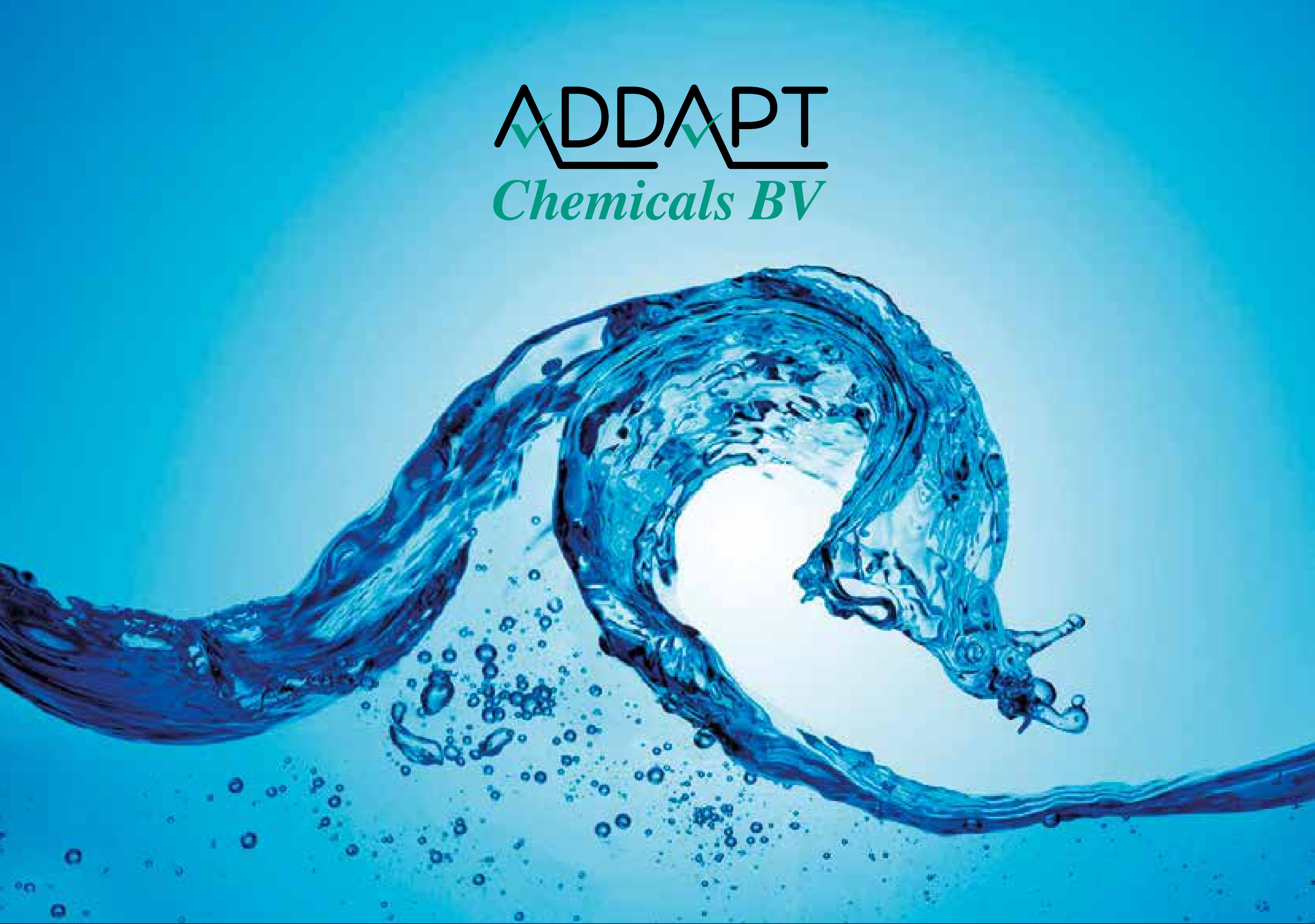


for tomorrow's
Technology

Wastewater Treatment Additives

for tomorrow's
World

Contents

1. Introduction

Natural Increasing living standard and consumption of goods is followed by the increase of waste products. This implies that water supply and wastewater treatment obtain high priority for all kind of industries. In order to keep up with fresh water supply, usage of wastewater treatment plants became a standard practise for the majority of the industries producing considerable amount of wastewater.

