Reclaimed water for producing 18-megohm-cm DI water for printed circuit board manufacturing

by:
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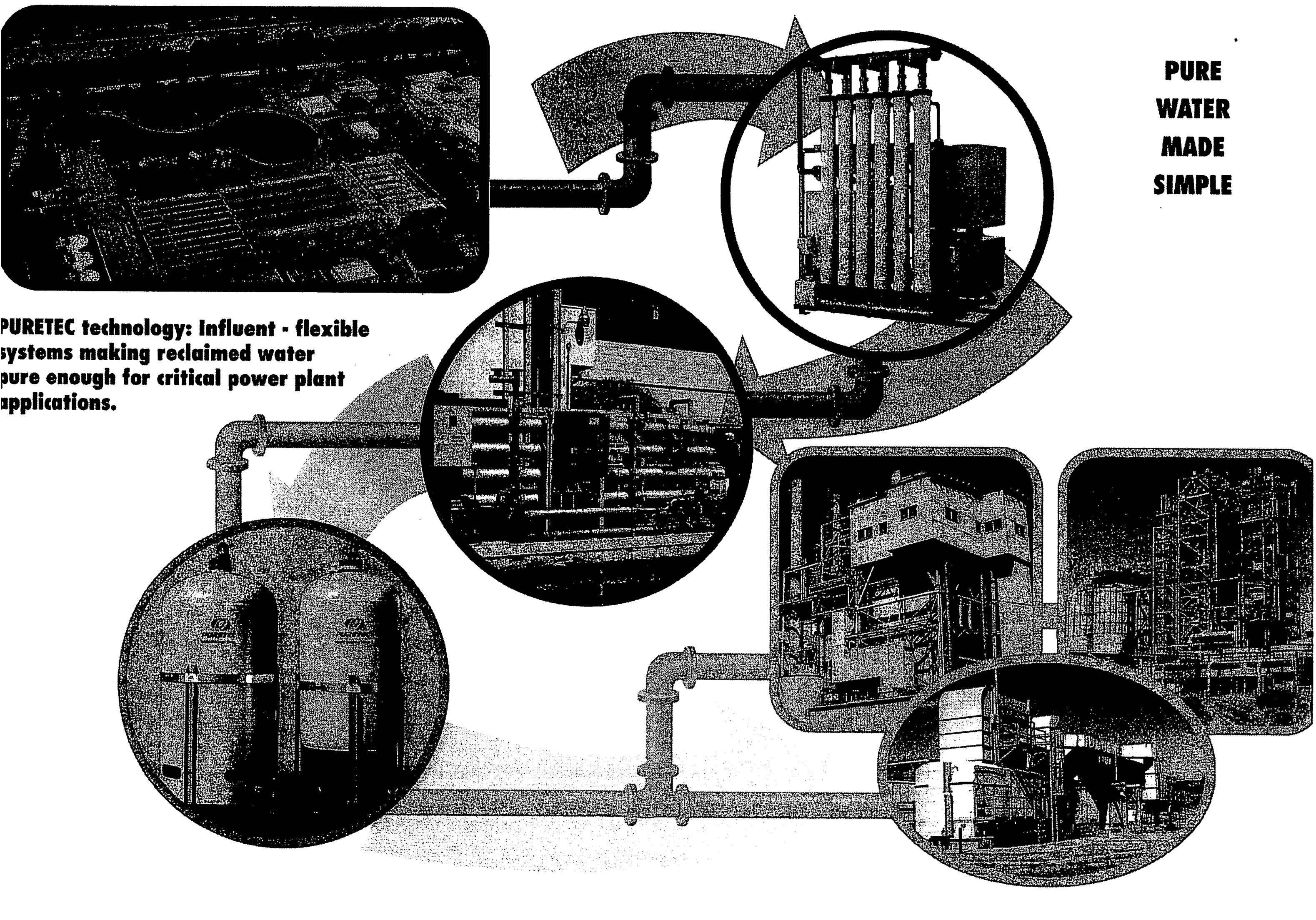

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WATER REUSE

RECLAIMED WATER FOR PRODUCING 18-MEGOHM-CM DI WATER FOR PRINTED CIRCUIT BOARD MANUFACTURING

In February 1997, a conventional reverse osmosis/deionization (RO-DI) system was installed for treating San Diego City potable water for an electronics firm with a large printed circuit board facility. The RO-DI system has operated for three years, providing an uninterrupted supply of 18-megohm-cm quality DI water as process water for the manufacturer. During the first quarter of 2000, the electronics firm finalized its negotiation with the City of San Diego for the use of the Title 22 reclaimed water, as part of the municipality's "Water for Industry" program.

