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"A REVUE OF SCALE FORMATION AND SCALE PREVENTION, WITH EMPHASIS ON MAGNETIC WATER TREATMENT"

1. Introduction

Scale formation is a well known problem in most systems where water is used. The most serious problems occur when water, with high calcium content, the source. In recent years several papers have been published on scale prevention. Among the scale preventing methods magnetic water treatment has gained renewed attention. Still, considerable doubts exist as to the validity of the claimed effects on scale formation. Both practical experiences and results from recent investigations confirm, however, the practical potential of this method.

2. Scale forming salts

2.1 *Calcium carbonate*

Calcium dissolved as bicarbonate has low solubility in water. The solubility varies with pressure, temperature and pH. Three well known crystalline structures of calcium carbonate are found in nature: Calcite, Aragonite and Vaterite.

With pH below 8.8, solubility increases with decreasing pH and decreases with rising temperature. A pH above 8.8 gives opposite dependence and solubility increases both with increasing temperature and pH[1].

Calcium dissolves as bicarbonate by the reaction:

$$CO_2 + H_2O + CaCO_3 \rightleftharpoons Ca(2+) + 2\,HCO_3(-).$$

High CO_2 content in the solution shifts the equilibrium towards the right, i.e. more $CaCO_3$ will thereby be dissolved. Increasing temperature forces CO_2 out of solution and calcium carbonate is precipitated. Changes in pH have similar effect.

Calcium carbonate is probably the most common compound found in scale, in systems such as: steam boilers, heat exchangers, evaporators, hot water heaters (califorifiers).

2.2 *Calcium sulphate*

Calcium sulphate exists as $CaSO_4 . n\ H_2O$ where n carries one of the following values: n = 2, n = ½ or n = 0. Solubility varies with temperature and pressure and maximum solubility is reached at 30–40°C. Higher temperatures cause lower solubility.

The formation of calcium sulphate scale is very likely the most important limitation in using evaporators for production of fresh water from salt water. Supersaturation in this case is primarily through evaporation. Calcium sulphate scale occurs also in crude oil production. Water, mixed with crude oil as it comes out of the well, often has a high calcium sulphate content. When the pressure drops, the salts precipitate in pump, valves, pipes, etc.

2.3 *Magnesium hydroxide and magnesium carbonate*

Scale from magnesium salts is relatively rare and causes limited problems as compared to calcium salts. Magnesium salts are mainly found in scale formed in steam boilers and evaporators.

2.4 *Barium sulphate*

Scale from barium sulphate is rare, but is found in the oil industry when producing crude oil from deep wells. The problem is also encountered in other industries, such as the paper industry[2]. Solubility in water is extremely low and varies with the content and concentration of other ions, temperature, pressure, etc.

This brief survey covers only some of the most common compounds found in scale. Silica, iron as well as other metal compounds may form scale, or become important in determining the scale forming mechanism.

3. Scale forming mechanism

Scale is formed when salts dissolved in water are precipitated, on a metal surface e.g. in steam boilers, heat exchangers etc. In order for scale to form, the water must contain a higher concentration of salts than the equilibrium concentration, i.e. the water is SUPERSATURATED.

Supersaturation alone, however, is not sufficient for precipitation to take place. The initial stage of precipitation is determined by NUCLEATION. Nucleation takes place either as heterogeneous nucleation (on impurities, seed crystals, metal surfaces etc), or as homogeneous nucleation (the nucleus is formed spontaneously from the mother phase). The nucleation is usually limited by the fact that sub-microscopic crystals have higher solubility than the equilibrium solubility. For this reason, a metastable region exists above the equilibrium solubility curve, see Fig. 1.

The solution may, therefore, stay supersaturated for longer periods without scale being formed. In a pure system, the width of the metastable region is given thermodynamically by the free energy of the formation of a nucleus (activation energy). The presence of metal surfaces and impurities usually promote the nucleation

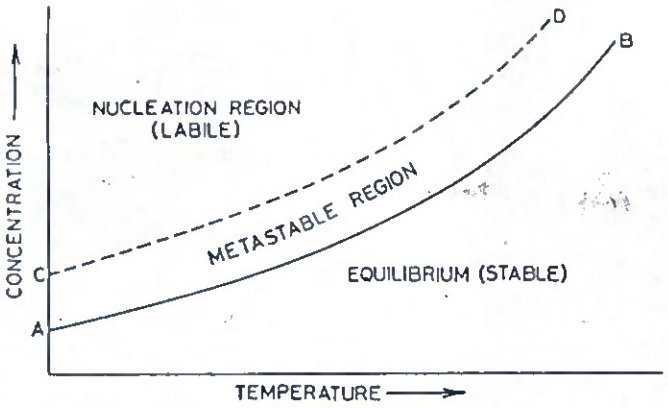

Fig. 1. Indicates the stable, metastable and labile (nucleating) region. The solid line A-B is the equilibrium concentration, the broken line C-D indicates the metastable limit.

