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COLLOID-A-TRON[®]



Patents pending

ABRE-G

Control of Sealing by
Colloid-a-Tron Device :
Mechanistic Experiments

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1. BACKGROUND

1.1 General

Fluid Dynamics manufacture and market a device, called the Colloid-a-Tron (CAT), that is claimed to reduce scaling from water that has been passed through it. The device consists of a bar of a special alloy containing mainly copper and zinc, but with additions of nickel and tin, mounted in the centre of a copper or galvanised mild steel tube that is inserted into the water flow system being treated. The mechanism by which the CAT produces its effect is not known. If the mechanism could be elucidated and proved scientifically this would considerably strengthen the appeal and therefore the sales of the device. It might also indicate how its performance could be improved.

In 1984 Harwell carried out an analysis of CAT performance data collected by Fluid Dynamics agents from a number of European countries. Although this data was very limited in its nature, Harwell was able, using a computer program to predict water chemistry equilibria, to suggest some possible correlations between reported performance and water chemistry.

Fluid Dynamics has maintained its contact with Harwell through membership of the Fouling Forum, and in March 1987 Messrs. R.J. Spencer and G. Outram visited Harwell to discuss possible further research to be carried out at Harwell under contract to Fluid Dynamics. A programme was agreed in June 1988, with three main aspects: the corrosion behaviour of the CAT alloy, possible adsorption of ions from water on to its surface, and its effect on nucleation of CaCO_3 from hard waters. This document reports the results of that programme.

1.2 Corrosion processes

Oxidation of most metals (the anodic process) in water must be accompanied by a cathodic process in which reduction takes place to balance the oxidation of the metal. The most common cathodic process is the reduction of atmospheric oxygen dissolved in the water to hydroxide ions, though in acidic environments hydrogen ions may also be reduced to give gaseous hydrogen. Under normal cooling water conditions the main cathodic process is reduction of oxygen. The hydroxide ions thus produced increase the pH, and also react with bicarbonate ions and carbonic acid present in the water, either naturally or from dissolution of atmospheric CO_2 , increasing the concentration of carbonate ions and thus the driving force for deposition of calcium carbonate.

Fluid Dynamics found that adding powdered CAT alloy to distilled water increased its pH from 7 to 10, and also that the pH close to the surface of a bar of the alloy was 0.3-0.5 pH units higher than in the bulk. The possibility therefore exists that corrosion processes in the CAT might influence the chemical equilibria in the water passing through it, and thus scale formation.

In samples of waters II, III, and IV that had been exposed to CAT powder difficulty was experienced in obtaining an end-point in the titration of (Ca+Mg). The problem was not encountered if the water had not been exposed to the CAT powder. It was found that satisfactory end-points could be achieved by heating the solution to boiling. Additional tests in which either a few mg of zinc chloride or zinc dust were added to a sample of water IV produced the same results as if the water had been exposed to CAT powder, and turned the colour of the solution from wine-red to purple.

It is seen that there are few, if any, significant differences between the concentrations of the ions in solutions that had been in contact with the CAT alloy powder, and those that had not. The total carbonate plus bicarbonate concentrations are more or less constant, though the ratio changes as a result of changes in the pH. Three possibly significant differences are those for Ca^{++} (but not Mg^{++}) in water I, and Mg^{++} (but not Ca^{++}) in waters II and III. If the first of these is significant, it is clearly very dependent upon pH, since a decrease by one pH unit from 8.5 to 7.5 removes the effect. The other two would appear to suggest that doubling the magnesium concentration increases the amount adsorbed by a factor of nearly three, which is unexpected. The failure of water IV to show a similar effect to water III must call this result into question. The uncertainty could be resolved by using a higher ratio of alloy surface to amount of salt dissolved.

It was noticed in some preliminary measurements that after 6 days precipitation had occurred spontaneously in waters I and II in contact with the CAT powder in a closed vessel, and was also beginning in waters III and IV under the same conditions. After 21 days precipitation was also noticed in waters I and II that had not been in contact with the CAT powder, and a day later a precipitate was noted in water III, though not in water IV.

