

Technical Information 311 Siliphos®



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Technical Information 311 Siliphos® Page 1 / 10



Index

- 1. Introduction
- 2. Siliphos system
 - 2.1. Dispenser size selection
 - 2.2. Types of Siliphos dispenser
 - 2.3. Treatment process
- 3. Health Considerations
- 4. Regulation and approvals
- 5. Technical benefit Protection of pipes
 - 5.1. Corrosion inhibition by Siliphos
 - 5.2. Scale inhibition by Siliphos
- 6. New Research Results on the Corrosion of Potable Water Mild Steel Pipes

Technical Information 311 Siliphos[®] Page 2 / 10



1. Introduction

The history of treating potable water with phosphates dates back to the early 19th century, and is more and more commonly applied, as the water becomes more and more rare, and its quality decreases due to a high rate of recycling. The drinking water supply is done from a great number of small and large size water works as well as by the private users themselves. Hydrological ground formations and pollution determine the quality of water. In some cases the use of surface water cannot be avoided, but in many cases suitable wells with an appropriate water quality are available. Of course, theoretically it is possible to add some naturally occurring ingredients to the water or remove some ingredients to bring the water to a suitable level of balance, but this is not only high in cost, but also requires a thorough analysis and different approach in all cases. Phosphates are the only natural ingredients in the water showing a positive improvement of the water in almost all cases of problems due to corrosion and scale. Adding phosphates to the water has a long history and will definitely also have a future.

Natural water ingredients	high level		low level	
	Corrosion behavior	CaCO3-scaling behavior	Corrosion behavior	CaCO3-scaling behavior
Hardness	decrease	increase	increase	decrease
рН	decrease	increase	increase	decrease
Alcalinity	decrease	increase	increase	decrease
Chlorides	increase		-,-	
Sulphates	increase		-,-	
Oxygen	increase		decrease	
Undissolved solids	increase		decrease	
Dissolved solids	increase	decrease	increase	increase
Phosphates	decrease	decrease	increase	increase

Adding phosphates to the water is technically not so simple. Usually phosphates have to be dissolved to make so-called stock solutions, which then are dosed with proportional dosing pumps to the water. Problems using this method are numerous, e.g. bacteria growth in the stock solution, inappropriately prepared stock solution with lumps inside, incorrectly operating dosing pumps, and very often dosing pumps which are broken and cannot be repaired due to the unavailability of spare parts.

Silicates reduce corrosion and the formation of brown water primarily in low flow through sections of drinking water systems or stagnation zones

Technical Information 311 Siliphos[®] Page 3 / 10



2. Siliphos[®] system

SILIPHOS[®] is a so-called sodium calcium polyphosphate, containing a well-balanced mixture of different inorganic phosphates and sodium silicates.

Siliphos[®] product types:

Siliphos $^{\circledast}\,$ - glassy spheres pieces with a diameter of about 2 cm

- Siliphos[®] II glassy spheres pieces with a diameter of about 2 cm and glassy granulated shiver with an average grit size of 2-4 mm
 - Siliphos II has a higher rate of solubility compared to Siliphos.

Siliphos[®] and Siliphos[®] II are slowly soluble and will be fed into water by a dispenser. The dosing rate should be between 2 and 5 ppm P_2O_5 equivalent to 3 to 8 ppm Siliphos[®].

2.1. Dispenser size selection

The solubility rate depends on water temperature, dispenser size and flow rate. The following recommendation results from practical experience and refer to cases of intermittent water consumption as is the case with most users of drinking water.

Hourly water consumption* (m ³ /h)	Content of dispenser (kg)	Dispenser size	Туре
< 0.1	0.5		
0.1 - 0.2	1		Transparent plastic for easy inspection
0.2 - 0.3	2		
0.3 - 0.4	3	small	
0.4 - 0.5	4	Sman	
0.5 - 0.6	5		
0.6 - 0.8	6		
0.8 -1.0	8		
1.5 - 2.0	15		
2.0 - 2.5	20		
2.5 - 3.0	25		
3.0 - 4.0	30	medium	
4.0 - 5.0	40		
5.0 - 7.0	50		
7.0 - 10.0	80		
10 - 13	100		
13 - 18	150		Welded steel fitted with sight glass and hammer finish
18 - 30	200		
30 - 100	500	large	
100 - 150	1000	paintwork	
150 - 200	1500		
200 - 250	2000		