The program was initiated to reduce the use of potable water, by encouraging industrial uses of reclaimed water. The pretreatment system for the RO-DI system required considerable modifications to accommodate quality standards needed for industry. The RO-DI system has been operating for the past 15 months, producing both desired quantity and quality (18 megohm-cm) DI water for the manufacturing facility. This article discusses modifications to the pretreatment system to accommodate characteristics of reclaimed water, operating data pertaining to pretreatment and the RO-DI system, and comments on the future use reclaimed water as an alternative source in other industrial applications.

Title 22 Water

Title 22 is a code of California regulations that includes the treatment requirements for recycled water that will be used for irrigation and industrial purposes. In order to comply with the regulations, domestic wastewater must be treated with the following processes:

- Oxidation to stabilize organic matter by adding oxygen.
- Coagulation to join particles together in the water to form lumps called "floc" making them easier to remove.
- Filtration, which cleanses the water further by passing the water through three different types of filters to remove the "floc".
- Chlorination, which disinfects the water by killing bacteria.

As a result of the Title 22 requirements, recycled water is odorless, colorless, and it meets the requirements for human contact. Regulations, however, do not permit human consumption (1).

Experience with City Water

In January 1997, the equipment supplier[a] entered into an agreement with the electronics firm to provide an RO-DI system producing 120 gallons per minute (gpm) flow and 2 megohm-cm quality DI water for the manufacturing facility. The pretreatment system consisted of automatic softeners with brine tank, activated carbon units and 5-micron (µm) cartridge filters. The RO system uses six pressure vessels, each with six 8-inch elements in a 4:2 array. The ion-exchange (DI) system included four mixed-bed portable units, two parallel trains, and two in series in each train.

During three years of operation, the performance of the RO-DI system was remotely monitored through the supervisory control and data acquisition (SCADA) system and the normal maintenance was provided. It included occasional backwash of carbon units, changing of 5-µm cartridge filters and the calibration of instruments on regular basis. The pretreatment was very effective in maintaining the silt density index (SDI) in the range of 2.5 and 3.5 to the RO system with the SDI values in the incoming city water ranging from 4.0 to 5.5. The total dissolved solids (TDS) measurements varied between 450 mg/L to 500 mg/L and the RO permeate TDS ranged between 7.0 milligrams per liter (mg/L) to 9.0 mg/L. The system produced 120 gpm permeate flow and the DI with the quality of 18 megohm-cm water without interruption.

Use of Reclaimed Water

Background on the "Water for Industry" program. With ever increasing demand for potable supply, the City of

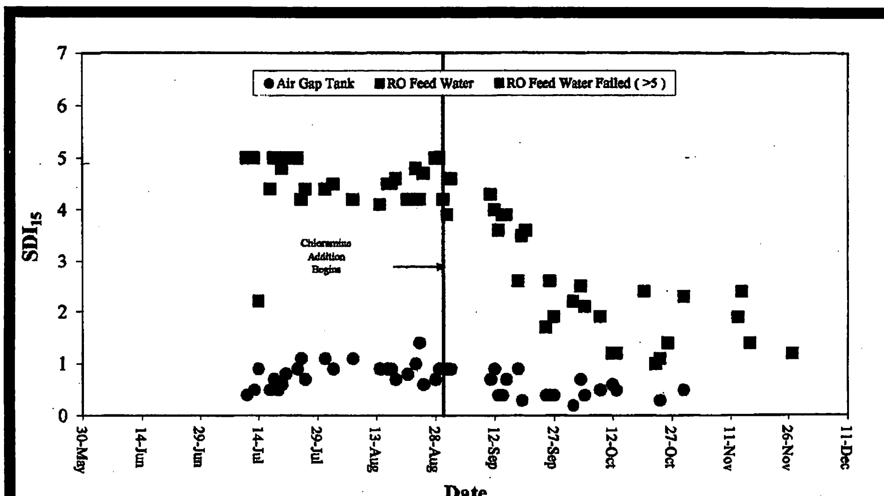

Figure 1. A comparison of SDI_{15} readings for reclaimed water.

