Colloid-A-Tron Physical Water Treatment

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Summary

Colloid-A-Tron works by precipitating scaling salts in the bulk of the water during its transit through the unit. The precipitated crystals tie up, and thus, reduce the concentration of free scale forming ions; in effect the water is 'part softened', reducing the risk of scaling at other sites in the treated system. The crystals are carried round the system as a particulate and will settle out in low flow regions such as cooling tower sumps and/or lost through bleed.

Colloid-A-Tron achieves this precipitation and softening through a significant increase in the pH, and as a consequence the calcium carbonate supersaturation ratio, in the water close to the surface of the device. This mechanism has been demonstrated and quantified by using controlled precipitation experiments. It has been validated through detailed examination of industrial and commercial case histories of both effective and ineffective applications.

Because of this effect mechanism, the water chemistry (pH, hardness etc.) needs to be suitable for Colloid-A-Tron to be an effective treatment method; the supersaturation ratio must be greater in the device than elsewhere in the protected system. Through the development of a detailed understanding of effect mechanism the compositional range for suitable application is predictable. A thermodynamic water simulation code has been developed which models the environment of any proposed application and indicates the likelihood of successful treatment and allows the evaluation of different plant operating conditions to increase this likelihood.

The understanding of the mechanism of action and the use of this code have resulted in Fluid Dynamics International becoming an intelligent supplier of water treatment to the water using industries.

1. Introduction

Physical water treatments such as Colloid-A-Tron have been considered with much scepticism despite strong evidence of successful applications throughout the World. The scepticism is, perhaps, not unreasonable since the physical devices have been somewhat 'hit or miss' in their effectiveness. Various mythologies have been proposed over the last 20 or so years to explain their effectiveness for hard scale prevention; many of these stretch the imagination.

Fluid Dynamics have also had applications failures in the early years of their 24 years of business. To resolve these failures, and to build up a portfolio of academic and technological support, they have commissioned several studies, notably at UKAEA Harwell, at Trinity College, Dublin, and currently at Ecole Superieure de Physique et de Chimie Industrielles de Paris to develop an understanding of how Colloid-A-Tron works - and where it doesn't. They have also developed a computer code based on the fundamental thermodynamics of hard waters which, when integrated with this understanding of the effect mechanism, can help in both the selection of applications and in offering guidelines for plant operation to improve the probability of successful water treatment. Experience in the past few years, throughout the World and across a wide range of industrial, commercial and domestic applications, has shown that this approach has been beneficial in terms of the quality in client service.

This paper considers the fundamental chemistry of the scaling process and how physical devices, but concentrating on Colloid-A-Tron, can influence the chemistry of hard waters and, thereby, reduce or eliminate hard water scaling problems. A simple experimental demonstration and quantification of the Colloid-A-Tron effect mechanism will be described and the application of the thermodynamic code to example applications will be illustrated. A number of case histories from various applications types are given.

The wide range of water compositions seen in practice cannot be treated by any one chemical or physical method; the operating environment must be well understood and the most appropriate solution applied. There are some applications that are best dealt with by chemical treatment, a large proportion that can be dealt with solely by physical devices and some where a combination might be appropriate. In view of the environmental issue of chemical additive discharges, it would seem most sensible to use non-chemical treatments wherever possible.

Even amongst the physical devices there is no single best device that can be successfully applied to all process streams and operating conditions. Given this, Fluid Dynamics International has also acquired the patent and manufacturing rights to the UK's leading magnetic treatment systems, the 'Magstream' and 'Clearscale' products previously manufactured by HDL Fluid Dynamics Ltd in Banbury.

2. Theoretical Considerations

The formation of scale on any surface in contact with hard water requires crystal growth to occur at the scaling site. If it does not, then any debris that accumulates can be readily removed by the water flow (given a reasonable flow rate and turbulent conditions). This deposition/removal of particulate has been studied over many years and the particulate deposit thickness, and hence the degree of the problem, can be estimated for a given particle size and Reynolds Number. However, if crystal nucleation and/or growth at the scaling site does occur then any deposited particulate, together with growing crystals, will cement into hard scale.

For scaling to occur three, quite separate, factors must be present:

(a) There must be a thermodynamic driving force for crystallisation.
This can be described as the attempt, by any system, to lower its energy state; it desires to reach a minimum, or at least a more stable state. If the water is overloaded (supersaturated) with respect to calcium carbonate the energy is lowered by the formation of crystals. Conversely if it is depleted (under saturated) it is lowered by dissolution of crystals. If it is in equilibrium (saturated) the crystal growth and dissolution rates will be equal.

