Yu, H., Doherty, W.O.S. and Sheikholeslami, R.
Proc. Aust. Soc. Sugar Cane Technol., Vol. 25, 2003

STUDIES ON THE INTERACTIONS OF CALCIUM OXALATE MONOHYDRATE AND SILICA SCALE COMPONENTS

By

H. YU[1], W.O.S. DOHERTY[2] and R. SHEIKHOLESLAMI[1]

[1]*School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW*
[2]*Sugar Research Institute, Mackay, Qld*

b.doherty@sri.org.au

KEYWORDS: Scale, Evaporator, HTC, Silica, Oxalate, Fouling Mechanisms.

Abstract

The current knowledge gap for scale control is due to the fact that conventional studies involve single-component systems and so do not adequately address the mechanisms associated with multi-component (i.e. composite) systems which exist in chemical industries. This paper describes composite fouling characteristics of calcium oxalate monohydrate (COM) and amorphous silica (SiO_2) in aqueous solutions under conditions similar to those of sugar mill evaporators. To complement these studies, a number of clarification experiments were carried out on 4th effect syrup. Results are presented for the fouling resistances of COM, SiO_2 and COM/SiO_2 mixtures and the physico-chemical properties of the scale. The amount of composite scale deposited and the scale texture is dependent on the initial COM and SiO_2 concentrations and their supersaturation ratios. The results also show that the presence of oxalate ions affects SiO_2 solubility. The implication of these results is that the variability in scaling rates that occurs during the season and between seasons may well be dependent on the COM and SiO_2 ratios.

Introduction

The sugar industry experiences scaling of evaporators, the extent of which varies from mill to mill. These encrustations are formed from the combined effects of several processes involving inorganic and organic molecules or ions. The type of the scale formed depends on a number of parameters, including the concentrations of scale-forming ions, the amount of dissolved and suspended solids, the pH and flow properties of the solution, the rate of evaporation, and the operating temperature (and pressure) of the system. Scale facilitates the corrosion of surfaces, restricts fluid flow, and because it has low thermal conductivity, reduces the quantity of heat transferred across the metal-fluid interface.

Calcium oxalate (COM) and amorphous silica (SiO_2) constitute the most intractable scale components formed on the calandria tubes of Australian sugar mill evaporators. The later vessels of a multiple-effect evaporator station are mostly affected as a consequence of high supersaturation and high sucrose content during juice evaporation (Doherty, 2000). A typical scale composition of the final effect in an evaporator set is shown in Table 1.

Table 1—A typical scale composition for the final effect of an evaporator set.

Component	Concentration (wt %)
Calcium oxalate	51.3
Silica	33.3
Hydroxyapatite	7.8
Organic matter	7.6

Previous studies on evaporator fouling of COM and SiO_2 (Crees *et al*., 1993; Walford and Walthew, 1996; Walthew *et al*., 1998) have focused on the deposition of a single component, despite the co-existence of these two species in evaporator scale. The presence of more than one compound has been reported to alter the structure and strength of scale (Andritsos and Karabelas, 1999). Thus, the study of composite systems will lead to a better understanding of the mechanisms governing scale formation in industrial systems.

To gain an understanding of the mechanisms governing composite fouling of COM and SiO_2, fouling experiments were conducted in a dynamic system by a simple approach. The approach involved concentrating the feed under subcooled nucleate flow boiling in a single vessel and so the scale formed was a mixture of scale components to be expected in a normal evaporator set, rather than being typical of any particular evaporator. The experiments were conducted in aqueous solutions of COM or SiO_2 alone and their binary mixtures. To complement these studies, clarification experiments with a factory's 4^{th} effect syrup in the presence of oxalic acid were carried out to compare the interaction between COM and SiO_2 in factory juice and in the aqueous systems of the fouling experiments of this study.

Experimental

Fouling experiments

The unit for the dynamic fouling tests is shown schematically in Figure 1. It comprises a closed-loop circulation system which includes a storage tank, a circulation pump, a double-pipe heat exchanger, a cooling heat exchanger, a series of pressure, temperature and flow measuring and control devices and a PC for control and data acquisition.

