Title: USE OF PHYTATE FOR WATER TREATMENT

Abstract: Use of phytate to inhibit the nucleation and growth in water of salts with one divalent cation selected from Ca²⁺ and Mg²⁺. This manages to prevent the crystallisation of calcium and magnesium salts by using very small amounts of product and without reducing the concentration of other essential mineral elements present in said water.
USE OF PHYTATE FOR WATER TREATMENT

Field of the Invention

This invention relates to methods of water treatment to prevent the formation of precipitates. In particular, this invention relates to the use of phytate to inhibit the nucleation and growth in water of calcium carbonate and of other salts with one divalent cation selected from Ca\(^{2+}\) and Mg\(^{2+}\).

Background of the invention

When a system contains amounts of solute exceeding that permitted by their solubility, that system is in an unstable situation from the thermodynamic point of view (supersaturated system) and sooner or later crystallises in order to achieve equilibrium. The time taken by a supersaturated system to precipitate ranges from seconds to years, and depends on kinetic factors.

A water is said to be hard when its content in dissolved Ca\(^{2+}\) and Mg\(^{2+}\) ions exceeds the content tolerated for the use to which the water is intended. In the case of drinking waters, the hardness is expressed as mg/L of Ca\(^{2+}\), and its maximum permissible value is 300 mg/L of Ca\(^{2+}\). Many drinking water supplies have a hardness in the order of 250 mg/L. The following table establishes a classification of water according to its hardness:
Hard water presents the problem of formation of precipitates (mainly calcium carbonate, but also other salts that co-precipitate) on the walls of the pipes and systems through which they circulate, reducing the life of household electrical appliances if such precipitated deposits are not removed at intervals, and even blocking pipes. This problem is accentuated where the water is hot, in which case there can be breakages or explosions due to overheating of the pipes or boilers. That is precisely why hard water cannot be used in steam boilers.

Furthermore, hard waters reduce the efficacy of detergents. Detergents are sodium or potassium salts of a long-chain fatty acid formed by the reaction of fats and oils with an alkaline compound. Such detergents are soluble in water or at least can be dispersed in it to form a colloid. However, the calcium and magnesium salts of long-chain fatty acids are insoluble in water, so that they precipitate and do not form foam.

Various methods exist for treating hard waters, mainly consisting in reducing the concentration of ions (also called water softening methods), such as ion exchangers, reverse osmosis systems, the formation of stable compounds and precipitation.

<table>
<thead>
<tr>
<th>Mg/L CaCO₃</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-75</td>
<td>Soft water</td>
</tr>
<tr>
<td>75-150</td>
<td>Not very hard water</td>
</tr>
<tr>
<td>150-300</td>
<td>Hard water</td>
</tr>
<tr>
<td>&gt; 300</td>
<td>Very hard water</td>
</tr>
</tbody>
</table>

Ion exchangers are generally zeolites and ion-exchange resins. The zeolites are natural or artificial aluminosilicates insoluble in water and chemically constitute fixed macroanions electrically neutralised by cations. The exchange is carried out by making the water
pass through a bed of a certain thickness, gradually encountering pure sodium zeolite. When the zeolite is exhausted it is regenerated with sodium chloride.

There also exist artificial exchangers such as permutites and exchange resins. The resins act in a similar way to the zeolites.

Reverse osmosis devices reduce the dissolved salts content in the water by applying a high pressure through a semi-permeable membrane. When a semi-permeable membrane separates two solutions of different saline concentration, the water circulates from the more diluted medium to the more concentrated medium, thereby setting up a pressure difference between each of the two sides of the membrane, a phenomenon known as osmotic pressure. The application of a higher pressure than this osmotic pressure reverses the flow, thereby providing one increasingly less concentrated solution and one increasingly concentrated solution.

Sometimes several polyamino acids (polyaspartic acid, polyarginine, polycysteine) are used, attached directly onto the surface of the pores in the membrane of hybrid reverse osmosis and nanofiltration systems in order to remove more effectively certain ions from the solution. In addition, the use of polyacrylic acid synergically with phytic acid to inhibit the formation of incrustations of calcium, magnesium and iron on the membranes of reverse osmosis systems has also been described (see, for example, Spanish patent no. 520.904/8).

