vosges di Moreno Beggio
Ionic Accelerators Department
Via Roma, 133
36040 - TORRI DI QUARTESOLO -
VICENZA - ITALY

ph. ++39-444-387119 r.a.
fax ++39-444-264228
mail : estero@vosges-italia.it
http://www.vosges-italia.it

REPORT ENEL RIT BRINDISI
BARI PLANT - CHEMICAL DIVISION

(translated from italian original)

NEW ara®™
super magnetic
water treatment systems

OBSERVATIONS ON THE INITIAL RESULTS OF THE MAGNETIC TREATMENT OF CARBON DEPOSITS WITH A VOSGES DEVICE

March 1994

INDEX

1. PREAMBLE

The importance of the problem of carbon deposits in cooled exchanger piping caused by particularly calcareous water has led in the Chemical Division of the Bari Plant to conduct research, initially theoretical in nature and later experimental, on possible alternative solutions that might resolve the technical problem more effectively and also provide economic advantages badly needed to limit the plant's running costs.

In this respect, a passive magnetic device, technologically more advanced than others currently on the market, has proved to be particularly interesting.

The feature that distinguishes this device from the large number of devices currently on offer is the creation of permanent magnetic plates, made from a samarium-cobalt alloy capable of producing a constant, intense magnetic field of 10.000 Gauss.

2. PROBLEM OF CARBONATE PRECIPITATION

2.0. General points

At the present time, the various types of magnetic, electromagnetic and electronic devices (continuous current electric polarization), and metal sleeves with or without sacrifical electrodes, use ferrite plates enriched with Neodymium, whose magnetic field tends to weaken over time due to the phenomena of demagnetization and corrosion of the ferrite itself.

The important effect of the magnetic field is not to alter the chemical equilibrium of the water but to interfere with the nucleation processes of crystals, acting on the levels of hyper-saturation within the germ, and to produce a change in the crystallo-chemical phase.

This effect is magnified if it is applied to saline types that display various polymorphous phases, including calcium carbonate, for the particular value of the ionic radius of 0,99 A°.

2.1. Notes on crystallo-chemistry

In its crystalline form, calcium carbonate may appear in three different phases, namely : calcite with crystallization in the triple-axis rhombohedral system (in this phase there is the crystallization of salts having an ionic radius of between 0,78 A° and 1 A°), aragonite with crystallization in the single-axis rhombic system (crystallization phase with salts having an ionic radius of between 1 A° and 1,43 A°), vaterite present in some sea organism structures whose crystal chemistry is connected with protein metabolism processes.

Of the three forms, the most probable at normal air temperature and pressure from a thermodynamic viewpoint is the stable calcite form.

When water is heated in thermal circuits, calcium bicarbonate normally decomposes and forms carbonates, which in turn form an adherent, compact carbon deposit on metal surfaces.

The formation of calcite results from the lack of an electronic doublet in the carbon atom; the carbon atom tends to eliminate this deficiency by capturing an electronic doublet from an atom having donating capabilities, as is the case for metals, which usually have free electronic doublets.

In most cases, this action is performed by the metallic element of the pipe, whose microscopically rugged surface favours the formation of crystalline germs, providing carbon with an electronic doublet and forming a metal-carbon bond which fixes the crystalline germ permanently to the piping; this germ will continue to grow.

This growth is due to the atoms that have a hand in the bond : a residual charge remains in these atoms, which generate dipoles; these dipoles in turn act as points of attraction and orientation for other molecules, which gradually accumulate there.

The grouping of molecules in the crystallization process does not come about at random, but takes place according to the orientation of existing electric dipoles and of the magnetic fields generated by electrons; molecule attack will be pointed in space according to the directions of greatest attraction and least magnetic interference.

On the basis of these electro-chemical aspects, the possibile influence of a magnetic field applied from outside causes a physical but not a chemical alteration to the structure, since this does not influence the solubility of compounds, and therefore does not affect the value of what is produced by solubility.

This influence, varying according to the intensity of the magnetic field, proves to be a decisive factor in the evolution and development of the crystalline germination.

2.2. Influence of magnetic field on crystallization

With regard to the phenomenon of solvation, every metal ion is surrounded by a certain number of water molecules due to the presence of electric dipoles, whose charged poles point in space according to the electrostatic attraction of the ions.

In this water-ion environment, the ion occupies the central cavity; the radius of this cavity ought to correspond to the crystallographic radius of the ion. In practice, by virtue of this phenomenon, the radius of the cavity is actually different.

The value of this radius is linked to the distance between the centre of gravity of the ion and the closest water dipole. This distance, which represents the actual radius of the ion, in reality depends on the orientation of the dipole itself.

The actual radius is greater than the crystallographic radius, and for cations - when no external force is applied - this difference corresponds to 0,1 A°.

The influence of a high intensity magnetic field capable of neutralising the magnetic fields produced by electrons prevents the free and harmonious orientation of dipoles.

Dipoles will therefore have to position themselves according to the lines of force of the applied magnetic field; this obliged orientation will influence the actual radius of the ion.

In the case of calcium ions, the forced orientation of dipoles brings about a considerable increase in the actual radius in relation to the crystallographic radius. In this way the ion acts as if it had an ionic radius of greater than 0,1 A°, giving rise to rhombic and not rhombohedral system crystals.

This deformation of the ion derives from the absorption of energy on the part of the system, which is transferred to the precipitate, consisting of the aragonite, metastable phase, with an energy content above that possessed by calcite.

But the anti-encrustation effect should not only be sought in the different crystallo-chemical ways of forming calcite and aragonite, since both of these, especially calcite, give rise to compact clusters and deposits.

