

NEXT GENERATION ANTI-CAKING: MESO TARTRATE

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Abstract: Presently $\text{Fe}(\text{CN})_6^{4-}$ is the world standard anti-caking agent for salt. Yet in membrane electrolysis $\text{Fe}(\text{CN})_6^{4-}$ has distinct negative effects since Fe deposits as $\text{Fe}(\text{OH})_3$ on or in the membranes increase power consumption and CN is partially transformed into harmful NCl_3 that may lead to explosions. The increasing number of membrane electrolyses worldwide enlarges the need for a powerful and effective anti-caking agent without the disadvantages of $\text{Fe}(\text{CN})_6^{4-}$.

This next generation anti-caking agent is Fe - meso Tartrate (Fe-mTA), in short mTA.

In this paper the original development and application of mTA is described as anti-caking agent for both chemical transformation salt and road salt. Customer's experience in operations with mTA-salt in large membrane electrolysis plants during the last four years is elucidated as well as practical experience with transport, unloading and storage. Presently optimization is executed to fine-tune the anti-caking properties of mTA further.

Introduction

Salt has a natural tendency to cake when exposed to varying temperature and humidity conditions. Especially at storage outdoors but even indoors salt hardens in time and handling becomes increasingly more cumbersome. Consequently combat of (the consequences of) caking has always been of importance in the salt business.

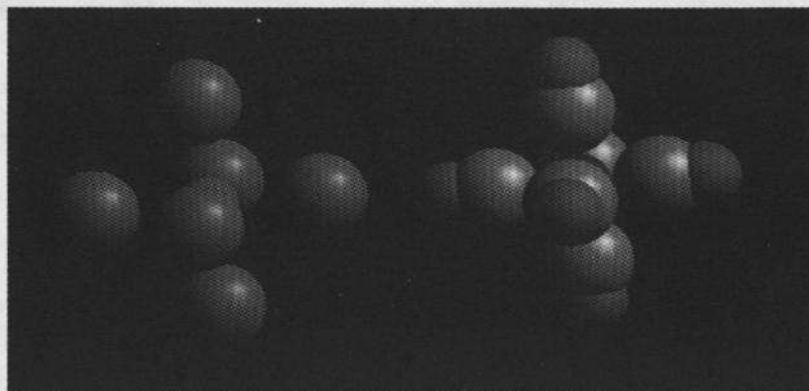
Until the discovery of anti-caking agents mechanical means were exercised at handling and transport.

In the 50's of the last century Royal Dutch Salt (KNZ now embedded within AkzoNobel) discovered and patented (1953 -

1957) $\text{Fe}(\text{CN})_6^{4-}$ as a very powerful and effective anti-caking agent for salt. Since then this first real anti-caking agent $\text{Fe}(\text{CN})_6^{4-}$ is the standard all over the world. $\text{Fe}(\text{CN})_6^{4-}$ is sold as Na_4 or K_4 salts named prussiates like $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\text{Na}_4\text{Fe}(\text{CN})_6$ and $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$.

The anti-caking action of $\text{Fe}(\text{CN})_6^{4-}$ is attributed to the same shape and nearly the same size (difference 0.09 Å) as the NaCl_6^{5-} cluster giving an almost perfect fit into the NaCl grid like a key in a lock. See picture 1.

As however the difference in positive charge (Na^+ and Fe^{2+}) has to be compensated electrically the NaCl crystal grid will be disturbed and caking is prevented (1).



Picture 1 **Shape of NaCl_6^{5-} cluster and $\text{Fe}(\text{CN})_6^{4-}$ ion**

Incentive for a new anti-caking agent

The incentive for a new anti-caking agent derives directly from the main application of

Salt + water + electricity
Hydrogen

2NaCl + $2\text{H}_2\text{O}$
(in mol)

salt e.g. the electrolysis process where salt is converted into chlorine, lye and hydrogen according to the reaction:

