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COMPARISON OF THE OPERATING CHARACTERISTICS OF TWO COOLING WATER SYSTEMS USING CHLORINE AND CHLORINE DIOXIDE BIOCIDES

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ABSTRACT

Tests using side streams from an industrial cooling water system have been made to compare the corrosion rates associated with the use of chlorine and chlorine dioxide biocides. Two streams were employed, a "once through" and a recirculating system employing a cooling tower. The water used on the plant originated from a canal. The results of the tests revealed differences in characteristics between the circuits, depending on the biocide used and the operating conditions. The data obtained demonstrated a higher corrosion rate of 1.5 mpy with chlorine compared to 1.0 mpv using chlorine dioxide. A change in chlorine concentration from 0.5 to 4.5 mg/l resulted in a 0.5 mpy increase in corrosion rate. There was no apparent change in the corrosion observed for an increase in chlorine dioxide concentration from 0.1 to 0.57 mg/l. A temperature rise of 38 to 43 °C did not seem to influence the corrosion rate of the chlorine dosed system, whereas a similar temperature rise using chlorine dioxide as the biocide, the corrosion rate was increased by 0.5 mpy. Higher deposition rates of scale were observed in the "once through" system compared with the system employing a cooling tower.

INTRODUCTION

Water is probably the most widely used industrial coolant. It is easily handled with no safety risks; in general readily available and relatively inexpensive. It does not expand or contract significantly within the usual operating conditions of temperature ($10 - 60^{\circ}$ C), and does not decompose. Water has the added advantage of a high heat capacity, enabling it to carry large quantities of heat per unit volume.

Unless appropriate steps are taken, its use can give rise to fouling in heat exchangers where its cooling properties are required. The fouling can result from the accumulation of micro organisms, the precipitation of inverse solubility hardness salts (scale formation), surface corrosion and particle deposition The usual method of fouling control is to use chemical additives to kill micro organisms, to inhibit corrosion and scale formation and the prevention of particulate matter deposition. Of interest is the interaction of these additives with each other under the operating conditions of the particular cooling water facility.

MATERIALS and METHODS

Two streams from an industrial cooling water circuit

were used in these tests. The origin of the water was from a near-by canal. The water to the pilot cooling tower unit was identical to the treated water fed to the full scale industrial cooling water circuit. The other stream representing a "once through" stream was taken from the discharge of the industrial cooling water circuit, The water was pumped under controlled conditions, through annular test sections. The annulus assembly consisted of an inner tube 19 mm O.D. containing in good thermal contact, a 2 kW electrical heater rod, mounted on the axis of an outer glass tube 28 mm I.D. The mild steel tube containing the heater represented the test surface.

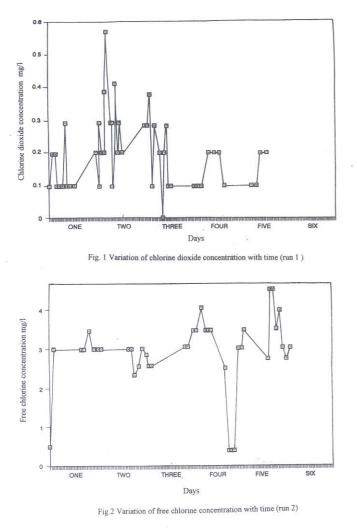
The heat load provided by the heated tube promotes a hostile environment making the test surface susceptible to corrosion and fouling processes, ideally suited to the assessment of water treatment programmes.

Both streams contained identical pipe work and layout, and test section geometry enabling a direct comparison to be made. Instrumentation on the individual test circuits provided continuous measurement of fluid flow, pH, conductivity, corrosion rates and temperatures of the flowing water and the test surfaces. Seven horizontally mounted test sections were employed in the tests.

Routine analysis of water samples was made throughout each test, using standard analytical methods. The analysis included; total alkalinity, free chlorine, hardness (calcium and total hardness) phosphates (total and ortho) and zinc.

