Field Experiences and Fabrication Techniques related to AL-6XN Alloy for SWRO Applications

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Abstract

Failure of metallic components in desalination plants results in forced shut down and loss in production. The failure of material is caused of localized corrosion, stresses, dissimilar metal combination or environmental attack. A proper material selection is the key to minimize the chances of corrosion of material and provide longevity to the plant. Superb corrosion resistance, good mechanical properties and cost effectiveness are the virtues of an excellent material selection.

Super Austenitic Stainless Steels or 6% molybdenum stainless steels, like AL-6XN, are heavily used for high pressure feed pipe systems in SWRO plants. AL-6XN alloy was designed to be a seawater resistant alloy and has been successfully used in a multitude of marine and offshore applications including process piping systems, heat exchanger equipment, drilling platforms, and desalination systems. Additionally, AL-6XN alloy has also been utilized for brine concentrators, wastewater evaporators, which contain similarly high chloride levels.

Alloying with 6.2 percent molybdenum, 20.5 percent chromium, 0.22 percent nitrogen provides a high level of resistance to localized corrosion by halides. As a result, AL-6XN can tolerate much more severe levels of chlorides than standard austenitic or duplex stainless steels without the onset of pitting or crevice corrosion. The combination of 24 percent nickel content and a nitrogen addition provide AL-6XN with its good welding and forming characteristics, which are superior to duplex and ferritic stainless steels of comparable corrosion resistance.

The corrosion resistance of AL-6XN in seawater service will be reviewed along with comparisons to other grades commonly used in SWRO applications. This includes the austenitic, duplex, and super duplex stainless steels. Various case studies are presented where AL-6XN has been successfully used in SWRO facilities and other related applications. Also, presented are cases where AL-6XN has successfully replaced SWRO equipment originally fabricated in other grades of stainless steel that suffered corrosion failures.

In addition to in service performance, fabrication practices and procedures are also discussed including welding, forming, and machining.

I. INTRODUCTION

The corrosion resistance of stainless steels makes them well suited for use in water treatment systems using reverse osmosis. Reverse osmosis systems are widely used for fresh water production for human consumption. While 316L stainless is useful for waters containing low levels of chlorides, its alloy content is insufficient to resist localized corrosion in waters containing elevated levels of chlorides such as seawater. Materials containing greater levels of chromium and molybdenum are necessary to resist localized attack in seawater systems, especially under crevice conditions. As a result, higher alloyed super austenitic stainless steels have been increasingly used to replace existing equipment and have been used as a standard alloy of construction for many components of SWRO equipment.

1.1 AL-6XN® Alloy (UNS N08367)

AL-6XN® alloy (UNS N08367) is a low carbon, high purity, nitrogen-bearing "super-austenitic" stainless alloy. The AL-6XN alloy was designed to be a seawater resistant material and has since been demonstrated to be resistant to a broad range of very corrosive environments. The high strength and corrosion resistance of the AL-6XN alloy make it a better choice than the conventional duplex stainless steels and a cost effective alternative to more expensive nickel-base alloys in applications where excellent formability, weldability, strength and corrosion resistance are essential. It is also a cost-effective alternative to less expensive alloys, such as Type 316, that do not have the strength or corrosion resistance required to minimize life cycle costs in certain applications. The high nickel and molybdenum contents provide improved resistance to chloride stress-corrosion cracking. Copper (Cu) has been intentionally kept to a residual level for improved performance in seawater. The high alloy composition of the AL-6XN alloy resists crevice corrosion and pitting in oxidizing chloride solutions to a degree previously achieved only by nickel-base alloys and titanium.

II. CORROSION RESISTANCE

2.1 Chemical Compositions & Laboratory Testing

The corrosion resistance has been reviewed in many papers published previously about AL-6XN alloy. It is widely accepted that increasing chromium, molybdenum, and nitrogen are beneficial in improving localized corrosion resistance in seawater. Table 1 provides the nominal chemistries of several austenitic and duplex, and super duplex (SDSS) stainless steels commonly used in water treatment systems. Rankings according to each materials pitting resistance equivalent (PREn) and critical pitting temperature (CPT) in the ASTM G 150 test in 1 M NaCl solutions are also provided. The PREn value is calculated using the following formula: PREn = % chromium + 3.3 x % molybdenum + 16 x % nitrogen