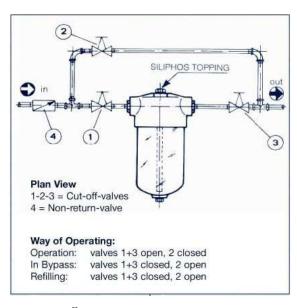
*average daily consumption divided by 24 hours

Technical Information 311 Siliphos® Page 4 / 10

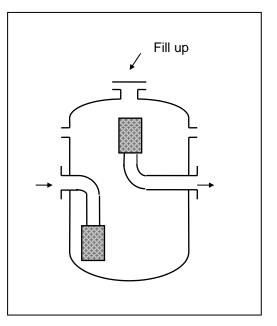


2.2. Types of Siliphos[®] dispenser

The following figures show the different types of dispenser.

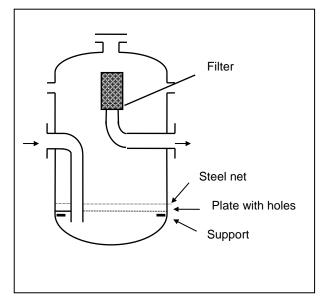


SILIPHOS[®] Dispenser (small/medium



SILIPHOS[®] Dispenser (medium size)

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SILIPHOS[®] Dispenser (large size)

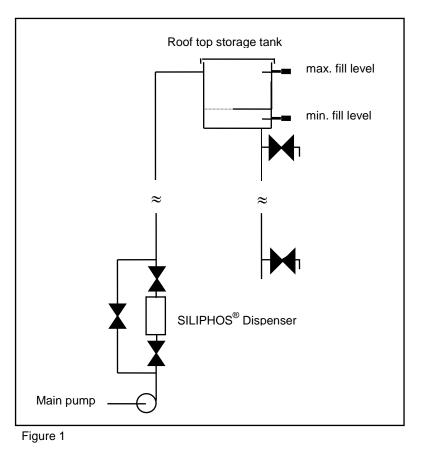
Technical Information 311 Siliphos[®] Page 5 / 10

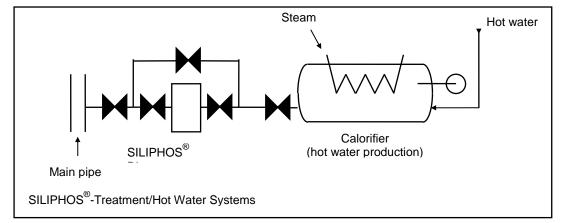


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2.3. Treatment process

The application is very simple. The solubility of SILIPHOS[®] is rather low; for this reason, it can be applied directly with special feeding equipment. After the main pump and before the roof top storage tank a simple container housing the slowly soluble SILIPHOS[®] is installed. See figure 1 and 2.







Technical Information 311 Siliphos[®] Page 6 / 10



This arrangement (the SILIPHOS[®] dispenser is installed before the roof top storage tank) yields to that the roof top storage tank acts as a diluting (buffer) tank in case the water is not flowing for a longer period of time and the P_2O_5 concentration in the SILIPHOS[®] dispenser exceeds 5 ppm.

The only service required is to fill up the SILIPHOS[®] dispenser once every three to six months with the SILIPHOS[®] spheres.

3. Health Considerations

Phosphates are natural minerals needed by the human body. There are absolutely no health considerations in case phosphate-treated potable water is consumed continuously. The phosphorus intake by the human body is per average $3,400 - 4,300 \text{ mg } P_2O_5$ per day. Based on the fact that per day two liters of water treated with max. 5 ppm phosphate (as P_2O_5) are consumed, the average daily P_2O_5 intake by potable water is 10 mg, less than 0.3 % of the total P_2O_5 intake. It should also be noted that the average phosphate intake per person and day should not drop below 1,500 - 2,000 mg P_2O_5 per day to avoid deterioration of the human body.

	P₂O₅ (mg/day)
Meat	446
Sausage	369
Milk	534
Cheese	300
Bread	696
Alcoholic beverage	469
Miscellaneous	1,000
Treated water	10
Total	3,824

Average daily phosphorus intake by the human body (Europe)

Technical Information 311 Siliphos[®] Page 7 / 10



Food
110 %
 $(3,200 - 4,300 \text{ mg P}_2O_5 \text{ per day})$ Bone material \downarrow $15 \% \downarrow \uparrow 15 \%$ \downarrow $15 \% \downarrow \uparrow 15 \%$ Digestion system \leftarrow \downarrow
35 % \leftarrow \downarrow
65 %

Phosphorus flow in the human body

Note: There is no difference between organic phosphorus and inorganic phosphorus as in the digestion system all phosphorous compounds are converted to ortho-phosphate.