because of lower activation energy. Therefore, in most cases the presence of different dissolved impurities determine the width of the metastable region, i.e. heterogeneous nucleation is the dominant mechanism during scale formation. In these systems the nucleation occur either on impurities suspended in the water, or directly onto the metal surfaces. When formed, the nuclei will develop into visible crystals (scale). The growth is determined by:

1. Diffusion of ions from the solution to the crystal solution interface.
2. Adsorption of ions/molecules from the interface onto the crystal surface.
3. Surface-diffusion to energetically favourable growth positions on the crystal surface and thereby incorporation into the crystal lattice.

Impurities (ions, organic components, greatly influence the rate of precipitation, the crystalline structure and the crystal habit. It is known that certain ions present in the solution in very low concentrations (e.g. 1 ppm), may adsorb onto the crystal surface and block the energetically favourable growth positions on the surface and thus completely inhibit further precipitation. This technique when used to prevent scale, is called: "Threshold treatment" (to be discussed later).

Suspended particles, both naturally found in water or the precipitate, may form a stable suspension. It is more likely, however, that the particles either will coagulate and settle as a sludge or adhere to a metal surface and thereby become an important component of the scale.

A decisive factor in determining the mechanical strength of the scale is the "Ostwald Ripening", i.e. the larger particles "swallow" the smaller ones. This is due to the fact that the larger particles are thermodynamically more stable.

All the phenomena described above are simultaneously involved when scale is formed and collectively determine the texture of the scale. Should one mechanism be inhibited, another will dominate. This is an important consideration when selecting effective methods for scale prevention.

4. Scale preventing methods

Methods for reducing or preventing scale formation should affect precipitation and thereby inhibit the scale forming mechanism in one or more of the following ways:

1. Reduced supersaturation, i.e. lowered content of scale forming salts.
2. Limited nucleation and growth on metal surfaces.
   - by increasing the rate of homogeneous nucleation, which cause the precipitation to occur in the body of the water
   - by improving the conditions for heterogeneous nucleation on impurities in the body of the water.
3. Inhibited growth of scale, for instance by adsorption of "impurities" in the favourable growth positions on the crystal surface.
4. Reduced adhesion between sedimentary products which may be a major part of the scale, i.e. by reduced mechanical strength of the scale.

In the following paragraphs both the most common chemical methods (and how they function), and the non-chemical methods, here restricted to magnetic water treatment, are discussed.

5. Chemical methods for scale prevention

5.1 *Selective salt removal*

Selective salt removal of water is attained either by adding specific chemicals or by using ion exchangers specifically designed for this purpose.

To remove calcium, magnesium and bicarbonate, chemicals such as calcium hydroxide or sodium hydroxide are added in order to achieve precipitation of the scale forming salts. The precipitation is carried out under carefully controlled conditions in a wide variety of equipment.

When using ion exchangers the content of scale forming ions is reduced by exchanging these with non-scale forming ions such as Na, hydrogen ions, etc. Nearly total demineralization (salt removal) is achieved by exchanging the cations with hydrogen ions and the anions with hydroxide.

5.2 *Scale inhibitors*

Commonly used are inhibitors based on phosphates, either organic or inorganic. Two methods are used: the amount of inhibitor per 100–200 mg of scale forming salts is in the range of 1 to 5 mg, "THRESHOLD TREATMENT". Alternatively the inhibitor is added in approximately the same amount as the scale forming salts, dependent upon the content of other ions, etc.

There exists no complete theory as to the mechanism for the scale inhibitory effect of these chemicals. It is, however, generally agreed that one or more of the following mechanisms are involved:

1. Adsorption of the inhibitor onto the crystal surface. Trials with some inhibitors indicate that the nucleation is not affected, whilst the subsequent crystal growth is completely inhibited. One believes this to be due to the adsorption of the inhibitor into growth positions on the crystal surface, which block the growth sites and thereby inhibit further crystal (scale) growth.
2. Adsorption reduced adhesion. The inhibitor is adsorbed on the surface of, for instance, suspended particles and reduces the adhesion between them. This coincides with the fact that certain tests show that the amount of scale is not drastically reduced, but that the hard, homogeneous scale is changed into powdery scale, i.e. the adhesion and thereby the mechanical strength of the scale is reduced.
3. The change of crystal habit. The inhibitor is incorporated into the crystal lattice causing a change of the crystal habit. The scale preventing effect of the inhibitor is believed to be tied to the change of the crystal habit and less adhesion between the "new" particles.
4. Complex formation. The inhibitor forms complexes

with scale forming ions, such as calcium ions, and thereby lowers the "effective" concentration of these.