This thermodynamic driving force is defined by the product of the actual concentrations of the Ca^{++} and CO_3^{-} ions divided by the concentrations of these species in equilibrium with a large crystal. This ratio is known as the supersaturation ratio (S_r).

$$S_r = [Ca^{++}]_a[CO_3^{-}]_a/[Ca^{++}]_{eq}[CO_3^{-}]_{eq}$$

Thus, for $S_r > 1$ the driving force is towards crystallisation.

(b) Suitable crystal nuclei must be formed (homogeneous nucleation) or be already present (heterogeneous nucleation).
To be stable, under even relatively highly supersaturated conditions, several hundred, or even thousands of calcium and carbonate ions must be present in an ordered structure. These agglomerates form over a period of time, during which they are inherently unstable and only a fraction of nuclei make the transition to become stable.

For homogeneous nucleation to occur a significant supersaturation must be present in the system; for many systems $S_r > 5$ is required.

Alternatively, scale crystals or other appropriate surfaces must be present that will act as sites for crystal growth. The presence of suitable surface for growth can enable scale nucleation to occur at a lower supersaturation than is demanded for homogeneous nucleation. Depending upon the suitability of the surface $S_r > 2$ but < 4 can be appropriate for heterogeneous nucleation.

This factor is the most important criterion for chemical inhibitor water treatment effect as many of the main chemical agents act in the disruption of the developing nuclei, thus making them less likely to transition into stable crystals.

(c) Once formed the stable nuclei must continue to grow.
New calcium or carbonate ions must move to the crystal surface and be incorporated into the lattice. This will occur where $S_r > 1$. Crystal growth can only occur at specific sites on

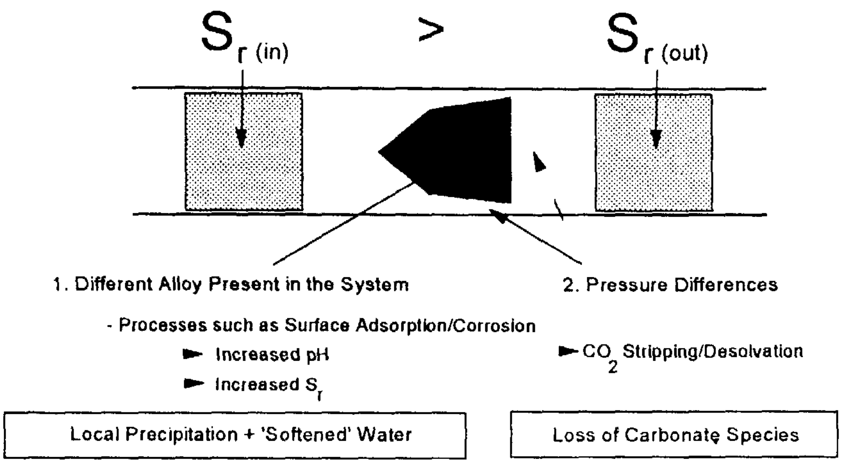
the water, because that is essential if the treatment is to be effective. Moreover, the mechanism must influence the chemistry of the water in such a way that at the site to be protected, which is likely to be remote from the device, the S_r is not sufficiently high for scaling to occur. In the following argument, the Colloid-A-Tron device will be used. It is the authors contention that the mechanism is common, perhaps to a varying degree, for all non-chemical water treatment devices.

3. Colloid-A-Tron Effect Mechanism

Colloid-A-Tron utilises a number of surface chemical and physical mechanisms in its operation. All of these are designed to contribute to the precipitation of scaling crystals during the passage of a hard water through the device.

The dominant mechanism is the patented Colloid-A-Tron alloy. This causes a significant increase in the pH of the water in the thin layer in contact with the device. This increase in pH raises the S_r of the water to a sufficient level that precipitation occurs in the water during transit through the unit. The precipitation ties up a proportion of the scale forming ions and the water is 'part softened'. The turbulence generated by the surface geometry of Colloid-A-Tron both help to entrain the precipitated crystals and can provide a secondary enhancement to the effect by desolvation of dissolved CO_2. Figure 2 illustrates these phenomena. The crystals are carried round the system as a particulate and settle out in low flow regions such as cooling tower sumps and/or lost through bleed.

