

Role of flow velocity on the scaling behaviour

J. Mathiyarasu

C. Boopathi

P. Subramanian and

N. Palaniswamy

The authors

J. Mathiyarasu, C. Boopathi, P. Subramanian and N. Palaniswamy are all based in the Corrosion Science and Engineering Division, Central Electrochemical Research Institute, Karaikudi, TamilNadu, India.

Keywords

Flow, Corrosion prevention

Abstract

The efficacy of antiscaling treatments under simulated flow conditions was studied by chronoamperometric technique. The effect of temperature and concentration on the scale forming behaviour of different compounds were also studied under the simulated flow conditions. In order to simulate the flow conditions a rotating disc electrode technique was employed. The mechanism of antiscaling behaviour of different chemicals was studied through electrochemical impedance spectroscopy. It was found that the flow velocity affected the efficiency of antiscalants. Polymer based compounds follow the growth modification adsorption mechanism, while compounds like EDTA and phosphonate follow nucleation modification absorption/chemisorption mechanism. Temperature and concentration of the scale forming compounds have a significant role in the scaling process, particularly at the low concentrations.

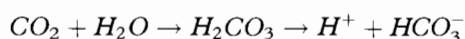
Electronic access

The current issue and full text archive of this journal is available at

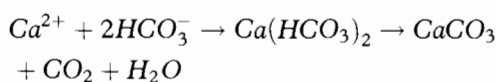
<http://www.emerald-library.com/ft>

Introduction

In industrial water treatment, the major task is to prevent the corrosion problem as well as the deposit formation. Scale can be defined as the adherent deposit of inorganic compounds precipitated from water onto metal surfaces. Generally, industrial cooling waters were found to contain dissolved calcium and magnesium cations (Jones, 1992). The dissolved carbon dioxide in water forms carbonic acid, H_2CO_3 and reduces the pH by dissociating to H^+ and the bicarbonate ion, HCO_3^- :



The bicarbonate ion forms an insoluble surface film containing $CaCO_3$:



Thus when calcium is deposited as $CaCO_3$ or $CaSO_4$, loss of production and increased maintenance expenses can result either due to poor heat transfer coefficient or shut down for the removal of scale. Therefore water treatment involving $CaCO_3$ dispersion in bulk solution, in such a way that the scale forming particles do not encrust the walls, is preferred.

One of the most accepted methods of avoiding such scale formation is by the addition of antiscaling chemicals or scale inhibitors. These antiscaling compounds, when added in certain quantity to a scaling water, reduce the formation of adherent scale.

Normally, in scale prevention, the concentration of antiscalants used in cooling water systems or in mains water is also an important aspect to be studied. There is often an optimal concentration for each specific antiscalant in any given medium. Many antiscalants/inhibitors are commercially available for use in preventing the formation of scale in the heat exchangers. Standard test methods (TM-03-74) proposed by NACE (n.d.) has been widely used to compare the effectiveness of these scale inhibitors. It is a laboratory screening test designed to measure the ability of antiscalants to prevent the precipitation of $CaCO_3$ and $CaSO_4$ from solution.

The author, J. Mathiyarasu, wishes to express his sincere thanks to CSIR, New Delhi, for the research project.

According to this NACE standard, the test solution is to be kept in constant temperature bath at 343 ± 1 K for the prescribed duration under static conditions. But in normal industrial practice the solution is under motion/flow conditions. Thus the effect of flow velocity on the scale inhibition was not considered in the NACE standard.

Hence, in the present investigations the effect of the scaling behaviour of calcium brine has been studied under simulated flow conditions by employing the chronoamperometric technique. The effect of temperature and concentration of the scale forming compounds present in the environment was also studied. The efficacy of certain scaling inhibitors under different flow conditions was evaluated. The final aim was to determine the mechanism of antiscaling behaviour of different compounds through electrochemical impedance spectroscopy.

Materials and methods

The scaling solutions were prepared as per the NACE standard. Before conducting the experiment the hardness of the test solution was determined by standard volumetric technique. The Langlier water saturation index (LSI) (Langelier, 1966) calculated for the untreated test samples gave positive value, indicating the possible scaling tendency of the water and confirming its suitability as test solution for evaluating the antiscaling behaviour.

