the authors concluded that there was a real risk of contamination of the water treatment sludge with cyanide. Monitoring was carried during a period of limited de-icing activity - in a more severe winter for example, there would have been a risk where the maximum permitted concentration of cyanide in sludge could be reached.

5 SNOW-MELT, INDUSTRIAL WASTEWATER AND SOIL CONTAMINATION

Contamination of water and soil by cyanides from de-icing salt can occur in a few other cases, as described in these studies.

Theoretical concentration of cyanide in snow-melt. Mass balance calculations predict that the cyanide concentration in snow-melt can exceed the desired maximum limits [39] in water, even at the lowest concentrations of YPS used to prevent caking. Only in cases where there are high levels of snowfall is sufficient dilution possible in order to lower the total cyanide concentration below the permitted limit.

Measured cyanide concentration in industrial wastewater (road salt dock). The concentration of cyanide measured in the wastewater from road salt storage can also be higher than permitted, as given at [40].

Snow-melt of urban areas. A monitoring study sponsored by the Water Environmental Research Foundation shows that snow-melt pollution by cyanide concentrations above the permitted limits can also occur. Snow samples were collected in commercial and residential zones [41].

Roadside soils along highways. A recent study [42] shows that the cyanide concentration in soil along main roads increases after winter operations. The authors did not detect concentrations above the permitted 50 mg CN/kg. The authors point to the risk of the 100% cyanide measured in some soil samples entering the groundwater. In such cases the maximum permitted concentration of cyanide in the water would certainly be exceeded. On the other hand the authors estimate the chance that this occurs as very low.

6 IRON TARTRATES AS AN ANTI-CAKING AGENT: INDUSTRIAL TESTS

Iron tartrates based formulations are used as a cyanide-free anti-caking agent for de-icing salt.



Figure 6 – The chemical formula for tartrate and a 3-D impression of a complexation product of tartrate with iron and water

The effectiveness of iron-tartrate as an anti-caking agent for different salt qualities for de-icing applications has been investigated. The next section describes the test performed by MVG, Ravenna, Italy.

6.1 Industrial test in big-bags (1 ton scale)

Wet rock, solar and vacuum salt was used for this test. An anti-caking agent in a concentration of 12 mg/kg salt (expressed as concentration of iron) was added before and after drying the salt. The treated salt was stored in big-bags in a covered warehouse. Big-bags were piled up and kept in storage for 1 year. During that year, the samples were monitored for free-flow ability and the formation of lumps. During the first two months, controls were carried out twice weekly; during the next two months the control was carried out once a week and finally once every fifteen days. Controls consisted in hitting the bags to verify the absence of any lumps and also a visual inspection of the product inside the bags. After one year the bags were emptied and the flow behaviour, as well as the presence of lumps was monitored.

6.1.1 Raw materials details

Salt origin	Average particle size mm	Humidity %
Solar	0-10	2.80
Rock	0-10	1.30
Vacuum	0-0.6	2.40

Table 5 – Raw materials details

6.1.2 Drying parameters

TURBO DRYER – SEA SALT

Air temperature dryer in	355 °C
Air temperature dryer out	107 °C
Speed dryer rotation	RPM 65
Dried salt temperature	76 °C
Salt humidity in	2.80%
Salt humidity out	0.15%

TURBO DRYER – ROCK SALT

Air temperature dryer in	305 °C
Air temperature dryer out	114 °C
Speed dryer rotation	RPM 70
Dried salt temperature	80 °C
Salt humidity in	1.30%
Salt humidity out	0.18%

FLUID BED – VACUUM SALT

Hot air temperature in	212 °C
Dried salt temperature	68 °C
Salt humidity in	2.40%
Salt humidity out	0.10%

6.1.3 Results

There were no significant differences in comparison to the normal product used (salt treated with sodium ferrocyanide) when using the drying lines. The physical behaviour of the salt was exactly the same during transport (belt conveyors, screw conveyors) and its behaviour in hoppers.

6.1.4 Smell and dust

Smell and dust also remained unchanged in comparison to ferrocyanide.