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TABLE A
Typical Reclaimed and City Water Compositions

Constituent	Reclaimed Water	City Water
Calcium (mg/L)	57	59.20
Magnesium (mg/L)	23	28.15
Sodium (mg/L)	147	71.65
Bicarbonate (mg/L)	48	119.6
Chloride (mg/L)	187	81.00
Sulfate (mg/L)	226	200.00
Silica (mg/L)	17.1	8.6
Nitrate (mg/L)	17.5	4.4
Other		
Ph	7.4	7.1
*TOC (mg/L)	8.8	3

San Diego initiated a program to promote replacement of potable water in industrial applications with reclaimed water through its "Water for Industry" program. Local industries were reluctant to use reclaimed water because of lack of experience in its use. Therefore, it became necessary to demonstrate the use of reclaimed water as a potential source for replacing potable water on an industrial site. For Phase I of the program, an electronics firm was selected as a demonstration facility to produce high-purity water from reclaimed water for the circuit board manufacturing facility.

Initial review of the characteristics of the reclaimed water indicated that in addition to being high in TDS it was also high in TOC. Further, the SDI tests to determine its suitability for the RO application, revealed that the SDI values at 5- and 10-minute intervals were very high and the 15-minute test (SDI_{15}) could not be completed due to plugging of the 0.45-µm pad. Detailed analysis of the reclaimed water and the potable water were conducted by San Diego (2). However, typical water analysis of reclaimed water and municipal water is shown in Table A. In order to render the reclaimed water qualitatively as good as the municipal water that entered the existing water treatment facility, San Diego conducted pilot tests. The tests included use of microfiltration, Jel Cleer, and Macrolite, followed by activated carbon. The goal was to establish appropriate pretreatment conducive to the existing RO-DI system. Microfiltration was selected as an effective means of pretreating the reclaimed water in producing required low SDI_{15} pretreated water for the existing RO system.

In the fall of 1999, the electronics firm signed an agreement with the city for the use of reclaimed water produced from its nearby North City water treatment facility. The pact required the city to provide reclaimed water not to exceed 1,000 mg/L of TDS and 10 mg/L of total chlorine leaving the treatment facility.

In the summer of 2000, Pall Corp.'s Microza microfiltration system was installed and commissioned. With a nominal pore size of 0.1 µm, the microfiltration membranes remove particulate material, including protozoa and bacteria. The microfiltration system consists of 20, 6-inch diameter modules that meet the flow requirement of 215 gpm of filtrate. Details of engineering specifications are provided in Reference 2.

Please note that using an air gap design, to avoid cross connections, municipal potable supply was incorporated as an alternate source in case of reclaimed water system failure. The microfiltration system produced a filtered water with an average turbidity of 0.03 Nephelometric Turbidity Units (NTU) during the start up and was continuously maintained with similar turbidity values.

Reclaimed Water Characteristics:
During the start up and commissioning of the microfiltration system, reclaimed water quality was monitored for key parameters. The TDS ranged 693 mg/L to 828 mg/L, total chlorine ranged 0.5 mg/L to 8.0 mg/L and the pH ranged between 7.1 and 7.5. Samples of reclaimed and city water were analyzed for major constituents and the results are shown in Table A.

Pretreatment System Modifications
Reviewing the initial data, it became apparent that the existing pretreatment system (auto soft granulated activated carbon [GAC] and 4-µm filter) needed to be modified to accommodate the fluctuating total chlorine content. Simultaneously, there was also a need to reduce the total volume of wastewater from the manufacturing facility. With these objectives in mind, automatic softeners were replaced with an antiscalant feed system. Sodium bisulfate feed was incorporated to neutralize the chlorine and activated carbon units were left as they were, to be used as an added insurance in case of a chlorine surge. With these modifications in place, initial operating data was gathered with the old RO elements that have been operating approximately 30 months without cleaning. It should also be pointed out that the carbon in the GAC units was changed and rinsed thoroughly prior to placing it into service.

For the first two months, the pretreatment data was monitored very closely by the city and the equipment supplier[a]. The results were in close agreement. The SDI_{15} data were collected from an air-gap tank (representing microfiltration effluent) and the RO feedwater after the 5-µm cartridge filters for several months. Results are shown in Figure 1. The findings indicated that the SDI_{15} values varied from 0.5 to 1.5 from the microfiltration effluent. Whereas, the SDI_{15} for the RO feed remained between 4.0 and 5.0 and exceeded the value of 5 on several occasions. Total chlorine data was also collected for the same period and are shown in Figure 2.