Carbon steel was used as the electrode material for all the electrochemical studies. It was encapsulated in Teflon to make it suit with the rotating disc assembly (diameter 13.5mm). Prior to every experiment, the specimens were polished to a mirror finish by various grades of emery papers (1/0 to 4/0). In order to obtain the flow conditions in the test solutions, a Tacussel rotating disc assembly was used with speed controller.

The effect of concentration of the calcium brine on the scaling behaviour of carbon steel was studied by varying the concentration of calcium hardness and at two different temperatures, namely 333K and 343K, which was the normal operating temperature range of heat exchanger systems. In all the experiments, the electrode was rotated at different speeds i.e. at 400, 900, 1,600 and 2,500rpm. These rotations were selected in

order to simulate both laminar and turbulent flow conditions as shown in Table I.

Different antiscaling chemicals were chosen to find out their efficiency as scaling inhibitors under flow conditions. They were 2-carboxyethyl phosphonic acid (2-CEPA), amino tri methyl phosphonic acid (ATMP), ethylene diamine tetra acetic acid (EDTA) and methyl methacrylate (MMA).

The efficiencies of these compounds were found in terms of the scaling time at 50ppm of the scaling solution, at 333K under different rotations. These antiscaling chemicals were added at a fixed concentration (50ppm) prior to the immersion of the electrode.

To study the mechanism of antiscaling behaviour of the above chemicals, electrochemical impedance spectroscopy studies have been carried out using a PAR model 6310. Prior to EIS measurements, the surface of the electrode was immersed in the scaling solution for half an hour in order to ensure the surface blocking by the scaling chemicals. Then the impedance of the electrode surface was measured by changing the frequency from 10mHz to 10kHz in static conditions. A fitting procedure to a model, based on a simplex algorithm was used to estimate the R_{HF} and C_{HF} (Gabrielli *et al.*, 1996).

Results

Effect of concentration and temperature

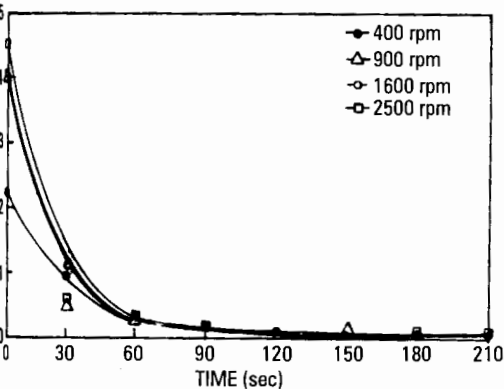
Figures 1a and 2a show a characteristic time versus current curve obtained for the brine containing 4,000ppm calcium ions at two different temperatures 333K and 343K. Similarly, these curves were recorded for 1,000ppm, 500ppm, and 50ppm of calcium ions at two different temperatures. The results are shown in Figures 1b-1d and 2b-2d.

The scaling time t_s and the residual current i_{res} derived from the above figures are given in Table II. From Table II, it was observed that there is no significant change in the t_s and i_{res}

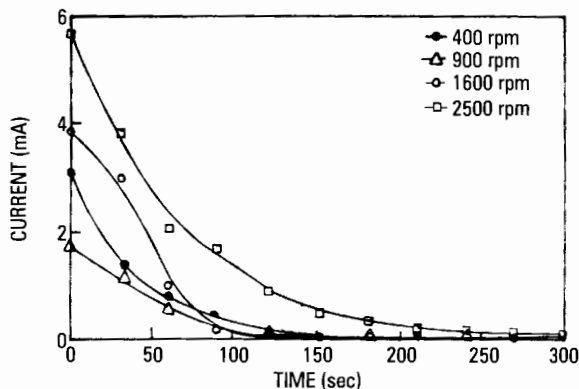
Table I Laminar and turbulent flow conditions

Rotation speed (Rev/min)	Angular velocity (rad/sec)	Reynolds number N_{Re}	Nature of flow
400	41.9	1909	Laminar
900	94.2	4292	Turbulent
1,600	167.2	7636	Turbulent
2,500	261.8	11912	Turbulent

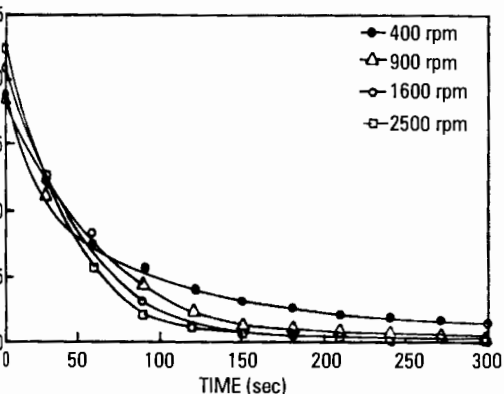
Chronoamperometric curves for carbon steel in calcium brine of various concentrations at 343K