Table 1 – Nominal Chemistries & PREn values for Various Stainless Steels

UNS Number	Common Name	Ni	Cr	Mo	N	Other	PREn	CPT °F
S31603	316L	10.2	16.4	2.1	-	0.02 C	24	68
S32205 S31803	2205	5.6	22.1	3.1	0.16	0.02 C	35	120
S32750	2507	7	25	4	0.27	0.02 C	42	180
N08904	904L	24	20.5	4.5	-		36	130
N08367	AL-6XN	24	20.5	6.2	0.22	0.02 C	44	172

2.2 Arabian Gulf Testing

The Saline Water Conversion Corporation, SWCC, conducted tests, on AL-6XN alloy in Arabian Gulf seawater and seawater concentrate (Al-Jubail RO reject brine) [1]. For comparison purposes, the 316L stainless steel was also tested under identical conditions. This corrosion performance evaluation of AL-6XN alloy was done employing immersion and electrochemical testing. During immersion tests under static conditions, the AL-6XN alloy did not show any perceptible weight change after a period of one year. Under dynamic conditions, samples exposed in a laboratory test loop for 30 days did not show any appreciable weight loss. The AL-6XN alloy exhibited high pitting resistance in potentiodynamic cyclic polarization tests. Tests in seawater and RO reject brine yielded E_{pit} of 1070 and 1058 mV, respectively, shown in Figures 1 and 2. Results from potentiostatic experiments show similar trends.

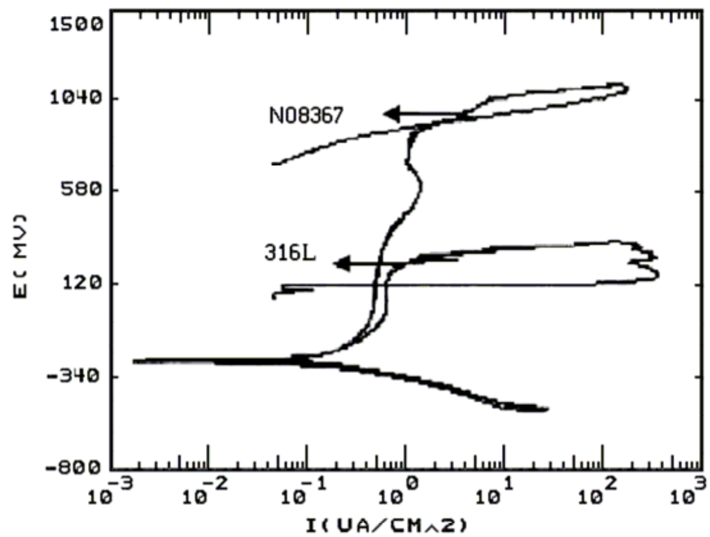

Figure 1 Polarization curves for AL-6XN and 316L in seawater

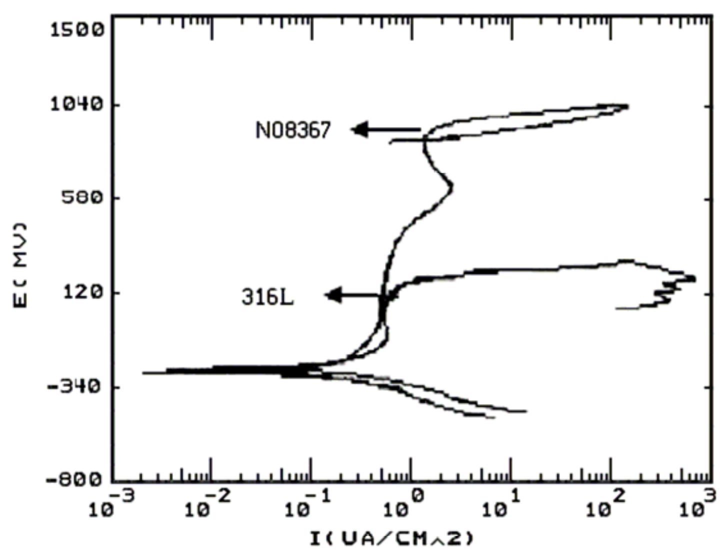

Figure 2 Polarization curves for AL-6XN and 316L in RO reject water

Crevice corrosion tests (CCT) carried out on plain alloy specimens in seawater and RO reject, using multiple crevice assemblies, showed no effect in both the media even after six months exposure. Autogenous welded samples of AL-6XN show weight losses of only seven and nine milligrams under torques of five and ten foot-pounds after six months of exposure indicating extremely high resistance to corrosion.