→ Chlorine + Lye +

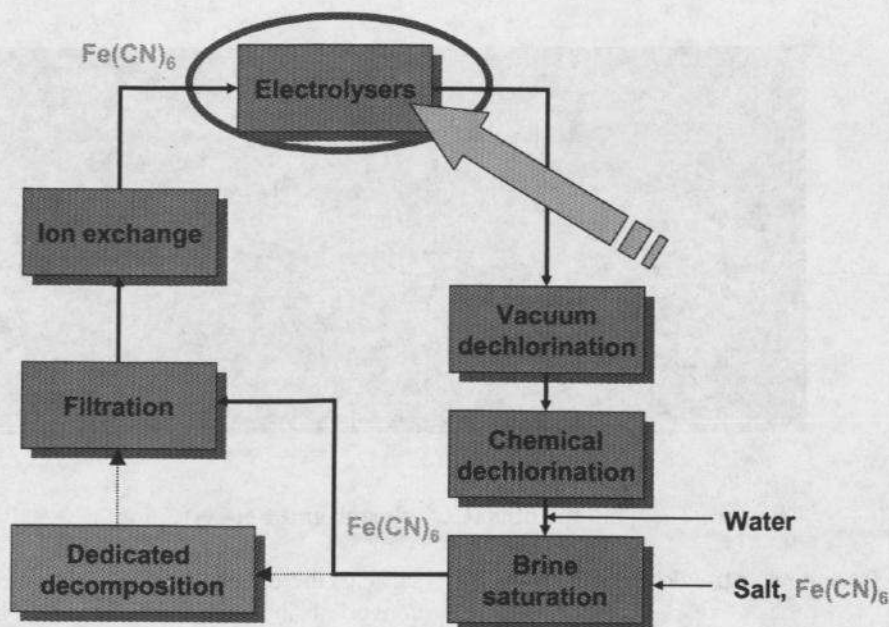
→ Cl_2 + 2NaOH + H_2

Originally this chlorine/alkaline electrolysis process was executed in diaphragm electrolysis plants using mostly brine without anti-caking agent and in mercury electrolysis plants using (dissolved) solid salt. However about 30-35 years ago membrane technology for chlorine electrolyses became increasingly mature.

Since that time a slow conversion from mercury electrolysis plants to membrane electrolysis plants took place which most probably will result eventually in a complete phase out of mercury electrolysis plants. Nowadays a still growing number of membrane electrolysis plants is erected to replace outdated mercury electrolysis plants as well as to increase chlorine production

capacity. In membrane electrolysis plants the fate of $\text{Fe}(\text{CN})_6^{4-}$ is quite different from its fate in mercury electrolysis plants and consequently it is essential to examine what exactly happens to $\text{Fe}(\text{CN})_6^{4-}$ in a membrane electrolysis.

$\text{Fe}(\text{CN})_6^{4-}$ enters the brine by dissolution of the salt in the dissolver. If $\text{Fe}(\text{CN})_6^{4-}$ is not decomposed in a dedicated destruction unit it passes the filter (that captures mostly iron hydroxide $\text{Fe}(\text{OH})_3$), the ion exchange columns and finally enters the electrolyzers. See picture 2 in which the principal electrolysis process flow for vacuum salt is depicted.



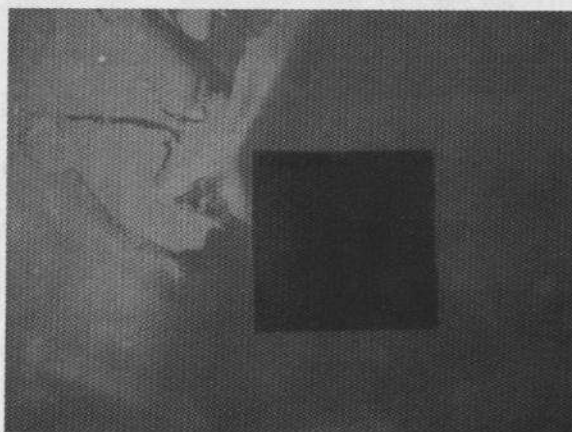
Picture 2 Flow sheet of a membrane electrolysis process for vacuum salt using Fe(CN)_6^{4-}

Subsequently at the elevated temperatures in the electrolyzers Fe(CN)_6^{4-} is decomposed into “free” Fe and cyanide (CN) by chlorine in statu nascendi. Cyanide is (partially) transformed into the harmful derivative: NCl_3 that may lead to explosions (2) even at ppm level in liquid Cl_2 .