Measurements of the pH of all four waters in closed flasks, with and without CAT powder, were made over a period of 72 hours, and are presented in Figure 3. This shows that the presence of the CAT powder led to increases in pH that were most marked for waters II, III, and IV.

3.4 Bulk precipitation studies with metal spinners

The pH values at which bulk precipitation was observed in the three waters I/II, III, and IV at 50°C with spinners of copper, zinc, and the CAT alloy are listed in Table 3. Similar results were obtained in the two cells. Bulk precipitation was observed within periods ranging from 17-56 minutes from the start of sparging the water at pH 5.5 with argon. The periods in general appeared to be shortest for copper and longest for the CAT alloy, but it is doubtful if the differences are significant.

Micrographs of the deposits from the waters I/II, III, and IV are presented in Figures 4, 5, and 6 respectively. These show that

Table 3

Bulk precipitation in the presence of spinners

Water	Spinner Metal	pH
I/II	Copper	8.2
	CAT alloy	7.5
	Zinc	8.1
III	Copper	8.45
	CAT alloy	7.85
	Zinc	8.25
IV	Copper	8.25
	CAT alloy	7.9
	Zinc	8.1

the individual crystallites were basically needle-shaped in all three waters, though with some differences in morphology. The shape of the crystals suggests that they were probably aragonite, rather than calcite (cubic) or vaterite (fan-shaped). Deposits formed in the presence of the zinc spinners contained some much finer material that had a much higher zinc content, and was probably a corrosion product of the zinc. With the exception of this material, the crystals formed in coils with the zinc or CAT alloy spinners were larger than those formed with the copper spinners. This would be consistent with the formation of a smaller number of nuclei at a lower supersaturation, followed by subsequent growth.

3.5 Nucleation on a heated surface

The pH values at which nucleation was observed were 8.3, 8.3, and 8.45 for waters I/II, III, and IV respectively, and were the same whether or not the CAT device was in the circuit. The morphologies of the deposits formed are shown in Figs.7 and 8, and show much larger sheaves of crystals than in the bulk deposits (Figs.4-6 and 7c). The deposit formed from water I/II without the CAT device in circuit (Fig.7a) also shows some cubic crystals, and x-ray diffraction examination of this coupon confirmed that the deposit was mainly calcite with a little aragonite, whereas that formed with the device in circuit was mainly aragonite with a little calcite, and the bulk precipitate formed on further increasing the pH was almost entirely aragonite (Fig.9).

4. DISCUSSION

4.1 General

The number of variables that could be investigated within the scope of the programme was limited, and did not cover the full range of temperatures under which the CAT device may be used. A number of the tests were undertaken under accelerated conditions

(e.g. at higher temperatures), and results from these tests must be considered as indicative of general behaviour rather than substantive.

4.2 Corrosion tests

The corrosion tests show that a current passes when the CAT alloy is coupled to copper. This does not by itself prove that the alloy corrodes, since the cathodic reaction could be solely the reduction of oxygen to hydroxide. This view is supported by similar changes in the magnitude and sign of the potential of the CAT alloy when the water is sparged with either argon or carbon dioxide. The changes are consistent with the CAT alloy acting mainly as an inert oxygen electrode, and with a lowering in the concentration of oxygen in the water. Perhaps the most convincing evidence for corrosion comes from the adsorption tests, where the same difficulties in analysing the waters for calcium and magnesium were experienced when the water had been exposed to the CAT alloy, zinc dust, or to zinc chloride. This suggests very strongly that some zinc, or possibly another component, dissolved from the CAT alloy.