RESULTS and DISCUSSION

Three "runs" were made using the test facility. Limits of 0.1 to 0.6 mg/l chlorine dioxide and 0.5 to 5.0 mg/l free chlorine are the recommended concentrations of the respective biocides for the two industrial systems, based on experience. A positive feed-back control was installed to maintain the respective biocide levels at ± 0.5 mg/l Nevertheless considerable difficulty was experienced in the maintenance of high or low chlorine dioxide concentrations in the cooling water. By contrast, in the chlorine dosing system, levels were found to be reasonably constant and the system responded well to the desired changes. The discrepancy between the two systems is attributed to the difference in volume of the mixing tanks where the biocide These effects are concentrations were controlled. illustrated in Figs.1 and 2.

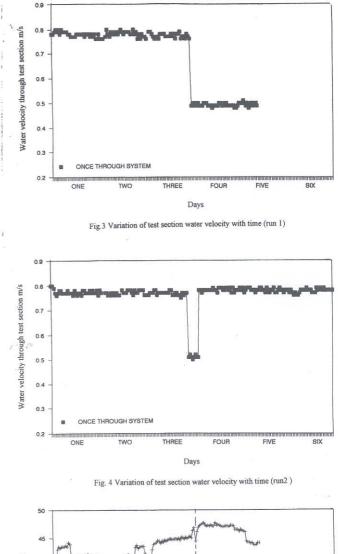


The "Once Through" System

Figs. 3 and 4 show the velocity in the system during the two tests. (runs 1.and 2) A step change was introduced approximately 72 hours after the commencement of the test. It would be anticipated that this would affect the temperature, due to the heat input from the electrical heaters in the test sections. Figs. 5 and 6 illustrate the temperature changes that were recorded.

The pH ranges for the two tests that were obtained were 6.5 - 7.2 and 7.6 - 7.9 respectively for the chlorine and chlorine dioxide biocide tests. The changes are illustrated on Figs. 7 and 8.

The corrosion rates for these tests are presented on Figs. 9 and 10 for chlorine dioxide and chlorine dosed systems respectively. Both show very high initial rates which then decrease exponentially for approximately 24 hours. The readings then gradually reach a reasonably steady value. The behaviour is common in corrosion probe (corrator) operation when virgin mild steel electrodes are inserted and a potential difference is applied to the instrument.



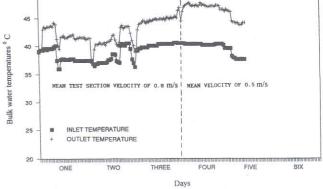


Fig. 5 Variation of bulk water temperature before and after flow through the test sections in the "once through" circuit (run 1)

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Two corrosion rate readings are provided for each system. Corrator 1 corresponds to fluid corrosivity prior to passage through the heater bank. Corrator 2 shows the effect of the 5° C temperature rise on the corrosion rates. An increase of 5° C does not appear to change corrosion rates of the chlorine dosed system, whereas a definite increase of approximately 0.5 mpy is apparent on Fig. 9 for the chlorine dioxide stream. Despite these temperature effects, higher corrosion rates are observed for the chlorine dosed system. Although there are variations of biocide concentration, particularly for the chlorine dioxide, the concentrations used are those necessary for microbial control, so that a comparison of the data is valid for the system under assessment. Chlorine dioxide corrosion rate readings appear to be independent of the biocide concentration used, over the range studied. A slight variation in corrosion rate is seen in the system using chlorine as the biocide, coinciding with the 0.5 to 4.0 mg/l step change in the biocide concentration. It is likely therefore, that the chlorine dosed unit is more sensitive to changes in biocide concentration.