Fig 2 Colloid-A-Tron - Effect Hypothesis



If the S_r at the Colloid-A-Tron is sufficiently high, the mass of precipitate produced can result in the water being softened to the extent that the water in the rest of the system becomes sub-saturated. Obviously the precipitate will begin to dissolve under these conditions, but it could also lead to the phenomenon of old scale dissolution and removal.

The proposed mechanism has been tested both by using controlled precipitation experiments and by examining industrial case histories of both effective and ineffective applications.

A quantifiable experimental demonstration of the effect of Colloid-A-Tron alloy on $CaCO_3$ crystallisation is through monitoring the bulk pH changes of supersaturated hard water that is being agitated by various alloy spinners. The hard water is produced by dissolving $NaHCO_3$ in deionised water. CO_2 is injected under pressure (in a soda siphon for example) to drive the pH down to around 5.5. $CaCl_2$ is similarly dissolved in deionised water and the bicarbonate solution added. The resulting solution is a simple, simulated hard water which is held subsaturated by the high CO_2 content; much as bore hole waters are.

Using an electrically driven paddle stirrer to agitate the solution the CO_2 is lost to the atmosphere in a controlled manner. The pH consequently increases due to the loss of carbonic acid and the saturation ratio will therefore increase. The pH will continue to increase until the S_r becomes sufficiently large to cause precipitation of $CaCO_3$. At this point the crystallisation will occur and there will be a marked change in the pH as the carbonate species equilibrium readjusts. Comparing the pH changes for a control alloy spinner, such as copper, with the Colloid-A-Tron alloy will highlight any differences in the crystal nucleating characteristics of the alloys.

Fig 3 Colloid-A-Tron Alloy
- Effect on Scale Precipitation

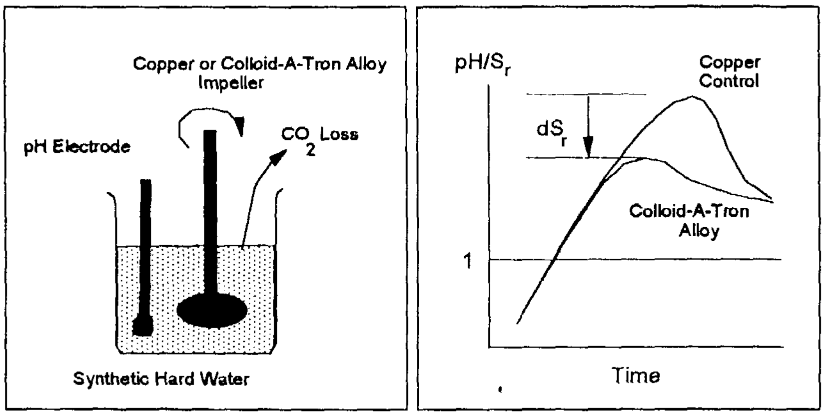


Figure 3 illustrates the experimental arrangement and the pH change profile for such a test. The effect of Colloid-A-Tron alloy is very marked. The Colloid-A-Tron agitated water precipitates at a pH much less than the control; typically in the range 0.2 to 0.5 below the control precipitation condition, depending upon the water composition and the rate of desolvation of CO_2. It is unlikely that Colloid-A-Tron is significantly affecting the fundamental nucleation thermodynamics of $CaCO_3$. It must be modifying the water chemistry in proximity to the surface, raising the pH, increasing the local S_r and thus nucleating crystals under conditions where the control is not.

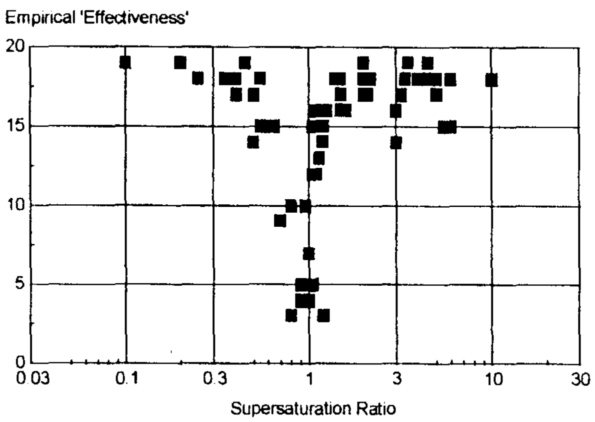
The experiment proves the effect mechanism of Colloid-A-Tron alloy.

