Biodegradable and Cyanide-free Anticaking Agent for De-icing Salt

Salt, Safety and the Environment

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Abstract

Sodium chloride is the most commonly used salt in the winter for keeping roads free of ice and snow. De-icing salt contains an anticaking agent to ensure that it is easy to spread and can be easily stored for prolonged periods. Presently ferrocyanide is the most commonly used anticaking agent for de-icing salt. As a result, a considerable amount of ferrocyanide enters the environment, which has raised environmental concerns. Ecosel®BioCare is an anticaking agent based on tartrate derivatives originating from the wine industry. This anticaking agent is cyanide free and readily biodegradable and therefore does not pose any risk to the environment. In this paper the anticaking mechanism, operational conditions, and industrial tests of Ecosel®BioCare are described.

Temperature and humidity variations occur during de-icing salt storage. When temperature is above 0 °C, salt bridge formation via dissolution and recrystallization of sodium chloride (NaCl) is the major caking mechanism. When temperature is below 0 °C, the formation of sodium chloride dihydrate is responsible for caking. Dihydrate crystals grow on the surface of the sodium chloride crystals, acting as glue between them.

Ecosel®BioCare has been tested in vacuum salt, rock salt, and sea salt stored in bag, pile, and vertical silo up to 1 year. It shows effective anticaking function for salt with moisture content up to 0.5%.

1. Introduction

The use of sodium chloride for roads de-icing activities 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-flowing during storage, transportation and spreading over the road surfaces. To make sure that salt is easy to handle, a small quantity of anti-caking agent is added to salt. The most commonly used anti-caking agent for de-icing salt is ferrocyanide ($Fe(CN)_6^{4-}$). This results in considerable amounts of ferrocyanide entering the environment each year. 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[1]. Cyanides and metal cyanide complexes are strong inhibitors of cellular metabolism and are not readily biodegradable[2]. Therefore the concentration 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.

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

Ecosel®BioCare, a complexation product of tartrates with iron chloride, has been developed as a cyanide-free alternative to ferrocyanide. In this paper the two additives as anti-caking agents in de-icing salts are compared.

2. Caking and anticaking mechanisms

Caking is the process by which free-flowing powders turn into lumps. For sodium chloride, when temperature is above 0 ^oC, salt bridge formation via dissolution and recrystallization is the main caking mechanism. As the weather in the winter can be very cold, the temperature of de-icing salt can drop below freezing point. For wet salt, as vacuum salt or sea salt, when temperature is below 0 ^oC, the formation of sodium chloride dihydrate ($NaCl{\cdot}2H_2O$) is responsible for caking. Very thin hexagonal dihydrate crystals grow on the surface of the anhydrous sodium chloride crystals[3], acting as glue between them.

Under freezing conditions, water and salt eventually form saturated brine and dihydrate crystals, as dihydrate is the stable form at temperatures below 0.1 ^oC (see Figure 1). At -21 ^oC or lower temperature, salt with 3% water transforms to dry salt containing approximately 7.9% $NaCl{\cdot}2H_2O$ crystals, which are composed of 3% H_2O and 4.9% NaCl. Wet salt with 3% water content contains 3.8% saturated brine (3% water and 0.8% dissolved NaCl). Therefore, 4.1% of NaCl crystals must dissolve to crystallize 7.9% of dihydrate.

To form dihydrate, however, both sodium chloride and water must be present. Inhibiting the dissolution of sodium chloride and / or decreasing the moisture content of the salt limits the dihydrate formation and thus prevents salt caking. When salt is dry, the amount of dihydrate formed is too little to glue crystals together, so salt remains free flowing under freezing conditions.