In conclusion, the use of iron tartrates as an anti-caking agent did not differ from the use of ferrocyanide as far as the production of dried salt with an anti-caking agent is concerned.

6.1.5 Free-flow ability and lumps

After one year all the samples were still free of caking and completely free-flowing.

6.2 Industrial test with a pile of rock salt (100 ton scale)

Iron-tartrate was added to approximately 100 tons of rock salt with the concentration of 12 mg Fe/kg salt. The average grain size was 0-5 mm and the salt humidity was approximately 0.25 %. The salt was stored in a pile in a covered silo and kept for one year. A comparative test was done with salt treated with 100 mg Fe(CN)₆/kg.

The compactness of each salt pile was tested with a friction tool during storage and by handling the salt after one year.

The spreading pattern of the salt was also tested. A designated road area of 12 x 20 metres was divided into sections of 4 m² in order to measure the total amount of salt spread, as well as the spreading pattern. The equipment was calibrated before spreading with the aim of spreading 15g/m². After the truck had performed the spreading action, the salt was gathered up using dedicated equipment. The salt collected in each section was dissolved in water and the amount of salt per section was determined by measuring the electrical conductivity of the salt solution.

6.2.1 Results

Salt preparation. It was possible to use the existing equipment for ferrocyanide for the preparation of the test sample.

Free-flowing. The salt pile treated with iron tartrates formed a brownish layer after a few days. This layer did not influence the colour of the bulk of the salt. The friction tool measured a higher compactness of the salt treated with iron tartrates with respect to the salt treated with ferrocyanide. On the other hand, handling the salt with a shovel at the end of the storage period went smoothly.

Spreading. No significant differences were observed in the spreading behaviour between the salt treated with iron tartrates or ferrocyanide.

