

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PREVENTION OF CALCIUM CARBONATE DEPOSITION IN WATER

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The present invention relates generally to the treatment of water and more particularly to the treatment of water to prevent the deposition of calcium carbonate in waters used for industrial purposes.

The carbonate hardness of natural waters consists to the main part of calcium carbonate in solution, which upon heating or upon addition of alkali, such as sodium hydroxide or sodium carbonate, is precipitated, causing in water distribution systems the undesired and disadvantageous scale formation.

Various processes have been resorted to, in order to overcome this evil, which, however, have not proved entirely satisfactory. The treatment by decarbonisation with lime, working according to the chemical equation



requires a relatively high investment of chemicals and, moreover, necessitates subsequent filtration of the precipitated calcium carbonate. Thus, this process takes too much time and is too expensive for application in cooling waters. The objections to the use of the decarbonisation process apply also to the treatment on basis of base exchange.

Another usual method for the inhibition of carbonate hardness provides the addition of hydrochloric acid, resulting in the formation of water-soluble, non-precipitable calcium chloride. For reasons of precaution in general only as much hydrochloric acid is added, as is necessary to maintain a slight excess of calcium carbonate in the water, since a remaining hardness of 2 to 3° does not or but scarcely tend to scale formation. In spite of this precaution it may be, that hydrochloric acid is—at least temporarily—present in excess, corroding metal tanks and pipe lines. It is a further disadvantage of the above-mentioned method that carbonic acid, liberated by this chemical process, has a highly-corrosive action.

Recently some methods have been developed and have turned out well, according to which deposition of calcium carbonate in waters for industrial purposes is prevented by adding to the water such agents, which delay or completely suppress the precipitation of calcium carbonate, without initiating certain chemical reactions based on certain stoichiometric proportions. Such materials are for example tannic acids, tannin, sulphite lye etc. The use of salts of phosphoric acids having a lower proportion of water molecules than orthophosphoric acid, such as so-

dium hexametaphosphate, has proved especially favourable.

The last-mentioned processes, however, are disadvantageous in as much as they cannot be used in all occurring applications, since it has been observed that in those cases where the rate of calcium ions in form of calcium bicarbonate exceeds a certain limit, deposition of calcium carbonate can, even by considerable increase of the additions, no longer be prevented.

Now it has been found that the process just described, if suitably combined with the hydrochloric acid process, can also be employed in those cases, in which—owing to the high content of calcium-bicarbonate—it appeared up to now impracticable. Instead of hydrochloric acid other inorganic or organic acids are capable of use, so far as they form with the metal ions of the alkaline earths contained in the water no insoluble or slightly soluble salts, for example the other halogen hydracids, chromic acid, thiosulphuric acid, sulphuric acid and above all their derivatives, such as amido sulphonic acids, sulphonic acids of aliphatic and aromatic compounds of the type of the fatty sulphonic acids, naphthalene sulphonic acid, alkylized naphthalene sulphonic acid, acid sulphuric acid esters of fatty alcohols, and unsaturated or oxy-fatty acids etc. Further be mentioned acetic acid, citric acid, tartaric acid etc.

The present process is generally carried out as follows: At first the necessary amount of acid so as to reduce the content of calcium carbonate to about 8 to 10° is added to the water. In this way it is far easier to avoid an excess of acid in the water than in the case the degree of hardness must be reduced to 2 to 3 by a general treatment with acid. Subsequent thereto, the substance which inhibits precipitation, for example tannin or a phosphoric salt, is added to the water in amounts usual with these methods. It is quite surprising that in the combined process these substances, for example phosphoric salts, develop their full effectiveness, even at a high rate of calcium ions, so far as the calcium ions are present to a considerable part in form of calcium chloride and not in form of calcium carbonate.

The effect obtained by the combination of the two processes may be explained by the assumption that carbonic acid, liberated upon addition of acid, acts reverting on the calcium carbonate, so as to displace the equilibrium in favour of soluble calcium bicarbonate. Moreover, upon addition of chemicals such as tannic acid and phos-

phates, a protective coating forms on the metal surface, which, too, acts against scale formation and reduces at the same time the danger of corrosion caused by acid or CO₂-vapours.

The method according to the present invention applies particularly to that type of waters, the carbonate hardness of which is beyond 15°, or which concentrate by evaporation during the working process to such a high degree that their hardness exceeds the critical limit. To such waters is now added in usual manner as much acid, for example hydrochloric acid, as to reduce the carbonate content to about 6 to 10°. Then the chemical which prevents deposition is added to the water having been treated with acid.

As especially favourable for the present use have proved phosphoric salts, for example the alkali metal salts of hexameta-, poly-, or pyrophosphoric acid as well as the salts of highly polymeric phosphoric acids (Tamman salts) besides tannic acids, tannin, sulphite lye etc. But also the slightly soluble salts of phosphoric acids, such as calcium metaphosphate, crystalline sodium metaphosphate, uranium metaphosphate, zinc metaphosphate, aluminium metaphosphate, double salts, such as sodium-calcium metaphosphate, sodium-magnesium metaphosphate, and calcium-magnesium metaphosphate, can be applied with advantage. Finally the slightly soluble salts of orthophosphoric acid, for example calcium orthophosphate, as well as the naturally occurring phosphate stones, for example apatite, are capable of use.

A preferred embodiment of the present invention provides the application of such an acid which forms with the metal ions of the alkaline earths contained in the water those salts, reacting in the sense of the second phase of the process. Among them be mentioned phosphoric acids, for example orthophosphoric acid, but above all those phosphoric acids having a low proportion of water molecules, such as pyrophosphoric acid, polyphosphoric acid, hexametaphosphoric acid,

and still higher polymeric metaphosphoric acids, since their calcium and magnesium salts, employed in amounts considerably below the stoichiometric proportion, have the distinct property of linking the coarse-disperse particles of calcium carbonate to each other, thus inhibiting precipitation with subsequent scale deposition. Organic sulphonic acids, tannic acids etc. belong also to this group. The particular advantage of this special embodiment consists in the remarkable simplification of the present process by substituting one single process for a 2-phase-treatment. To a water, having a carbonate hardness of 18 to 20° for instance, hexametaphosphoric acid is added in an amount so as to reduce the hardness to 12 to 15°. In this case the second phase of treatment becomes superfluous, since the forming calcium and magnesium hexametaphosphate suppresses the precipitation of metal ions of the alkaline earths in form of carbonates.

In the case of a relatively high carbonate content, mixtures of phosphoric or other expensive acids with any acid of inferior quality, for example hydrochloric acid, can be used, in order not to waste the acid of superior quality, but to keep its consumption within narrow limits. Thereby it is only essential to take care that the quote of primary acid is as high as to form calcium salt in a fair amount, viz. about 3 mg. per litre. If the water to be treated has a carbonate hardness of about 30°, it is necessary, for that primary acid becomes efficacious, to add that amount of acid-mixture by which hardness is reduced to at least 15°. The acid of superior quality, however, is not required to constitute the whole amount, by which hardness sinks down from 30 to 15°, but a mixture of for example hydrochloric acid and metaphosphoric acid, in which metaphosphoric acid is contained only to a very small percentage, wholly serves the purpose.

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