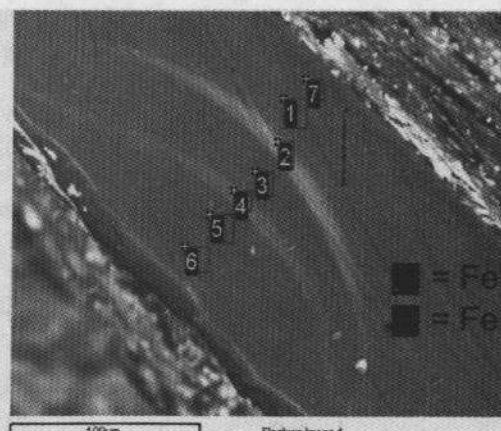
The positively charged Fe ion will deposit as a solid in the form of Fe(OH)_3 on or in the membranes (see picture 3) and even coat the

electrodes (3) depending on the acidity of the original brine.

The Fe deposition increases the electrical resistance in the electrolysis cell yielding a voltage increase. As the current in the electrolysis cell is normally held constant the power consumption increases linearly and so do the electrical energy costs.



Overview



Cross section

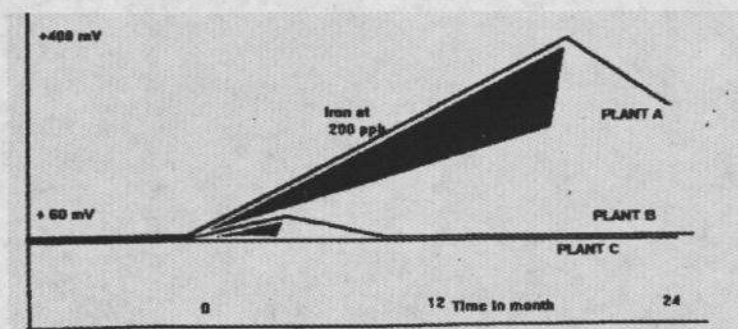
Picture 3 Fe deposition on and in membranes.

The overview shows in the back ground a membrane used in an electrolysis plant without Fe(CN)_6^{4-} in the feed brine. The cross

section shows a Scanning Electron Microscope (SEM) picture.

Already in 1997 the detrimental voltage increase that may result from $\text{Fe}(\text{CN})_6^{4-}$ was convincingly shown by Van der Steegen and Breuning (4). See picture 4 in which the voltage increase as caused by 200 ppb Fe is

given for plant A originally operating on rock salt (400 mV in 18 months) as well as for plant B originally operating on solar salt (60 mV in 3 months). At both plants no acidification of the anolyte was applied.



Picture 4 Voltage increase of 200 ppb Fe

Overall the detrimental effects of Fe depend mainly on pH of the brine, current density, type of membrane, type of electrolysis cell and frequency of shutdown.

It is noted that the adverse effects become more severe at lower pH.

Alternatively a dedicated decomposition unit using active chlorine at $\sim 100^\circ\text{C}$ may destruct $\text{Fe}(\text{CN})_6^{4-}$ before it reaches the electrolysis cells. This solution however also generates costs resulting from investment for

the decomposition step, chemical and energy use and at times disposal of waste heat.

So the conclusion must be that one way or the other $\text{Fe}(\text{CN})_6^{4-}$ generates costs!