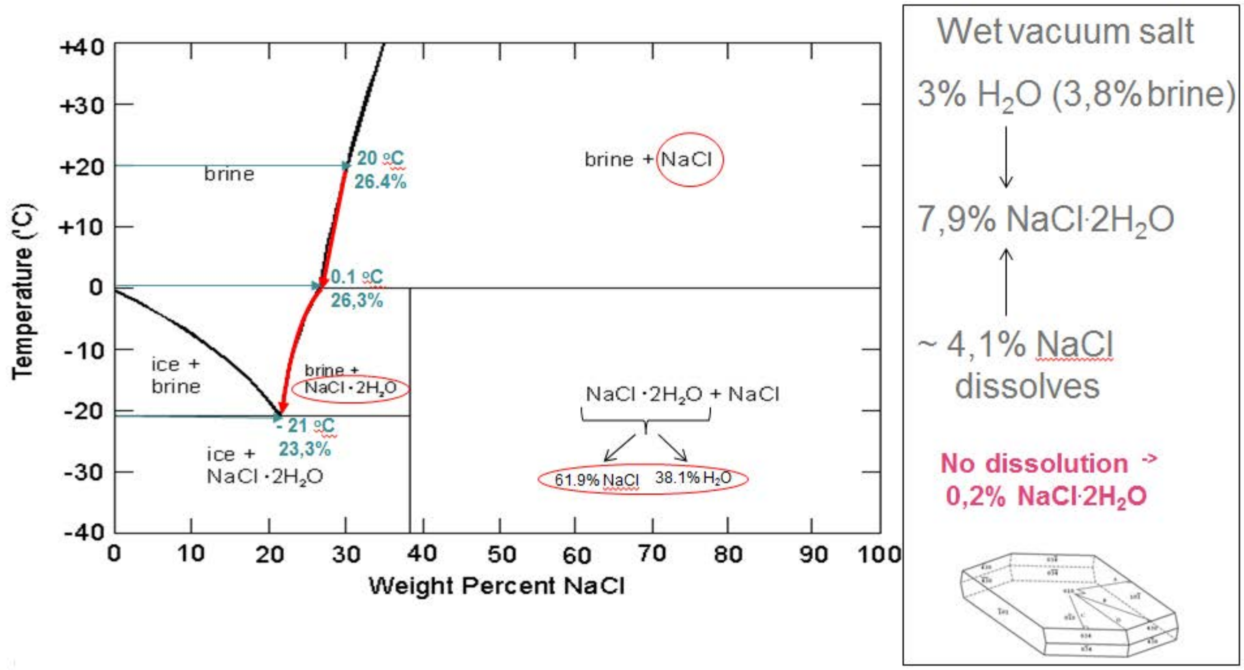

Figure 1: NaCl phase diagram and NaCl dihydrate formation

2.1. Ferrocyanide

$Fe(CN)_6^{4-}$ ion has the same shape and nearly the same size as the $NaCl_6^{5-}$ cluster giving an almost perfect fit into the NaCl grid like a key in a lock. See Figure 2. The anti-caking action of $Fe(CN)_6^{4-}$ is attributed to the difference in positive charge (Na^+ and Fe^{2+}). As this difference has to be compensated electrically, the NaCl crystal grid is disturbed and caking is then prevented[4-5].

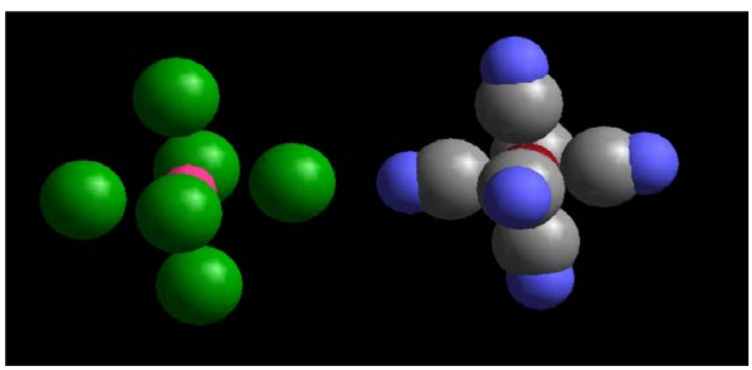

Figure 2: Shape of $NaCl_6^{5-}$ cluster and $Fe(CN)_6^{4-}$ ion

The presence of $Fe(CN)_6^{4-}$ at the crystal surface inhibits nucleation and crystal growth in supersaturated solution and limits crystal dissolution in undersaturated solution. The effectiveness of inhibition function depends on the concentration of anti-caking agent at the surface. When the degree of supersaturation becomes higher than a certain threshold, inhibition of nucleation and growth cease and crystallization starts. Therefore, the critical relative supersaturation is defined as a limit, above which three-dimensional nucleation occurs. Likewise, when the degree of undersaturation becomes higher than a certain threshold, inhibition of dissolution ceases and crystals start to dissolve. Similarly, the critical relative undersaturation is the limit, under which dissolution of NaCl occurs.