The data indicated that there was a wide variation in the total chlorine content ranging from 0.5 mg/L to 8 mg/L. Variations in total chlorine residuals were abrupt and values varied from 1 mg/L to 8 mg/L within a two-day period. In spite of abrupt changes in the total chlorine residuals, sodium bisulfite feed was able to cope with fluctuation and did not allow any chlorine to pass through the activate carbon units. However, the RO elements, being old, started to show higher pressure drops and the elements were cleaned in order to reduce pressure drops and gain permeate flow. The results were not encouraging. Details of the data are also shown in Reference 2.

Higher SDI_{15} values observed in the RO feed with the injection of sodium

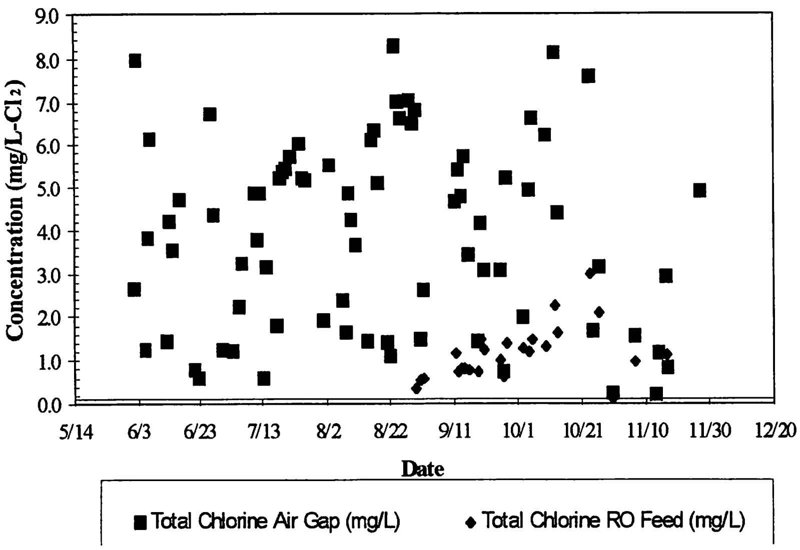

Figure 2. Total chlorine residuals for reclaimed water.

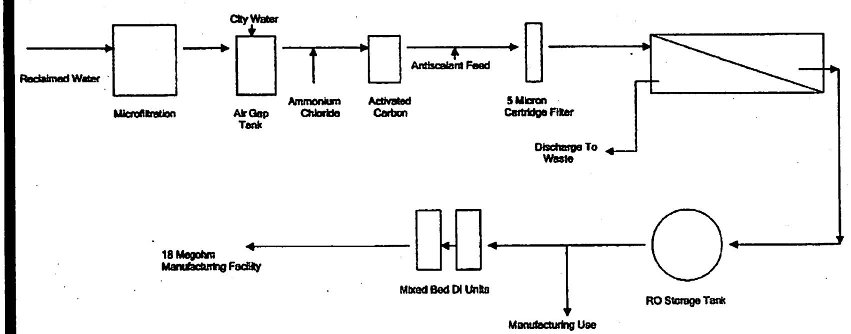

Figure 3. A simplified process flow diagram.

bisulfite and the activate carbon units as pretreatment were primarily attributed to slough age of sub-micron particles of carbon in the effluent as evidenced by the color of micron cartridge filters, and the suspected biological activity in absence of any chlorine residuals entering the activated carbon. Based on the above data, it was postulated that in order to control the bioactivity, the pretreatment system need to be modified so that it could allow chlorine to pass through GAC.

Conversion of Chlorine to Chloramine

In natural waters, inorganic chloramines are formed by reaction of chlorine with free ammonia occurring in potable and wastewaters. The oxidation potential of free available chlorine is much higher then that of chloramines and varies with pH. The oxidation potential of chloramine is much lower than that of free chlorine. Therefore, the germicidal efficiency of chloramines is considerably much lower than that of free chlorine. The reaction rate is almost instantaneous, based on reaction rates calculated for a 99% conversion of a free chlorine to a monochloramine at 25 °C. That is based on a molar ratio of 0.2×10^{-3} mol/ hypochlorous acid (HOCl) and 1.0×10^{-3} mol of ammonia (NH_3), between pH 7. and 8.3 the reaction is almost instantaneous. Details are provided in Reference 3.