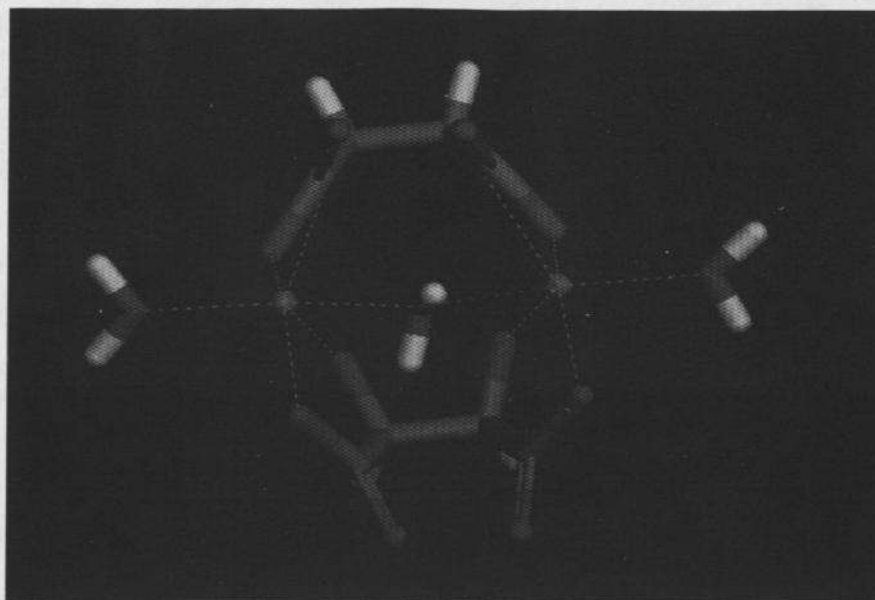
An exciting way to avoid the negative effects of $\text{Fe}(\text{CN})_6^{4-}$ is its substitution by an anti-caking agent without the disadvantages described above. Realising the need and challenge AkzoNobel's R&D salt started several years ago a quest for an anti-caking agent particularly customized for the membrane electrolysis process.

A new anti-caking agent

The technical demands imposed on a new anti-caking agent are extremely challenging as shown below;

- Strong anti-caking action at a few ppm dosing level.
- Good solubility in water or brine
- Not poisonous, preferably food grade.
- Colorless.
- Odorless.
- Non volatile.
- Easily destructible to non harmful chemicals (H_2O , CO_2 , HCl , etc.) at (membrane) electrolysis processes.

In addition the new anti-caking agent needed to be patentable to reinforce the intellectual property position of AkzoNobel. Finally the new anti-caking agent needs to be economically attractive as salt is a very cheap commodity product. After considerable R&D efforts a high-quality anti-caking agent for salt was found and patented (5). See picture 5. This anti-caking agent is Fe - meso Tartrate (Fe-mTA), in short mTA, and its probable anti-caking mechanism has been described (6). Fe realizes the actual anti-caking action by Fe oxychloride complexes but mTA is essential for transporting Fe to the salt surface without being precipitated as $\text{Fe}(\text{OH})_3$. Surprisingly Fe-DTA and Fe-LTA have no or only inadequate anti-caking properties. This difference in behavior of the 3 different stereo isomers of tartrate is presently subject of investigation.



Picture 5 Fe - meso Tartrate complex

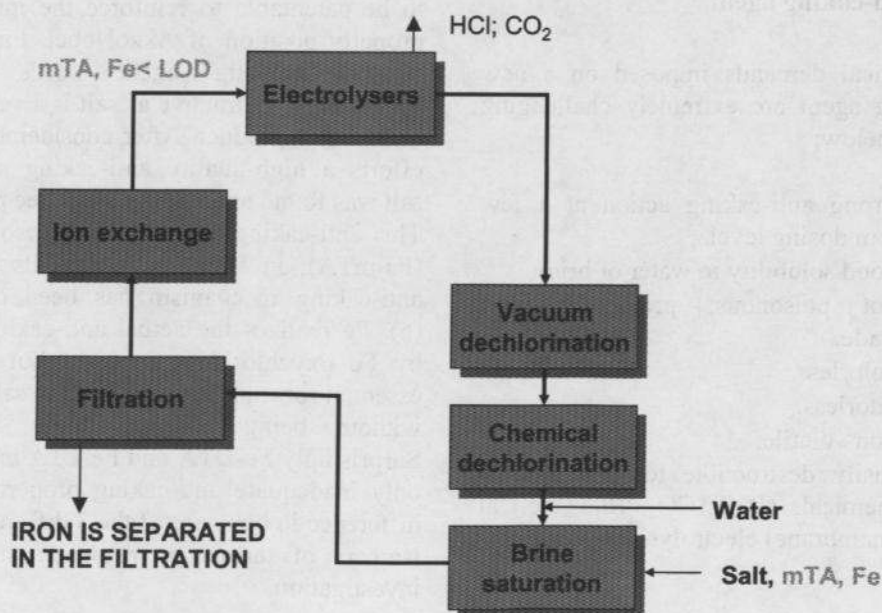
As mTA is commercially only available in small quantities at totally unacceptable prices a production process had to be invented. Although this initial production process yields only about 30 - 35 % mTA the final solution was applied as anti-caking agent for salt processed in a large scale commercial Chlor/Alkali membrane plant. mTA is easily bio degradable as it can be derived from the food grade renewable by-product LTA which makes it natural and environmental friendly. Also young tamarind