During purification of the wastewater, there is an increasing tendency of foam-build up. Usage of Foam Control Agents is highly recommended in order to achieve an optimised wastewater treatment process. The increasing number of waste treatment plants and the very strict environmental restrictions for industrial waste leads to a strong increase in Foam Control Agents (FCA).

The composition of wastewater varies dramatic and it is advised to split the wastewater in industrial applications. Industrial wastewater again, differs strongly from communal wastewater. Communal wastewater consists mainly of non-ionic and anionic surfactants. Because of the high diluting factor, the communal wastewater does show a high foam tendency. This in contrast to the industrial wastewater, which shows a high concentration of industrial waste, dissolved in the water.

The increase in foam tendency of industrial wastewater can be found in:

- Larger wastewater quantities;
- Higher content of foaming substances in the wastewater;
- Biodegradation becomes more difficult; therefore more intensive treatment is required.

The chemical industry consumes the highest amount of water (one third of the fresh water consumption). About 80% of this fresh water is used for cooling processes. The chemical process takes 16% of the used water in account and only 2% is used as boiling feed water and drinking water for employees.

Chemical industries that produce and/or handle emulsions based systems and industries handling methyl cellulose do produce wastewater with a strong foam tendency.
Running a wastewater treatment plant is not an easy task because of the different kind of chemicals dissolved in the wastewater. Adequate inoculums have to be selected enabling one to biodegrade the chemicals dissolved in the wastewater. The composition of the industrial wastewater also alters many times. This asks for a fast change in treatment of the wastewater. For this reason there are many different wastewater treatment processes available. A correct choice of the treatment leads to a very effective biodegradation of the chemicals. Below the most well known treatment processes are discussed in brief.

2. Water treatment methods

2.1 Mechanical-chemical treatment

Solids have been removed from the wastewater and water was collected in large basins in order to allow solids to settle to the bottom. This was the version of a wastewater treatment plant.
Later, flocculants were used in order to improve the settling of the solids and a better clarification was achieved. This (very simple) treatment of wastewater is still in use.

2.2 Biological treatment

Majority of industries is using a so-called biological clarification in combination with the mechanical-chemical treatment. The biological treatment is a foam active process and requires Foam Control Agents. The principle is the same as applied in fresh water and seas: micro organism use the pollution as nutrient and produce by using oxygen (aerobic) cell substances and carbon dioxide or without oxygen (anaerobic) manure gas (methane).
Water treatment plants apply the aerobic process. Sometime a combination of both methods is applied. The supply of oxygen can be achieved in different ways. The most convenient and easiest way is by stirring. The stir process adds also to the foam tendency. The presence of oxygen is, of course, the key to an optimised biodegradation process.

3. Industrial sewage system set-up

The communal sewage plants are all similar because the wastewater composition from this source is more or less the same. Industrial sewage systems can differ because the wastewater composition often differs dramatic from each other, i.e. it depends what kind of industry is attached to the sewage system. In some cases the communal wastewater and industrial wastewater is pre-mixed with each other in order to keep the running cost low (no extra sewage system for the communal wastewater). In this case the composition of the wastewater is also kept uniform; this is an advantage for the micro organism used in the sewage systems (adaptation of the micro-organism).

Industrial sewage systems consist of different treat stages:

- Pre-treatment;
- Pre-settle;
- Biological stage;
- Final sedimentation.

4. Wastewater pre-treatment

Many chemical production processes include the usage of acids or lye. For this reason, the majority of the incoming wastewater has to be neutralised first. The neutralisation takes part after the settling of the rough dirt has been collected.

5. Pre-settle

The dissolved heavy metal will separate as hydroxides after the neutralisation reaction. These hydroxides are collected together with other solids during the so-called pre-settle process.
The pre-settle process is carried out in pre-clarification ponds. The process can be accelerated by the usage of flocculants. The pre-clarified water is now pumped into the biological pond. During this pump activity, the water passes different kind of sieves and filters in order to filter out more, small sized solids.