With the above chloramine chemistry in mind, it was concluded to introduce ammonium chloride in the ratio of chlorine to ammonia of 1:5. However, prior to implementing the conversion, several concerns were expressed as to the impact of chloramine on RO elements, on the RO permeate quality, and subsequent affect on the printed circuit boards and the ion-exchange resins. After several internal discussions with all parties involved, including membrane manufacturers, the following consensus was reached, as summarized here.

1. The presence of chloramine in the RO feed below 5 mg/L may not have a deterrent effect on the elements – oxidative degradation. In fact, chloramine being a mild oxidant may help in controlling bioactivity in the elements.
2. Chloramine being partially rejected by the elements, RO permeate will contain 40% to 50% of chloramines compared to chloramines concentration in the RO feed, and it will be absorbed by the ion-exchange resins.
3. Chloramine being a mild oxidant compared to chlorine, its impact on the ion-exchange resins was considered minimal.

Because of the fluctuating total chlorine content of the reclaimed water, ammonium chloride if introduced in excess beyond the stochiometric requirements, would be rejected effectively by the RO membranes and cause no harm.

Chloramines and Activated Carbon

The use of activated carbon for the removal of free chlorine is a well-established means of dechlorination. The reaction of free chlorine with activated carbon is instantaneous. In contrast, the absorption of chloramines by the activated carbon requires considerable contact time for complete removal.

In view of the above, the following modifications were incorporated in the pretreatment system. Sodium bisulfite feed was replaced with ammonium chloride feed and the activated carbon units with their new carbon were left untouched. Initially, the RO-DI system was operated with old RO elements to stabilize the pretreatment system. For a simplified process flow diagram, see Figure 3.

During the first week of operation after the above modifications, the SDI_{15} in the RO feedwater ranged between 4 to 5, while the effluent from microfiltration unit produced an SDI_{15} value of 1.0. With continued operation, the SDI_{15} values gradually started to drop. Total chlorine residuals in the effluent of microfiltration ranged 1 mg/L to 9 mg/L and the chlorine residuals in the RO feed averaged below 1 mg/L, indicating the carbon units were effectively removing the chloramines. With the gradual decreasing trend in the SDI_{15} values in the RO feed, combined with the difficulty in maintaining the required RO permeate flow with the old elements, it was time to replace the elements in the RO system.

In consultations with the membrane

TABLE B

Date	Temp °F	Pressure Feed Press.	Conc. Press.	ΔP	TDS Feed	TDS Perm	SDI	Total Chlorine Residual Chloramine Into GAC	Total Chlorine Residual Chloramine Into RO
2000									
09/25-10/01	81	142	110	32	788	13.5	2.1	5.75	0.4
10/02-10/10	80	146	114	32	811	12.9	2.48	7.23	1.2
10/11-10/21	78	148	113	35	1156	14.4	1.7	17.8	4
10/23-10/26	78	147	114	33	843	12.66	1.4	4.33	2
11/02-11/28	73.5	155	121	34	840	13	2	3.4	2.75
12/01-12/26	71.5	167	131	36	884	14.44	1.9	5.5	3.6
2001									
01/02-01/30	68	176	140	36	850	12	1.54	3.38	2
02/02-03/02	66.25	179	142	37	970	13	1.4	3.71	3
03/02-03/20	66	178	140	38	1018	13	1.7	4.33	3.33
04/04-04/24	70.5	170	133	37	964	14	1.55	3.8	2.6
05/02-05/22	73.5	160	124	36	975	14	1.75	6.55	3.25
06/05-06/26	76	149	108	40	850	16	1.82	5.2	3.5
07/03-07/24	80	141	105	36	818	16.5	1.29	5.75	3.25
08/01-08/28	81	140	99	41	825	18	2.12	3	2.4
09/05-09/25	82	140	98	42	800	17.87	3.35	5.25	3.3
10/02-10/17	76	146	103	43	875	14	3.59	5.5	2.5
10/25	78	154	106	48	800	13.5	4.6	5	3
10/30	76	162	110	52	850	12	2.8	7	3
11/07-11/27	73.5	170	115	55	855	12	4.35	2	2

manufacturers, Hydranautics CPA3, 8-inch elements were selected due to their higher surface area and its ability to withstand up to 4 mg/L to 5 mg/L of chloramines in the RO feed. The RO elements were replaced in September 2000.