The annular test section consists of a central stainless steel heating tube of 0.019 m OD and 1.6 m long, and a glass outer wall to allow visual observation of the deposition process during the experiment. All other pipings and fittings in the water systems were manufactured from stainless steel to prevent corrosion. The test solution was heated by a counter-current flow of saturated steam (100–200 kPa) obtained from a regulated steam supply system. An in-line cooling unit was used to obtain the heat balance within the flow loop and keep the bulk temperature of the feed constant (80^oC) throughout a run. All experiments were conducted at a constant solution flow rate (0.41 m/s) and heat duty (7.0 kW) using two automatic control valves operated by a data acquisition and control system. To reduce the magnitude of data fluctuation, all experimental measurements were averaged over a 10–20 min. period.

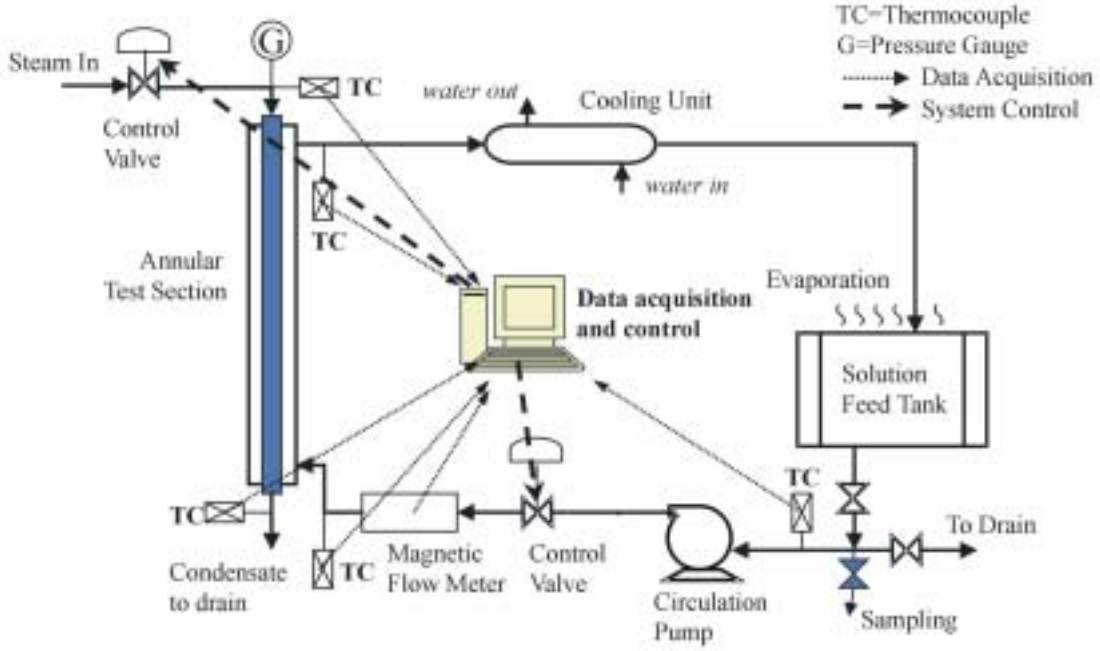

Fig. 1—A schematic diagram of the dynamic test unit.

The chemicals used in this study were analytical grade calcium chloride, sodium oxalate and sodium silicate. Hydrochloric acid/sodium hydroxide was used to adjust the pH of the stock solutions to 6.5 before they were added to the feed tank. The key operating conditions such as temperature (80^{o}C as in the 4th effect of a quintuple evaporator set), effective temperature difference ()T) which is the temperature difference between the vapour in the vapour chest and the boiling solutions in the tube (24^{o}C), COM/SiO_2 initial supersaturation (SS) ratio (0.6–3.0) and concentration factors (CF, the degree of concentration) were maintained in the range comparable to those usually encountered in the later effects of a sugar mill evaporator (Table 2). Single (i.e. COM or SiO_2 solutions) and binary (i.e. mixture of COM and SiO_2 solutions) systems were tested using identical experimental conditions. In the binary systems, COM was used as the controlling species with the SS varying from 1 to 5.3 in the presence of a fixed SS of 1.7 for SiO_2 (Table 2). Details of solution preparation, determination of COM and SiO_2 concentrations and test procedures have been described elsewhere (Yu *et al*., 2002a).

The degree of scale formation can be quantified in terms of the fouling resistance (R_f), by equation 1, which relates R_f to the overall heat transfer coefficient (htc) U_t measured at a particular time.

$$R_f = \frac{1}{U_t} - \frac{1}{U_o} \qquad (1)$$

where R_f is the fouling resistance, U_t is the htc after the evaporator has operated for a time t, and U_o is the initial htc when the evaporator is clean.