In order to treat water hardness chelating or sequestering agents are also widely used. These agents combine with the metallic ions (calcium chelating agents are preferably used) in the water. The metallic ion is surrounded by the sequestering agent and a complex of anionic charge forms. This reduces the effective concentration of the ion, so that the supersaturation in relation to certain salts is reduced, thereby preventing
the formation of solid deposits and reduction in the efficacy of detergents. Among the chelating agents used are the phosphates. Tripolyphosphate was usually used in detergents, combining with the calcium and magnesium through the formation of soluble complexes, though also sequestering the iron and dissolved manganese (that interfere in detergence). Certain environmental aspects have led to the use of other alternative sequestering agents such as ethylenediamine tetraacetic acid (EDTA).

The above techniques and methods are based on reducing the concentration of the ions responsible for the water hardness. In the case of ion exchangers, reverse osmosis and precipitation the ions are removed directly, also causing the precipitation of other ions that are beneficial for human health. In the case of the chelating agents, recourse is usually had to substances that harm the environment or are toxic for human consumption.

Summarised description of the invention

An object of this invention is to provide an alternative to the existing methods, allowing the formation of precipitates in the water to be prevented but without altering its ionic composition.

In particular, this invention relates to the use of myo-inositol hexaphosphate to inhibit nucleation and growth in the water of calcium carbonate salt and of other salts with one divalent cation selected from calcium and magnesium.

Before moving on to discuss the details of this invention, definitions of the specific terms related to the main aspects of the invention are provided.
Definitions

In this invention, "phytate" or "myo-inositol hexaphosphate" is taken to mean the molecule that corresponds to the formula

![Chemical structure](image)

and its corresponding salts, which include but are not limited to salts of sodium, potassium, calcium, magnesium or calcium-magnesium salts.

Myo-inositol hexaphosphate (phytate) is a natural product that accumulates in the seeds of cereals, vegetables and nuts and that has many beneficial effects for health, such as its antioxidant effect or a preventive effect for certain types of cancers.

In this invention, "crystallisation inhibitor" is taken to mean a substance that is capable of reducing or preventing the formation of a nucleus or development of such a nucleus into a crystal. This inhibiting effect is due to the fact that the phytate is adsorbed on the nucleus undergoing formation or the growing crystal and inhibits their development. As explained in detail below, this is a purely kinetic factor that does not alter the supersaturation of the compound and, therefore, does not remove ions from the water.

In this invention, "turbidity" is taken to mean the presence of precipitated particles of calcium or magnesium salts in suspension in a liquid, not being adhered to any surface.
In this invention, "dispenser" is taken to mean any system that allows a substance to be placed in the water in known doses.

In this invention, "devices and facilities for the administration of water" is taken to mean any system used for domestic or industrial water supplies, including but not limited to ducts, pipes, wells, cisterns, household electrical appliances or tanks in which the water is stored temporarily.

Figures

Figure 1 shows the inhibiting effect of phytate on the crystallisation of salts in a sample of synthetic water having a concentration of calcium lower than 300 mg/L and a concentration of carbonate of 350 mg/L. The concentrations of phytate used were: 0 mg/L (■), 1 mg/L (▲) and 2 mg/L (●). Figures 2 and 3 pertain to a chemical analysis of the water treated with phytate, showing that at increasing concentrations of phytate the concentration of calcium and carbonate in solution was greater, thereby demonstrating that phytate added to the water prevents crystallisation of the calcium salt.

Detailed description of the invention

The general objective of this invention is to prevent the formation of calcium carbonate and other salts that may coprecipitate in cisterns, wells, pipes, ducts, household electrical appliances and taps, as well as other points that frequently undergo deposits of precipitates of calcium carbonate and other salts along the water-circulation route and that give rise to deterioration and
poor functioning of said installations and devices, with
the expense involved for the consumer in repairing and/or
replacing them.

In particular, the object of this invention is the
use of phytate to inhibit nucleation and growth in the
water of salts with one divalent cation selected from
calcium and magnesium.

In a preferred embodiment, said salt with one
divalent cation is calcium carbonate.

The objective of incorporating phytate is to
prevent the formation of precipitates of calcium carbonate
and of other calcium and magnesium salts thanks to the
inhibiting action of the phytate on crystallisation.

It is well-known to a skilled person in the art
that the crystallisation of solids is the result of the
action of three factors: supersaturation (driving force of
crystallisation, thermodynamic factor), the presence of
promoting substances (kinetic factor) and the presence of
substances that inhibit crystallisation (kinetic factor).