Results and Discussion

Detailed operating data was collected on the RO-DI system for a period of 15 months after the installation of new RO elements with the pretreatment stabilized beginning in September 2000 through November 2001. Data for the key operating parameters are shown in Table B and are plotted in Figures 4 and 5. Note that the data grouped together each month are the averages of four to five sets of readings. Other data, not shown in the table, along with the highs and lows where warranted will be mentioned in the discussions/comments. Please note that the reclaimed water delivered to the manufacturing facility from the treatment facility should contain no more than 1,000 mg/L of TDS and 10 mg/L of total chlorine. Further the electronics firm was guaranteed to receive 120 gpm of RO permeate operating at 75% recovery.

TDS. Reclaimed water TDS concentration varied an average of between 788 mg/L and 1,018 mg/L. Most of the values were around 800 mg/L to 825 mg/L. Instantaneous increases in TDS were recorded as high as 1,156 mg/L. The TDS variations were attributed to fluctuations in the treatment processes at wastewater treatment facility.

SDI_{15} – effectiveness of pretreatment. The SDI_{15} values were taken of the inlet of the RO feed after the 5-µm cartridge filter housing. The effluent from microfiltration showed turbidity—0.04 to 0.05 NTU and the SDI_{15} values ranged between 0.8 to 1.0. However, with the addition of ammonium chloride and the activated carbon, after the 5-µm filter RO feed showed a much higher SDI_{15} values, indicating some particulate contribution from the activated carbon units.

Upon reviewing the SDI_{15} data of the RO feed, the SDI_{15} values have been fairly low, ranging from 1.2 to 2.5 for the first year of operation, most of the values averaged around 1.7. Although these values are high considering, the SDI_{15} from the microfiltration effluent, they are still low compared to the original SDI_{15} values of the reclaimed water without any pretreatment. It should also be pointed out that the average SDI_{15} values observed for the reclaimed water 1.6 to 1.7 were considerably lower than that of the potable water with old pretreatment softeners/GAC in place. The SDI_{15} values averaged between 2.5 to 3 and at times 4.0.

Total chlorine/chloramine. The total chlorine residual data gathered during the entire period showed a significant variation in its concentration leaving the microfiltration unit. The total chlorine residual entering the microfiltration varied from less than 1.0 mg/L to 9 mg/L within the period of a day. At one time for a two-day period, the total chlorine exceeded 20+ mg/L. This fluctuation was attributed to a nitrification upset at the municipal treatment facility. It should be noted, according to the operating personnel at the facility, that the total chlorine concentration will vary depending on the reclaimed water consumption for irrigation and other public uses along the way from treatment facility to electronic firm. It should also be noted that the ammonium chloride feed system was adjusted to cover up to 10 mg/L of total chlorine.

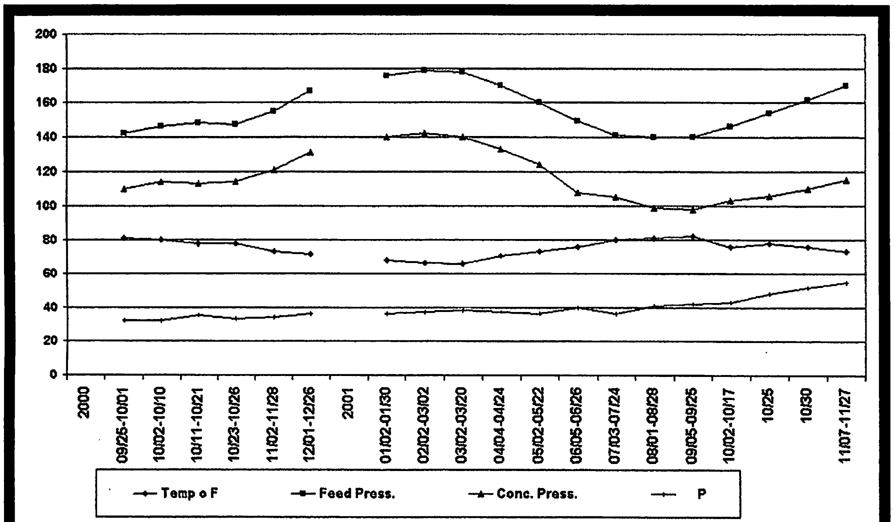

Figure 4. Plots of key operating data from the treatment system.

