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Technical Memorandum No. 14

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Subject: Corrosivity Testing of Desalinated Water and Comparison to Water Supplies of Marin Municipal Water District
MMWD Seawater Desalination Pilot Program
K/J 0468029

Background

As a part of the overall Desalination Pilot Plant Program a laboratory study was conducted to assess the relative corrosivity of conditioned reverse osmosis (RO) treated water as compared to that of the Marin Municipal Water District's (MMWD) Central Marin Reservoirs and Russian River surface source water supplies.

There are several aspects of the corrosivity of the water that are of importance which include (Ryder 1990):

- Health effects – compliance with the Lead and Copper Rule (LCR) of the Federal and State Safe Drinking Water Act Regulations:
- Aesthetic – Discoloration of distributed water as primarily related to leaching of iron from distribution pipes causing red water or of copper laterals and consumer plumbing systems causing blue water and sometimes a metallic taste to the water.
- Economic – Accelerated corrosion and pitting of iron and steel distribution pipes or storage tanks, and pitting of copper piping of consumer systems, and increased interior roughness causing capacity loss or higher pumping costs.
- Environmental – Minimization of toxic heavy metals in wastewater discharged to Marin Wastewater Treatment Plants with subsequent discharge to the San Francisco Bay from corrosion and leaching of copper, lead, nickel, zinc, chromium, etc. primarily from consumer plumbing systems.

MMWD has had an ongoing effective corrosion control program for many years for internal and external corrosion of distribution piping, tanks, etc. as well as consumer plumbing systems. This is achieved by both pH adjustment and addition of a zinc orthophosphate corrosion inhibitor to the treated or delivered water.

LCR testing reported in the 2005 Water Quality Report showed a range for copper of 0 – 0.21 mg/l with an average of 90th percentile of 0.12 mg/l, which is less than ten percent of the allowable action level of 1.3 mg/l (MMWD 2005).

The lead testing indicated a range of 0 to 22 µg/l, with a 90th percentile of 6 µg/l, which is less than half of the 15 µg/l allowable action level of the LCR.

There are also few reported instances of discoloration of water or aggravated, pitting of distribution or corrosion plumbing system pipes due to internal corrosion within the service area of MMWD. Similarly, the concentration of heavy metals – copper, due to water piping internal corrosion is not now a reported difficulty at the County's wastewater treatment plants. However, there were past difficulties of excessive copper at the Northern Marin Wastewater Treatment Plants until the Sonoma County Water Agency increased the pH in Sonoma Aqueduct Water to over 8.0 about ten years ago.

The relative benign internal corrosion conditions of the MMWD's present water supplies are an important factor to consider in the prospective use of desalinated water, so that it will not significantly degrade present conditions. This is of significant concern for many water agencies in the United States, in blending desalinated water with surface and groundwater supplies as is recently reported for the Tampa Bay Area (Imran 2006).

Water Quality and Corrosivity

An analysis of the proposed finished water objectives of the pilot plant finished water was described in Technical Memorandum 7. The objective was to provide a finished water quality similar to that of MMWD's Marin Reservoir and Russian River water supplies. One objective was to have a taste of the desalinated water similar to that of the other sources, so that changes of supply would not be particularly noticeable to consumers. Another objective is that the corrosivity of the water would be relatively similar, so there would not be aggravated corrosion, or destabilization of pipe scales causing red discolored water upon changes of supply or direction of flow as well as continuing to meet objectives of the LCR and other corrosion control objectives. Technical Memorandum 7 described the Water Corrosion Control Objectives and various corrosion indices, which are also calculated herein this memorandum.