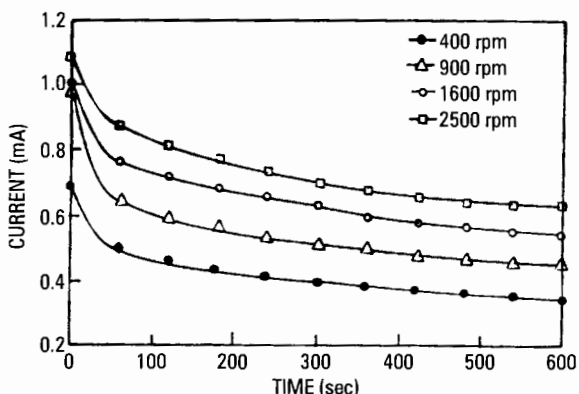
(a) 4000 ppm



(b) 1000 ppm



(c) 500 ppm



(d) 50 ppm

with respect to rotation at higher concentration. However at lower concentrations of scaling solution, velocity has a great role in residual current and in the scaling time. The i_{res} also increases with the increase in flow velocity. Temperature also has certain influence on the t_s and i_{res} , particularly in the low concentration.

Effect of scaling inhibitors

The current versus time was recorded for the addition of various antiscaling compounds and they are given in Figures 3a-3d. The parameters t_s and i_{res} obtained from the above figures are also given in Table III. It was observed that all the antiscalants gave a constant current with time. Therefore it was difficult to establish the scaling time in all the cases except in 2-CEPA and ATMP.

The i_{res} was found to be less in 2-CEPA and ATMP when compared to the other chemicals. In all the cases, rotation greatly affects the residual current.

Electrochemical impedance studies

The impedance of the electrode measured after 30 minutes of immersion in the solution and

the Nyquist plots obtained are given in Figures 4a-4e. It was explained that the high frequency time constant allows a pseudo high frequency resistance R_{HF} and a pseudo high frequency capacitance C_{HF} which were related to the coverage of the scale. The low frequency time constant may be related to the oxygen diffusion in bulk solution.

Without addition of antiscalant, the impedance shows diffusion limiting rather than a single time constant. The addition of MMA shows a semicircle and the resistance values were found to be 400KOhm. On the other hand 2CEPA, ATMP and EDTA show a rising curve proving that the diffusion process occurs at the electrode-electrolyte interface.

Discussion

When a fluid carrying suspended particles, flows in contact with solid surfaces, the particles tends to be transported to the wall and after adhering to it, form a more or less stable deposit, subject to the fluid shear stress forces (Oliveira *et al.*, 1993). Due to costs and

Figure 2 Chronoamperometric curves for carbon steel in calcium brine of various concentrations at 333K