III. SERVICE EXPERIENCE

3.1 Tampa Bay [2]

A reverse osmosis (RO) seawater desalination plant was built to help the Tampa, Florida area meet its water needs. Tampa Bay Water owns and operates the USA's largest desalination plant, which is rated at 25 MGD. The project started to operate at the end of 2002. The salinity of the source water from Tampa Bay ranges from 16-34 ppt on average. The temperature of the water from the power plant cooling water discharge to the RO pretreatment ranged from 98-105 °F.

Figure 3 Filter Vessel constructed using AL-6XN Material

Due to the pressure and the water's corrosiveness, AL-6XN alloy is used in critical locations throughout the pretreatment and reverse-osmosis processes to help to fight the corrosive effects of the seawater. The cartridge filter vessels, shown in Figure 3, and the high pressure piping on the RO skids were constructed of AL6XN. This materials selection is based upon the 30-year design life for the plant. To date, the AL-6XN components of the plant have shown no corrosion.

3.2 Trinidad

The largest RO seawater desalination plant in the Western Hemisphere was constructed in Trinidad. The plant was designed to produce 109,000 cubic meters of water per day (28.8 million gallons a day) for the Water and Sewerage Authority of Trinidad and Tobago. AL-6XN pipe was chosen for the critical pretreatment piping in this plant [3]. This project began operation at the end of 2002. Shortly after startup, localized corrosion was encountered under the gaskets in a significant fraction of the compression couplings. The cause of this never was disclosed publicly but tacitly was attributed to startup issues. The replacement pipes were also fabricated from AL-6XN material. Subsequently, AL-

6XN material was also chosen for an expansion that raised the output of this plant to approximately 40 million gallons per day.

3.3 Bahamas Desalination

Waterfields Company Limited operates a seawater RO plant that produces 2.64 million gallon per day for Nassau, Bahamas. The plant provides 20% of Nassau's fresh water needs. This plant started operation in 1997. Seawater feed is extracted from wells and contains 39,000 ppm total dissolved solids. Initially, the plant was constructed using 316L stainless. Some 316L stainless components failed by pitting within six months, and were replaced with AL-6XN material in 1997. The AL-6XN material has been in service since then with no reported failures.

3.4 Affordable Desalination Collaboration

The ADC was formed in 2004 with its charter being to demonstrate that SWRO was economically competitive with other means of supplying fresh water to Southern California. Rolled Alloys was an initial member of the ADC along other notable companies such as Poseidon Resources, Energy Recovery Inc., Carollo Engineers, Pentaire, and Piedmont Pacific. In addition, several government agencies were also members. Rolled Alloys supplied AL-6XN pipe and fittings for the ADC facility [4], which is located at Port Hueneme, California. This material was used in the high-pressure seawater intake lines and the brine discharge lines.

The tests results gathered, after years of operation, proved that SWRO was indeed cost effective with pumping Colorado River water from Nevada to Los Angeles. The AL-6XN material was chosen for this application for its outstanding corrosion resistance and proven record in seawater service. It has operated performed without issue.

3.5 Florida Keys Aquaduct Authority – Stock Island

This is a 2.18 MGD (8,252 m3/d) Stock Island Plant. The system operates at 35-40% recovery and each 0.5 MGD (1,892 m3/d) train is equipped with a 650 HP (485 kW) diesel driven, multistage vertical turbine pump to provide 850 to 1000 psi (59 to 69 bar) operating pressure. Each SWRO train has a reverse running energy recovery turbine to recover 200 HP (150 kW), and the total diesel fuel consumption is 1.39g/kgal (1.39L/m^3).

Harn R/O recently made some additional modifications including the replacement of the feed, permeate and concentrate lines with higher performance materials; the feed and concentrate lines were made from AL6XN alloy [5].

Figure 4 Brine Discharge Piping Using AL-6XN pipe

3.6 St. Kitts

A 1.25 million gallon per day reverse osmosis desalination plant was installed at the Marriott St. Kitts Royal Beach Resort & Spa. The plant was installed to provide potable and irrigation water for the 648 room resort and its eighteen hole golf club. The plant design utilized four trains each rated for 250,000 gallons per day with the option to add a fifth train. AL-6XN alloy was utilized for all of the high-pressure piping. The plant started full production in February 2004. No corrosion issues with the AL-6XN piping have been experienced.