Table 2—Operational conditions of evaporators in a sugar mill (Doherty, 2001 pers. comm.) in comparison to this work.

Conditions	Sugar mill evaporator			This work
	3rd effect	4th effect	5th effect	
Conc. factor (CF)	1.5*	2.0*	3.0*	1–10
Initial (feed) supersaturation				
COM [a]	2–7	4–12	5–22	1–5.3
Silica [b]	1–5	2–6	3–11	1.7
Overall range of supersaturation (3rd effect feed – 5th effect exit)				
COM	2–66			1–53
Silica	1–33			1–17
Initial COM/SiO_2 SS ratio (3rd effect feed)	0.5–3.5			0.4–2.0
Temperature (^oC)	100	80	54	80
Pressure (kPa)	98	50	15	101
)T (^oC)	12	20	26	24

* Approximate values based on the changes in the sucrose conc. (wt %) in a sugar mill evaporator; [a]COM supersaturation is calculated as: [COM]/19 (19 is the solubility (ppm) of COM at 80^{o}C in the single systems and for the binary systems this is ~30 ppm); [b]Silica supersaturation is calculated as: [SiO_2]/290 (290 is the solubility (ppm) of SiO_2 at 80^{o}C in the single and binary systems).

The overall heat transfer coefficient, U, was determined from the heat duty, q (kW), the heat transfer surface area, A (m^2) and ΔT_m, the log-mean-temperature-difference (^oC) for a counter current arrangement (Eqn. 2).

$$U = \frac{q}{A\Delta T_m} \qquad (2)$$

After each run, the scale deposited on the heated tube was removed (by scraping the scales off the surface using a knife) and characterised by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). Prior to the start of each experiment the tube was cleaned with hot caustic soda (2%, w/v) followed by dilute acid (pH = 1).

Removal of scale-forming components

The fouling experiments were conducted in aqueous solutions not factory juices or syrups where the interactions between COM and SiO_2 may be different. Ideally, factory juice should have been used to complement the fouling experiments. As a few thousand litres of juice were required, it was impracticable to preserve such volume before use in the test rig. Besides, juice deteriorates after a short period of time. As such, clarification experiments (at 80^{o}C similar to the temperature of the fouling experiments) were conducted with factory syrup in the presence of oxalic acid to determine whether COM and/or SiO_2 will be precipitated and hence reduce scale formation. Two batches of syrups (1 and 2) were collected from two factories.

Clarification flotation (because of the brix of the syrup) experiments in the presence of oxalic acid using a standard batch settling kit were carried out at 80°C with last effect syrup from a sugar mill. Each series of tests included a control test when only phosphate (250 ppm P_2O_5 on brix), lime saccharate, anionic flocculant (10 ppm on brix) was added and the mixture equilibrated at 80°C for 15 min. The flocculated material was removed by filtering through an 8 μm membrane and the filtrate analysed for inorganic ions and oxalic acid.

Results and discussion

Fouling rates

Figures 2 and 3 show the fouling resistance and supersaturation curves obtained for COM/SiO_2 single systems. The onset of COM fouling occurred almost immediately after the experiments began (CF above 1.0). This is not surprising because of the low solubility of COM. The magnitude of the fouling resistances, R_f for the three COM concentrations were in the order 50 ppm > 20 ppm ~ 100 ppm. The values were in the range 0.05-0.1 $m^2.K.kW^{-1}$. It is suggested that the higher R_f values at 50 ppm of COM are probably due to the formation of a higher proportion of metastable colloidal COM particles than at 20 or 100 ppm of COM since the equilibrium SS of COM at 50 ppm was higher than those at 20 and 100 ppm (Yu *et al*., 2002b). This suggestion was arrived at from the results obtained when COM solutions were filtered through a series of membrane filters (pore size 0.005–2.5 μm) and determining the COM concentration after each filtration (data not shown).