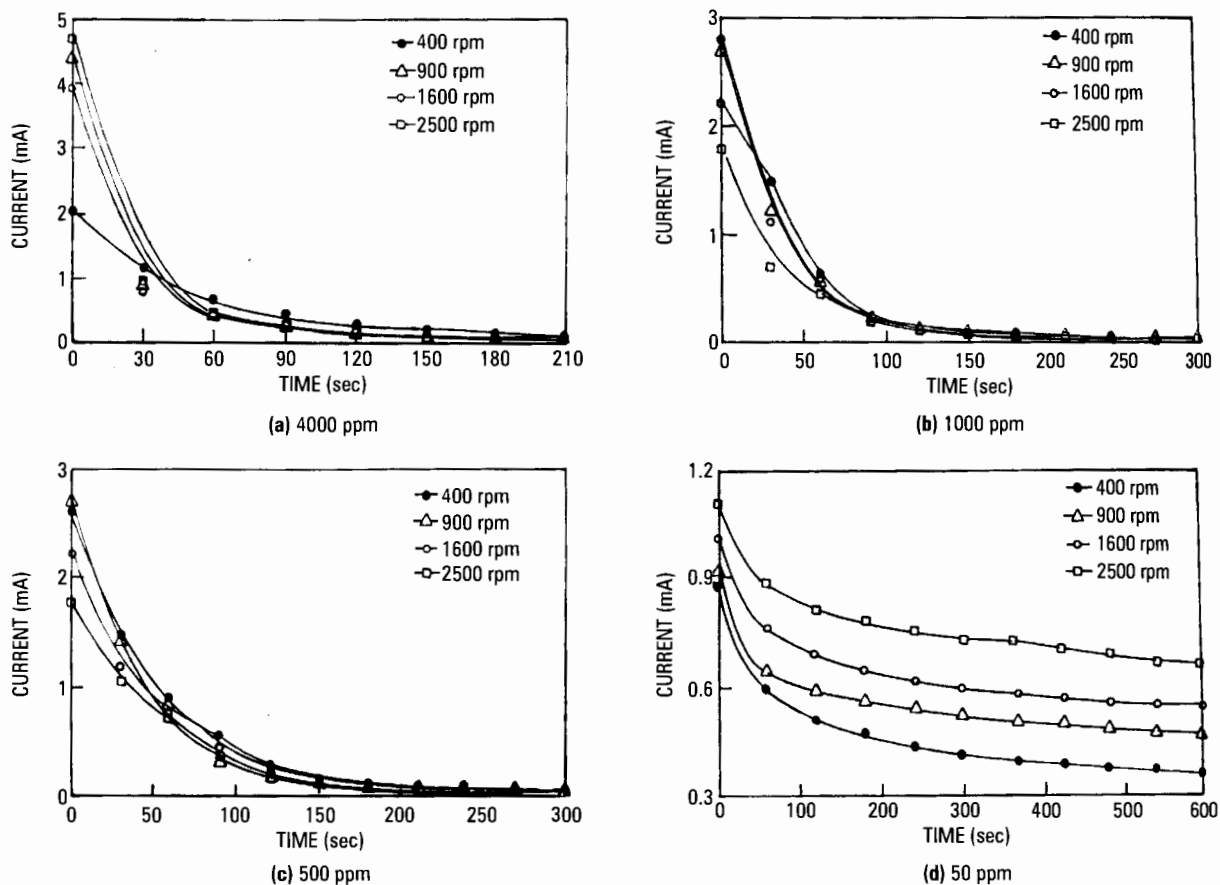


Table II Effect of temperature and rotation on the scaling behaviour of calcium brines of various concentrations

Conc. of brine	Temperature 343 K								Temperature 333 K							
	400 rpm		900 rpm		1,600 rpm		2,500 rpm		400 rpm		900 rpm		1,600 rpm		2,500 rpm	
	t_s	i_{res}	t_s	i_{res}	t_s	i_{res}	t_s	i_{res}	t_s	i_{res}	t_s	i_{res}	t_s	i_{res}	t_s	i_{res}
4000 ppm	49	0.51	40	0.52	37	0.56	43	0.57	69	0.17	41	0.10	41	0.07	42	0.07
1,000 ppm	56	0.1	90	0.07	83	0.02	93	0.04	83	0.02	60	0.02	56	0.02	55	0.01
500 ppm	60	0.19	83	0.08	80	0.04	73	0.04	68	0.03	70	0.02	59	0.03	80	0.02
50 ppm	100	0.35	100	0.46	150	0.57	186	0.64	82	0.38	90	0.48	130	0.55	164	0.67

Notes: t_s – in seconds; i_{res} – in mA

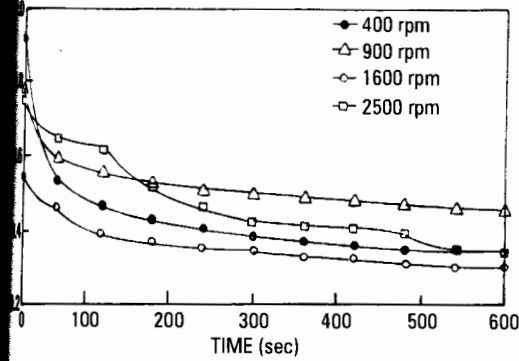
difficulties of treatments involving removal of scale inducing salts, the internal addition of antiscalant is the most common and effective scaling control method in industrial cooling water system (Jamiala Runadi and Muller Steinrager, 1993).