3.7 Carlsbad, CA Demonstration Plant

Poseidon Resources operates a SWRO pilot plant at the site of Southern California Edison's Carlsbad Power Station. This plant was initially fitted with a type 316L stainless piping system. Within six months of start up the 316L material began to experience corrosion failures. The piping system was replaced in 2004 with AL-6XN being selected as the replacement material. Its selection based largely on its extensive use in Poseidon's Tampa Bay Desalination Plant. The AL-6XN material has been in continuous use at Carlsbad since 2004, without any service issues.

IV. FABRICATION

4.1 Fabrication Background

While material selection is important, of equal importance is the use of correct weld filler metals and fabrication techniques to construct the equipment. Overall the procedures for fabricating AL-6XN are quite similar to those used on 300 series austenitic stainless steels. There are some differences that should be understood, however, to ensure a quality fabrication and avoid unnecessary added costs and delays during fabrication.

4.2 Welding

4.2.1 Filler Metals

Welding without fillers over alloyed in molybdenum, can lead to microsegregation of Cr and Mo in the weld bead. This can result in reduced corrosion resistance. Autogenous welds in 6% molybdenum stainless steels have greatly reduced pitting corrosion resistance when compared to the base metal. Autogenously welded 6% molybdenum stainless steels have comparable corrosion resistance as a 4.5% molybdenum grade such as type 904L in laboratory testing. The sample coupon shown in Figure 5 was constructed of AL-6XN and S31254 coupons welded via gas tungsten arc welding (GTAW) autogenously on one side and with 625 filler on the other. Testing in accordance with ASTM G 48 for 72 hours was then performed on the specimen in the 10% $FeCl_3$•$6H_2O$ solution at 50°C (122°F).

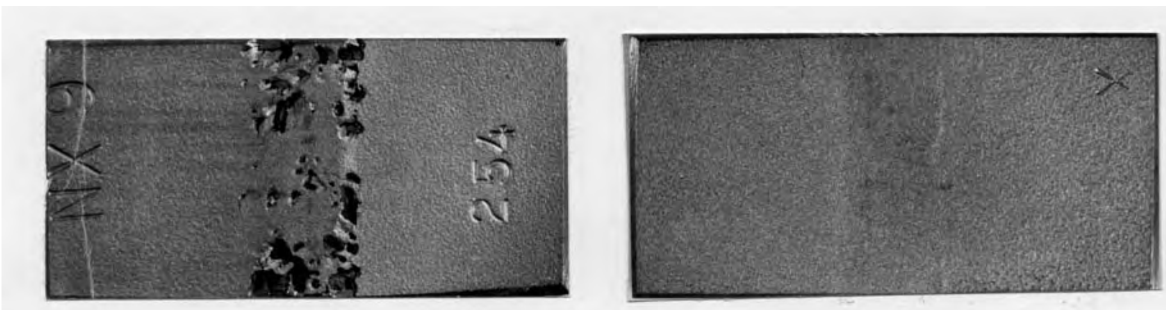

Figure 5 Sample condition after corrosion testing for 72 hours in 10% $FeCl_3$•$6H_2O$, at 50°C (122°F). The autogenous weld is shown at left and the GTAW weld with 625 filler is at right.

AL-6XN must be welded with over alloyed filler metal for best corrosion resistance. To compensate for the segregation of molybdenum and chromium, use of a weld filler such as 625 (ERNiCrMo-3) wire or 112 (ENiCrMo-3) electrodes with nine percent molybdenum is common. It is also acceptable to use even higher molybdenum fillers such as alloy 22 (EniCrMo-10) to weld AL-6XN. Such fillers with greater than 13.5% molybdenum provide additional corrosion resistance in the weld. The lower chromium alloy C-276 (ERNiCrMo-4 wire) is not suggested for welding AL-6XN. C-276 weld filler does not match the chromium content of the AL-6XN alloy base metal.

Welding of AL-6XN alloy without filler metal is permitted when the weld is to be subjected to post weld annealing at 1150-1200°C (2100-2200°F) followed by rapid quenching. This is normal practice for the manufacture of ASTM B 675 pipe, but quite impractical in vessel and field fabrications. In thin sheet fabrications such as for bellows acceptable autogenous welds have been made by using an argon shielding gas with 3 to 5% nitrogen to maintain corrosion resistance.