For threshold treatment it is likely that one of the first three mechanisms discussed above is the most important one. When using large amounts of inhibitors, complex formation is believed to be the reason for reduced scale growth.

5.3 *Use of acid*

Acid may be used to decrease the pH value, and thereby allowing a higher concentration of calcium carbonate to be kept in solution. This method has no effect on calcium sulphate. Increased corrosion rate will become a serious side-effect.

5.4 *Use of seed crystals*

Seed crystals are fed into the water in order for the precipitation to take place on these, and not on boiler walls, for instance. The surface area of the seed crystals and the crystalline structure, greatly influenced the efficiency of the method. Factors such as adhesion, temperature, the presence of different ions and growth inhibitors, are important parameters.

6. Non-chemical methods for scale prevention—magnetic water treatment

A "definition" of non-chemical methods, not precise, but acceptable for our purpose is:

A method based on mechanical (e.g. vibrations), electrical or magnetic principles. One might add that the method is often controversial.

Our discussion is limited to a system which is based on the use of a magnetic field, hereafter referred to as magnetic water treatment. The last part of this paper will discuss different aspects of magnetic water treatment (MWT) i.e. scale prevention is achieved by passing the water through a magnetic field, with the field strength in the range 1,000–10,000 Gauss. The effect on scale formation is claimed to last four hours after the water has passed the magnetic field.

MWT is today the most frequently used non-chemical method. Considerable doubts, however, still exist as to the reality of the effect on scale formation. In the following paragraphs we discuss different aspects of MWT, such as:

- Practical experiences from installations where Polar units are used. Polar is a magnetic unit produced by Olaf Fjeldsend A/S, Sandefjord, Norway. References are given.
- Different theories to explain the observed scale preventing effect. Both explanations found in company literature and theories published in scientific literature are discussed.
- Reports from laboratory experiments completed or underway in Olaf Fjeldsend's laboratory in Sandefjord, Norway.

6.1 *Practical experiences with magnetic water treatment*

Polar is used successfully in the cooling system of a ferro silicum furnace at A/S Hafslund, Norway[3]. Serious scale problems developed after only a few months of operation. A Polar unit was installed in 1970 and the cooling system has operated without any scale problems for the last 10 years.

Six months after installing Polar in an air-conditioning system with major scale problems (Adelaide, Australia), the following was noted: Old scale came off in layers without new scale being formed[4].

Results from installations in bottle washing machines clearly show that the method may be used successfully to prevent scale in nozzles, pipes, hot water tanks, etc.

Polar has been installed in several water works in order to reduce scale where lime slurries are used to increase the pH (in drinking water) as required by the authorities[5,6].

This is a small cross-section of the many areas of application for Polar. The method is used in industry, shipping (over 1000 ships) and private homes. Polar prevents scale in equipment such as: steam boilers, heat exchangers, pipe systems, hot water heaters, coffee machines, washing machines and dish washers, etc.

A trial with a Polar unit was conducted in Andebu, Norway in 1978 using well water and two boilers. Steam was allowed to escape and feed water was added through two Polar units: one with a field strength of approximately 6000 Gauss, the other unit not magnetized.

Results of test:

1. Upon completion of the test, the water in each boiler was filtered. The filtrate was dried and weighed, thereby indicating the amount of scale forming salts which did not form hard scale. The container using treated water *always had more filtrate than the container using untreated water.* In other words, the container using treated water always had less scale.
2. Four small copper mesh nets were placed in each boiler. These were collected after 3-6-12 and 24 hours. Fig. 2 shows the results. From the pictures we see that less scale is formed in the container using treated water.

The test also disclosed certain limitations on the effectiveness of the method, with respect to high concentrations of certain silicates and sulphates.

In the literature, a large number of similar reports on the use of MWT are found. These reports primarily describe results such as[7,8,9]:

- Reduced or no scale formation.
- Old scale loses its mechanical strength and dissolves.

A number of negative reports also exist. The most frequently quoted one is probably the report published in the nineteen-fifties by a scientific group at MIT (USA), based on tests using different non-chemical methods[10]. Also magnetic units were tested and reportedly showed no change in the scale formed either by structure or amount.