NACE suggested a laboratory-screening test to determine the ability of scale inhibitors to prevent the precipitation of $CaSO_4$ and $CaCO_3$ from solution in static conditions. These tests may be run at various concentrations to determine the minimum dosage required for scale control in order to obtain a better composition of inhibitors under laboratory condition. However the scale inhibitor concentration requirement for

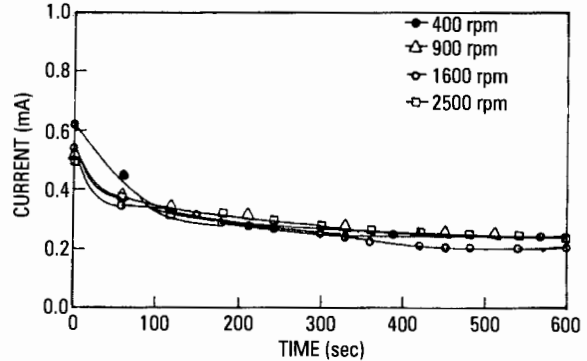
a practical condition will probably be different from the values determined under static conditions in the laboratory.

In the present study the concentration of the scaling compounds present in the environment do not affect the t_s and i_{res} except in the lower concentrations (50ppm). At 50ppm concentration, there is a linear relationship between the flow velocity and scaling time. At higher concentrations, due to the reactivity of $CaCO_3$, the scaling process takes place within a few seconds, irrespective of the flow velocity. The temperature also has an important role on the scaling behaviour. In general the scaling time was found to increase with increase in temperature.

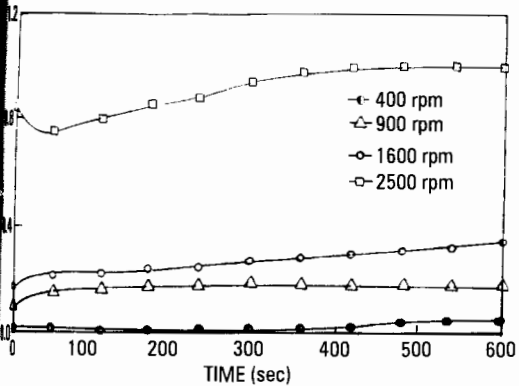
3 Chronoamperometric curves for carbon steel in 50ppm calcium brine at 333K with the addition of various antiscalants



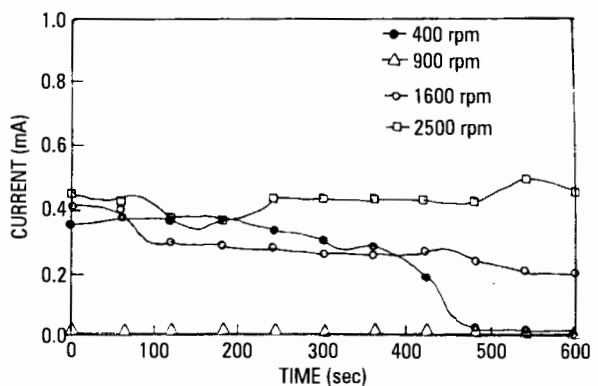
(a) 2-CEPA



(b) ATMP



(c) EDTA



(d) MMA

Influence of various antiscalants on the scaling behaviour of membranes at various rotations

Antiscalant	Temperature 333 K							
	400 rpm		900 rpm		1600 rpm		2500 rpm	
	t_s	i_{res}	t_s	i_{res}	t_s	i_{res}	t_s	i_{res}
2-CEPA	75	0.34	123	0.46	202	0.29	228	0.35
ATMP	208	0.22	140	0.70	106	0.25	200	0.28
EDTA	-	0.02	-	0.18	-	0.34	-	0.89
MMA	-	0.38	-	0.38	-	0.31	-	0.41

t_s - in seconds; i_{res} - in mA

As a general rule, it can be said that lower fluid velocities and higher temperatures favour deposition by the transport process, while higher velocities and lower temperatures enhance the dispersion process (Pinheiro, 1987). However the high fluid velocities usually enhance the removal rate of the scale. The effects of temperature in the detachment of deposits are often associated with the increase/decrease of the solubility of the solids.