The magnitude of the current flowing between the CAT alloy and the copper shows that the amount of corrosion of the CAT alloy is small enough (a few micrometres per year at most) for no significant corrosion to be likely to be observed in installed units. The considerable drop in the current observed, even during the relatively short duration of the tests, suggests that the surface of the alloy rapidly passivates. The change in sign of the current in water IV, which would be expected to be the most corrosive because of the higher chloride and sulphate contents, could possibly cause some breakdown of the passive film of corrosion product that probably forms on the surface of the CAT alloy. It cannot be ruled out that a similar reversal of sign might have been observed with the other waters if tests had been carried out for long enough. These observations suggest that it would be worthwhile to examine the surface of units that have been in service for some time, to look for evidence of corrosion or deposition on them.

4.3 Adsorption measurements

It would not appear from the adsorption tests that the CAT alloy adsorbs significant amounts of the ions in the waters. The weight of powder added to each flask, assuming it to consist of equal perfectly smooth spheres, would have had a surface area of c.0.1 mm². The true surface area was not determined, but was probably at least an order of magnitude larger, a factor that would have been further increased by any corrosion. Assuming a surface site area 10⁻¹⁰ m² (one square Angstrom) and a monolayer coverage, this would correspond to a drop in concentration in the water of 0.3 millimoles/litre, which should have been detected for any of the ions present except, possibly, bicarbonate.

4.4 Nucleation studies

The observation of bulk precipitation at lower pH values with the CAT metal spinner than with zinc or copper, and the larger crystal sizes than with copper, both indicate that nucleation takes place at lower supersaturations in the presence of the CAT alloy. The fact that the zinc spinner gave larger crystals, while not producing bulk precipitation at a lower pH than copper, is not understood. It is clear from the bulk precipitates that the zinc spinner had suffered significant corrosion in waters III and IV. It suggests that bulk precipitation is not purely concerned with any selective corrosion of this element in the CAT alloy.

In this connection it may be significant that a sample of the CAT alloy, polished for metallographical examination of the grain size to determine its relation to the particle size of the powder supplied, showed that it apparently consisted of two phases, one of which appeared to have solidified before the other during casting. Differences in the composition of these phases could lead initially to selective corrosion of one of them, implying that the CAT metal contains its own anodes and cathodes, and does not need to be connected to another conductor for corrosion to take place. This would explain the increase in pH observed in all the waters containing CAT alloy powder, presumably due to oxygen reduction.

The observation that calcite was the main component of the deposit from water I/II on the heated surface in the absence of the CAT device, and mainly aragonite in its presence, or in the bulk precipitate, is unexplained. At the surface temperatures concerned aragonite is the most likely species to be formed, with calcite being more likely at lower temperatures. It would be worth examining the deposits formed from the other waters, and some formed at lower temperatures, to establish whether this is a general result. Controlled tests under conditions that would normally lead to calcite formation, in which small concentrations of the individual component ions in the CAT alloy were added to the water, would help to establish if they played a role in determining the crystal structure of the deposit.

5. CONCLUSIONS

- (1) In all of the waters tested a small current flows between a bar of the CAT alloy connected to a copper tube, but this rapidly decays and in water IV reversed its sign within 24 hours. The magnitude of the current would correspond to a uniform corrosion rate not exceeding a few micrometres per year.
- (2) The potential of the CAT alloy in the waters tested varied with their composition, but appeared mainly to depend on the concentration of dissolved oxygen.
- (3) It does not appear that significant adsorption of any of the ions in the waters tested took place on the surface of the CAT metal.
- (4) Spinners of CAT alloy led to bulk precipitation at lower pH values in all the waters tested than those of copper or zinc. This, and the larger crystals observed, suggest that the CAT alloy or its corrosion products promote nucleation in bulk solution.

6. RECOMMENDATIONS FOR FURTHER INVESTIGATIONS

- (1) Detailed analyses of the surfaces of CAT alloy bars from devices that have been successfully employed in service for a substantial period should be undertaken to see if they have the same properties as the new ones used in this work.
- (2) The corrosion behaviour of the individual phases in the CAT alloy should be investigated to establish their possible role in the device's action, possibly using the Harwell laser electrochemical microscope.
- (3) The effects of flow, and thus of mass transfer coefficient, on corrosion of the CAT alloy should be investigated, possibly using a rotating disc, which produces well-defined flow conditions.
- (4) Further crystallographic studies should be undertaken on deposits formed with and without CAT devices in circuits at different temperatures, to obtain a better database to demonstrate the possible action of the device in promoting the formation of aragonite rather than calcite.
- (5) Nucleation tests should be undertaken to establish the possible roles of CAT alloy corrosion products in promoting the formation of aragonite (or even vaterite) under conditions where calcite is normally found.