Ferrocyanide is a poor anticaking agent for the $NaCl\cdot 2H_2O$ crystals and hardly has any effect on crystal growth or nucleation of dihydrate. However, ferrocyanide inhibits the dissolution of the NaCl crystals and thus prevents the majority of the $NaCl\cdot 2H_2O$ formation. This is the reason why a high dosage level of ferrocyanide (75 ppm) is needed for de-icing salt. When the dissolution of NaCl is prevented by ferrocyanide, only 0.2% of $NaCl\cdot 2H_2O$ forms, which is only from the NaCl presented in brine around the crystals. This 0.2% of $NaCl\cdot 2H_2O$ is not enough to glue NaCl crystals, so salt remains free flowing. However, when salt containing ferrocyanide is kept for long time at -15 ^oC or below, it also cakes. This is because in tough conditions the degree of undersaturation becomes higher than the critical relative undersaturation, so NaCl dissolves and then $NaCl\cdot 2H_2O$ forms, as the stable crystal form under 0^{o}C is the dihydrate crystal.

2.2. Ecosel®BioCare

Ecosel®BioCare is a 100% biodegradable anticaking agent patented[6] by AkzoNobel, in which the main component is a complexation product of sodium tartrates and iron (III) chloride (iron tartrate). The recommended dosage level is 106 mg iron tartrate per kg of salt (equivalent to 12 ppm calculated as Fe).

Tartrates are present in plants and fruits like grapes, bananas and tamarinds. The natural occurrence of the stereoisomers already points to the *ready* biodegradability of these substances. Indeed, the stereoisomers are degraded in Closed Bottle tests (OECD 301D) within two weeks. The ready biodegradability is also found with complexation products with iron chloride. Readily 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[7]. This short half-life and mineralization of tartaric acid 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 make this degradation in anaerobic conditions. In conclusion, tartrates are readily biodegradable and environmental friendly. Once they enter the soil they become part of the natural low molecular weight organic acid pool naturally present in soil.

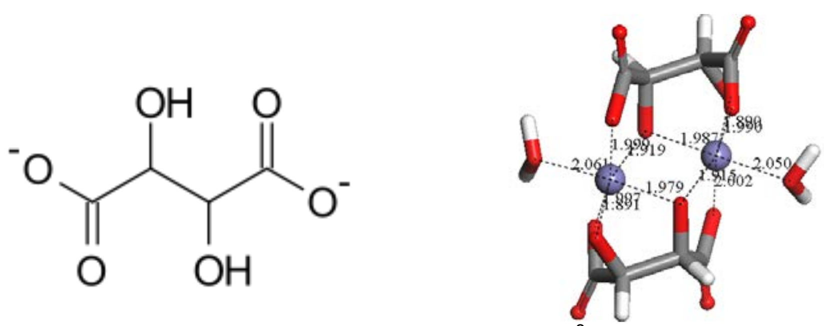

Figure 3: Chemical formula of tartrate and the 3-D structure[8] of the tartrate complex with iron and water

The anticaking agent Ecosel®BioCare (see Figure 3) effectively inhibits crystal growth of sodium chloride[9]. Experimental results show that dosing level of 6 ppm (calculated as Fe) inhibits crystal growth about 83%, which is about the same as ferrocyanide at the dosage level of 2.5 ppm (calculated as $Fe(CN_6)^{4-}$). 12 ppm Ecosel®BioCare (calculated as Fe) inhibits crystal growth of sodium chloride even more effectively, reaching to 98%.