6. Biological stage

The active sludge in the biological pond is responsible for the biodegradation. This biodegradation is mainly an aerobic process. There are many different ways to add oxygen to the biological pond in order to optimise the biodegradation.

6.1 Surface aeration

This is the most widely used process. The water goes in to ponds with a 3 to 4 m. depth. At the surface there are large “stirrers (aerators), which produce a high turbulence. The turbulence leads a high amount of oxygen into the biological pond. This process leads to a high foam activity. In order to prevent a strong foam activity, the operators use Foam Control Agents. The stirrers are responsible for a good distribution of the Foam Control Agent. The usage of an active Foam Control Agent is critical because the presence of foam decreases the air supply dramatically.

6.2 Submerged aeration

The ponds have a depth of 6 to 8 meters. The air supply is achieved via large nozzles, which blow air in the liquid. The advantage of this technique that the air distribution is more effective as in the previous mentioned method (stirring). This method also asks for an effective Foam Control Agent.

6.3 Tower biology

Tower-biology refers to the latest technology in wastewater treatment. The biodegradation takes place in steel containers, which measure 30 meters, height. The principle is similar to a fermentation tower for yeast production. Advantages of this technology are:

- Better oxygen utilisation;
- Space saving construction;
- Odourless process. The containers are closed. The produced gases and excess of oxygen are treated afterwards.

6.4 Other aeration techniques

A few other systems are in use; however, they never became common systems in the wastewater treatment process such as: “second aeration stage droppers” (towers filled with so-called “droppers” where the wastewater is added from the top to the liquid stored in the wastewater tower.
All the above systems deal with standard air. In very special cases, pure oxygen is added to the wastewater. It is obvious that these ponds are covered in order to keep the oxygen in the pond and a minimum will evaporate.

7. Final sedimentation

The activated sludge and clarified wastewater have to be separated after the biodegradation. The water is transferred into the final sedimentation ponds. Flocculants are added to the waste in order to accelerate the sedimentation process. A part of the activated sludge transferred back to the biological pond, the remaining sludge is de-watered and treated together with the primary sludge.

A problem can occur when the sludge floats on top of water ponds, i.e. the entrapped air prohibits the settling of the sludge. To prevent that the sludge will be carried away together with the water, the ponds do have a skimmer, which holds back the sludge, which floats on top of the water.
However this is a problem, which finds its roots in the dissolved air in the water. The obvious solution is to use anti foam, which acts as deaerator as well. The lack of air in the water reduces the problem of floating sludge on the water. See the reference chart for suitable deaerator (Foamstop 150N; Foamstop 600N; Foamstop CCB).

8. Foam Control Agents

During the biodegradation process, many gases evaporate from the liquid. This leads to foam development. In order to control the foam activity Foam Control Agents are selected.

8.1 Foam Control Agent usage

The majority of the dosage points are at the biological treatment ponds. These ponds do contain the micro organism as well, so it is extreme important that not all the air is taken from the liquid. A too low content on oxygen will lead to a reduced activity of the micro organism or even non-active micro organism. For this reason, the correct choice of Foam Control Agent, which leads to good anti foam properties and a balanced air content, is the key to a successful biodegradation.

The Foam Control Agent should be very effective (low extra addition of organic material) and be biodegradable as well. Mineral and preferably biodegradable Vegetable oil based Silicone free Foam Control Agents are preferred.

8.2 Selection of Foam Control Agents

The composition of the wastewater might vary over a period of time and most industrial sewage systems are different from each other, for this reason it is recommended to test the Foam Control Agent at small scale before it is used in larger scale.
The evaluation should carry out with fresh wastewater. Wastewater, which has been biodegraded already at a certain stage, is not a good reference. The test can be carried out in the laboratory.

9. Scaling and Anti-scalants

Scaling means the deposition of particles on a surface like for instance a membrane, causing it to plug. Without some means of scale inhibition, reverse osmosis (RO) membranes and flow passages within membrane elements will scale due to precipitation of sparingly soluble salts, such as calcium carbonate, calcium sulphate, barium sulphate and strontium sulphate. Crystallization of sparingly soluble salts such ascalcium carbonate and calcium sulphate dihydrate is known to occur when certain surface and ground waters are used as the water source in membrane desalination processes. Most natural waters contain relatively high concentrations of calcium, sulphate and bicarbonate ions.