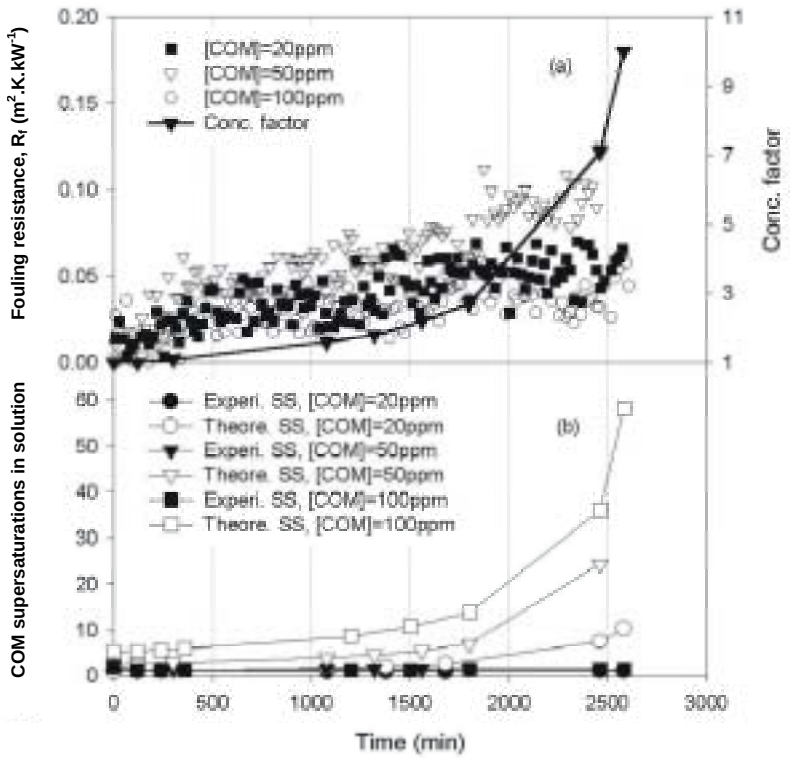

Fig. 2—COM fouling in single systems.

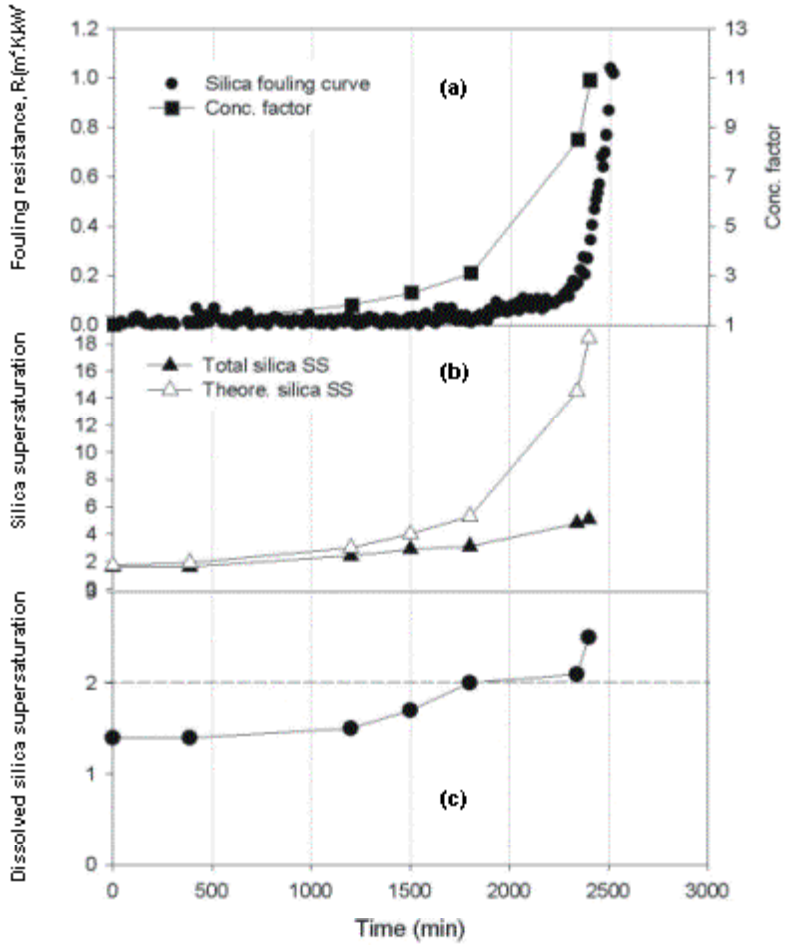

Fig. 3—Silica fouling at initial conc. of 500 ppm.

Additional information on silica fouling is shown in Figure 3c. It is seen that SiO_2 SS ratios is below 2.0 at CF 1.0–3.0 then markedly increased from 2.0 to 2.5 as R_f steeply rose to ~ 1.0 $m^2.K.kW^{-1}$. It may be inferred from these results that direct deposition of molecular silica may have occurred at low CF, while deposition of colloidal SiO_2 species occurred at high CF which resulted in the steep rise in R_f (Yu *et al*., 2002b).