In the formation of aragonite, molecules will position themselves according to the lines of force of the magnetic field due to the presence of an electric dipole; this alteration will cause a steric impediment to the construction of the crystal lattice, since it will not be able to position itself freely in space and cluster according to the lines of attraction of electric dipoles present in molecules.

These attractions make up the intramolecular forces that cause crystalline cohesion.

The absence of these attractions leads to the formation of amorphous deposits, appearing as a soft, inconsistent powdery substance, made up of a series of very small crystals having a very light acicular habitus that may easily be removed by means of the fluodynamic action of the water.

2.3. Effect of magnetic field on existing carbon deposits

Another important aspect of the action of magnetic fields is that pertaining to the effects on carbon deposits already existing in the circuit.

Although calcium carbonate is insoluble, it may become soluble under certain chemical conditions. In practice, continuous conditions of dynamic equilibrium are created between the calcium carbonate precipitate and water hardened by calcium.

There are indeed continuous exchanges between calcium ions generated by the dissociation of the minimum amount of soluble calcium carbonate and the calcium ions contained in the water, with the re-formation of an altered calcium carbonate, owing to the prior influence of the magnetic field, and the consequent transformation from the calcite to the aragonite phase.

Owing to the limited solubility of calcium carbonate, this form of kinetics is very slow; important roles in this process are played by time and the state of carbonate agents on the various surfaces.

3. INITIAL EXPERIMENTS

3.0. General points

With a view to testing the results of theoretical research, tests were carried out on water samples subjected to the action of the high intensity magnetic field using a device containing samarium-cobalt plates lent by the Vosges company, and on untreated water samples.

Tested water possessed high encrustation characteristics (Stiff-Davis index of 2.1), with a high content of calcium bicarbonate; this water is currently supplied to the cooling circuits of evaporation towers.

In the first series of tests, performed in the laboratory, equal volumes of treated and untreated water were subjected to gradual heating until the thermal conditions of total precipitation were reached (80°C), in one litre glass containers.

To prevent excessive local temperatures, the sample was lightly “stirred” during the entire heating phase by magnetic means.

Following total precipitation, the sample was allowed to cool slowly, then the solution was filtered by means of a final washing of the precipitate with demineralised water.

This operation was necessary in order to remove possible impurities due to impregnated saline water, which would have caused erroneous information in the crystallographic exam using X-rays and the EDS.

3.1. Analysis of untreated water samples

There were significant asperities and roughness on the sides of the glass containers. When the container dried, this white-coloured formation took on a consistent and compact appearance.

The microscopic exam on a slide with polarised light at a magnification of 400 X revealed a heterogeneous distribution of crystals with an extended prismatic habitus and high degree of nucleation (pluri-acicular clusters with evolving crystallization germs).

The crystallographic exam revealed a large proportion of calcite and a lesser proportion of aragonite.

Further exams based on studies using the electron microscope with EDS microprobe revealed the presence of large quantities of strontium, held responsible for the aforementioned slight formation (phenomenon of isomorphism).

3.2. Analysis of water samples treated with magnetic field

In this case, the sides of the glass containers, once water had been removed and the container dried, were covered by a very light impalpable formation that was easily removed with a finger or a slight sprinkling of water.

The microscopic exam on a slide with polarised light at a magnification of 400 X revealed a homogeneous distribution of crystal sizes and an extended prismatic habitus some 20-25 times lower than the case described in point 3.1.

The crystallographic exam using X-rays revealed a presence of aragonite only.

3.3. Precipitation test during continuous flow and under thermal load

To test the behaviour of water treated with a magnetic field and of untreated water, a circuit was created, consisting of a glass apparatus in which a quartz resistance probe having a power of 400 Watts was placed in the upper part of the apparatus, immersed in water.

Water delivery was regulated so as to maintain a constant temperature of 80°C.

In both cases, the test lasted four days on a continuous basis.

During the test, samples were taken of discharged water in order to measure the variation of ion calcium and the content in suspended solids.

In the first test, to study the behaviour of untreated water, the sides of the quartz heating probe were covered with a moderate carbonate formation, very difficult to remove and extremely compact.

The covering was removed with an acid treatment.

The analysis of calcium on the filtered sample showed variable values, with a 15-20% reduction compared with the initial value.

The content in suspended solids varied from 2-5 ppm.

In the second test, in which the magnetic device was placed in the circuit, the surface of the quartz probe was covered with a light powdery stratum that could easily be removed with running water or soft paper.

The analysis of calcium on the filtered sample showed a variation that was on average the same as the previous case.

The content in suspended solids varied from 10-15 ppm.

3.4. Test performed on boiler affected by carbonate scaling

In order to verify the action of the magnetic field on existing carbon deposits in circuits subjected to considerable thermal stress, a device was installed at the entrance of the drinkable water supply of the boiler located in the company canteen, which has a capacity of 1000 litres and a water temperature of around 90°C.

Before the device was installed, the heating element was removed and viewed to assess the degree of scaling.

A considerable formation of compact carbonate was discovered, amber in colour owing to the presence of ferric oxides.

The inner surfaces proved to be completely covered by the same deposits, obstructing vision of the zinc layer.

When cleaning tanks and kitchenware units, cleaning staff generally use acid-based detergents which, staff say, are not always sufficient unless they are accompanied by a vigorous use of abrasive pads.

After 50 days, the boiler was reopened.

The heating element was this time found to be devoid of carbonate deposits; a considerable quantity of carbon deposits was found on the boiler base, which proved to be very crumbly in texture.

The inner zinc surfaces were also free of deposits.

Cleaning staff declare that during the test period they did not use acid-based detergents, nor did they scrub thoroughly the sides of the tank.

4. CONCLUSIONS

These initial tests carried out on a magnetic device used to prevent the formation of carbon deposits deriving from the precipitation of carbonates produced satisfactory results.