In membrane desalination operations at high recovery ratios, the solubility limits of gypsum and calcite exceed saturation levels leading to crystallization on membrane surfaces. The surface blockage of the scale results in permeate flux decline, reducing the efficiency of the process and increasing operating costs. To avoid scaling difficulties, it is essential to restrict the fractional recovery of purified water below a threshold limit at which there is a risk of scale precipitation. In view of the economic benefit of high water recovery, the effective solubility limits of scaling salts, and hence the allowable water recovery, are usually extended by anti-scalant treatment.

There are three methods of scale control commonly employed:
- Acidification;
- Ion exchange softening;
- Anti-scalant addition.

Acidification: acid addiction destroys carbonate ions, or removing one of the reactants necessary for calcium scale precipitation (sulphate). This is very effective in preventing the precipitation of calcium scale, but less effective in preventing other types of scale. Additional disadvantages include the corrosion by the acid, the cost of tanks and monitoring equipment and the fact that acid lowers the pH of the RO permeate. ADDAPT Chemicals BV offers Phosphate esters (PEX-080B and PEX-106) which, when used neat, can be used against Calcium scale. Contrary to “pure” acids, they exhibit enhanced corrosion inhibition.

Ion exchange softening: this method utilizes the sodium which is exchanged for magnesium and calcium ions that are concentrated in the RO feed water, following the chemical equations:

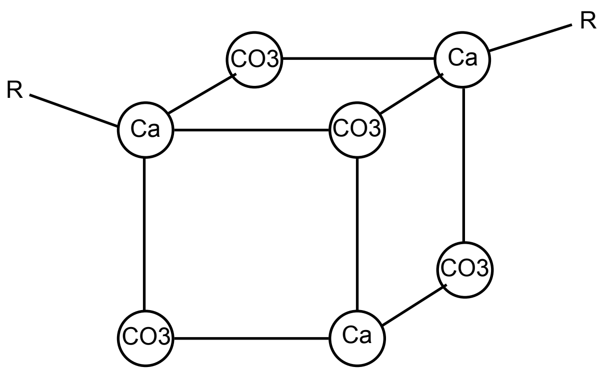
$Ca^{2+} + 2NaZ \quad 2Na^{+} + CaZ_2$

$Mg^{2+} + 2NaZ \quad 2Na^{+} + MgZ_2$ (NaZ represents the sodium exchange resin)

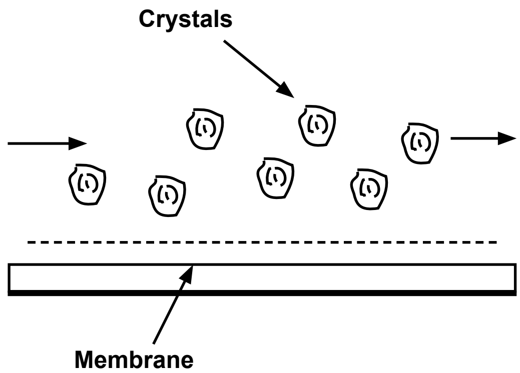
When all the sodium ions have been replaces by calcium and magnesium, the resin must be regenerated with a brine solution. Ion exchange softening eliminates the need for continuous feed of either acid or anti-scalant.

Anti-scalants: they are surface active materials that interfere with precipitation reactions in three primary ways:

- **Threshold inhibition:** it is the ability of an anti-scalant to keep supersaturated solutions of sparingly soluble salts.
- **Crystal modification:** it is the property of an anti-scalants to modify crystal morphology, resulting in soft non adherent scale. As a crystal begin to form at the sub microscopic level, negative groups located on the anti-scalant molecule attack the positive charges on scale nuclei interrupting the electronic balance necessary to propagate the crystal growth. When treated with crystal modifiers, scale crystals appear distorted, generally more oval in shape, and less compact.
- **Dispersion:** dispersing is the ability of some anti-scalants to adsorb on crystals or colloidal particles and impart a high anionic charge, which tends to keep the crystals separated. The high anionic charge also separates particles from fixed anionic charges present on the membrane surface.