The conditioning of the reverse osmosis (RO) permeate water was described in a memorandum to MMWD of 13 March 2006 and included the addition of the following chemicals to second pass RO permeate as found by an RTW corrosion control model (RTW 1990):

- Calcium chloride (CaCl) 80 mg/l
- Sodium carbonate (Na_2CO_3) 37 mg/l
- Sodium bicarbonate ($NaHCO_3$) 80 mg/l

- Sulfuric Acid (H_2SO_4) 3 mg/l

In addition, the chemicals used to provide a chloramine residual for disinfection and for corrosion inhibitors typical of what is used in the present treated MMWD source water would be added, i.e.:

- Zinc orthophosphate 1.1 mg/l as phosphate
- Chlorine (Cl_2) 1.5 mg/l
- Ammonium chloride (as N) 0.37 mg/l

In actual practice chemical additions the conditioning or stabilization of the desalinated water would most likely be a combination of hydrated lime (calcium hydroxide [$Ca(OH)_2$]) and carbon dioxide (CO_2) to elevate pH, calcium, and alkalinity close to MMWD's other water source supplies. However, for the corrosion loop testing, more stable alkalinity sources other than CO_2 were selected as determined by an RTW model.

The conditioned RO permeate desalinated water, finished water obtained by the MMWD staff at the San Geronimo WTP (as typical for Marin Reservoir Water), and finished water from the Ignacio Pump Station (termination of the Sonoma Aqueduct for the Russian River source) were all tested for corrosivity to steel, copper, and lead by a linear polarization pipe loop test assembly set up at Kennedy/Jenks Consultants (KJC) Pacific Environmental Laboratory facility, beginning in April 2006 and extending into June 2006 as described herein.

Samples of each of the water sources at the beginning and end of the two week L.P. corrosion pipe loop testing were obtained for analyses the results of the water quality of the water used in the corrosion tests is shown in Table 1.

These data show that the temperature of the water was elevated somewhat during the tests to ambient conditions of the laboratory room; and that there was some evaporation and increase in concentration of the mineral constituents of the water. However, because each source sample was exposed to the same conditions, for comparative purposes these changes should not impact the overall conclusions.

The calculation of the corrosion indices indicated that both the Desal and Marin Reservoir water were under saturated with calcium carbonate as shown by negative Langelier Indices calculated for 60°F typical cold water. The Ryznar Index above 8 indicates an increasing probability of red water from iron or steel corrosion. The Larson Index above 0.4 indicates a tendency for pitting corrosion by a predominance of the strong acidic anions (sulfate and chloride) as compared to the weak acidic bicarbonate anion (Ryder 1985).

In contrast the Russian River source has a positive Langelier Index, and a lower, favorable Larson Index, although this does not necessarily correlate with corrosivity (Vik 1996).

All of the water sources indicated that there is little tendency for copper pitting corrosion. All of these water sources are dosed with a zinc orthophosphate corrosion inhibitor, which tends to minimize corrosion effects or both metals and concrete (Ryder 1985). Thus, despite having negative Langelier Indices, and elevated Ryznar Indices, the waters exhibit relatively low corrosivity to iron, copper, and lead based upon MMWD's experience and test results for LCR compliance.

A comparison of the water tested to the average and typical range projected for the SWRO desalination facility and historic water quality for the Marin Reservoir and Russian River sources is shown in Table 2. These data indicate that all of the test concentrations were within the usual range for nearly all constituents. Thus, the testing, albeit limited, is in a range of expected water conditions and thus it should be representative of what can occur in the system and likely a rather accurate predictor of comparative corrosion conditions to be experienced by the three water sources.

Corrosion Testing

The use of an electrochemical corrosion assessment technique was proposed as a practical measure to evaluate the comparative corrosivity of the desalinated water to Marin Reservoir and Russian River source values. This method of real-time corrosion assessment is now extensively used in water system corrosion evaluations (Reiber 1996); and quoting from AWWARF Internal Corrosion of Water Distribution System book:

> "Electrochemical Corrosion Assessment – Corrosion is an electrochemical process and electrochemistry can be a powerful tool in its assessment. Electrochemical techniques can determine the underlying rate of corrosion as well as characterize the surface reactions that control or limit it. – The electrochemical methodologies that have found widest application in distribution system corrosion assessment are those based upon polarization measurements – potentiodynamic scans, linear polarization and impedance spectroscopy – two other nonpolarization electrochemical measures (electrochemical noise and electrical resistance have had limited application in distribution systems. – Linear polarization assessment data form is polarization resistance, (Rp) the operating principle is a single point polarization sequence – linear relationship between the Rp and corrosion rate. LP can provide intermittent online corrosion rate measurements, it has variable precision based upon accuracy of the anodic and cathodic Tafel polarization constants. Probes are two or three electrode types LP instrumentation provide a useful indictor of relative change in corrosion rate over time and relatively simple and inexpensive."