XRD studies (described later) on the deposited materials showed COM to be crystalline while SiO_2 to be amorphous. Amorphous materials have lower thermal conductivities than crystalline materials (Honig, 1963).

Figures 4 and 5 present the data obtained for COM/SiO_2 composite fouling in the binary systems containing 20, 50 and 100 ppm of COM. The binary system containing 50 ppm of COM shows a gradual increase in R_f up to 500 min. followed by a sharp increase in slope before a very rapid increase after 2000 min. The reason for the transition at 2000 min. was not determined. The increase in R_f for the binary systems with COM at an initial concentration of 20 and 100 ppm only started after 2500 min. and the increase was small relative to that with 50 ppm of COM. The reliability of the experimental data was determined by having a duplicate run for one of the binary systems (data not shown). The results indicate that the R_f data were reproducible with 90% of the data points having less than 10% deviation, a low magnitude considering the sources of errors expected.

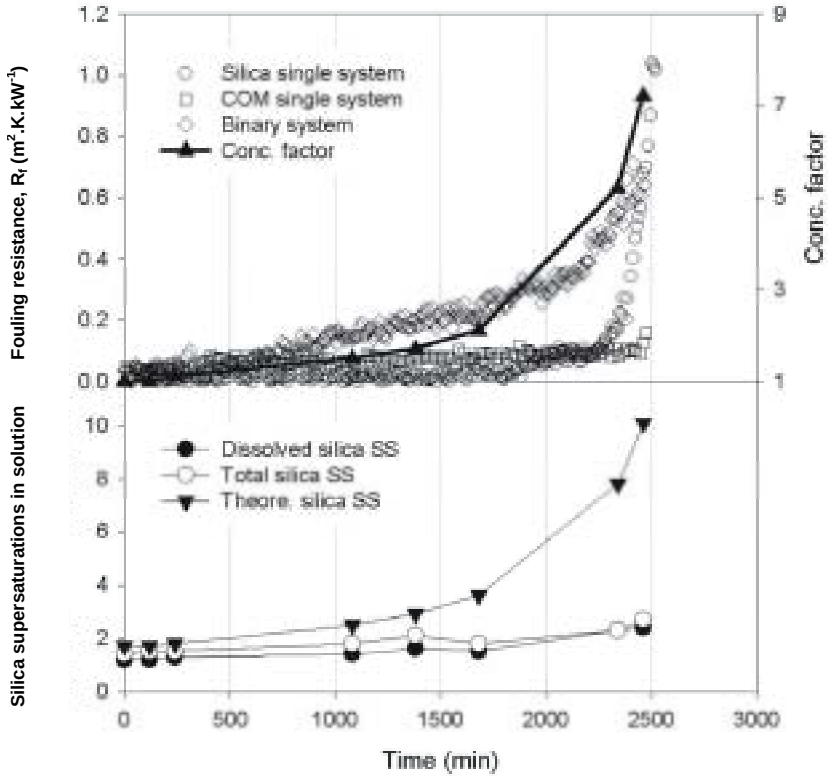

Fig. 4—Composite fouling of COM/SiO_2 at initial SiO_2 conc. of 500 ppm and initial COM conc. of 50 ppm.

Interestingly, the R_f values for the binary system containing 50 ppm of COM were higher than those obtained for either COM or SiO_2 single systems implying a synergistic effect between the two scale components. This synergy was not obtained when the initial COM concentration of the binary system was 20 or 100 ppm (Figure 5). In fact, at these COM concentrations, the R_f values were lower than those of SiO_2 single system, a phenomenon associated with antagonism (i.e. negative interaction).

The effect of co-precipitating species enhancing scale formation has previously been reported (McGarvey and Turner, 1999). The deposition rates of silt and hematite particles were enhanced by the co-precipitation of calcium carbonate (McGarvey and Turner, 1999). They reported that the increased deposition rate of silt is due to the reduced energy barrier between negatively charged silt particles and a negatively charged stainless steel wall. The reduction in the surface charge of the silt particles was associated with the deposition of calcium carbonate onto the particles. So, the high composite fouling rate observed for the binary system containing 50 ppm of COM and 500 ppm of SiO_2 in this study may be due to a lower interfacial energy between the surface area of heat exchanger tube and COM/SiO_2 colloidal particles through charge-neutralisation between the positively charged COM particles and the negatively charged SiO_2 particles (Callejas-Fernandez *et al*., 1991; Tadros and Lyklema, 1969).