Ecosel®BioCare has limited effect on crystal growth and nucleation of dihydrate. In addition, it does not prevent NaCl dissolution. Thus, Ecosel®BioCare is not applicable to salt containing high moisture content stored at temperature below freezing point. The operational window of Ecosel®BioCare has been well studied. The results are described in next section.

3. Operational window of Ecosel®BioCare

The maximum water content of salt that remains free flowing under freezing conditions is determined experimentally by performing freezing tests of Ecosel®BioCare treated salt with different water contents.

All freezing experiments were performed on pharmaceutical grade salt with varying water contents, from 0 to 3% water. 12 ppm Ecosel®BioCare calculated as Fe was added to salt. Salt was thoroughly mixed at room temperature, added in Grainer tubes and put into a freezer at -15 or -20 °C. After 1 or 2 days the samples were checked to determine whether they were completely frozen, free flowing or in between. All the samples had 5 replicas, each Grainer tube containing 30 g of salt.

All the samples were analyzed and marked according to the additive performance from 1 to 4 as described in Table 1.

Performance mark	Description
1	completely free flowing salt
2	free flowing salt with small lumps
3	only small part of the sample is free flowing
4	completely hard and frozen salt

Table 1: Performance evaluation

Each replica was analyzed and marked separately and then the average performance was calculated. Figure 4 shows the results of the performance of all the Ecosel®BioCare treated samples.

The results show that caking increases with water content. This can be explained by the higher dihydrate content. It can also be seen that caking becomes more severe with lower temperature (shift from blue curve to the green curve in Figure 4) or longer storage time (shift from blue curve to the red curve in Figure 4). The samples that were kept for 2 days at -15 °C looked very dry, which indicates that the brine that was liquid at room temperature transformed almost completely to sodium chloride dihydrate at -15 °C. This is confirmed also by experiments where the samples were kept for 4 days at -15 °C and caking was very similar to the samples kept for 2 days at -15 °C. It means that the thermodynamic equilibrium was not reached yet after 1 day, but it was reached after 2 days at -15 °C.

The time that the samples stay in the freezer is important due to the stochastic nature of nucleation. The volume of the sample is small and there are not too many available nucleation centers[10] for the dihydrate crystals. Therefore, it is a matter of time before the dihydrate starts forming, but once it starts it grows and the water in the sample is consumed. The amount of dihydrate eventually formed depends on the temperature according to the phase diagram. On a bigger scale the probability of nucleation is much higher[10] and the thermodynamic equilibrium can be reached faster, which means that in practical situation, the caking behavior will be close to the worst case on lab scale.