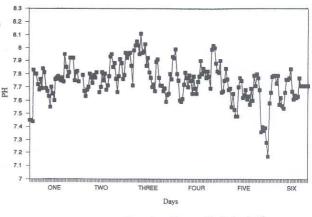
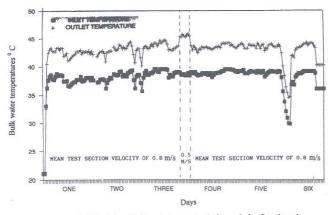
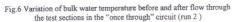
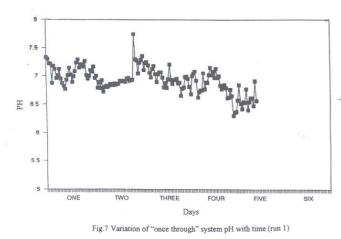
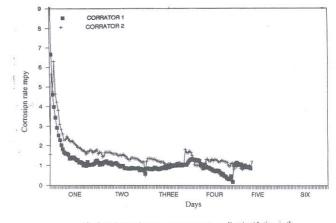


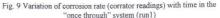
Fig.8 Variation of "once through" system pH with time (run2)











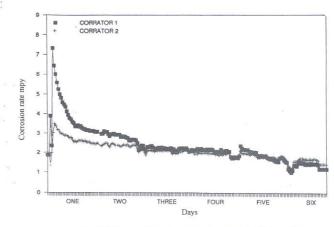


Fig. 10 Variation of corrosion rate (corrator readings) with time in the "once through" system (run2)

Comparison of the "Once Through" and Recirculating Systems

A separate test (run 3) was carried out to compare directly the operation of the "once through" and circulating systems. Unpassivated mild steel tubes were used in this experiment. The test sections were exposed to a water flow velocity of 0.5 m/s. One test section was enclosed in a larger diameter tube so that the water velocity was 0.2 m/s to provide some limited data on the effect of velocity on the results.

A temperature difference of approximately 7° C through the test sections was maintained in the experiment although some variation was apparent due to the variable duty of the main industrial system.

Table 1 provides typical data on the water quality of the pretreated "make up" water to the system and common to both cooling water circuits. The table indicates a reasonable control of pH was obtained. The free chlorine concentration residual of 0.15 to 2.5 mg/l, confirms that acceptable microbial control was obtained. Pretreatment included zinc phosphate corrosion protection and a dispersing agent.

Table 1 Daily analysis of the "make up" water

SAMPLE		MAKE-UP SUPPLY WATER						
DAY NUMBER	1	2	3	4	5	6		
Calcium H	· 351	312	312	354	350	336		
Total H	360	378	394	416	390	388		
Conductivity (micromhos/cm)	1000	960	990	960	890	910		
m-alkalinity	199	164	181	188	196	188		
рН (-)	7.7	7.1	7.3	7.8	7.3	7.2		
Free Chlorine	0.2	0.15	2.5	2.5	2.5	0.6		
O-Phos (F)	122	-	0.4	0.1	0.2	0.2		
O-Phos (U)		0.6	1.0	0.3	0.3	0.3		
T-Phos (F)	-	-	0.4	0.3	0.4	0.3		
T-Phos (U)	-	0.6	0.8	0.4	0.5	0.3		
Zinc (F)	-		0.05	0.07	0.07	0.06		
Zinc (U)	0.06	0.06	0.07	0.09	0.07	0.07		

Water Analysis values are expressed as mg/l unless

F represents 0.45 µm pore filtered sample. U represents unfiltered sample. H represents Hardness.

H represents Hardness. O-Phos represents Ortho-phosphate T-Phos represents Total-phosphate

The "make up" water data reveal high levels of calcium hardness, total hardness, conductivity and m-alkalinity which reflect a substantial salt content in the canal water. In contrast, relatively low concentrations of phosphates are recorded. These data are consistent with concentrations present in the majority of industrial water sources not subject to phosphate corrosion inhibited treatment or adjacent to agricultural land. Since the data on the total phosphate analysis includes ortho phosphate, it may be concluded that the more stable ortho form predominates. It has to be stated that a degree of experimental error is apparent in these data. Tables 2 and 3 give data for the two systems.