The most viable explanations for this phenomenon is that the Colloid-A-Tron alloy is either corroding, generating OH^- through the corrosion reaction, or has an adsorption layer that produces an elevated pH as part of the electrical double layer. Studies at Harwell have shown that for a wide range of waters, fresh and saline, the corrosion is negligible, certainly far less than would be required to produce the results seen in the precipitation test. Therefore, the surface adsorption/double layer phenomenon is the mechanism for the pH change. This has been further confirmed by zeta potential measurement of powdered Colloid-A-Tron alloy.

Because of this effect mechanism, the water chemistry (pH, hardness etc.) needs to be suitable for Colloid-A-Tron to be an effective treatment method. Colloid-A-Tron would be expected to be most effective if the water passing into it is already close to saturation or supersaturated. As the supersaturation increases, at least up to a point, Colloid-A-Tron becomes more effective; with chemicals large increases in inhibitor concentration would become necessary. The effects of foreign ions on Colloid-A-Tron effect is unclear; their presence will alter the nature and thickness of the charged double layer around the Colloid-A-Tron surface in which the crystal nucleation occurs; it would be expected that moderate concentrations of these ions might improve effectiveness whereas they 'poison' many chemical treatments.

The presence of mineral particulate and other colloidal bodies inevitably present in waters will offer sites for hetero-nucleation of scale crystals. Colloid-A-Tron effect may be enhanced by such particulates in that the S_r threshold for nucleation may be lowered. The generation of colloids may also allow Colloid-A-Tron to be effective against scales other than calcareous scales. In contrast, through using chemical scale inhibition methods, these particulates will be absorbers of inhibitors. This will result in the particulates not becoming effective heteronuclei for scale growth and they will adsorb significant quantities of inhibitor which can lead to breakdown in scale prevention.

Fig 4 Colloid-A-Tron - Empirical Effectiveness as a Function of Water Chemistry



However, the water composition may be such that Colloid-A-Tron is an ineffective treatment. If the change in pH is insufficient to raise the S_r to the point where precipitation will occur, this will be the case. An analysis of over 200 applications water compositions was carried out and there was a strong correlation between the ineffective applications and S_r. Figure 4 shows some of this data.

This study is further evidence that the effect mechanism proposed is correct. Fluid Dynamics International have, therefore, a simple methodology to identify high risk applications and so improve success rates.

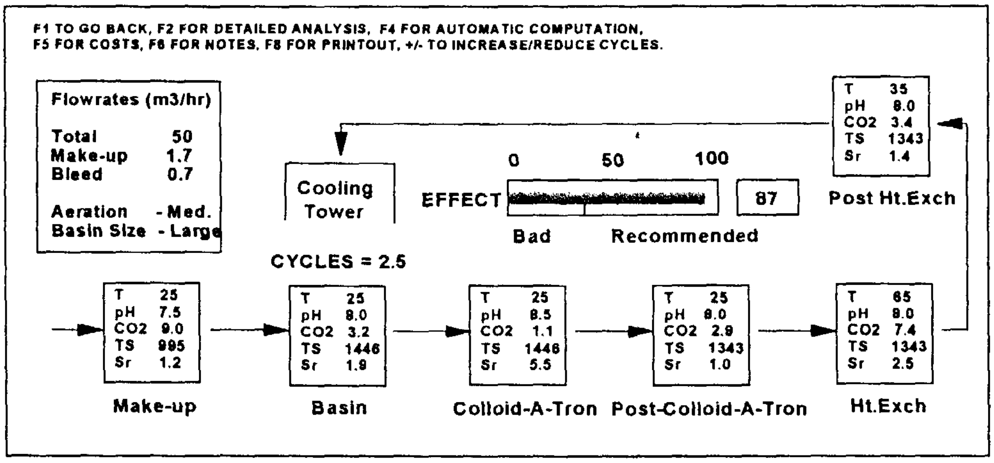
4. Detailed Water Modelling

Having established an understanding of the effect mechanism, together with an interpretation of how this impacts a range of applications it is possible to develop a detailed water simulation code that can be used as part of customer selection and service.

Considerable thermodynamic data on aqueous solutions has been generated by (for example) the US Geological Survey. Fluid Dynamics International has used these data of ionic equilibria as a function of temperature, ionic strength and pressure to build a comprehensive PC based model of the significant species in the waters used in heat exchange plant and other applications in the Fluid Dynamics International portfolio. A standard water analysis of the supply, or recirculating, water is made and the data loaded into the model. The S_r associated with the water at various locations in the plant is calculated and the likelihood of successful treatment is assessed.