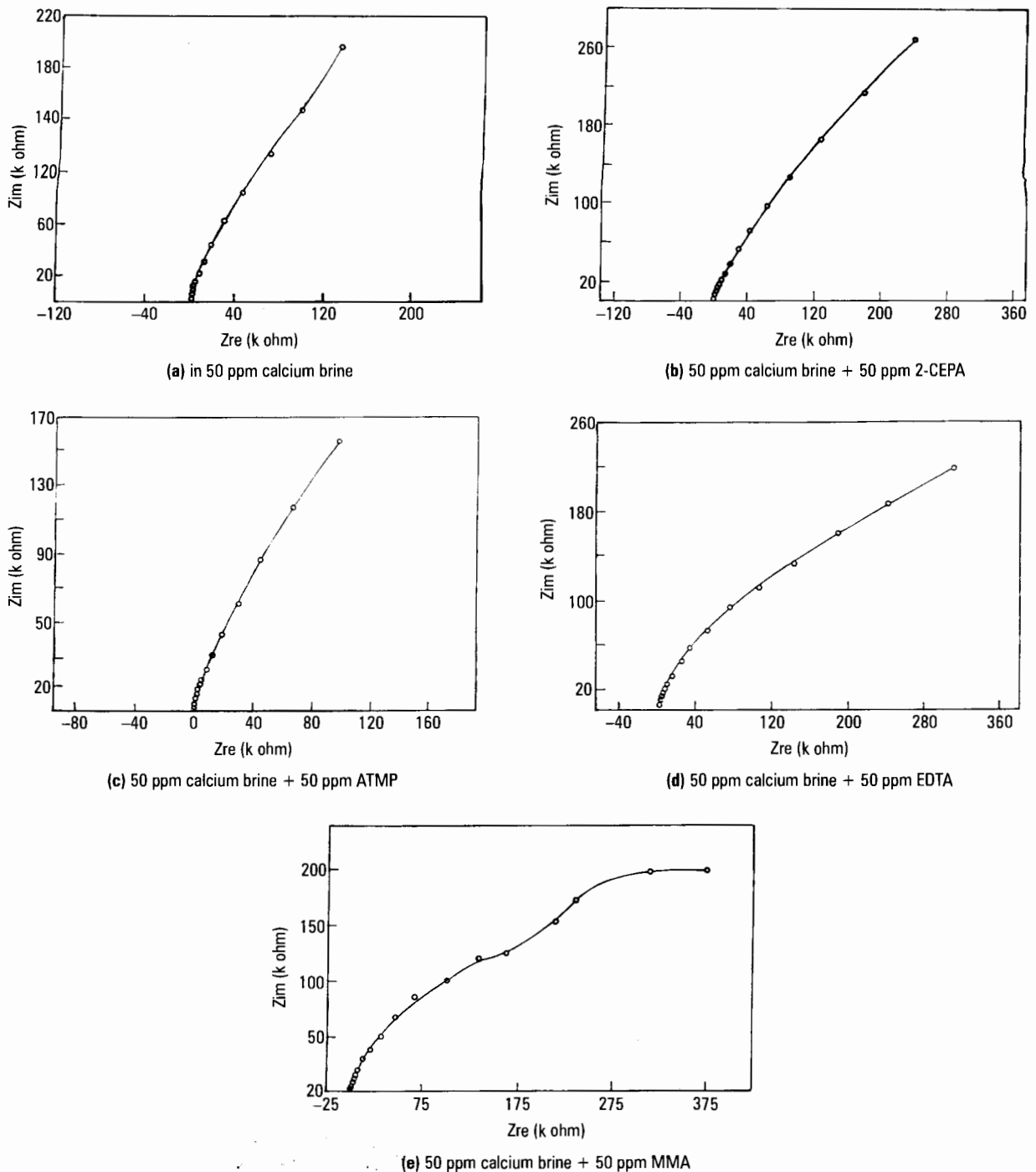
Antiscalant additives prevent solid accumulation at the heat transfer surface. Most of the antiscalants are multifunctional and inhibit the complex scaling mechanism in more than one-way. However, the suppliers of

the materials rarely provide the nature of the chemical and the mechanism by which an antiscalant behaves. Therefore the selection of the antiscalant would be significant, if behaviour of the system in the absence and in the presence of scale are known. Generally antiscaling additives control the scale by two ways. One by growth modification mechanism and another by nucleation modification mechanism.