fruit contains a significant amount of mTA (7) and is edible.

Application

Chemical transformation salt

With the new anti-caking agent available the principal electrolysis process flow becomes as follows;



Picture 2 Flow sheet of a membrane electrolysis process for vacuum salt using mTA. (LOD = Level Of Detection)

Now the dedicated decomposition unit for $\text{Fe}(\text{CN})_6^{4-}$ can be avoided or taken out of operation as the Fe-mTA complex is weak and easily destroyed at the dissolution of the salt. Iron liberated from the Fe-mTA complex is precipitated as $\text{Fe}(\text{OH})_3$ and subsequently removed at filtration. In most cases the existing filtration capacity is more than sufficient to handle the limited increase in amount of $\text{Fe}(\text{OH})_3$. mTA is mostly converted to HCl and CO_2 in the electrolysis cells and no chlorinated components are formed (8).

Additionally a membrane electrolysis plant can now be operated under more acidic conditions resulting in both less chlorate and less oxygen formation. Apart from the higher chlorine efficiencies less chlorate eliminates the need for a chlorate destruction unit and less oxygen greatly reduces (anode) corrosion thus increasing the lifetime of the electrodes and gaskets. So mTA salt enables operation of a membrane electrolysis plant at higher current density, higher acidification, no chlorate destruction and low oxygen in the chlorine produced.

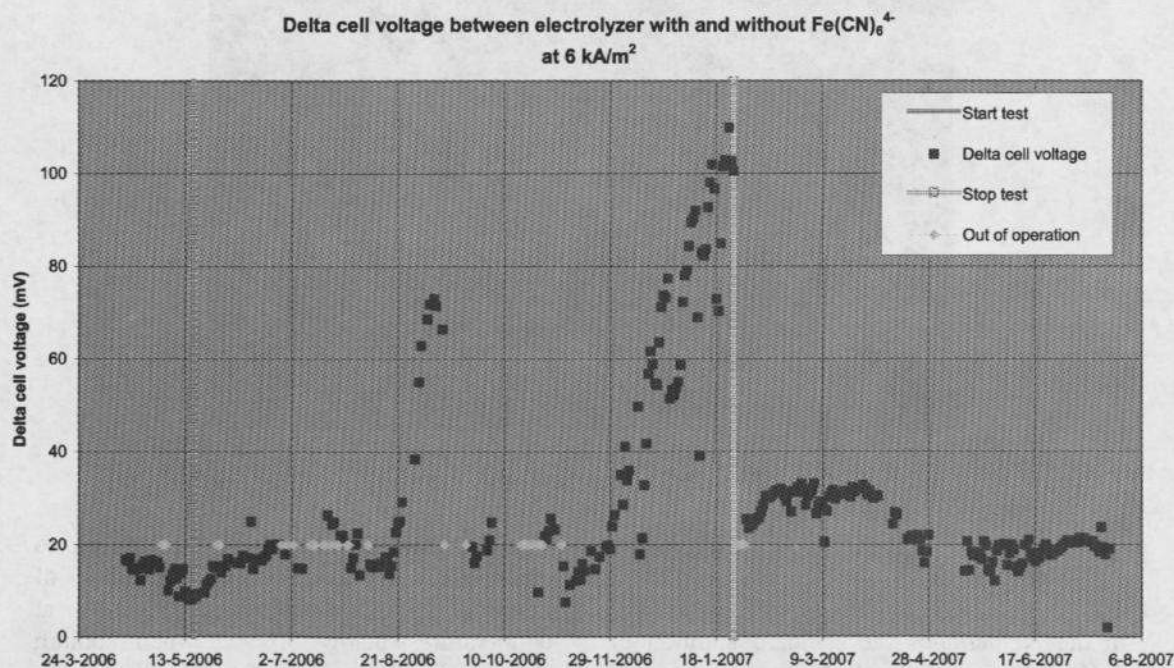
After completion of extensive large scale tests of mTA in mercury, diaphragm and membrane electrolysis the decision was taken to use further only mTA vacuum salt in a large scale Chlor/Alkali membrane plant of which the capacity just was to be extended.