Table 2 Daily analysis of the "once through" system water

SAMPLE		ONCE THROUGH WATER							
DAY NUMBER	1	2	3	4	5	6			
Calcium H	181	193	290	320	290	268			
Total H	223	225	326	375	354	316			
Conductivity (micromhos/cm)	1290	1190	1090	1090	1090	1150			
m-alkalinity	38	28	89	87	94	52			
рН (-)	7.7	7.0	7.8	7.9	7.4	7.5			
Free Chlorine	0.1	0.1	0.15	0.25	0.05	0.25			
O-Phos (F)	-	-	3.5	3.2	2.8	4.6			
O-Phos (U)	-	14.2	5.0	4.4	4.2	5.8			
T-Phos (F)	-	-	2.4	6.5	7.5	9.0			
T-Phos (U)	-	22.0	4.1	10.5	11.4	15.5			
Zinc (F)	-	-	0.21	0.26	0.20	0.28			
Zinc (U)	0.54	0.40	0.20	0.32	0.29	0.34			

Water Analysis Values are expressed as mg/l unless stated.

F represents 0.45 µm pore filtered samples. U represents unfiltered sample. H represents Hardness. O-Phos represents Ortho-phosphate. T-Phos represents Total-phosphate.

Table 3. Daily analysis of the circulating circuit water

SAMPLE	COOLING TOWER							
DAY NUMBER	1	2	3	4	5	6		
Calcium H	389	651	810	705	590	580		
Total	-	-	780	810	705	690		
Conductivity (micromhos/cm)	1550	1780	1820	2500	1760	1650		
m-alkalinity	38	111	93	233	76	68		
рн (-)	7.1	8.2	8.1	8.9	7.8	7.8		
Free Chlorine	<0.1	<0.1	0	2.5	0	0		
O-Phos (F)	-	-	13.0	6.5	5.9	6.1		
O-Phos (U)	-	14.0	13.8	11.5	6.1	6.5		
T-Phos (F)		-	5.4	7.0	6.6	10.0		
T-Phos (U)	-	13.5	10.2	12.0	6.9	10.5		
Zinc (F)	-	-	0.80	0.50	0.37	0.48		
Zinc (U)	0.79	0.39	0.80	0.90	0.44	0.50		

Water Analysis values are expressed as mg/l unless stated

F represents 0.45 µm pore filtered sample. U represents unfiltered sample. H represents Hardness. 0-Phos represents Ortho-Phosphate. T-Phos represents Total-Phosphate.

The close agreement of calcium hardness, total hardness and conductivity measurements between "make up" and "once through" systems, indicates a very low concentration factor in the latter likely to be due to the negligible evaporation. It is also important to note that the calcium and total hardness analysis for "make up" water slightly exceed those of the "once through" system whereas, the reverse trend is exhibited by the conductivity measurements. This is generally accepted to be characteristic of calcium deposition. The reasonably close agreement of the two sets of data indicate that this effect is not pronounced.

Tables 2 and 3 illustrate that a greater degree of fluctuation is exhibited by the cooling tower water calcium hardness, conductivity, pH, m- alkalinity and zinc levels compared to the "make up" and "once through" water samples. This is likely caused by the variable evaporative losses due to changing heat loads and process operating conditions. The increases in calcium hardness and conductivity levels indicate that the salt concentration effects of cooling tower evaporation far outweigh salt depletion via the "make up" supply/ purge system between days 1 and 4 of the test. The cooling water purge rate was increased on day 4 to stabilise the situation.

The calcium hardness and conductivity data between days 3 and 4 for the recirculating water system exhibit a contradictory trend. The rise in conductivity denotes the continued concentration of all dissolved salts, including calcium. The simultaneous fall in calcium hardness signifies the initiation of calcium deposition, the conductivity being maintained by the remaining dissolved salts, such as sodium, zinc, aluminium, and magnesium. The contribution of magnesium salts is probably responsible for the less dramatic fluctuation of the total hardness values (the total hardness including the combined concentration of available calcium and magnesium).