There is now a trend to utilize to a greater degree, electrochemical corrosion techniques for online real-time measurement (Hairston 2006). Electrochemical noise measurement is gaining popularity, although LP is still a very viable rugged and economical technique to quickly assess the relative corrosivity of water to metals; and the one proposed and utilized for the recent MMWD waters.

A Metal Samples Model M51500L LPR data logger was used in the corrosion testing. Two inch corrosion plugs into which cylindrical rod electrodes of various metals are attached; all obtained from Metal Supplies, Inc.

A corrosion pipe loop test assembly was fabricated from 2-inch diameter PVC pipe, into which steel, copper, and lead LP probes were inserted, and test water for the three sources circulated from a 30 gallon tank by a pump, as shown in Figure 1.

The tested water was obtained from the Desal Pilot Plant, the San Geronimo WTP and Ignacio Pump Station, and each sequentially independently tested for two week periods.

Nine electrode probes of each metal were tested and of the following compositions:

Mild Steel	-	ASTM 1018	-	carbon steel
Copper	-	CDA 110	-	>99.5% pure copper
Lead	-	L10000	-	>99% pure lead

Three electrodes were used in individual probe assemblies for each water. They were arranged in the order of first steel, then copper, then lead (or lead solder) as would be typical of sequential exposure in distribution and plumbing systems, while also avoiding possible adverse galvanic conditions when copper would proceed steel or iron in a piping system.

The test water was first introduced into the 30 gallon storage tank, and circulated for a week to provide an initial passivation of the test loop. Then linear polarization readings of cathodic and anodic corrosion rates utilizing the three probes (Metal Samples 2000) with a 10 mvolt offset potential were read at seven, ten, and fourteen days. Cathodic and anodic corrosion rate readings tended to be within ten percent; and the average corrosion rate of the two was used for comparison and listed in Table 3.

The Metal Samples LP logger also has a feature where the reference electrode of the three probes is blocked out and a 20 millivolt potential difference between the two remaining, test and reference electrodes. This measurement provides a rough indication of pitting rate and a pitting index based upon the ratio of forward and reverse polarizing currents (Metal Samples 1998; Young 2003; Boffardi 1995).

The reason these are rough measurements of pitting is that there are other possible sources of asymmetric polarization which include: non-uniform flow characteristics, scale deposition, small differences in electrode composition, presence of surface inclusions or electrode surface roughness. Despite these possibilities, the “pitting rate” and pitting index of the LP data logger were recorded following a one minute polarization stability period at the last (14 day) test period.

A summary of the corrosivity evaluation is presented in Table 3, which displays the LP tested overall corrosion rate for the three electrodes at 7, 10, and 14 days for each water source, as well as the two-electrode “pitting rate and pitting index for the 14 days.” It is of interest to see that the corrosion rates for the metals were reliably stable after 14 days; so it would appear that the 14 day test was of sufficient duration to obtain comparative data (Reiber 1996).

The appearance of the probes, and as shown in the photographs (Figures 2, 3, and 4) are also of interest.

The last column of Table 3 is an overall evaluation of the type and degree of corrosion found by the LP tests and appearance.

The comparative corrosion data are of distinct interest and include:

1. The steel corrosion rates were all relatively uniform and relatively low for the three water sources. The corrosion rates for the Desal and Russian River sources were nearly the same, while that for the Marin Reservoirs somewhat less as measured and as evident in the photograph (Figure 2).

2. The corrosion iron rust deposits were orange colored Geothite (FeOOH) with darker tubercles of Magnetite (Fe_3O_4).

3. The predominant type of corrosion of steel was pitting and tubercle formation as is evident in the photographs.

4. The copper corrosion rates for all three water sources were very low and tended to be uniform corrosion producing a slight burnish of cuprite scale (Cu_2O).

5. The measured copper corrosion rate and appearance of the conditioned desalinated water was lower than the other water sources.

6. Lead corrosion rates for conditioned RO permeate water of the Desalination pilot plant were significantly lower than for the Marin Reservoir or Russian River source waters, although it had the highest pitting rate and pitting index.