So the existing decomposition unit for $\text{Fe}(\text{CN})_6^{4-}$ was closed down and to date more than 5 Mton of mTA vacuum salt has been processed successfully.

Supplementary to establish the detrimental consequences of $\text{Fe}(\text{CN})_6^{4-}$ on membrane electrolysis processes on industrial scale once and for all the effect of dosing of $\text{Fe}(\text{CN})_6^{4-}$ to the feed brine of just one electrolyser (resulting in a Fe concentration of ± 45 ppb) was investigated.

The performance of this one electrolyser was compared to another electrolyser which had the same header, same cells, same membranes, same current densities, same feed brine and the same process conditions but no $\text{Fe}(\text{CN})_6^{4-}$ dosage. Inclusive stops the dosage was continued for 8 months and all other effects were excluded by subtracting the cell voltage of the electrolyser without $\text{Fe}(\text{CN})_6^{4-}$ dosage from the cell voltage of the electrolyser with $\text{Fe}(\text{CN})_6^{4-}$ dosage.

The result is given in picture 6 and it shows clearly that the addition of $\text{Fe}(\text{CN})_6^{4-}$ to the specific electrolyser causes the measured cell voltage to increase (50 mV in 4 weeks in August 2006 and 90 mV in 7 weeks in December 2009), as all other process conditions were equal for both electrolyses.



Picture 6 Δ cell voltage in time

In addition table 1 gives an overview of the average Fe concentrations in and on the membranes after respectively 5 and 8 months. The latter was at the end of the $\text{Fe}(\text{CN})_6^{4-}$

dosage period. Whether or not any Fe was removed by rinsing of the membranes just before removal from the electrolyzers is not known.

	Reference		$\text{Fe}(\text{CN})_6^{4-}$ dosage	
	after 5 months mg/m^2	after 8 months mg/m^2	after 5 months mg/m^2	after 8 months mg/m^2
Fe	470	450	2100	2480

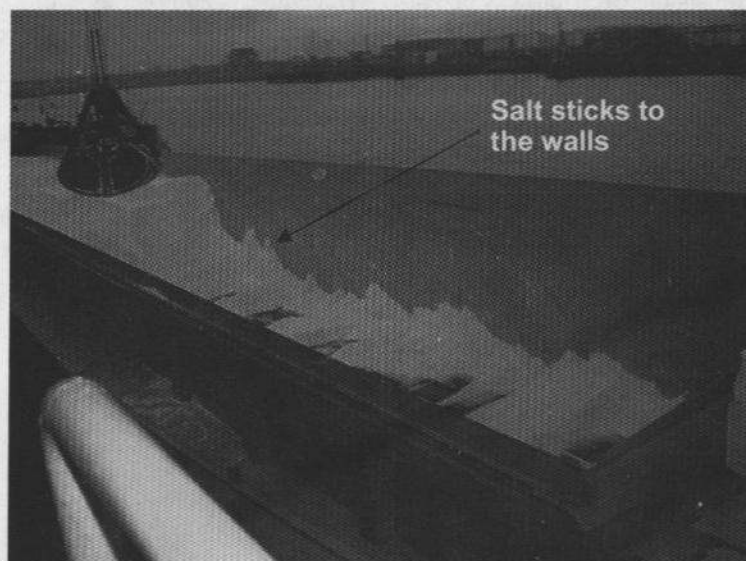
Table 1. Fe analysis in membranes after dosage of 45 ppb Fe as $\text{Fe}(\text{CN})_6^{4-}$

It should be noted however that presently mTA vacuum salt is not yet as free-flowing as standard $\text{Fe}(\text{CN})_6^{4-}$ vacuum salt. Picture 7 clearly shows that mTA vacuum salt has a tendency to stick to the walls and to form salt walls. Also the unloading speed decreases as the crane is not filled up completely.

