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POLYAMIDE 11 COATINGS: AN ALTERNATIVE TO STAINLESS STEEL TO DECREASE OPERATING AND CAPITAL EXPENDITURE IN WATER TREATMENT PLANTS USING MEMBRANE TECHNOLOGIES

POWLEKANIE POLIAMIDEM 11 JAKO ALTERNATYWA STOSOWANIA NIERDZEWNEJ W STACJACH UZDATNIANIA WODY STOSUJĄCYCH TECHNIKI MEMBRANOWE

Polyamide 11 is a high performance material with unique functional properties. Actually its semi crystalline structure brings to the material both the hardness of thermosetting materials and the flexibility and impact resistance of thermoplastics. Manufactured originally from a natural renewable resource: castor oil, it is the only engineering bio plastic available on the market. While giving an effective protection to metallic surfaces, it provides as well a surface aspect, which is aesthetic and smooth. It is available in powder form, without any shelf storage life. Various processing technologies are available, which allow its application on different types of metallic substrates in order to obtain an optimum protection. The main application processes include dipping in fluidized bed, electrostatic spraying on cold substrates or spraying on preheated substrates.

Polyamide 11 has been used in water industry for coating pipes, pumps, valves and fittings since 1967. For treatment of water, waste water and sea water, Polyamide 11 coated mild steel piping system has been found as a technical alternative to the more expensive stainless steel piping. Its unique properties bring to the water companies, the municipalities and the industries numerous benefits including the preservation of the water quality, the protection of the parts during handling and storage, the decrease of maintenance cost as well as the saving of energy. Those benefits have been proven through relevant usage references in the water industry.

Besides, in order to solve corrosion issues and decrease the cost of their piping systems, some innovative companies involved in membrane filtration technology, including salt water and brackish water reverse osmosis, have specified polyamide 11 coated piping system to replace 316L and super duplex. Actually, even those very expensive stainless steel grades can face pitting corrosion and their resistance to seawater and membrane cleaning agents are limited. The better chemical and corrosion resistance of polyamide 11 combine with its lower bring benefits that allow them to decrease both operating and capital expenditure. Relevant references include the new water ultra filtration plant of

Moscow in Russia with a capacity of 275 000 m3/day or in the Okinawa reverse osmosis seawater desalination plant of 40 000 m3/day in Japan.Summary of the research paper for the XX-th Jubilee-National, VIII-th International Scientific and Technical Conference "Water Supply and Water Quality"

1. Introduction

The ever-increasing consumption of water throughout the world for both domestic and industrial use combined with its scarcity due to the climate change requires new innovative solutions for water and wastewater treatment. Membrane filtration technologies have permitted to address those issues. We can mention reverse osmosis membranes decreasing the cost of desalination as well as the ultra-filtration membranes allowing the removal of pesticides in river and underground water. Membrane technologies play also a major role in regards to the challenges raised by the strengthening of wastewater regulations. Whereas the development of those technologies appears as a real breakthrough, some innovations are still required to make them more affordable. This paper introduces the polyamide 11 coatings and describes its benefits throughout 40 years of relevant usage references within the water industry. We will show how it can give the opportunity to engineering companies and subcontractors to decrease both OPEX and CAPEX in water treatment plants using membrane technologies.

2. Polyamide 11 coatings

2.1. Material presentation

Polyamide 11 is a high performance thermoplastic material with excellent functional properties. It is marketed under the brand name of Rilsan®. It is obtained by the polycondensation of 11-amino undecanoic acid, which is coming from a vegetable origin: castor oil. It contributes to sustainable development in that:

- It is bio-based high performance bioplastics-100% of carbons in polyamide 11 are organic and coming from plant based renewable resources (ASTM 6866)
- Its production from primary energy sources and primary raw materials requires less fossil energy than most performance polymers.
- Its production from primary energy sources and primary raw materials generates much less CO2 and other greenhouse gases emissions than other performance polymers.