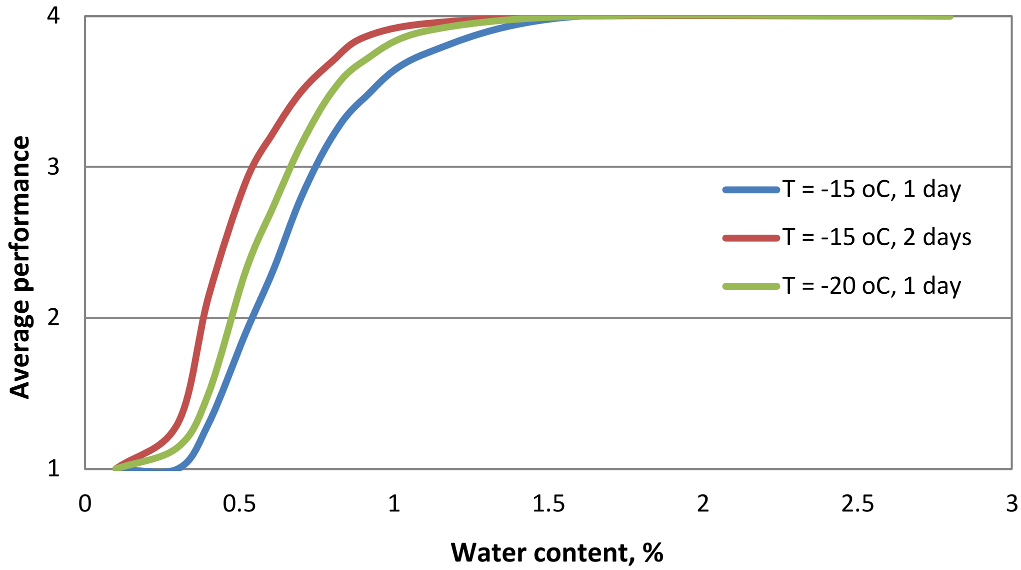

Figure 4: Caking of Ecosel®BioCare treated salt as a function of water content

All experiments were performed with vacuum salt. Although rock salt and sea salt are not tested, it is expected that all types of salt with (it should be either moisture or water content) lower than 0.5% are free-flowing, even if the crystal size distribution also plays a role in caking. It is expected that vacuum salt is the worst case scenario, as the other types of salt have bigger particles which decrease the glueing effect of dihydrate.

4. Industrial tests

The anticaking performance of Ecosel®BioCare for de-icing applications was further investigated in industrial scale. The test was performed together with MVG, located in Ravenna, Italy.

4.1. Industrial test in big-bags (1 ton scale)

Dry rock salt, sea salt and vacuum salt (see Table 2) were used in this test. 12 ppm Ecosel®BioCare calculated as Fe was added to the different types of salt samples. The treated salt was stored in big bags in a covered warehouse. Big bags were piled up and kept for 1 year. During storage, the samples were monitored to check their flowability and caking status. Controls consisted in hitting the bags to verify the absence of any lumps and in a visual inspection of the product inside.

After one year the bags were emptied and the flow behavior was monitored, as well as the presence of lumps.

There were no significant differences in comparison to the usual salt treated with sodium ferrocyanide. The flowability of the salt samples was exactly the same, when handled via belt conveyors, screw conveyors and hoppers. After 1 year all samples were free of caking and completely free-flowing.

Salt type	Average particle size, mm	Moisture content , %
Sea	0-10	0.15
Rock	0-10	0.18
Vacuum	0-0.6	0.1

Table 2: Raw materials details

4.2. Industrial test with rock salt in a heap (100t scale)

Ecosel®BioCare was added to 100 t of rock salt at the concentration of 12 ppm Fe. The average grain size was 0 - 5 mm and moisture content was 0.25%. Salt was stored as a heap in a covered silo and kept for 1 year. A comparative test was done with salt containing 100 ppm ferrocyanide.

The compaction of each salt pile was checked using a friction tool during storage and by handling of the salt after 1 year. The friction tool measured a strong compaction in the salt heap treated with Ecosel®BioCare compared to that treated with ferrocyanide. However, the handling of the salt with a shovel at the end of the storage went smoothly. It shows that Ecosel®BioCare performs effectively as anticaking agent in this test setup.

4.3. Industrial test with rock salt (40 kt scale)

40 kt of dry rock salt (grain size: 0-7 mm) was treated with 12 ppm Ecosel®BioCare.

The salt was transported by ship for several days and then stored outside under a plastic cover. A reference salt pile treated with ferrocyanide was stored at the same condition.

Compaction and caking measurements showed that the salt treated with Ecosel®BioCare was more compact than the one treated with ferrocyanide. Handling of the salt treated with Ecosel®Biocare went smoothly.

5. Conclusions

Ecosel®BioCare is an alternative anticaking agent to ferrocyanide for de-icing salt applications. Being readily biodegradable and cyanide free, this anticaking agent avoids some of the concerns related to the use of the more traditional ferrocyanide.

Laboratory tests showed that vacuum salt treated with Ecosel®BioCare with moisture content up to 0.5% is free flowing at temperatures as low as -20 °C. Other types of salt were not tested, but is expected that any type of salt treated with Ecosel®BioCare (12 ppm calculated as Fe) with a water content of maximum 0.5% will be free-flowing and easy to handle.

Sea salt, rock salt and vacuum salt with moisture content up to 0.25% was industrially tested. The results showed that salt containing Ecosel®BioCare was free flowing after one year of storage. No differences in handling were observed between salt treated with Ecosel®BioCare and ferrocyanide, when salt was stored in big-bags. In case of bulk storage, the salt could still be handled after one year of storage, even if salt containing Ecosel®BioCare became more compacted.

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