Unloading from ships equipped with belt discharge systems at the ships bottom proved to be cumbersome at a few occasions

depending on the degree of salt compaction at sailing. So transport with self-unloading ships is not recommended presently. These disadvantages have been taken care of by customers by small adaptations in their operations.

Naturally R&D is presently focussed to improve the propensity to flow to reach ultimately free flow ability of mTA vacuum salt.



Picture 7 Unloading with crane

Road salt

In the Netherlands the standard addition of $\text{Fe}(\text{CN})_6^{4-}$ for road salt (both vacuum and rock) is in the range 40 – 100 mg/kg which is roughly 30 times more than the standard addition of $\text{Fe}(\text{CN})_6^{4-}$ for electrolysis salt.

This substantial increase is necessary to compensate the limited effectiveness of $\text{Fe}(\text{CN})_6^{4-}$ as anti-caking agent at temperatures below 0.1 °C when sodium chloride dihydrate ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) is formed. Logically $\text{Fe}(\text{CN})_6^{4-}$ added to road salt yields low concentrations of $\text{Fe}(\text{CN})_6^{4-}$ dissolved in (surface) water when the road salt dissolves.

Fortunately $\text{Fe}(\text{CN})_6^{4-}$ naturally has low or no toxicity to humans or aquatic life due to its high chemical stability. However conversion of $\text{Fe}(\text{CN})_6^{4-}$ to toxic free CN^- under the influence of sunlight may occur.

Except for the direct environment of road salt storages most investigations show that $\text{Fe}(\text{CN})_6^{4-}$ in road salt is not a factual problem due to dilution and volatilization of free CN^- (after reaction to HCN). Yet a "cyanide free" anti-caking agent would certainly be appreciated both by the road authorities and by the general public for environmental reasons. mTA certainly is such green "cyanide free" alternative for $\text{Fe}(\text{CN})_6^{4-}$ in road salt and so mTA salt is recently explored for its properties in de-icing applications.

Storage

So far storage tests only have been conducted using **regular** mTA vacuum salt as applied at the electrolysis process, so no higher dosage. As expected preliminary results indicate that this **regular** mTA vacuum salt should not be stored as road salt for considerable periods of time due to lumps and crust formation. Like with $\text{Fe}(\text{CN})_6^{4-}$, the concentration of mTA must be increased to be effective under de-icing conditions. Presently long term storage tests are being executed applying higher dosages of mTA to road salt.

Spreading

Shortly (within 2 months) after storage **regular** mTA vacuum salt was spread several times as road salt resulting in normal spreading patterns. A year later a second spreading test with both standard road salt (± 75 ppm $\text{Fe}(\text{CN})_6^{4-}$) and **regular** mTA salt revealed again normal spreading patterns despite the already mentioned lump formation of mTA salt. These lumps partly broke in the hopper thus yielding salt fragments up to 5 cm that bounced on the road surface for several meters. So **regular** mTA vacuum salt spreading is highly comparable to standard vacuum road salt (± 75 ppm $\text{Fe}(\text{CN})_6^{4-}$). In the future higher dosages of mTA to vacuum road salt will certainly diminish lump formation.

Future developments

A number of major developments are noteworthy.

- Improvement of the propensity to flow of mTA salt to obtain free-flow ability.
- Further optimization of the anti-caking properties of mTA salt by fine-tuning e.g. the ratio of Fe to mTA and total Tartrate.
- Execution of storage and spreading tests to establish optimal dosages of mTA to vacuum or rock salt for de-icing purposes.
- Fundamental R&D to reveal the underlying anti-caking mechanism at molecular level in cooperation with an university. This investigation may lead to third generation anti-caking agents.

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