6.2 *How is MWT explained in literature?*

When the water (at a given time) has passed through a magnetic field with a field strength of 1,000–10,000 Gauss, the following has been observed:

1. The precipitated salts do not form hard scale, but rather a sludge which can be easily removed. Alternatively scale with low mechanical strength is formed.
2. The influence of the magnetic field on the water is reported to last for several hours after having passed through the field: "THE MEMORY EFFECT".

These observations gained from use of the method must lie within the framework of an acceptable theory. What is "altered" by the magnetic field, must therefore, have extended relaxation time and should be tied to conditions which are vital as to how scale is formed.

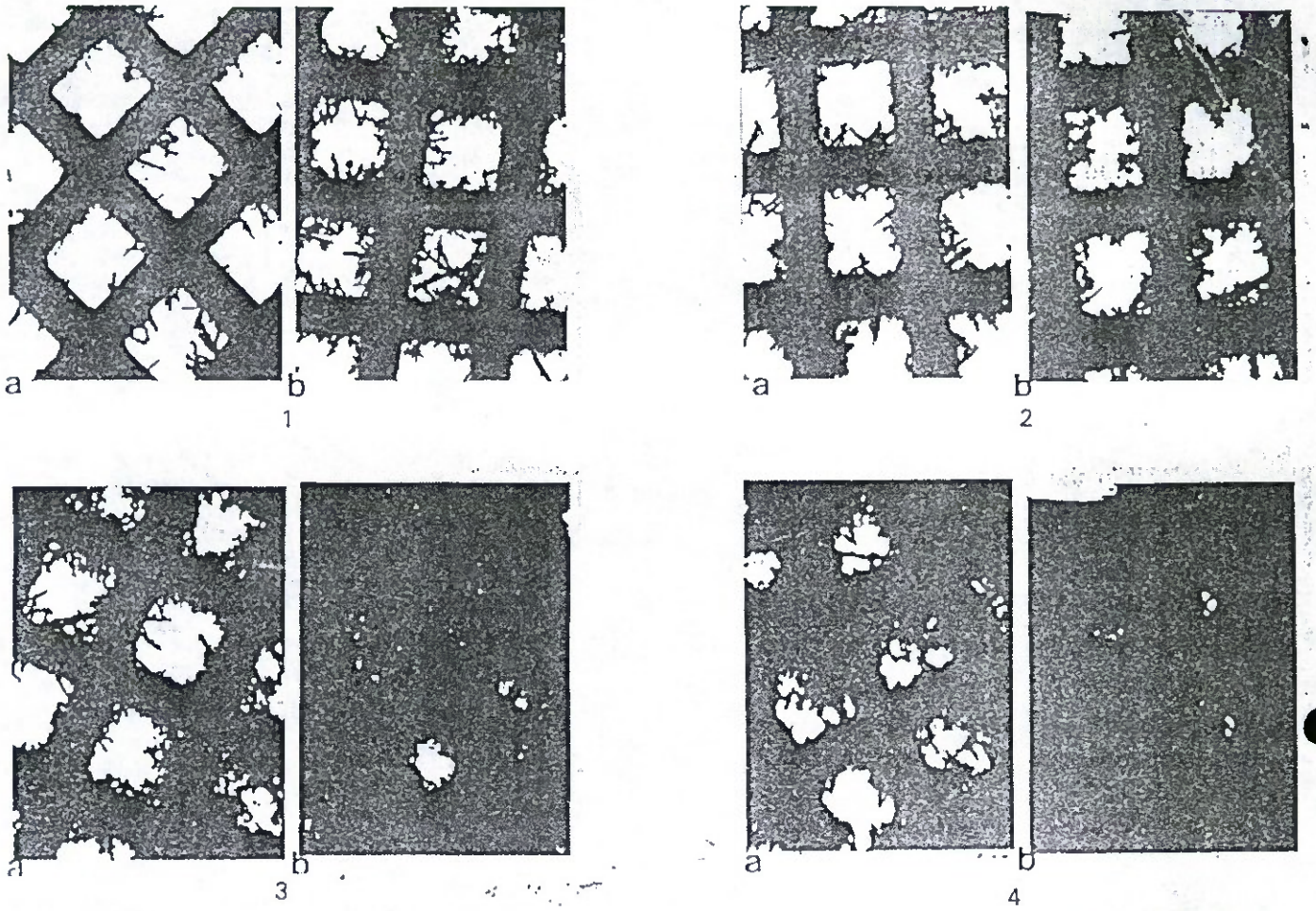

Fig. 2. Picture showing the mesh of sampling nets which were placed in two boilers, one using magnetically treated water (a), the other untreated water (b). Nets, numbered 1-4, were taken from the boilers after 3-6-12-24 hours respectively. Mesh dimension is approximately 0.2 mm. It is clearly seen that MWT significantly decreases the rate of scale growth. The fact that scale in untreated water is difficult to see from these photos.