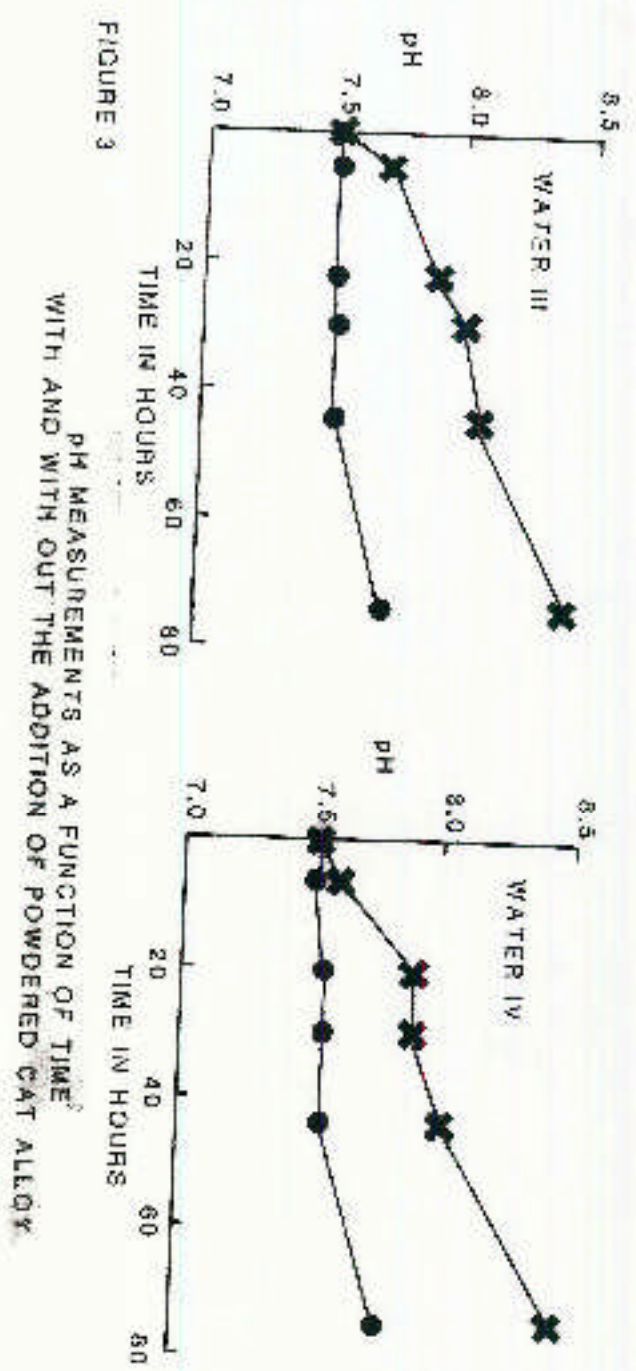
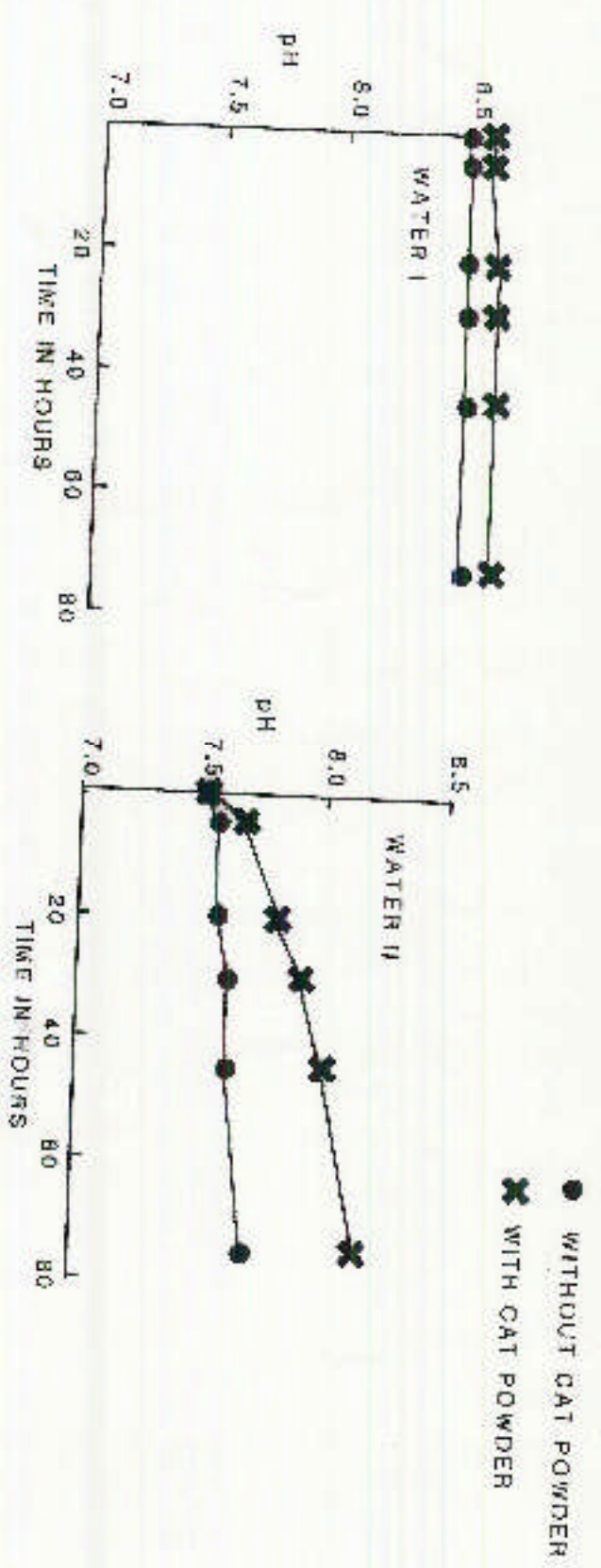
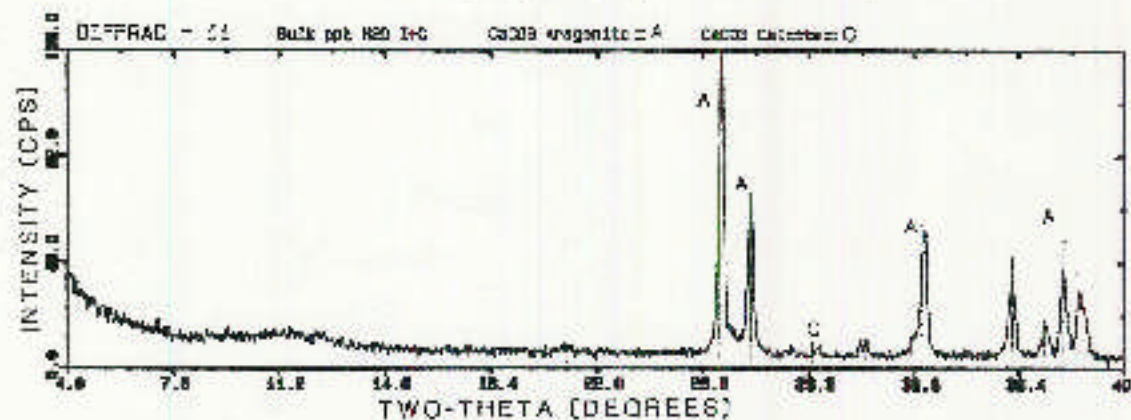
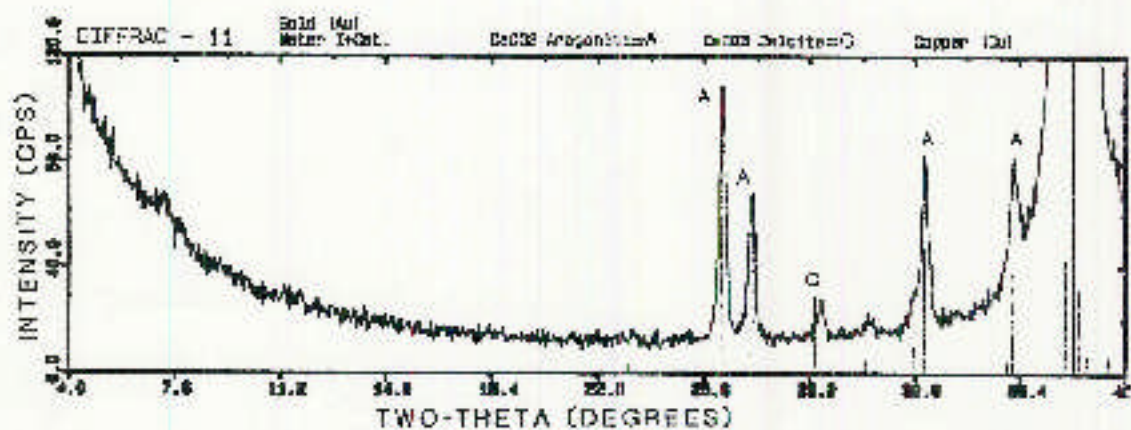
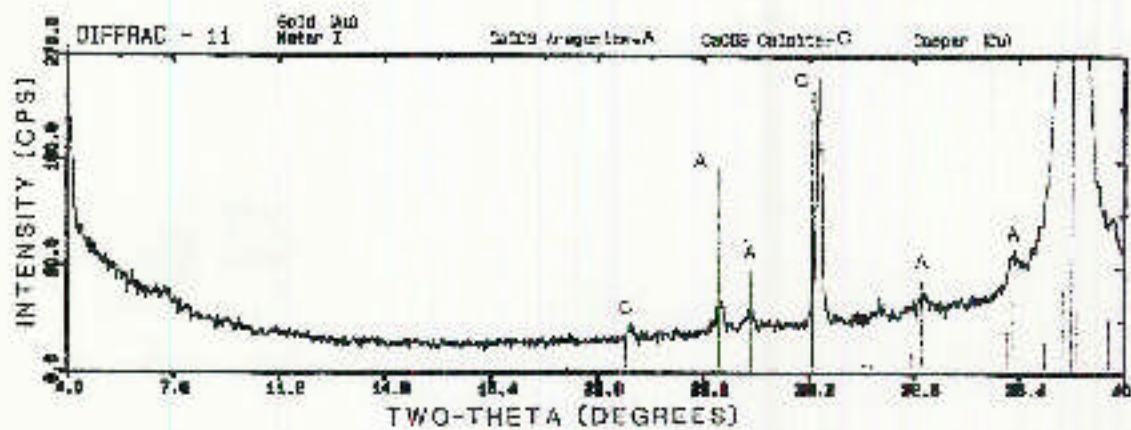


FIGURE 3
 PH MEASUREMENTS AS A FUNCTION OF TIME
 WITH AND WITHOUT THE ADDITION OF POWDERED CAT ALLOY



X-RAY DIFFRACTION PATTERNS OF DEPOSITS FORMED FROM WATER 1/10
 a) SURFACE DEPOSIT FORMED IN THE ABSENCE OF THE CAT DEVICE
 b) SURFACE DEPOSIT FORMED IN THE PRESENCE OF THE CAT DEVICE.
 c) BULK PPT. FORMED IN THE PRESENCE OF THE CAT DEVICE.

FIGURE 9