A further refinement of the expert system is one which allows the supply water to be loaded and the code simulates various operating conditions and concentration cycles so as to optimise the operating conditions in a heat exchange plant. Figure 5 illustrates the PC screen showing the conditions in the plant for a typical hard water. The S_r at the Colloid-A-Tron and at the heat exchanger are assessed to ensure that it is high enough to give rise to precipitation at the first but below this point at the second. Experience from a wide range of plants has shown where these thresholds are and it has highlighted the importance of basin size and cooling tower aeration on the atmospheric equilibration of the CO_2 in controlling the characteristics of the plant.

Fig 5 Application of Water Model to Typical Heat Exchanger Application



The model, and its commercial interpretation, is an integration of the fundamental science of water thermodynamics and scale nucleation and growth and the World-wide service experience of Colloid-A-Tron.

For 'once through' applications the mechanism can be modelled, though less effectively, as a simple nomogram of pH vs. Hardness. Figure 6 shows this approach and underlays the ranges of waters found in practice. The vast majority of potable waters lie in the 'treatable' regions. There are some that are at an S_r that is too low for Colloid-A-Tron to cause crystallisation, which incidentally are unlikely to scale on heated surfaces, and some which have such elevated S_r that the Colloid-A-Tron itself is at risk of being scaled up, and subsequently becoming ineffective. Experience in domestic and commercial applications of this type has shown good agreement with the nomogram.

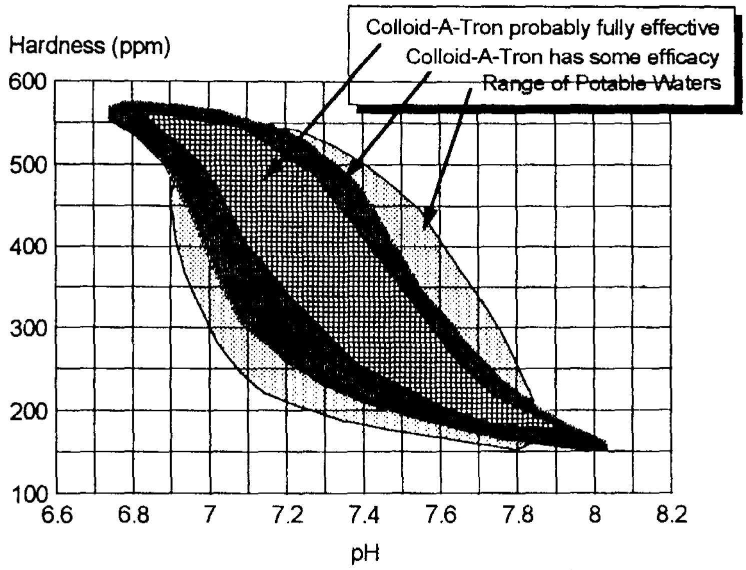


Fig 6 Nomogram for Initial Assessment of 'Once Through' Applications

Through this integration of the understanding of the effect mechanism, the considerable experience in industrial and commercial operation and the water code, Fluid Dynamics International now achieves better than 95% success rates in new applications.

5. Case Histories

5.1 Domestic Hot Water Systems in Apartment Flats, Ballymun, Dublin.

- Calcium and Magnesium scale was forming on the heating coils of the hot water calorifiers.
- Descaling treatment was required every three weeks.
- Scale also formed on the internal walls of water cylinders, pipe lines and hand valves, the latter had to be replaced every 6-9 months.
- Installation of a 3" Colloid-A-Tron on the cold water feed pipe eradicated the scaling problem throughout the system.
- Several savings arose: no manual cleaning of the calorifiers (2 days every three weeks), no mechanical damage to the coils and chambers (a risk with the

mechanical scale removal), no scale associated valve replacement required, no loss of hot water due to drainage for calorifier checking and valve replacement and a 20% reduction in fuel oil.
- Dublin Corporation has now installed Colloid-A-Tron to the other 35 Apartment blocks in the district.

5.2 Air Compressor Coolers, Kellogg Gmbh, Bremen, Germany.
- Scale was forming in the cooling water tubes in the heat exchangers of the three Atlas-Copco air compressors.
- Descaling treatment was required annually.
- Installation of 1 1/2" Colloid-A-Tron units in each of the three circuits has removed the problem. Some sludge removal is necessary from low turbulence areas, but this is by compressed air blower rather than mechanical cleaning.
- Colloid-A-Tron units have now been installed for hot water production areas of the food processing plant.