4.2.2 Welding Processes to Be Avoided

In addition to avoiding autogenous GTAW welding, there are other practices that should be avoided during the fabrication of AL-6XN material and many corrosion resistant alloys in general. Oxyacetylene welding should not be used. AL-6XN alloy is susceptible to carbon pick-up from the flame. Carbon lowers the corrosion resistance. In plasma welding, too minimal an amount of filler metal is added to the joint for good corrosion resistance in AL-6XN. Plasma welds require a full anneal to remove chromium-molybdenum segregation and restore corrosion resistance. Carbon-arc air gouging poses a considerable risk for carbon pickup on the surfaces of cut edges when using this technique. This carbon can lower the corrosion resistance of AL-6XN. In general, carbon-arc gouging should not be used on any corrosion resistant alloy. GTAW “wash” passes to improve the aesthetics of a weld joint should be avoided as the remelted area can have undesirable levels of molybdenum segregation and reduced corrosion resistance.

4.3 Machining

AL-6XN alloy and other austenitic grades are quite ductile in the annealed condition. However, chromium-nickel alloys work harden more rapidly and require more power to cut than do the plain carbon steels. Chips tend to be stringy, cold worked material of relatively high ductility. AL-6XN is refined to very low sulfur levels (0.002% typical). This makes the chips quite "gummy".

Machine tools should be rigid and used to no more than 75% of their rated capacity. Both the work piece and cutting tool should be held rigidly. Tool overhang should be minimized. High speed steel or cemented carbide tools should be sharp and reground at predetermined intervals. Turning operations require chip curlers or breakers.

Feed rate should be high enough to ensure that the tool cutting edge is getting under the previous cut thus avoiding work-hardened zones. Slow speeds are generally required with heavy cuts. Approximate speeds for turning and milling and drilling are roughly 2/3 that of 304L stainless. Lubricants, such as sulfur-chlorinated petroleum oil, are suggested. Such lubricants may be thinned with paraffin oil for finish cuts at higher speeds. The tool should not ride on the work piece as this will work harden the material and result in early tool dulling or breakage.

4.4 Hot & Cold Forming

Cold working is the preferred means of forming AL-6XN. Plate can normally be press brake bent over a radius equal to the plate thickness. AL-6XN is roughly 50% stronger than 316L stainless so greater force will be required for forming and shearing operations. Additionally greater springback can be expected. With sheared plate, it is good practice to remove the shear burr, to avoid cracking. As with other austenitic stainless and nickel alloys, bending over a sharp male die may cause the material to crack. Heat treatment after cold working operations is usually not required.

Hot forming or forging of AL-6XN should be performed from a starting temperature of 2275°F (1246°C). Finish forging before the stock drops below 1850°F (1010°C). Fairly heavy scaling occurs at temperatures above 2100°F (1150°C). In order to dissolve any potential secondary phase precipitates occurring from the hot forming operations, the material should be subsequently annealed.

4.5 Annealing & Heat Treatment

AL-6XN is a fully austenitic alloy and cannot be hardened by heat treatment. Annealing is performed either to soften the material after heavy cold work, remove harmful secondary phases potentially formed during hot working operations, or minimize alloy segregation from autogenous welding. Most AL-6XN fabrications are normally placed in service without annealing. Annealing is done at 2050-2150F (1121-1177°C), followed by water quenching. The cooling rate from the annealing temperature is important. Slow cooling can markedly decrease the corrosion resistance of AL-6XN.

AL-6XN is more tolerant of time at temperature than duplex and super duplex stainless steels. The fully austenitic structure of AL-6XN requires longer time at temperature before deleterious phases such as sigma precipitate in levels sufficient to degrade corrosion resistance and mechanical properties. AL-6XN does not suffer embrittlement at 885°F (474°C) that occurs in the duplex family of stainless steels. Heavy sections of AL-6XN are less sensitive to time at temperature during welding and heat treatment. As a result there is less potential for reduced corrosion resistance with AL-6XN fabrications than competing duplex and super duplex grades. Annealed AL-6XN alloy typically has a charpy impact toughness of 240 ft-lbs [5] . By comparison duplex stainless steels have a room temperature charpy impact toughness around 180 ft-lbs in the annealed condition. Figure 6 compares the effect of time and temperature on the impact toughness of duplex stainless steels and AL-6XN alloy. At 900°C (1652°F), superduplex requires a minute or less at temperature to reduce impact values by 50%, whereas AL-6XN alloy maintains more than 50 percent of its toughness after an hour at temperature.