Growth modification

This involves the use of various habit modifiers like organic polymers and other substances to distort the crystal structures of various types of scale (Woerner and Holzer, 1981; Schuck and Godlewski, 1978). The modification of crystal growth rate, crystal size and crystal morphology generally results in a loose and less adherent scale, which is more easily dislodged by the process fluid. The mechanisms that influence crystal growth by the antiscalant are based on adsorption or inclusion phenomena. In the present study MMA has been found to follow the above mechanism. The i_{res} was found to vary from 0 to 0.2mA, which shows that the surface of the electrode was active, which is due to the non

Figure 4 Electrochemical impedance of carbon steel electrode measured after one hour



absorbance of both the scale and the antiscalant compound. Further, it was evidenced by Nyquist curve, which gave a single time constant semicircle. This reveals that the surface was highly active. Therefore these antiscalants may adsorb during the growth of a crystal and hence the scaling behaviour was highly altered. However the flow velocity changes the i_{res} showing that efficiency decreased with increasing velocity.

Nucleation modification

In this mechanism, the solubility of the scale can be increased by the addition of certain chelants or chemically reactive compounds to the cooling water (Helmsteffer and Holzer, 1987).

In the present investigation EDTA and phosphonates (2-CEPA/ATMP) are found to follow the above mechanism. The addition of EDTA increases the solubility of the scale and hence prevents scaling. The phosphonates

also form a soluble complex with Ca^{2+} ions but these complexes adsorb on the electrode surface and thus prevent scaling of the electrode surface. The above discussion may be evidenced by the chronoamperometric and impedance measurements.

In chronoamperometric curves, the residual current was found to be higher for EDTA and it reveals that the electrode surface was free from any adsorption. In the case of phosphonates, initially it was found to be 0.4mA but with time the current values attain zero value, which suggests that adsorption of the complex over the electrode surface takes place.

It was also found that the tendency for scale formation in the scaling solution decreases strongly with increase in EDTA concentration. However, solubility, enhancement through chelants is usually limited by cost (van Rosmalen, 1981), effectiveness on iron and silicate deposits and corrosion potential (Gibson and Hwa, 1984; Kelly *et al.*, 1983).

The use of phosphonates to enhance solubility has been more successful in recent years. The phosphonate adsorb the growing crystal through chemical reaction/chemisorption. Thus the advantages of phosphonates are effective at much lower concentrations. However, the flow velocity can affect the i_{res} .

Conclusions

The following conclusions can be made:

- Velocity does not have any significant contribution to the scaling process at higher concentration of scale forming solutions.

- At lower concentrations, the scale formation was affected by flow velocity.
- The chronoamperometric measurements could be effectively used for the evaluation of antiscaling chemicals at lower concentrations, by measuring the scaling time and residual current.
- MMA inhibits the scale formation through a growth modification – adsorption process.
- EDTA and phosphonates follow a nucleation modification – adsorption/chemisorption process.

References

- Gabrielli, G., Keddam, M., Perot, H., Khalil, A., Rosset, R. and Zidoune, J. (1996), *J. Appl. Electrochemistry*, Vol. 26, p. 1125.
- Gibson, I.R. and Hwa, C.M. (1984), *45th Int. Water Conf.*, p. 361.
- Helmstetter, G.J. and Holzer, R.A. (1987), *39th Int. Water Conf.*, p. 299.
- Jamiala Runadi, M. and Muller Steinrager, T.H. (1993), *Corr. Reviews*, Vol. 11 No. 1-2, p. 25.
- Jones, D.A. (1992), *Principles and Prevention of Corrosion*, Macmillan publishing company, New York, 1992.
- Kelly, J.A., Lin, M.L. and Flasch, G.W. (1983), *44th Int. Water Conf.*, p. 194.
- Langelier, W.F. (1966) *J. Amer. Water Works Assn.*, Vol. 28, p. 1500.
- NACE (n.d.) Standard TM 03-74, NACE, Houston, TX.
- Oliveira, R., Melo, L., Pinheiro, M., Vieira, M.N. (1993), *Corr. Reviews*, Vol. 11, No. 1-2, p. 55.
- Pinheiro, J.D. (1987), "Fouling of heat transfer surface", in Kakac, Bergles and Mayinger (Eds), *Heat Exchangers: Thermal Hydraulic Fundamentals and Design*, McGraw-Hill, New York, NY, pp. 1013-35.
- Schuck, J.J. and Godlewski, I.T. (1978), *39th Int. Water Conf.*, p. 277.
- van Rosmalen, G.M. (1981), *AIChE 74th Annual Meeting*, pp. 209-33.
- Woerner, I.E. and Holzer, R.A. (1981), *Proc. 42nd Int. Water Conf.*, p. 28.