There is an extensive bibliography describing the
stages in a crystallisation process (see, for example,
Söhnel 0., Garside J. [1992] Precipitation: basic
principles and industrial applications, Butterworth,
Oxford; Grases F., Costa-Bauza A., Söhnel 0. [2000]
Crystalización en disolución. Conceptos básicos, Editorial
Reverte SA, Barcelona). Briefly, the process of
crystallisation within a solution consists of the
following stages:

a) Nucleation: this is the first of the
crystallisation stages and consists in the formation of
groups of atoms, molecules or ions that constitute a new
solid phase. Until these groupings attain a certain
critical size (10-100 structural units) they are not
stable and dissociate again, leaving the free ions in
solution. However, when due to the successive
incorporation of atoms, molecules or ions that critical size is reached, a minimum stable core (nucleus) is said to have formed. There are two types of nucleation:

a.1. Homogeneous nucleation: this is the formation of a solid within a solution as a consequence of its supersaturation, i.e. the substance is in solution in amounts exceeding those permitted by its solubility product, and is a consequence of the sequential collision of several particles of the future solid until what is known as a minimum stable core is formed;

a.2. Heterogeneous nucleation: it corresponds to the formation of a solid within a solution on the surface of a pre-existing solid particle of chemical composition different from that of the solid undergoing formation;

b) Crystalline growth: once nucleation has taken place, the nucleus formed grows by successive incorporation of atoms, molecules or ions. It is a simpler stage than the preceding one because growth takes place on a pre-existing particle that is already stable (while in the nucleation stage the nucleus can split off before attaining critical size); and

c) Secondary processes: once the crystal has formed, various processes take place, such as recrystallisation, ageing or secondary aggregation. The latter consists of grouping of the solid particles (crystals) already formed, giving rise to other larger ones.

In accordance with this invention, the phytate acts kinetically, preventing nucleation and growth (the initial stages of crystallisation). In particular the phytate, owing to its affinity for divalent cations, among them calcium, is adsorbed on the crystalline nucleus under formation or on the growing crystal, preventing or delaying its formation (initial stages (a) and (b)). The addition of phytate does not alter the mineral composition
of the water and moreover, advantageously, a natural product (the phytate) is incorporated in very small amounts and has many properties that are beneficial for the health.

In the procedures and devices in the state of the art, such as ion-exchange systems (exchange resins or zeolites) and reverse osmosis system, the objective is to carry out what is known as "water softening" (i.e. acting on the supersaturation). In these cases, the objective is to remove the ions responsible for the formation of precipitates in the water (carbonate, sulphate, calcium, magnesium, etc). The removal of said ions involves the loss of other mineral elements essential for the organism. This aspect is of particular importance in the case of water for human consumption.

On the other hand, the water treatment of the state of the art act on the level of supersaturation, so that the ions responsible for the formation of a solid are either removed or sequestered (as it happens if complexants such EDTA are used), and those that act kinetically prevent secondary aggregation (the last stage of the process of formation of crystals). However, with the method of this invention, the crystallisation of calcium salts is prevented by inhibiting nucleation (homogeneous or heterogeneous) by using very small amounts of product, leaving the concentration of other essential mineral elements present in the water undiminished. Advantageously, therefore, with the object of this invention the formation of precipitates of calcium carbonate and other salts is prevented.

In one embodiment of this invention, the amount of phytate is less than 10 mg per litre of water to be treated.

In another preferred embodiment, the amount of phytate ranges between 0.1 and 5 mg per litre of water to
be treated.

Preferably, said phytate is used in an amount that ranges between 0.1 and 2 mg of phytate per litre of water to be treated.

In one embodiment of this invention, using a laboratory crystalliser, it was observed that with synthetic water of totally controlled composition, 1 mg/L of phytate completely prevents crystallisation of the calcium carbonate when the concentrations of calcium were less than 300 mg/L (see Figure 1) and the concentration of carbonate was 350 mg/L. It should be taken into account that a hard drinking water contains ranges of calcium of 100-120 mg/L and of carbonate of 200-500 mg/L. The recommended pH ranges are 6.5-8.5, but the maximum permitted value is 9.5.