The excellent properties of polyamides and in particular polyamide 11 are a result of the amide linkages in the chain, which allow a strong interaction between the chains by hydrogen bonds. Low creep, high ductility and mechanical strength, excellent resistance to abrasion, fatigue and ageing as well as high barrier properties are a direct result of these strong inter-chain interactions. A polyamide will absorb a greater amount of water when its amide group number is higher, weight being constant. Polyamide 11 thus compares advantageously to standard nylons such as 6 and 66. Notably, its significantly lower water absorption results in better ageing resistance, lower density, higher chemical resistance, very good dimensional stability with time and limited changes in the electrical properties and mechanical properties. Comparative data are given in Table 1.

Tab. 1. Comparison of different polyamides.

	PA 66	PA 6	PA 11
Melting point (°C)	255	215	188
Density	1,14	1,13	1,03
Flexural modulus (MPa) 50 % Relative Humidity/23°C	2800 (1200)	2200	1300
Water absorption at 23°C 50 % Relative Humidity In water immersion	2,5 8,5	2,7 9,5	1,1 1,9
Charpy notched impact ISO 180/1A 23°C - kJ/m^2 - 40°C – Kj/m^2	5,3 (24) ×	8 (30) ×	23 13
ISO 527 Tensile stress (MPa) Tensile elongation (%) Elongation at rupture (%)	87 (77) 5 (25) 60 (300)	85 (70) 15 - 200	36 22 360

It is manufactured both in granules and powder form. Granules are transformed by conventional process (extrusion, injection…) to be used in industries including oil and gas, transportation and sports. Among the various application where polyamide 11 granules are used, we should notice offshore flexible pipes and umbilical, gas transportation pipe, air brake tubing, sport shoes and ski upper layer. This paper will deal with polyamide 11 powders, which are used for metal coating application for years in a great variety of applications and sectors:

- It has been used for more than 15 years as a durable coating to protect dishwasher basket due to its excellent resistant to various food products, dishwashing detergents and thermal cycles.
- Because of its low coefficient of friction, excellent abrasion and chipping resistance and its behavior under compression, Polyamide 11 has been used for years in the transportation industry as a durable protection for components exposed to high mechanical and chemical strains (spline shafts, steering column or sliding door rail, fuel line coating…) or for noise reduction purposes (seat components, sun roof cables…).
- Polyamide 11 is also used as a coating for roller for litho offset printing machine because of its machining ability, its wear resistance as well as its inertia to ink and cleaning solutions. Its unique surface properties allow getting a homogeneous

and very thin layer of ink on the litho plate leading to an excellent printing quality.
- Polyamide 11 has been used since 1967 for the steel protection in fluid transfer industry including water treatment and transportation, oil extraction and gas transportation.

2.2. Application process

Comparing to conventional thermosetting materials, polyamide 11 is a thermoplastic, which means that the coating application consists in a simple change of physical state through the first melting of the polymer, which then solidify and form a film on the surface of substrate. No chemical reaction and thus optimized control of application conditions are required to obtain the designed mechanical properties. The application thereof brings no pollution to the application workshop and both the powder and coating release no volatiles, organic substances or odors.

Various processing technologies are available, which allow its application on different types of substrates in order to obtain an optimum protection. The main application processes include dipping in fluidized bed, electrostatic spraying on cold substrates or spraying on preheated substrates. When requiring optimal anticorrosion properties, as it is typically for water treatment industry, a water-based primer should be applied prior to polyamide 11 to form what we will call later in this paper “the polyamide 11 system”. The different processes are describes in the scheme 2.