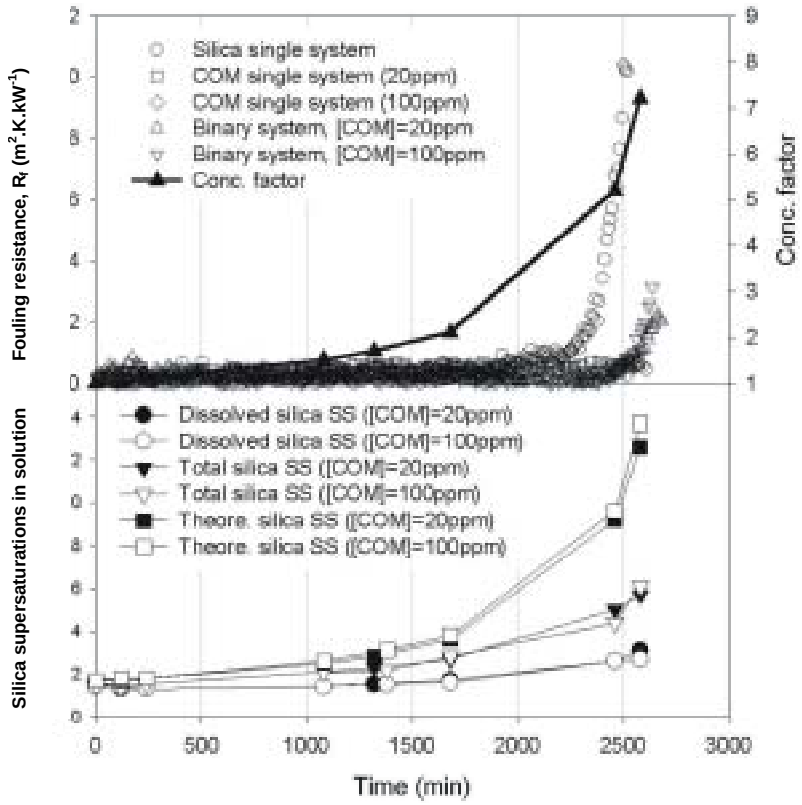

Fig. 5—Composite fouling of COM/SiO_2 at initial SiO_2 conc. of 500 ppm and initial COM conc. of 20 and 100 ppm.

The low fouling rates observed for the binary systems containing COM of 20 and 100 ppm were probably due to the formation of colloidal COM/SiO_2 particles with surface charges that remained sufficiently high to prevent particle deposition. Also, for the binary system containing 100 ppm of COM, the high COM concentration may have led to rapid aggregation and precipitation of COM/SiO_2 complexes in the bulk solution rather than on the tube wall owing to the fact that the kinetics of COM precipitation will be rapid at this concentration (Yu *et al*., 2002b).

The physical properties of fouling particles such as size and shape may also have an impact on scale deposition as they determine the particle transport regime as well as the attachment efficiency of particles to the surface (Epstein, 1988; Yiantsios and Karabelas, 1998). Hence, the different composite fouling rates observed in the binary systems may also be related to the variations in the size distribution of particles formed at different initial COM supersaturation levels.

Physico-chemical properties of scale

Visual examination, SEM and XRD studies were carried out to examine the effect of COM on the physico-chemical properties of the composite scales. The amounts of scale deposited onto the surface of the heat exchange tube were found to be small for all the COM single systems, in accordance with the low COM fouling resistances observed. Visual examination of the tube surface during the later stage of the SiO_2 fouling experiment found that the silica scale had a rippled surface. This rippled layer of deposit contained aggregates of large particles and was partially swept away upon draining the test section to remove the tube, revealing a uniform inner layer of hard scale.

For the composite scales, only the one obtained at an initial COM concentration of 50 ppm led to a complete coverage of tube surface. This scale (see Figure 6) was more tenacious than the inner layer scale formed in the SiO_2 single system. Composite scale formed at initial COM concentrations of 20 and 100 ppm were composed of large isolated clusters, which appeared to be less tenacious than the scale obtained with 50 ppm of COM. Under the sub-cooled flow boiling heat transfer, bubble formation on certain nucleation sites of heat exchange surface could be observed, especially at the upper end of the test tube, which was closer to the steam inlet. The deposit accumulation was generally found to be thinner in this area, possibly as a result of increased scale removal by extra bubble dynamics.