Let us look at three categories of explanations given by manufacturers of equipment used for MWT:

Changes in the electron structure of dissolved ions or molecules caused by the magnetic field are given as an explanation. This is obviously wrong. First of all, the energy of interaction between a magnetic field of 1,000 to 10,000 Gauss and molecules in solution would be many orders of magnitude too weak to cause changes like this. Furthermore, the typical lifetime for such changes is in the order of 10^{-10} second or shorter.

Another "possible" explanation is that the magnetic field causes the water molecules (or dissolved molecules) to align themselves in the field. This improved order is said to remain in water also after it has passed the magnetic field. Firstly, the energy of interaction between, for instance, a water molecule and the magnetic field is in the order of 10^{-5} of the hydrogen bonds, i.e. negligible. Secondly, there is no reason to expect relaxation times longer than 10^{-6}–10^{-10} second.

A third explanation offered claims that MWT affects impurities suspended in the water. This explanation suggests, for instance, that suspended particles are changed in such a way that:

- the particles are made more hydrophilic.
- the conditions for nucleation and thereby growth on these suspended impurities are enhanced.

The last explanation comes close to our own hypothesis based on experimental work. We believe that some changes in the surface or interface of dissolved collodial particles take place, which in turn gives rise to increased precipitation in the bulk of the water (discussed later).

Generally, we feel that most of the attempted explanations are to a very small degree based on technical or scientific insight. It can safely be said that the people behind many of these "theories" often lack the knowledge they pretend to possess. It should be kept in mind, however, that although most of the "theories" are wrong, it does not follow that the method as such does not work.

Theories not so different from those discussed above, are found in scientific literature. One may assume that some of the statements made by manufacturers are taken from this literature, but much of this matter is misinterpreted by the producers. We shall comment on some of the theories published in scientific journals.

It is proposed that the magnetic field is the source of structural changes in the water. Based on the above mentioned energy considerations, it is very unlikely that changes in the water structure caused by the magnetic field may take place. V. I. Klassen and his group, nevertheless present two papers where they study IR-adsorption. They found that the IR spectra are changed when treating water with a magnetic field i.e. that MWT is the source of structural changes in the water[11 12]. There is reason to believe, however, that these measurements are wrong and that the results are due to impurities dissolved in the water[13].

Changes in structure of water proximate to an interface, is set forth as a possible theory by W. Drost-Hansen et al.[14]. This "theory" is not based on experimental work on MWT, but rather on work Dr. Drost-Hansen and co-workers are doing to study other properties of structurally modified interfacial water, referred to as: "Vicinal water". Dr. Drost-Hansen