4. Regulations and approvals

Drinking water is water intended for human consumption. It must comply with national legislation. The national legislation for EU member states is based on the EC Drinking Water Directive 98/83/EC. Raw materials used for conditioning products must be in accordance with DIN EN standards and included in national positive lists if existing. DIN EN standards especially for 'chemicals used for treatment of water intended for human consumption' contain general description and purity criteria. The limits for conditioning products differ from country to country.

The purity of Siliphos[®] and Siliphos[®] II for the treatment of drinking water is in accordance with the EC-Standard (DIN EN 1208) as well as the requirements of the FAO/WHO Expert Committee on Food Additives (7th and 19th Report).

Further there are some approvals from various countries for using Siliphos in drinking water treatment.

- Siliphos II is NSF-listed since 1991 as 'Drinking Water Treatment Chemical'.
- Approval in Turkey from Ministry of Health Ankara in April 1984, Ministry of Health Denizli in November 1985, Ministry of Health Itmir in March 1986
- Approval in Czech Republic Ministry of Health Prague in January 1991
- Approval in Slovakia Ministry of Health Bratislava in March 1991
- Approval in Poland Hygienic Institute of Poland, Warsaw in December 1994

Technical Information 311 Siliphos[®] Page 8 / 10



5. Technical benefit - Protection of pipes

5.1. Corrosion inhibition by Siliphos[®]

Water missing certain natural ingredients or having an unfavorable composition (buffer capacity, calcium amounts, neutral salt contents, etc.), cannot form a corrosion inhibiting layer inside the pipes. The phosphates contained in SILIPHOS[®] consist of a well-balanced blend of many species of food grade organic phosphates, authorized to be used for potable water treatment. Because of their well-balanced composition they inhibit the cathodic corrosion process, leading to a synergistic effect.

In presence of calcium and iron, phosphates form a dense, uniform, hard to dissolve layer separating the water and the oxygen in the water from the iron-metal. For the formation of this corrosion protective layer the total composition of the water is of minor importance.

The real mechanism still remains unexplained, but following are some assumptions of a possible mechanism:

1. 2Fe ²⁺	+ 2H ₂ O + O ₂	\rightarrow	2Fe(OH) ₂	
2. 2NaH ₂ PO ₄	+ Ca(HCO ₃) ₂	\rightarrow	Ca(H ₂ PO ₄) ₂	+ 2NaHCO ₃
3. Ca(H ₂ PO ₄) ₂	+ 2Fe(OH) ₂	\rightarrow	CaFe ₂ (PO ₄) ₂	+ 4H ₂ O

A slowly soluble calcium iron phosphate is deposited on the pipe surface, forming the desired corrosion inhibiting layer.

5.2. Scale inhibition by Siliphos[®]

SILIPHOS[®] acts as "Threshold Inhibitor" in sub-stoichiometric amounts, thus stabilizing water and preventing CaCO₃-scale from forming.

As a guideline it can be said that SILIPHOS[®] prevents CaCO₃-scaling up to water hardness of 360 ppm as CaCO₃ and up to a water temperature of 80[°] C.

Removing Existing Scale

Actually SILIPHOS[®] is not a fast descaler. Existing hard brown scale is insoluble iron oxide/hydroxide. In case of flow changes these iron oxide/hydroxide scale will be washed out. The formation due to corrosion is faster than the wash out. Over time the layer increases. SILIPHOS[®] will prevent new iron oxide/hydroxide scale formation, and loosen/soften existing scale deposits, which thus are flushed off by the natural turbulence of the water flow.

It is to be noted that the descaling process by SILIPHOS[®] is very slow, thus the Fe³-content in water will not increase during the initial treatment, above levels encountered before using the SILIPHOS[®] treatment. The time needed for the descaling process depends on many factors like composition and amount of scale and is hard to be forecasted. Time may vary from 4 days to 6 months or even more.

Setting up a special treatment schedule for each case is a must. Kurita Europe APW and the representing distributors are any time willing to assist.

Technical Information 311 Siliphos[®] Page 9 / 10



As a general guideline it can be said that, in general, brown scale (iron oxide/hydroxide) can be totally or partially removed, whereas it is hard to remove white scale (calcium carbonate, calcium silicate). As far as white scale is concerned in most cases only further build-up increase of scale is prevented.