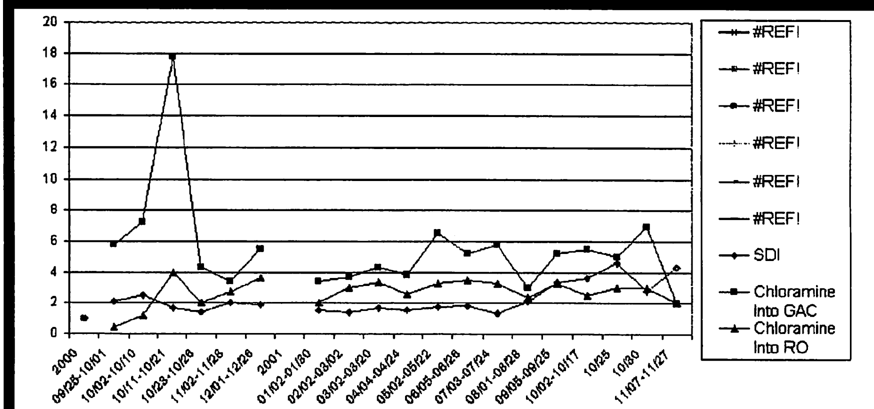

Figure 5. Plots of key operating data from the treatment system.

Effectiveness of chloramine reduction by activated carbon units. Overall data of chloramine reduction through the activated carbon units show that approximately 50% of chloramines were removed in the activated carbon unit, allowing 50% of the total chloramines to enter the RO unit. Initially, during the first two-month period, chloramines removal efficiency was much higher, probably due to the carbon being new. However with continued operation removal efficiency dropped significantly. In some instances, as low as 20% to 40% removal efficiency. During the entire 14 months of operation, the RO elements were never exposed to a chloramine concentration of exceeding the limit of 5 mg/L set forth by the membrane manufacturer.

In October/November 2001, the SDI_{15} values increased in the inlet of the RO in spite of the chloramines residual 2.0 to 3.0 mg/L in the RO feed. With this increase in the SDI_{15} values, there was a corresponding increase in the RO feed pressure to maintain the required permeate flow of 120 gpm. This increased pressure drop observed in recent months is most probably due to increased bioactivity in the carbon units. In addition, for the past months, the manufacturing facility has experienced frequent shutdowns for extended periods (3 to 4 days on occasions), providing a conducive environment for bioactivity. Further, because the manufacturing facility is the primary user of reclaimed water from the main supply line, that water tends to stagnate in the transfer line, thus allowing dissipation of chlorine and promoting further bioactivity.

Operating pressures. With new elements in the RO system, initially the RO feed pressure was 142 psig and the concentrate pressure was 110 psig with a pressure differential of 32 psig. With continued operation for the next 2 months, no significant difference in the RO feed and concentrate pressure was observed. It should also be noted that during the first two-month period that the water temperature dropped from 82 °F to 78 °F, requiring the increase in RO feed pressure from 142 to 147 psig. As the winter progressed till end of March with a continued drop in the temperature from 78 °F to 66 °F, there was a corresponding increase in feed pressure from 147 to 178 psig to maintain the required 120 gpm RO permeate flow. During the same period, the pressure differential between the RO feed and the concentrate feed increased from 32 psig to 38 psig, which was considered normal. For the next 6-month period (April through September), which had a steady rise in feed temperature from 70.5 °F to 81 °F, the operating feed pressure dropped from 170 psig to 140 psig, and the pressure differential averaged 38 psig. However, in October and November 2001, the RO feed pressure had to be increased to maintain the desired permeate flow. The pressure differential continued to increase, suggesting a need to clean the membranes.

Permeate TDS. During the entire period, in spite of variations in the TDS content, the RO permeate TDS averaged 14 mg/L, with the following low and high values of 12 mg/L and 18 mg/L.

DI quality. The RO permeate, containing an average 14 mg/L TDS, is deionized using portable mixed-bed units of two trains, each operating two units in series. The DI tanks have consistently produced 18 megohm-cm DI water for the manufacturing facility.

In summary, the RO-DI system over the past 14 months has operated well providing an uninterrupted supply of 18 megohm DI water quality for the manufacturing facility treating reclaimed Title 22 water. The above operating experience and data gathered will help in future applications using the reclaimed water. However, it should be pointed out that the long-term performance of RO membranes and the impact of DI water quality on high-density microchips needs further study.

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ments and confirming initial data. Additional thanks to E. Kingston and J. Russell for collecting the data and maintaining the RO-DI system.■

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Endnote

[a]Puretec Industrial Water of Ventura, Calif., supplied the treatment equipment.

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