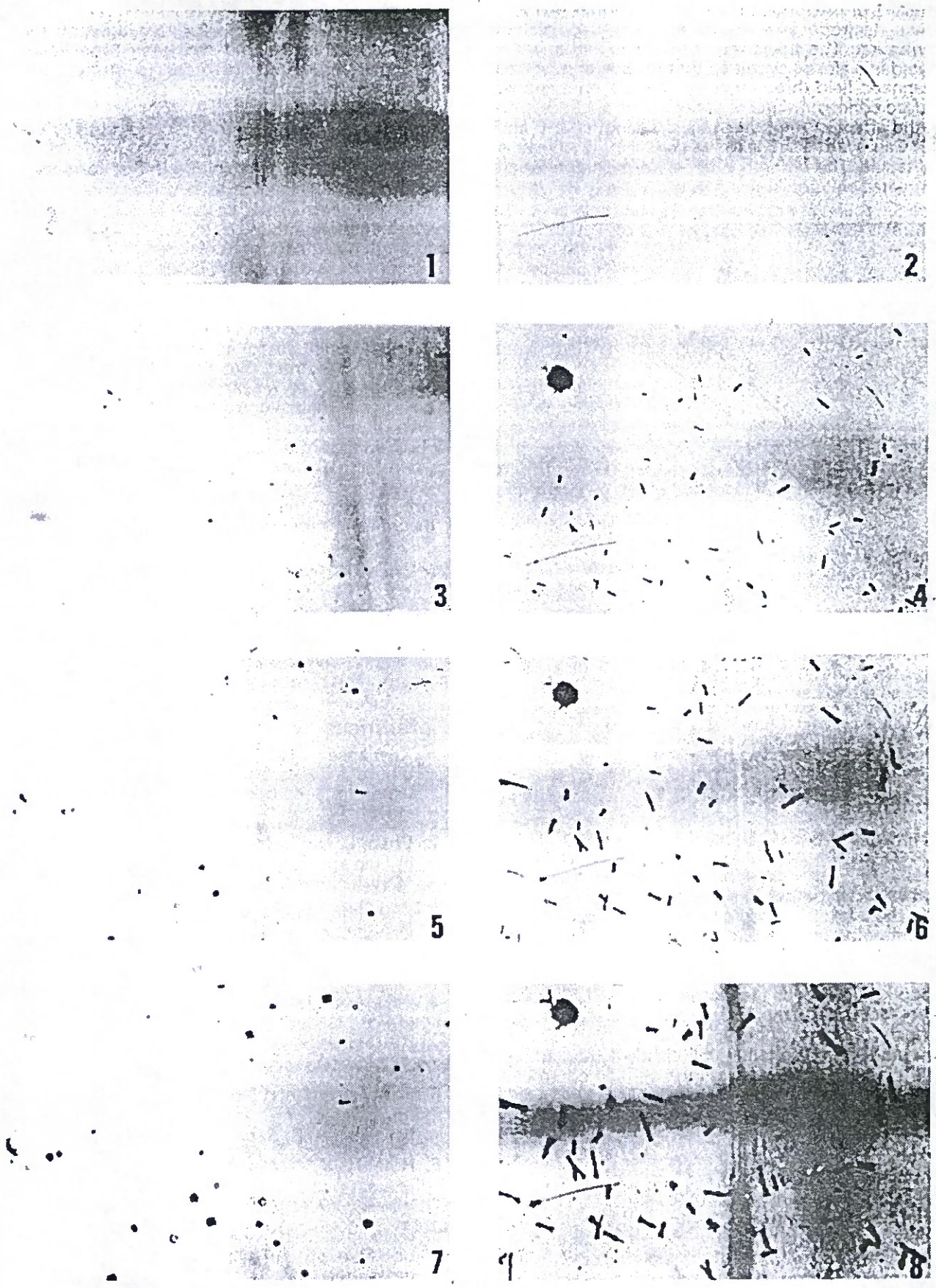

Fig. 4. Shows creation and growth of calcium carbonate crystals in the growth cell. Pictures with odd numbers are for treated water, even numbers for untreated water.
Nos. 1 and 2 are taken after 52 minutes, nos. 3 and 4 after 229 minutes, nos. 5 and 6 after 315 minutes and finally 7 and 8 after 430 minutes. There are fewer crystals with simpler crystal habit in magnetically treated water than in untreated water.

Fig. 4 shows, based on results from two comparable experiments, that less crystals are found in treated water (10,000 Gauss) than in untreated water. The treatment promotes the formation of calcite, whereas a more complex crystal habit is found in untreated water, the latter appears to have a "head' of calcite and a "tail" of needle-like crystals similar to aragonite.

Finally, we shall look at an experiment where the rate

assumes that the thickness of the vicinal water is approximately 0.1 μm. There is reason to believe, however, that the thickness is not more than a few molecule layers, i.e. a factor of 10^{-2}–10^{-3} thinner than what Dr. Drost-Hansen assumes. The theory, therefore, appears doubtful.

A third theory considers the magnetic unit as a sacrificial anode. The effect of the method is in these theories believed to be due to ions dissolved from the anode which in turn influences the subsequent crystal growth. The theory that the magnetic unit acts as a sacrificial anode, i.e. increases the concentration of certain ions in the water, is based on the general knowledge of the influence of trace elements on precipitation. It is well known that the rate of precipitation of, for instance, calcium carbonate is strongly affected by certain ions, even when these are present in very low concentrations. This effect should be understood in the context of the aforementioned "threshold treatment". It is known that for instance Fe(3+), Fe(2+), Mg(2+) and Zn(2+) have such an affect on the calcite structure of calcium carbonate. There is no doubt that trace elements generally are an important factor in scale formation, however, this theory alone, *cannot* explain the effect of commercial magnetic units on scale formation.

Another similar theory considers the unit as a sacrificial anode producing high local pH. It is assumed that an increased pH will cause some precipitation of calcium carbonate to take place near the anode, producing seed crystals which will cause precipitation to take place in the bulk of the water and thereby reduce the scale formed on the metal surfaces of boilers, etc. It is correct that an increased pH in a zone near a sacrificial anode under given conditions causes precipitation to take place. This change in pH will, in most cases be ineffective or under the most favourable conditions give only temporary relief from scale since: Firstly, the zone of increased pH will be relatively narrow, the amount of scale forming material able to precipitate in this zone, will therefore be negligible. Secondly, most of the precipitation will take place on the anode itself and render the anode inactive.