Plugging effect

Old pipeline systems often contain invisible holes only plugged by loose iron oxide deposits, through which water leaks. SILIPHOS[®] will harden this deposit plug and to some extent, prevent the leaking of water, but it will definitely prevent the small holes from increasing in size. This effect is uniquely achieved with the composition of several phosphates contained in SILIPHOS[®].

Decolorization of Brown Water

Brown water (containing Fe_2O_3 below 0.3 ppm as Fe^{3+}) can be decolored by addition of SILIPHOS[®]. This effect is very important during the initial treatment and in case the incoming water contains already a certain Fe^{3+} -load. SILIPHOS[®] is adsorbed to the small iron oxide/hydroxide particle, thus preventing them from agglomeration and coloring the water brown.

6. New Research Results on the Corrosion of Potable Water Mild Steel Pipes

According to newer investigations, good corrosion inhibiting layers or films contain a minimum of 25 $\% \text{ Fe}^{2+}$ regarding the total iron - cations. A great part of this Fe^{2+} constitutes of FeCO_3 (Siderite). Based on this, it is concluded that the structure and kind of corrosion products are responsible for the formation of good corrosion inhibiting layers. A further important part are the carbonic acid and their derivatives, since the OH-formed in the cathodic reaction react with bicarbonate according to the following equation:

 $OH^{-} + HCO_{3}^{-} \rightarrow CO_{3}^{2-} + H_{2}O$

The secondary reactions can be summarized as follows:

Ι.	$Ca^{2+} + CO_3^{2-}$	\rightarrow	CaCO₃	(Calcite)
II.	$Fe^{2+} + CO_3^{2-}$	\rightarrow	FeCO ₃	(Sidderite)
III.	1/2O ₂ + H ₂ O + 2FeCO ₃	\rightarrow	2FeOOH + 2CO ₂	(Goethite)
IV.	2Fe ²⁺ + 1/2O ₂ + 3H ₂ O	\rightarrow	$2FeOOH + 4H^{+}$	(Magnetite)
٧.	$3Fe^{2+} + 1/2O_2 + 3H_2O$	\rightarrow	$Fe_3O_4 + 6H^+$	(Magnetite)
VI.	1/2O ₂ + 3FeCO ₃	\rightarrow	Fe_3O_4 + $3CO_2$	(Magnetite)

Technical Information 311 Siliphos® Page 10 / 10



According to this newer theory the formation of siderite and not calcite is the key reaction in the corrosion process. Only if a considerable part of the secondary reaction leads according to equation II to the formation of siderite, good corrosion inhibiting layers can be expected. The primary formation of insoluble Fe^{2+} components also assists in the formation of mixed Fe^{2+}/Fe^{3+} oxides, which also show a good inhibiting effect. Reactions III and IV and thus do not negatively influence the formation of corrosion inhibiting layers.

Deposition of siderite which is by factor 100 less soluble than $CaCO_3$, results by the actual corrosion process which yields Fe^{2+} and OH^- . The pH-value at the metal surface thus increases, and CO_3^{2-} -ions for the formation of siderite are available.

Direct oxidation of Fe²⁺ according to equations IV and V will always be preferred to siderite formation, resulting in loose non-uniform layers giving no corrosion protection, if the pH on the metal surface is very high and the carbonate concentration very small.

This explains the influence of the buffer capacity of the water on the corrosion rate.

Based on the before-mentioned findings, the following conclusions can be made on the formation of corrosion protective layers (without the addition of treatment chemicals):

 In natural water high bicarbonate concentrations are always accompanied by high buffer capacities and relatively low pH-value. Due to the high buffer capacity the so-called "surface alkalinity" is low, resulting in a slow oxidation of the Fe²-formation of siderite, is preferred to calcite formation. In the presence of oxygen, the siderite can be partially or fully oxidized.

The forming corrosion inhibiting layer decelerates the diffusion of oxygen more strongly than a layer of FeOOH \cdot H₂O developed by the direct oxidation of iron.

 Low bicarbonate concentrations and low buffer capacities result in unfavorable layers. The formation of Fe²⁺ is decelerated and its further oxidation to Fe³⁺ accelerated because of a higher "surface alkalinity" and pH-value.

Due to a further reaction of the Fe²⁺, mainly calcite is formed on the metal surface, and only loose, non-uniform layers giving no corrosion protection do result.

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