In another embodiment of this invention, using a model that simulates the circulation of water inside a pipe, it was found that the presence of 2 mg/L of phytate in circulating water that contained 136 mg/L of calcium and 350 mg/L of carbonate at a pH = 8.00 gave rise to a 95% reduction in the development of precipitates of calcium carbonate and of 92% of magnesium salts at 30°C, while 5 mg/L of phytate under the same conditions of concentration and pH, but working at 65°C, gave rise to 98% reduction of development of precipitates of calcium carbonate.

In still another embodiment of this invention, it was found that the addition of 1 mg/L of phytate to the water of a 10000-litre tank recently filled with water from a naturally fed well ([Ca\(^{2+}\)] = 107.7 mg/L, [carbonate] = 311.1 mg/L, pH = 7.92), totally prevented the development of turbidity/microparticles in suspension and precipitates in the bathroom and kitchen installations (taps, bath tubs, etc.) during the week it took to consume said water. Furthermore, chemical analysis of the water
with the phytate treatment revealed that at increasing concentrations of phytate the concentration of calcium and carbonate in solution was greater, thus showing that phytate added to the water prevents crystallisation of said salt owing to its inhibiting ability.

In still another embodiment, the phytate is supplied to the water to be treated in a dispenser for household or private use.

In a second aspect, this invention relates to a dispenser that contains myo-inositol hexaphosphate for preventing the formation of precipitates of calcium carbonate and of other calcium or magnesium salts within devices and installations for the administration of water.

In a third aspect, this invention relates to a detergent composition that contains myo-inositol hexaphosphate for preventing the formation of precipitates of calcium carbonate and of other calcium or magnesium salts within devices and installations for the administration of water.

Examples of embodiments of the invention

Example 1 (homogeneous nucleation)

10 ml of synthetic water was introduced into laboratory crystallisers prepared according to the following table:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO$_4$$\cdot$7H$_2$O</td>
<td>40</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>3</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$$\cdot$2H$_2$O</td>
<td>80</td>
</tr>
<tr>
<td>CuSO$_4$$\cdot$5H$_2$O</td>
<td>0.2</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>2</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>Variable (see Figure 1)</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>490 (equivalent to 350 mg/L carbonate)</td>
</tr>
</tbody>
</table>
Each solution was prepared in such a way as to contain 0, 1 or 2 mg/L of phytate. 15 seconds after preparation of the water, turbimetry measurements were taken using a photometer (Metrohm 662) equipped with a reflector optic fibre cell of optical pitch 2 x 10 mm and using monochromatic light (550 nm). The crystallisation processes were carried out at 25°C and the pH of all the solutions was adjusted to 9.8.

Figure 1 shows the results obtained. As it can be observed, at a concentration of 1 mg/L of phytate the crystallisation of the calcium carbonate was prevented completely when the concentration of calcium was lower than 300 mg/L and the concentration of carbonate was 350 mg/L.

**Example 2 (heterogeneous nucleation and growth)**

Synthetic water (see table of Example 1) (a) was made to circulate for 48 hours (30°C) and (b) for 24 hours (65°C) through a 20 cm copper pipe in length, 4 mm inner diameter and 6 mm outer diameter. The test was carried out with concentrations of calcium of 100 and 200 mg/L. The pH of all the solutions was adjusted to 8.00 and the synthetic water was renewed every 24 hours.

After 24 or 48 hours, the precipitate formed on the walls of the pipe was dissolved with IM HCl and the calcium determined by atomic emission spectroscopy using inductively coupled plasma (ICP-AES).

Thus, it was found that the presence of 2 mg/L of phytate in the circulating water that contained 136 mg/L of calcium and 350 mg/L of carbonate at pH 8.00 gave rise to a 95% reduction in the development of precipitates of calcium carbonate at 30°C, while 5 mg/L of phytate under
the same conditions of concentration and pH, but working at 65°C gave rise to a reduction of 98% in the development of precipitates of calcium carbonate.

As it is well known, the greater the temperature of the water the greater will be the precipitation and deposition of the calcium and magnesium salts in the pipes, household electrical appliances, etc., with the disadvantages involved for consumer.

As this example shows, the phytate is equally effective at moderate temperatures (30°C) as it is at high temperatures (65°C). This aspect is of particular significance in the case of household electrical appliances (such as washing machines), and pipes, etc., through which hot water circulates.