6.3 *Laboratory experiments on MWT*

No measurements based on commonly accepted chemical methods, have so far shown any chemical change to take place in the water, due to MWT. Therefore, the activity to find methods to study reproducible effects of the magnetic field on a salt solution has been increasing during the last years. In our laboratory we have chosen to study the time dependent phenomena such as the rate of precipitation etc. This has been studied both for magnetically treated and untreated water.

We will discuss three experiments done in our laboratory. These will, we trust, widen the acceptance of the method and be one step towards a theory to explain the observed effect, i.e. that a magnetic field of 1,000–10,000 Gauss cause significant changes in naturally hard water and that there is a memory effect.

F. Ellingsen and H. Kristensen measured the effect of MWT on the rate of precipitation of calcium carbonate in naturally hard water[15]. When magnetically treated, the water was placed in the laboratory for 10 minutes. This was to test the existence of the memory effect. Hydroxide was added to achieve supersaturation. An electromagnet with field strength variation of 0–10,000 Gauss was used. We found:

1. The rate of precipitation was dependent upon the magnetic field strength, see Fig. 3A.
2. A "turning point" was established, i.e. below a given pH, the rate of precipitation increased, while at higher pH, the rate decreased, see Fig. 3B. We now believe that it is possible to correlate the "turning point" to the point where the zeta potential crosses zero. The zeta potential is the potential between the double layer of ions which surrounds a particle in solution and the solution itself:
3. The precipitation rate was surface controlled.

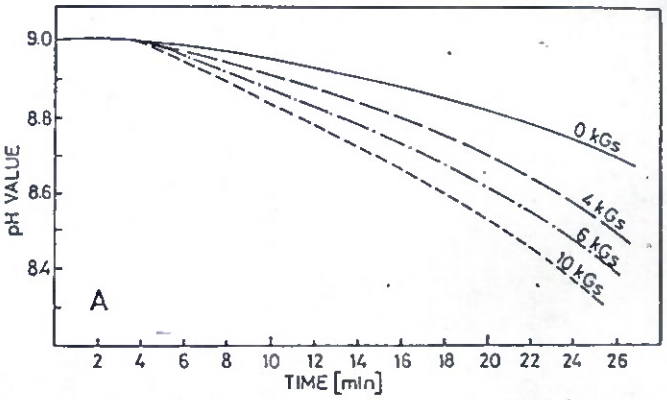

Fig. 3A. Shows the pH-change vs. time for four different field strengths. Increasing the magnetic field strength accelerates the rate of precipitation.

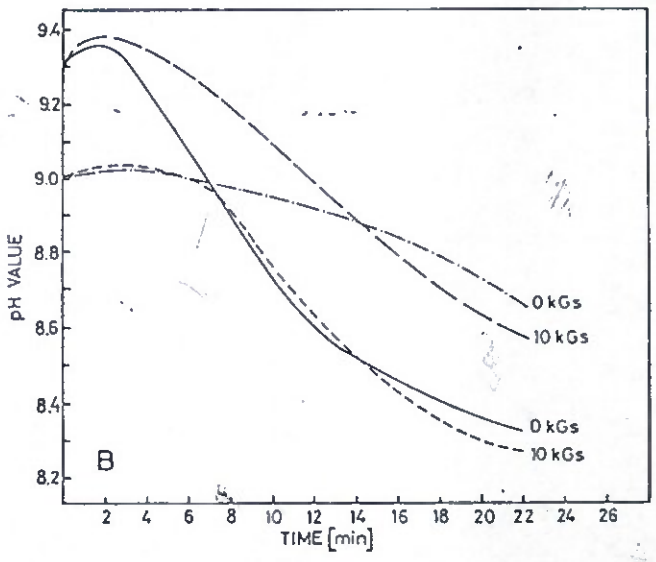

Fig. 3B. Gives an example of "the turning point". For treated water a pH of 9.0 shows forced precipitation whereas a pH of 9.3 inhibits precipitation.

4. A connection between the effect of MWT, turbidity (reduced visibility in the water due to suspended materials), and the oxygen content was established. Increased turbidity and oxygen content increased the effect.