7. There was an adherent gray scale, which is probably a complex combination of lead carbonate, lead oxide and possibly lead phosphate. However, the fact that it is an

adherent scale would tend to lessen the concern of lead particulate sloughing from lead soldered pipes, or brass fixtures.

8. The appearance of all of the lead probe coupons was relatively the same.

Findings and Conclusions

1. The linear polarization corrosion pipe loop testing for steel, copper, and lead indicated that properly conditioned desalinated water would likely be no more corrosive than existing Marin MWD sources from the Marin Reservoirs or Russian River.

2. Copper corrosion was very low and uniform rather than pitting type corrosion for all sources.

3. Lead corrosion was also low and adherent films developed for all sources.

4. Steel corrosion was moderately low, with shallow pits and tubercles quickly formed for all sources; however the conditioned desalinated water appears no worse than the current supplies and should not aggravate existing corrosion rates or pipe scales; however, it still may be necessary to slowly blend the water sources to minimize any adverse effects.

5. There is no direct correlation of this short term electrochemical corrosion testing with Lead and Copper Rule testing or iron and steel pipe and reservoir corrosion experience; but the tests conducted on the conditioned desalinated water indicate the probability that present conditions with existing water sources should not worsen by the use of desalinated water or its blends with fresh surface water sources.

Table 1: Marin Municipal Water District Desalination Pilot Plant Water Quality of Desalinated and Present Source Waters of Corrosion Linear Polarization Pipe Loop Testing

Characteristic	Units	Desal Water[1]		Marin Reservoir[2] Water		Russian River[3] Water	
		Before[4]	After[5]	Before	After	Before	After
General							
Temperature	°C	10	20	10	20	10	20
pH	units	-	7.70	7.81	-	8.24	-
Total Dissolved Solids	mg/l	140	220	120	-	180	-
Total Hardness	mg/l $CaCO_3$	55	74	62	-	59	-
Total Alkalinity	mg/l $CaCO_3$	65	92	59	-	148	-
Cations							
Calcium	mg/l	22	29	9.3	-	24	-
Magnesium	mg/l	-	< 0.1	9.4	-	-	-
Sodium	mg/l	-	51	22	-	25	-
Anions							
Bicarbonate	mg/l	79	112	72	-	180	-
Chloride	mg/l	36	51	28	-	8.3	-
Sulfate	mg/l	8.2	13	7.5	-	13	-
Corrosion Indices							
pH $CaCO_3$ Saturation	pHs	8.46	8.21	8.87	-	8.07	-
Langelier Saturation Index	LSI	-	-0.51	-1.06	-	+0.17	-
Ryznar Index	RI	-	8.72	9.93	-	8.10	-
Aggressive Index	AI	-	11.12	10.95	-	12.13	-
Larson Index	LI	-	0.91	0.80	-	0.17	-
SO_4/CL Ratio	Ratio	-	0.16	0.20	-	1.17	-
Copper Pitting Propensity	CPP	0	+1	+2	-	-1	-
Sampled[6]		4/19/06	5/3/06	5/12/06	-	6/7/06	-

Notes:

(1) Conditioned water of desalination pilot plant water.
(2) San Geronimo WTP treated water.
(3) Ignacio Pump Station treated water.
(4) Before corrosion pipe loop testing.
(5) After 14 days of corrosion pipe loop testing.
(6) (Cruse 1985).

Technical Memorandum No. 14

24 October 2006
K/J 0468029
Page 9

Table 2: Marin Municipal Water District Desalination Pilot Plant
Comparison of Water Quality of Corrosion Loop Test Water with Typical Supply Waters