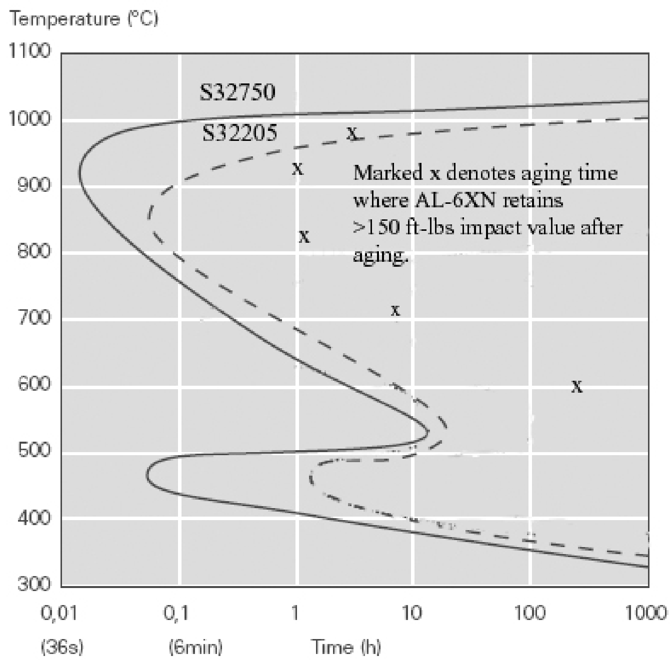

Figure 6 Curves for reduction of impact toughness to 50% for duplex compared to solution-annealed condition. AL-6XN values related to >150 ft-lbs minimum impact value shown for comparison [6], [7]

Figure 7 Long radius elbow showing surface pitting from catastrophic oxidation during improper annealing

High molybdenum alloys such as AL-6XN are subject to catastrophic oxidation during open air annealing. Stagnant areas, where molybdenum trioxide is trapped on the surface, may develop broad pits 0.020-0.030" (0.5-0.8 mm) deep. Pale yellow smoke or dust in the furnace is the molybdenum trioxide. To minimize this attack, permit air to circulate freely about the parts. Do not pack the furnace full of work piece. It is also recommended to not re-anneal material that is heavily scaled.

V. CONCLUSIONS

1. AL-6XN has been utilized for a variety of both large scale, resort scale, and skid mounted RO units successfully replacing other lower alloyed materials. Lower molybdenum stainless steels such as 316L do not possess the corrosion resistance required for seawater service.

2. AL-6XN and other high molybdenum stainless steels need to be welded using fillers over alloyed in molybdenum to ensure corrosion resistance matching the base metal.

3. Autogenous welds, plasma welding, carbon arc gouging, oxyacetylene welding, and TIG wash passes should be avoided when fabricating AL-6XN and other similar corrosion resistant alloys.

4. The machinability of AL-6XN is somewhat more difficult than 300 series stainless. Its higher nickel and low sulfur result in the need to use speeds roughly 2/3 that of 304 stainless.

5. AL-6XN is less sensitive to time at temperature than duplex stainless steels. As a result, there is less risk for reducing corrosion resistance and ductility during welding or heat treatment of AL-6XN fabrications.

VI. REFERENCES

1. A. U. Malik, I. N. Andjijani, F. Al-Muaili, and R. J. Gerlock, "Corrosion Performance Evaluation of Super-austenitic Stainless Steel UNS N08367", IDA World Congress on Desalination and Water Reuse, Bahrain, March 8-13, 2002.

2. J. F. Grubb and R. J. Gerlock, "Use of a 6% Mo Alloy in Desalination", CORROSION 2003 Paper No 03258, NACE, Houston, TX

3. C. Kutzler, Water & Wastewater International, November 2003

4. J.P. MacHarg, "ADC Spreads the Word", Desalination, Volume 1, Issue 1

5. Water Desalination Report, Volume 43, Number 31, August 20, 2007

6. Duplex Stainless Steels, Outokumpu Publication 1008EN-GB:5. Centrum Tryck AB, Avesta, Sweden. February 2007.

7. J.F. Grubb, “Elevated Temperature Stability of a 6% Mo Super Austenitic Stainless Alloy”, CORROSION 96 PaperNo. 426, NACE, Houston, TX