In the second experiment, water, slightly supersaturated with calcium carbonate, was circulated through a crystal growth cell. The centre of the cell was made from glass. Water passed at a low rate through an opening (4 mm) between two glass plates which constituted the top and bottom plate. Precipitation was either initiated by heterogeneous nucleation on the bottom plate or by nuclei simply "dropping" out of the solution down to the bottom plate (nuclei formed on impurities). Crystal growth on the bottom plate was studied and pictures taken through a light microscope, see Fig. 4. To treat the solution, an electro-magnet with a field strength of 0 or 10,000 Gauss was used. The treatment took place just before entering the growth chamber.

of solubility of calcium carbonate is measured. An ion-selective electrode is used to measure the calcium concentration. The suspension of calcium carbonate is circulated in a closed circuit so that the solution passed the magnetic field three times per minute on average. Controlled concentrations of various salts are added, to study the effect of impurities. Field strengths of 0 and 10,000 Gauss are used alternatively. Fig. 5 shows a typical result. The difference between the treated and the untreated solution is clearly seen.

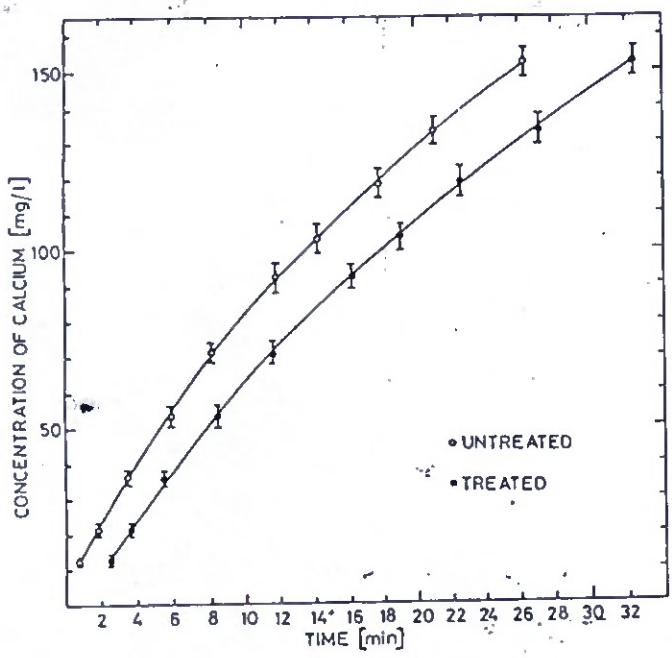

Fig. 5. Shows the concentration of calcium carbonate as a function of time. In this experiment 0,3 mg/l Fe^{3+} in the form of chlorides, was added. The difference in the rate of solubility between treated and untreated water is evident.

7. Conclusion

We believe that MWT changes the properties of either the surface or the double layer surrounding colloidial particles. All our experimental works seem to strengthen this hypothesis.

Both the rate of precipitation and solubility are, among other factors, dependent upon available surface between the growing crystals and the solvent. In practice, parts of the surface are often blocked by adsorption of impurities (as discussed earlier). This will limit the "access" to the surface and, thereby change the surface controlled kinetics.

In the study of precipitation, it is clearly demonstrated that the magnetic field changes the surface controlled rate of precipitation. We were also able to relate the magnetic field effect to both turbidity and the zeta potential of calcite. Furthermore, preliminary analysis of the solubility experiment indicates that MWT alters what above is called the "access" to the surface. All these results strengthen our hypothesis.

The tendency we found for treated water to promote formation of calcite is recently confirmed in a work presented by Dr. Kyzling and co-workers[16]. The mechanism of this is not clearly understood.

8. Summary

Much has been done to investigate and prevent scale, but the future still holds many unanswered questions. With numerous parameters, often unknown or uncontrollable, the study of scale, as an example of crystal growth, is considerably more complicated than what is normally studied in a laboratory. The formation of scale should, therefore, be seen in connection with general problems in crystal nucleation and crystal growth. There is a definite need for conducting controlled tests where one changes and measures the effect of the individual parameters in order to study their interconnection in a more complex system such as natural water.

There is, however, no room for doubt as to the effect of the magnetic field with respect to kinetics of different processes occurring in solution. Our research clearly shows the effect on the rate of dissolution of calcium carbonate. Furthermore, it is shown that magnetic water treatment influences both the rate of precipitation and promotes the formation of calcite.

It can be said that MWT has a weaker theoretical base than is the case with most chemcial methods employed. However, the many positive reports from users as well as results obtained in several laboratories, leave no doubt as to its significant effect on scale formation. We trust that the experiments referred to above, as well as research in progress, will bring us closer to a complete understanding of the phenomen.

We have found certain limitations from the application of the method, such as the content of certain silicates and sulphates. This is important and reduces the failure percentage of the method, but much work remains before the method may be called "theoretically" understood.

Acknowledgement

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