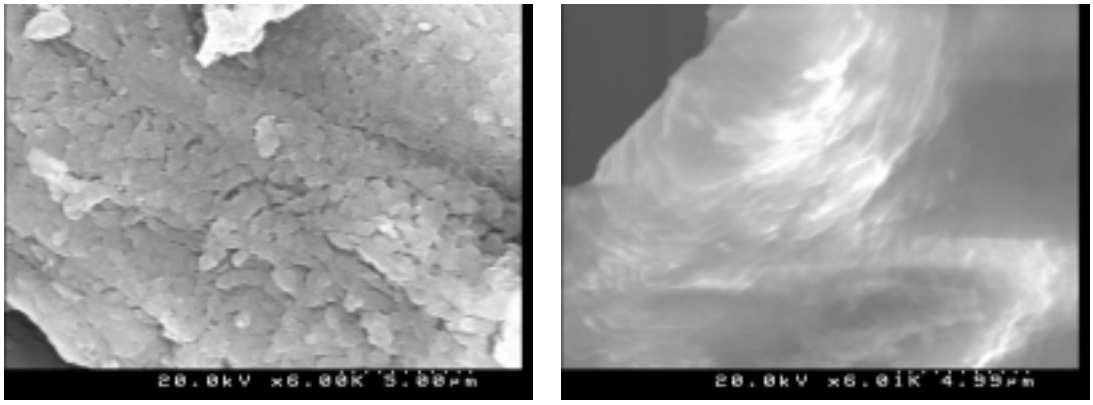

Fig. 6—SEM cross-sections of SiO_2 scale and composite scale, (a) SiO_2 scale and (b) composite scale at 50 ppm of COM.

X-ray powder diffraction analysis was conducted on SiO_2 and composite scales to identify the crystalline phases. The XRD spectra of all the scales gave a smooth broad peak or 'halo' with a 2θ value of approximately 23^o due to the presence of amorphous silica (Nakamura *et al*., 1995). However, this peak appeared to be narrower for the composite scales compared to that of the SiO_2 scale perhaps due to the re-organisation of SiO_2 molecules into a less disordered arrangement (Nakamura *et al*., 1989). The rearrangement of Si-O-Si structural units may have been caused by oxalate ions. The spectra for the composite scales at 50 and 100 ppm of COM were also found to contain additional sharp peaks (2θ values of 14.9^o, 24.4^o, 31.7^o, 38.3^o and 45.4^o) due to the presence of crystalline COM (Kontoyannis *et al*., 1997). The spectrum for 20 ppm of COM composite scale did not show characteristics COM peaks because of the low amount of COM formed.

Effect of adding oxalic acid to factory syrup

Table 3 shows the effect of adding oxalic acid during the clarification of 4^{th} effect syrup. It shows that the presence of oxalic acid (after 20 min. on addition) resulted in changes in SiO_2 content when compared to the same syrup clarified in the absence of oxalic acid. In one set of data (errors less than 2%), it increased SiO_2 content (by up to 117%) and in another set of data it reduced SiO_2 content. This may be due to the type of SiO_2 species in the syrup. The solubility of SiO_2 in water at 80^oC is 290 ppm (Yu *et al*., 2002b). This means that a large proportion of the SiO_2 in the clarified 4^{th} effect syrup (2) will be in the colloidal state, more so in the syrup (Table 3) as SiO_2 solubility is lower in sucrose solution than in water.

There were only marginal differences in the oxalic acid concentrations of the clarified syrups compared to the control where no oxalic acid was added (Table 3). It is therefore apparent from the results of Table 3 that the presence of oxalate ions affects the solubility of SiO_2 and hence would impact on scale deposition in sugar mill evaporators. As such, this work to a certain degree does validate the fouling experiments which showed definite COM and SiO_2 interactions. It must be added that in an earlier work by the authors (Yu *et al.*, 2002b), the presence of SiO_2 slightly inhibited the crystal growth of COM and increased COM solubility.

Table 3—The effect of added oxalic acid on CaO and SiO_2 on clarified 4th effect syrup.