The onset of calcium deposition in the cooling tower test section coincides with an unusually high pH of 8.9 on day 4. Such a value is probably due to the effect of system concentration and the relatively high "make up" water pH of 7.8. The solubility of the various metal ions, particularly calcium ions, decreases with an increase in alkalinity. It is therefore likely that the combination of high pH and salt concentration initiates the deposition of calcium salts. The increase in purge rate on day 4 produced a decrease in pH and a further fall in the calcium concentration on days 5 and 6. The fall of the calcium content is not considered to be due to deposition because of the reduction in conductivity also observed.

Fluctuations in calcium hardness and conductivity in the cooling tower circuit, can be seen to be followed by the zinc and phosphate analysis in Table 3. The filtered zinc concentration follows the calcium hardness concentration for days 3 to 5 i.e. a reduction is observed prior to increasing the purge rate. This may be due the possibility of zinc deposition which would be detrimental, due to the accompanying reduced effectiveness of the corrosion inhibition. It is likely that the "reacted" zinc is not bound to the surface in this instance, because unfiltered analysis results increase till day 4 when the increased purge was applied. The levels of filtered and unfiltered zinc analysis are reasonably similar after the purge increase, indicating a high degree of solubility and therefore maximum inhibition effectiveness. A comparison with the "once through" system data confirms the consistent maintenance of zinc solubility under conditions of the lower concentration factor and pH.

The ortho phosphate data exhibit identical trends to the zinc where decreases in filtered ortho phosphate precede the results of the unfiltered analysis by one day. The formation of zinc phosphate and particularly calcium phosphate, are common reactions in cooling water circuits. The results of the calcium hardness, zinc and ortho phosphate analysis, as well as visual observation of the uniform pale cream deposit on the test sections of both systems, suggest the possibility of such a process.

In contrast, in the recirculating system the analysis of the total phosphate is not consistent with the trends of the ortho phosphate concentrations. A gradual decrease in the concentrations is noted in the unfiltered total phosphate analysis from day 2, which resembles the magnitude and trend of the ortho phosphate from the unfiltered samples, suggesting that most of the additive exists in the ortho phosphate form. The total phosphate analysis of the filtered sample shows an increase from days 3 to 6 and the concentrations are lower than the corresponding ortho phosphate data. Such a phenomenon is also apparent for the "once through" circuit, but these findings are of course, not theoretically possible. It is likely that these anomalies in the data are due to experimental error.

The controlled deposition of calcium salts, such as calcium phosphate, is commonly practised in corrosion inhibition programmes, including the additive used in this work. The deposition is due to the inverse solubility and stability of calcium compounds. The effect is to promote the preferential "scaling" of the hotter heat transfer surfaces where the beneficial properties of the corrosion inhibitor are most needed! The prevention of excessive calcium deposition is of paramount importance however, so that adequate heat transfer can be maintained. The combination of high operating temperatures and high calcium hardness and conductivity levels in the "make up" water supply necessitate the use of a chemical dispersant in conjunction with the zinc phosphate treatment.

Considerable difficulty was encountered in maintaining free chlorine concentrations within the required range of 0.2 to 0.4 mg/l in the recirculating water. It is possible that the incoming "make up" water was of variable quality that caused the difficulty, as indicated by the figures contained in Tables 1 and 2. The chlorine demand is influenced by the microbial content of the incoming water supply.

Table 4. Microbial analysis (run3)

		ISOLATED SPECIES (cells/ml)						
SAMPLE SOURCE	DAY NUMBER	PSEUDOMONAS SPECIES	NON- TROUBLESOME TYPES	AEROBIC SPORE FORMING	TOTAL			
MU	3	-	-	-	<10			
	5	-	-	-	<10			
PCT	3	3850	92050	100	96000			
	5	-	-	20	20			
OT	3	-	20	20	40			
	5	-	-	20	20			

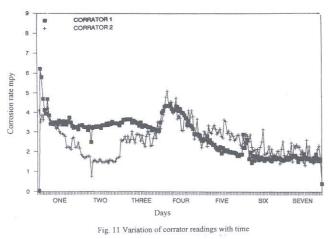
Table 4 suggests that although chlorine levels in the "once through" system are low, the extent of the microbial contamination is far less than for the recirculating circuit. It is noticeable that cell counts in the recirculating system decrease dramatically after the high level treatment in days 3 to 5. It is evident that the constant biocide dosing and the low ambient temperatures of the "make up" water yield the lowest cell count.