Threshold Mechanism



Dispersing

During the past two decades, new generations of anti-scalants (AS) have emerged commercially, in which the active ingredients are mostly proprietary mixtures of various molecular weight polycarboxylates and polyacrylates. Optimal molecular weights have been reported in the range of 1,000- 3,500.

It is often stated that anti-scalants adsorb onto formed crystals or associate/complex with incipient nuclei (or crystals) and that these phenomena govern the inhibition of scale formation affecting the crystal morphology. The precise mechanism of scale inhibition is not clearly understood at this time. However, it is known that in supersaturated solutions of sparingly soluble salts, a significant delay in crystal nucleation and subsequent growth is observed in response to AS treatment. This delay is referred to as the induction-time of the system, which occurs at remarkably low threshold dosages in the order of 1-10ppm. The scale inhibition capability of anti-scalants is related to chemical structure, molecular weight, active functional groups and solution pH parameters.

An important factor in determining the success of surface and ground water desalination is the optimization of anti-scalant treatment with respect to type and dosage. Prior to field testing or even laboratory studies on the performance of RO processes, it is important to identify the proper anti-scalant to use and the dosageinduction time relationship for the expected level of supersaturation.

ADDAPT Chemicals BV offers Descal 900 (Polyacrylate) and PEX-080B/PEX-106 (when neutralised) as AS. When used at threshold levels they effectively inhibit the precipitation of many scale-forming minerals and also modify the crystal morphology. Both of these properties play key roles in keeping heat exchanger or evaporator surfaces scale-free.

10. Conclusion

ADDAPT Chemicals BV offers a wide range of Foam Control Agents and Antiscalants, which are suitable for different kind of industrial water treatment and desalination plants. The plant manager should forward already what kind of wastewater is treated in the plant, preferred with the rough composition of wastewater (for example if it is non-ionic, cellulose or starch based).

The kind of Foam Control Agent nowadays used, gives a good indication what kind of wastewater is treated. Attached flow chart gives already an indication what kind of Foam Control Agent could be evaluated for an effective treatment and leading to an optimised biodegradation.

Note

FS 150N	Foamstop 150N	Not suitable for cationic based sewage systems; Water soluble
FS 600N	Foamstop 600N	Water soluble
CCB	Foamstop CCB	Vegetable oil/PAG based
MP 21	Foamstop MP 21	Polyol based
VF10N	Foamstop VF 10N	Based on Vegetable oils; biodegradable, from renewable resources, non-VOC
VF35N	Foamstop VF 35N	Based on Vegetable oils; biodegradable, from renewable resources, non-VOC
SIN 265	Foamstop SIN 265	PAG based
SIN 360	Foamstop SIN 360	PAG based
SL 10	Foamstop SL 10	Silicone emulsion (10%)
Descal 900	Descal 900	Polyacrylate Mw. ~3500
PEX 080B	Phosphate ester	Oil soluble, water soluble upon neutralisation
PEX 106	Phosphate ester	Water soluble

11. Selection guide

	Foamstop grade								
Sewege type	FS 150N	FS 600N	CCB	MP 21	VF 10N	VF 35N	SIN 265	SIN 360	SL 10
Communal; Standard	●	●	●	□	●	●	□	✖	●
Communal; High detergent content	●	●	●	□	□	●	✖	✖	●
Balanced active substances	●	●	●	●	●	●	✖	✖	✖
Industrial; High detergent content	●	●	●	□	□	●	✖	✖	●
Industrial; High cellulose content	✖	✖	●	✖	●	●	●	□	●
Industrial; high protein level	✖	✖	●	□	●	●	□	□	□
Cooling water, high Biocides level	✖	●	●	●	●	✖	□	✖	●
Scum deaerating	□	●	●	□	●	●	✖	●	●
Desalination	✖	✖	✖	●	✖	✖	✖	✖	✖

● Highly recommendable   □ Recommendable   ✖ Less recommendable

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