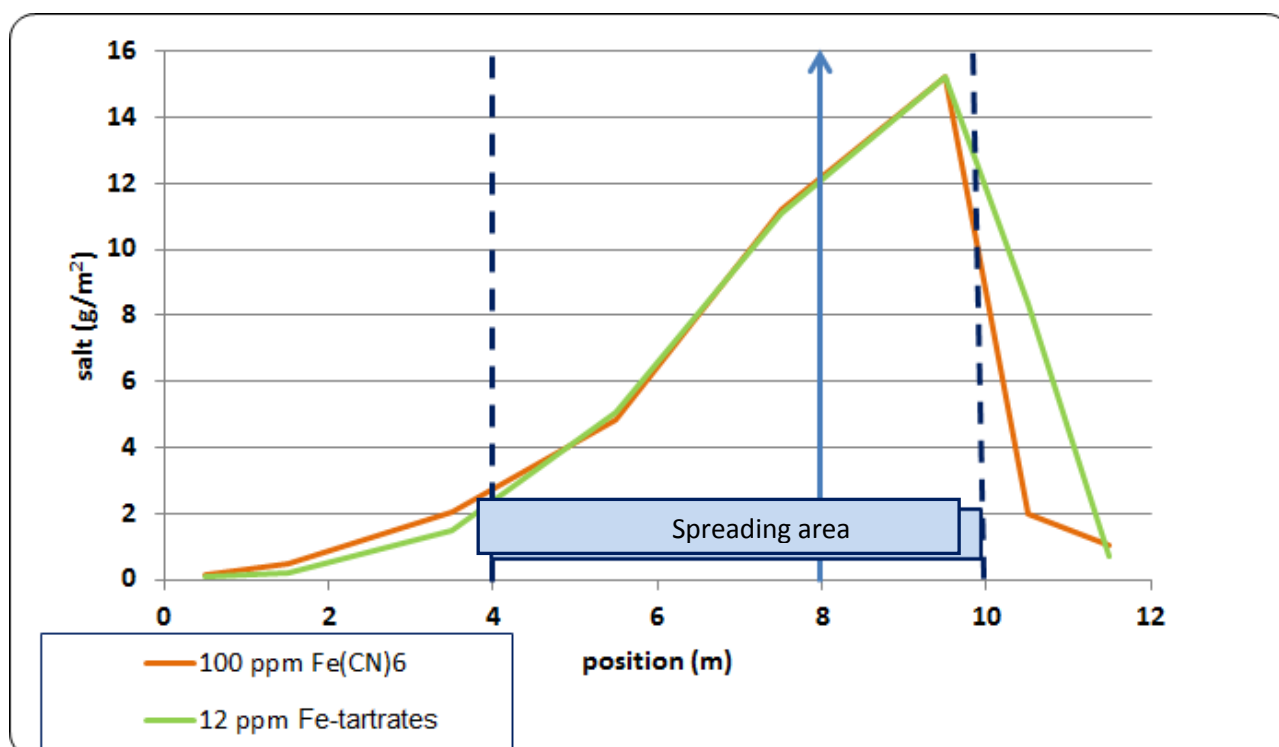


Figure 7 - Spreading pattern of de-icing salt treated with ferrocyanide (orange line) and iron tartrates (green line). The blue arrow indicates the direction of the spreading truck and the centre of the distribution disk. The positions “4” and “10” simulate the sides of the road.

6.3 Industrial test with rock salt (40,000t scale)

40,000 tons of dry rock salt (grain size: 0-7 mm) was treated with 12 ppm iron tartrates. The salt was transported by ship for several days and then stored outdoors under a plastic cover. A reference salt pile treated with ferrocyanide was stored under the same conditions. After some weeks a crust developed on the salt pile. Measurements for compactness showed that the salt treated with iron tartrates was more compact than the salt treated with ferrocyanide. Handling the salt treated with iron tartrates went smoothly, irrespective of the formation of the crust, or the increased compactness inside the pile.

7 ANTI-CAKING AGENTS AND TECHNICAL SPECIFICATIONS FOR DE-ICING SALT

The product *specification* of de-icing salt often differs from country to country and from one administrative region to another (state, province, city, municipality and highway departments). Specifications might include anti-caking agents, and where they are included, the application may be mandatory or recommended.

Sometimes of the *guidelines* from Knowledge Centres such as CROW in the Netherlands or TL-Streu in Germany are followed; these guidelines differ regarding their views on anti-caking agents. For example, the guidelines for anti-caking agents in de-icing salt in three European countries namely, the Netherlands, Germany and United Kingdom, go from advising no specific anti-caking agent, through to only using ferrocyanide, or both ferrocyanide and a cyanide-free alternative.

<i>Country</i>	<i>Anti-caking agent for de-icing salt</i>	<i>Knowledge Centre for national guidelines</i>
<i>The Netherlands</i>	K/Na ferrocyanide or equivalent cyanide-free	CROW
<i>Germany</i>	K/Na ferrocyanide	TL-Streu
<i>United Kingdom</i>	Not stated	British Standards Institution

Table 6 - Example of three national guidelines and the recommendations they give for anti-caking agents for de-icing salt. Either ferrocyanide, or a cyanide-free alternative are stated, as well as giving no specific recommendations for a specific anti-caking agent.

Some authorities have included biodegradable and cyanide-free anti-caking agents in their tenders. In some cases this type of anti-caking agent is indicated as a preference, and in others it is mandatory. Guidelines for sustainable purchasing help stimulate authorities into choosing biodegradable anti-caking agents.

8 CONCLUSIONS

Iron tartrates anti-caking agents are an alternative to ferrocyanide for de-icing salt applications. Being ready biodegradable and cyanide free, this anti-caking agent avoids the concerns related to using the more traditional ferrocyanide. Dry de-icing salt treated with iron tartrates is free-flowing after one year in storage. No differences in handling were observed when the salt was stored in big-bags. In the case of bulk storage, the salt can still be handled after one year's storage, even where the compactness of the salt increases and a brownish salt crust forms over the pile. Cyanide-free anti-caking agents are sometimes included in the product specifications of national guidelines for de-icing salts, although ferrocyanide is the one that is usually stated.

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