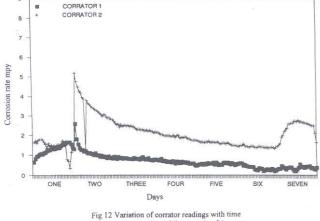
In-situ corrosion readings for the two systems are presented on Figs. 11 and 12. Both sets of data gradually decrease with time although the corrosion rates show more fluctuation in the cooling tower circuit than the readings for the "once through" system. Corrator 1 and 2 figures show the corrosion rates before and after flow through the test sections. Fig. 12 demonstrates a definite temperature dependence on the corrosion rates in the "once through" system, where a 5° C rise results in a doubling of corrosion rate. It is also interesting that the unexpected increase in the corrator 2 rates between days 6 and7 corresponds exactly with a 3° C increase in the exit temperatures on days 6 and 7.

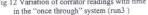
A similar temperature dependency is not apparent in the data from the recirculating circuit however the readings from corrators 1 and 2 approximate the corrator 2 data on the "once through" system between days 6 and 7.

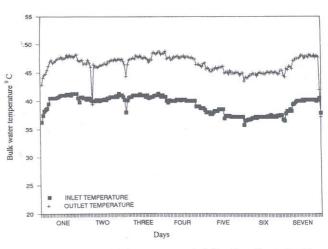
Corrators 1 and 2 on the cooling tower circuit give corrosion rates that are highest between days 3 and 4. It is significant that this coincides with the highest conductivity data in Table 1, suggesting that the dissolved salt concentrations strongly influence the corrosion rate. It is likely that the concentrations of certain ions, such as iron are the main contributors to this effect.

Table 5 includes data on tube corosion and deposition rates for the 7 test surfaces. The exact bulk water temperature in each tube is not known, but a 5° C temperature difference between the inlet and the outlet is apparent for both systems from the data contained on Figs. 13 and 14.











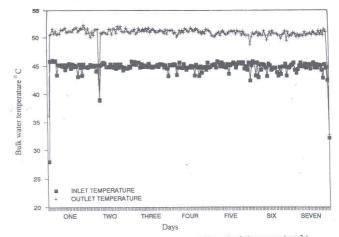


Fig. 14 Change in bulk water temperature in the recirculating system (run 3)

Table 5 Deposition rates of deposit elements in both systems.

SYSTEM TYPE	TUBE	WEIGHT LOSS AT 800°C (% w/w)	ELEMENTAL DEPOSITION RATES (mg/cm ² yr)						
	POSITION		Iron	Calcium	Phosphorous	Zinc	Silicon	Sulphur	
	1	20.7	54.86	4.91	4.04	3.87	1.39	1.01	
60	2	7.2	25.98	1.43	1.41	0.84	0.37	0.17	
Recirculating	3	8.5	21.58	1.69	1.35	0.88	0.33	0.33	
Ino	4	14.0	27.85	5.43	2.13	1.35	0.55	1.48	
eci	5	11.2	27.76	2.48	1.91	1.26	0.50	0.48	
8	6	8.9	26.18	2.04	1.80	1.18	0.45	0.28	
	:7	10.9	25.88	2.86	2,21	1.32	0.40	0.60	
"Once through"	1	23.3	92.97	10.84	12.08	1.00	1.46	1.36	
	2	25.9	114.68	13.38	12.07	1.19	1.50	1.91	
	3	15.1	64.46	8.17	6.97	0.79	0.99	1.27	
	4	20.8	95.64	9.36	10.50	0.98	1.14	0.99	
	5	34.6	124.26	2.09	9.67	0.97	0.79	0.10	
	6	20.9	80.68	6.84	9.50	0.72	1.17	0.58	
	7	55.4	139.43	27.28	21.06	1.46	2.38	5.17	