Example 3 (homogeneous and heterogeneous nucleation)

The test was carried out with a 10000 L capacity tank with the inner walls coated with a layer of cement. This tank is used to supply three families, and under normal conditions is refilled on a weekly basis. The tank was filled regularly from a natural well and phytate added so that the concentration inside the tank would be in the 0-1 mg/L range. During the week of use of each concentration of phytate, the remains of precipitates of calcium carbonate in the house taps and bathroom accessories were evaluated qualitatively. Moreover, 48 hours after filling the tank a sample of water was taken from a tap of one of the three families and a quantitative determination of the pH, calcium and bicarbonates was carried out.

Thus, it was found that the addition of 1 mg/L of phytate halted the development of turbidity/microparticles in suspension and calcium precipitates in the water installations (taps, bathtubs, etc.). Furthermore,
chemical analysis showed that at increasing concentrations of phytate, the concentration of calcium and carbonate in solution was greater, thus showing that the phytate added to the water prevented precipitation of said salt due to its inhibiting ability.

**Example 4**

The previous 3 examples show that the inhibiting effect of phytate against the crystallisation of calcium carbonate in water occurs in very low concentrations. Apart from dispensers, detergents can also be used in order to incorporate phytate in water, with the purpose that the final concentration of phytate in water (not in the detergent) is around 10 mg/ml, preferably lower than 5 mg/ml and, especially, between 0.1 and 2 mg/ml.

With the purpose of attaining this concentration in water, the following detergent compositions are proposed by way of illustration and not limitative in any way.

**Composition 1**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium lauryl sulphate</td>
<td>3.5%</td>
</tr>
<tr>
<td>Dodecylbenzenesulphonic acid</td>
<td>11.8%</td>
</tr>
<tr>
<td>Coconut fatty acid diethanolamide</td>
<td>0.3%</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>2.9%</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>0.6%</td>
</tr>
<tr>
<td>Phytate</td>
<td>0.1%</td>
</tr>
<tr>
<td>Water</td>
<td>q.s.</td>
</tr>
</tbody>
</table>
Composition 2

Sodium lauryl sulphate 3,5%
Dodecylbenzenesulphonic acid 11,8%
Coconut fatty acid diethanolamide 0,3%
Diethanolamine 2,9%
Sodium hydroxide 0,6%
Phytate 0,5%
Water q.s.
CLAIMS

1. Use of myo-inositol hexaphosphate to inhibit the nucleation and growth in water of salts with one 5 divalent cation selected from Ca\(^{2+}\) and Mg\(^{2+}\).

2. Use according to claim 1, wherein said salt is calcium carbonate.

3. Use according to claim 1, wherein nucleation is homogeneous.

4. Use according to claim 1, wherein said nucleation is heterogeneous.

5. Use according to any of claims 1 to 4 to reduce the turbidity of the running water.

6. Use according to any of the preceding claims, wherein said myo-inositol hexaphosphate is administered to the water in the form of an aqueous composition.

7. Use according to any of the preceding claims, wherein said myo-inositol hexaphosphate is administered in an amount lower than 10 mg per litre of water to be treated.

8. Use according to claim 7, wherein said ratio ranges between 0.1 and 5 mg of myo-inositol hexaphosphate per litre of water to be treated.

9. Use according to any of claims 7-8, wherein said ratio ranges between 0.1-2 mg of myo-inositol hexaphosphate per litre of water to be treated.

10. Use according to any of the preceding claims, wherein the myo-inositol hexaphosphate is applied in the form of a dispenser within devices and installations for the administration of water.

11. Use according to claim 10, wherein said device is a household electrical appliance.

12. Use according to any of claims 10 to 12, wherein said installation is a heating element.
13. Dispenser that contains phytate to prevent the formation of deposits of precipitates of calcium carbonate and of other calcium or magnesium salts adhering within devices and installations for the administration of water.

14. Device according to claim 13, wherein said device is a household appliance.

15. Device according to any of claims 13-14, wherein said installation is a heating element.

16. Detergent composition that contains myo-inositol hexaphosphosphate to prevent the formation of deposits of precipitates of calcium carbonate and of other calcium or magnesium salts adhering within devices and installations for the administration of water.

17. Use of myo-inositol hexaphosphosphate in detergents to prevent the formation of deposits of precipitates of calcium carbonate and of other calcium or magnesium salts adhering within devices and installations for the administration of water.
FIGURE 1

Absorbance

[Ca^{2+}] (mg/L)
FIGURE 2

[Graph showing calcium concentration (mg/l) against phytate concentration (mg/l).]