Syrup	Amount of oxalic acid added prior to clarification (ppm on brix)	CaO (ppm on brix)	SiO_2 (ppm on brix)	Oxalic acid in clarified syrup (ppm on brix)
Clarified 4th effect syrup 1	None	3163	130	56
	20	3251	245	–
	50	3232	222	62
	100	2957	282	–
Clarified 4th effect syrup 2	None	3468	677	93
	20	3371	431	110
	50	3713	487	101
	100	3490	538	117

The use of oxalic acid in this study demonstrates that if it is produced in the factory during processing, it may impact on the composition and nature of scale formed in the evaporators.

Conclusion

The interactions between COM and SiO_2 in aqueous solutions and intermediate syrup have been studied. The results show that the amount and texture of scale formed is dependent on the initial concentrations of COM and SiO_2. The variability in scaling rates that occurs during the season and between seasons may well be dependent on the COM and SiO_2 ratios. Therefore, determining the COM and SiO_2 ratios in juice and intermediate syrup might help factory staff predict scale formation and scaling rates. Further work is underway to investigate the composite fouling characteristics of COM and SiO_2 in synthetic sucrose solutions.

Acknowledgments

The financial support of the Australian Research Council (ARC) and the Sugar Research Institute (SRI) of Australia are gratefully acknowledged.

REFERENCES

Andritsos, N. and Karabelas, A.J. (1999). The influence of particulates on $CaCO_3$ scale formation. J. Heat Transfer, 121: 225–227.

Callejas-Fernandez, J., de las Nieves, F.J., Martinez-Garcia, R. and Hidalgo-Alvarez, R. (1991). Electrokinetic characterisation and colloidal stability of calcium oxalate monohydrate dispersions in the presence of certain inhibitors. Progress in Colloid and Poly. Sci., 84: 327–333.

Crees, O.L., Cuff, C., Doherty, W.O.S. and Senogles, E. (1993). The effects of polymeric additives on the crystallisation of compounds present in evaporators. Proc. Aust. Soc. Sugar Cane Technol., 15: 141–149.

Doherty, W.O.S. (2000). Chemical cleaning of sugar mill evaporators. Proc. Aust. Soc. Sugar Cane Technol., 22: 341–346.

Epstein, N. (1988). Particulate fouling of heat transfer surfaces: Mechanisms and models. Fouling Science and Technology, Kluwer Academic Publishers: Dordrecht, The Netherlands.

Honig, P. (1963). Principles of Sugar Technology, Vol. 111, page141, Elsevier, Amsterdam.

Kontoyannis, C.G., Bouropoulos, N.C. and Koutsoukos, P.G. (1997). Urinary stone layer analysis of mineral components by Raman spectroscopy, IR spectroscopy and X-ray powder diffraction: A comparative study. Applied Spectroscopy, 51: 1205–1209.

McGarvey, G.B. and Turner, C.W. (1999). Synergism models for heat exchanger fouling mitigation. Int. conf. on understanding heat exchanger fouling and its mitigation, Pascoli, Italy.

Nakamura, T., Sameshima, K., Okunaga, K., Sugiura, Y. and Sato, J. (1989). Determination of amorphous phase in quartz powder by X-ray powder diffractometry. Powder Diffraction, 4: 9–13.

Tadros, T.F. and Lyklema, J. (1969). The electrical double layer on silica in the presence of bivalent counter-ions. Electroanalytical Chem. and Interfacial Electrochemistry, 22: 1–7.

Walford, S.N. and Walthew, D.C. (1996). Preliminary model for oxalate formation in evaporator scale. Proc. S. Afr. Sugar Technol. Assoc. 231–235.

Walthew, D.C., Khan, F. and Whitelaw, R. (1998). Some factors affecting the concentration of silica in cane juice evaporators. Proc. S. Afr. Sugar Technol. Assoc., 223–227.

Yiantsios, S.G. and Karabelas, A.J. (1998). The effect of gravity on the deposition of micro-sized particles on smooth surfaces. Inter. J. Multiphase Flow, 24: 283–293.

Yu, H., Sheikholeslami, R.and Doherty, W.O.S. (2002a). The deposition of calcium oxalate and amorphous silica scale under dynamic conditions which simulate sugar mill evaporators. In: Proc. 9th APCChE Congress and CHEMECA 2002, CD-ROM paper 389, Christchurch, New Zealand.

Yu, H., Sheikholeslami, R. and Doherty, W.O.S. (2002b). Mechanisms, thermodynamics and kinetics of composite fouling of calcium oxalate and amorphous silica in sugar mill evaporators – A preliminary study. Chem. Eng. Sci., 57(11): 1969–1978.