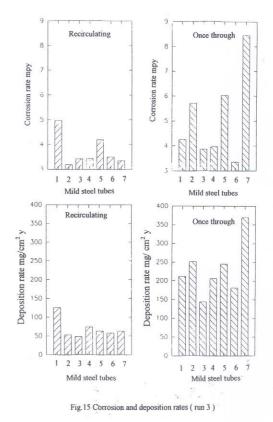
The influence of temperature on deposition and corrosion processes is not well defined by the results given on Fig.15 in contrast to the data from the corrators. From the figure it is clear that deposition and corrosion rates for the cooling tower circuit test section 1, are substantially higher than the other sections despite exposure to the lowest bulk water temperature. The difference may be due to the lower water velocity of 0.2 m/s compared with the velocity in all the other tubes. Comparison of the results in the two systems indicates that the "once through" deposition and corrosion rates are much higher for the majority of the test sections. This is an encouraging result since the bulk water temperatures are approximately 5° C higher than in the "once through" system.

Table 5 gives the elemental analysis of deposits taken from the test sections in the two systems. It may be seen that higher deposition occurs in the "once through" system, for all the elements except zinc. Although the controlled deposition of some compounds such as those containing calcium and phosphate is beneficial, the data in Table 5 together with visual observation suggest, that excessive deposition on the test surfaces in the "once through" system occurred.

The deposition of iron on all surfaces is greater than any of the other elements analysed, and reflects the significant amount of corosion products. The trends follow the corrosion rate results on Fig 15. This is also encouraging since it indicates that the iron content in the deposits agree closely with the test section corrosion rates assessed by direct weighing before and after the deposits had been removed at the conclusion of the tests.

Deposition rates of calcium are substantially lower than iron. Significant amounts of phosphate and zinc are also apparent on both sets of test sections. It is probable that the presence of both elements is the result of the treatment using zinc phosphate chemicals, as the "make up" water contains low concentrations. Silicon and sulphur are not present in the treatment additives. It is likely therefore that they originate in the water supply from the canal.

An assessment of the organic content of the deposits was made and the results are presented in Table 5 as the weight loss at 800° C. The organic material includes microbial matter, as well as organic residues from the canal water.



CONCLUSIONS

The following summarises the results of this study:

- 1. A tighter control of biocide concentration could be obtained by a chlorine based programme 0.5 to 4.5 mg/l compared to the use of chlorine dioxide in the concentration range of 0 to 0.57 mg/l.
- 2. Higher corrosion rates of 1.5 mpy were obtained for the chlorine dosed system compared with 1.0 mpy for the chlorine dioxide treatment. A change of chlorine concentration from 0.5 to 4.5 mg/l resulted in an increase in corrosion rate of 0.5 mpy. There was no apparent increase of corrosion when the chlorine dioxide concentration was raised from 0.1 to 0.57 mg/l.
- 3. An increase of temperature from 38 to 43° C did not appear to influence the corrosion rate for the chlorine dosed system in the concentration range 0.5 to 4.5 mg/l. For the identical temperature range a 0.5 mpy increase in corrosion rate was observed for the chlorine dioxide dosed system in the concentration range of 0.1 to 0.57 mg/l.
- 4. Higher deposition and corrosion rates were observed in the "once through" system compared to the recirculating circuit despite a 5° C lower operating temperature. Deposition rates of 144 to 370 and 48 to 126 mg/cm² were obtained for the "once through" and recirculating systems respectively. The corresponding corrosion rates were 3.35 to 8.45 and 3.2 to 4.95 mpy for the "once through" and recirculating system respectively.

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5. In the cooling tower circuit deposition rates of 126 and 48 to 76 mg/cm²y at 0.2 and 0.5 m/s respectively were obtained demonstrating the influence of velocity on the deposition process.