5.3 Steam Generation Boilers, Webster and Horsfall, UK.
- Following successful scale protection of wire drawing machines at the facility for many years, Colloid-A-Tron was employed to protect a number of boilers.
- Boiler inspection and reintroduction to service required acid pickling to remove scale, this was carried out on an annual basis.
- Installation of a 1 1/2" Colloid-A-Tron on the boiler feed pipe 2 years ago has resulted in no scale build up and no need for acid pickling.
- The lack of requirement for acid pickling has resulted in a more rapid return to service for the boilers and the life of the boilers will be extended.

5.4 Steam Generation Boiler, Kentdown Mushrooms, UK.
- Despite use of a combination of chemical treatments and part softened supply water, the Minipac 4 Boiler suffered severe scaling.
- Descaling treatment, both mechanical (drills and chisels) and chemical (acid) was required every three to six months.
- Installation of a 1" Colloid-A-Tron between the boiler feed pump and the boiler has stopped all scaling. No chemical treatment is used.
- Annual inspection, since 1989, has shown no sign of scale development, no cleaning is required and the boiler is rapidly returned to service.

5.5 Computer Suite Humidifier, Pfizer, UK.
- Vapour generator electrodes in humidifier bottles scale up and cease to work.
- Bottle replacement was required every 3 months.
- Installation of Colloid-A-Tron XT has eliminated scale build up of the electrodes and prevented hard scale in the bottles.
- The bottles now operate for over 1 year and a mild chemical clean has enabled bottle reuse. This application has delivered a 200% return on investment in the first year.

6. Discussion and Conclusions

Scale formation from hard waters is controlled by the fundamental thermodynamics and kinetics of the water chemistry. For any hard water the key elements in this are the carbonate species concentrations which are volatile as functions of either temperature and/or pH. Colloid-A-Tron exploits this volatility by producing near surface increases in pH due to the surface chemistry of the patented alloy.

Under suitable conditions Colloid-A-Tron operates by the generation of crystals in this near surface region of increased pH, and therefore of high supersaturation. The flow conditions in the Colloid-A-Tron must be sufficient to remove the formed crystals into the bulk of the water and so reduce the risk of the device itself becoming scaled. The formation of calcium carbonate precipitate removes scaling salts from the solution equilibrium; the mechanism can be compared to lime softening. During the formation of crystals, solvated CO_2 will be produced and the design of Colloid-A-Tron, providing rapid local pressure variations, will allow a fraction of this to be desolvated. This secondary mechanism makes the formed crystals more stable by reducing the local carbonic acid level and the remainder of the bulk water less supersaturated by reducing the overall pH slightly.

If the reaction goes far enough, the treated water can remain under-saturated even at the heat exchanger surface and give rise to the phenomenon of 'old scale' removal or dissolution. The water passing the heat exchanger needs to have a lower S_r than it would without the Colloid-A-Tron in the circuit if the device is to have any effect and it should be below the crystallisation threshold for Colloid-A-Tron to be completely effective.

In principle the effect will work for any water (fresh, sea, brackish etc.) if the parameters involved in supersaturation control, pH and temperature, are achieved for a short 'reaction time' in the 'active region'. Supersaturation of the order of 3 to 5 for a few tenths of a second would be more than sufficient. It is now clear that, for the most part, the compositional range is predictable for suitable application. Physical water treatments such as Colloid-A-Tron have met with considerable success in a very wide range of applications throughout the World. The scepticism with which they are considered is unreasonable; there is a good and demonstrable scientific basis for their effectiveness. It is the lack of appreciation of these mechanisms, often by the physical water treatment industry itself, and the inherent constraints on the selection of suitable application that has led to the 'hit or miss' in their effectiveness. Successful water treatment requires a high level of understanding of the water environments experienced throughout the industrial plant, the effect mechanisms of the various treatment methods need to be understood and analysed and the most appropriate method selected and managed to match the requirement.

Fluid Dynamics International have developed a thermodynamic water simulation code which models the environment of any proposed application and indicates the likelihood of successful treatment. The understanding of the mechanism of action and the use of this code have resulted the removal of the 'Black Magic' associated with physical water treatment and has resulted in Fluid Dynamics International being an intelligent supplier of water treatment to the water using industries.