Characteristic	Units	SWRO Treated Water			Marin Reservoir Water			Russian River Water			Remarks
		Test[1]	Average[2]	Range	Test	Average	Range	Test	Average	Range	
Characteristic											
pH	-	7.7	7.9	7.8-8.2	7.81	7.8	7.8-7.9	8.24	8.1	7.8-8.4	All close to average
Total Dissolved Solids	mg/l	140	120	60-180	120	119	86-136	180	171	148-186	All close to average
Total Hardness	mg/l $CaCO_3$	55	60	50-110	62	62	52-74	59	105	96-112	RR less than average
Total Alkalinity	mg/l $CaCO_3$	65	60	50-110	59	61	49-70	148	119	110-125	RR more than average
Cations											
Calcium	mg/l	22	24	20-44	9.3	-	-	24	-	-	
Magnesium	mg/l	< 0.1	<0.1	< 0.1-0.1	9.4	-	-	-	-	-	
Sodium	mg/l	36	30	10-50	22	16	11-25	25	20	16-23	All close to average
Anions											
Bicarbonate	mg/l	79	73	61-134	72	74	68-85	180	145	134-153	RR more than average
Chloride	mg/l	23	50	10-70	28	21	10-37	8.3	8	7-10	SWRO less than average
Sulfate	mg/l	5	-	-	7.5	12	<0.25	13	13	11-14	All close to average
Corrosion Indices											
pH $CaCO_3$ Saturation	pHs	8.72	7.9	7.75-8.25	8.87	8.84	8.44-9.19	8.07	7.99	7.98-8.26	SWRO above average
Langelier Saturation Index	LSI	-0.51	0	-0.5+0.5	-1.06	-0.94	-0.64-1.29	+0.17	+0.11	-0.14+0.42	All close to average
Ryznar Index	RI	8.72	7	6-8	9.93	9.87	9.08-12.68	8.10	7.99	7.94-8.82	SWRO Above average
Aggressive Index	AI	11.12	11.5	11-12	10.95	11	10.8-11.3	12.13	12	11.8-12.2	All close to average
Larson Index	LNI	0.91	0.3	0.25-0.4	0.8	-	-	0.17	-	-	

Notes:

(1) All test waters at running of corrosion pilot loop testing.
(2) From Table 1, Proposed General Mineral Objectives – K/J Technical Memo No. 7, 3 January 2006.

Table 3: Marin Municipal Water District Desalination Pilot Plant
Water Corrosivity Evaluation by Linear Polarization Analysis(1)

	Corrosion Rate(2) – mils per year						
Material	7 days	10 days	14 days	Pitting Rate(3) Mils per year	Pitting Index(4)	Probe Appearance	Corrosivity Type(5) and Rating(6)
1. Test 1: Desalinated Water							
Steel	11.25	9.90	9.70	44.85	1.1	Orange red with dark brown tubercles	Low pitting and tubercles
Copper	0.04	0.01	0.01	0.45	0.8	Slight tan burnish (Cu_2O)	Very low – uniform
Lead	0.44	0.20	0.56	13.0	2.2	Grey adherent scale	Moderate-pitting
2. Test 2: Marin Reservoirs' Source							
Steel	6.52	7.12	7.26	30.6	1.1	Brown scale with tubercles	Low – pitting and tubercles
Copper	0.015	0.075	0.05	0.085	0.8	Tan burnish	Low – uniform
Lead	0.67	0.55	0.75	7.00	1.3	Grey adherent scale	Moderate – pitting
3. Test 3: Russian River Source							
Steel	9.55	10.70	9.87	42.85	1.1	Orange brown scale with tubercles	Low – pitting and tubercles
Copper	0.05	0.01	0.015	0.10	0.4	Tan burnish	Very low – uniform
Lead	1.31	1.07	1.10	11.75	0.9	Dark grey adherent scale	Moderately high pitting

Notes:
(1) Metal Products, Inc. MS1500L LPR Data Logger.
(2) Average of Cathodic and Anodic LPR of 3rd – Last reading.
(3) Pitting rate 2 electrode probe after 1 minute – 14 days exposure.
(4) Pitting Index of 2 electrode probe analysis – 14 days exposure.
(5) Corrosivity Type – Uniform or pitting basins on pitting index <1 uniform and >1 increasingly pitting.
(6) Corrosivity Rating – Steel 5 to 10 mpy loop, 10 to 20 mpy moderate, > 20 mpy, heavy; copper: very low <0.1 mpy, low 0.1 – 0.2 mpy; lead: low 0.1 – 0.5 mpy, moderate 0.5 – 1 mpy, heavy >1 mpy; Bradford (2002).

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