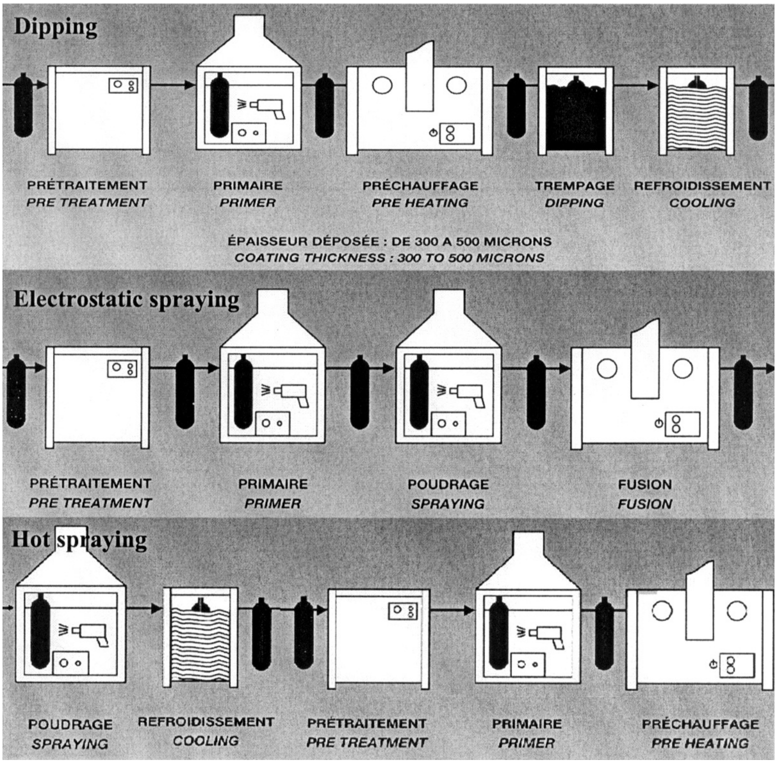


Fig. 1. Polyamide 11 application process

The most suitable process to coat components for water treatment plants remains the dipping in a vertical fluid bed of powder (often as deep as 7 meter- see picture 3). Both internal and external coatings could be achieved in one step on tubes and elbows up to 6 m length and having diameters larger than 1 m. A uniform overall thickness is obtained due to the sharp melting peak of polyamide 11, typically a nominal thickness of 350μm ± 50 μm. In order to ensure the performances of the coated parts and to provide relevant tools to engineers for risk management, standards from all over the world (Holland—KIWA K-759, USA—AWWA C-224, Japan—JWWA WSP-067, Australia—AS/NZS 4158, Europe—EN 10310) covers the following points:

- Effect of coating materials on water quality according standards in force (NSF 61, WRAS…)
- Coating material performances (resistance to impact, water immersion, corrosion…)
- Application procedure (surface preparation, primer application, coating)
- Quality control on coated parts (Appearance, thickness, holiday detection, adhesion…)

Fig. 2. Vertical fluid bed of polyamide 11

3. Polyamide 11 in water industry

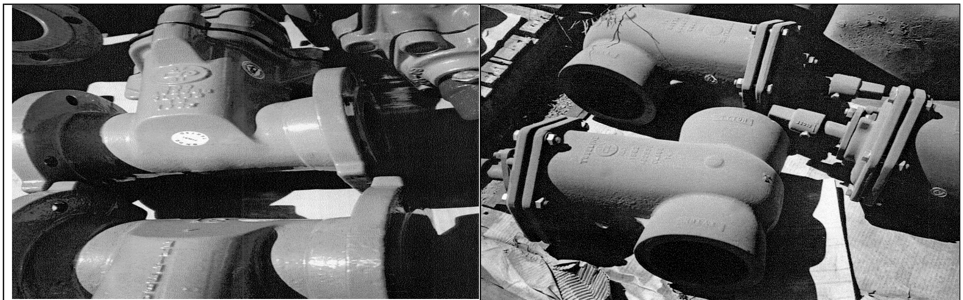
Polyamide 11 has been used in water industry for coating pipes, pumps, valves and fittings since 1967. It is internationally acknowledged as a coating material that can be used with confidence by the engineer and designer to combat corrosion, without sacrificing the economy and strength of basic metal substrates. Its unique properties allow providing to water companies, municipalities and industry the following benefits:

3.1. Water quality preservation:

Polyamide 11 coating does not release any hazardous compound. It has been evaluated and found to comply to various regulatory requirements, for example, WRAS and DWI in UK, DVGW-KTW and DVGW-W270 in Germany, ACS according to Circular DGS/VS4/N°99.217 in France, KIWA-ATA in Holland, JWWA WSP 067-2001 in Japan, NSF61 in US and AS4020 in Australia.

3.2. Easier handling of coated pieces

Polyamide 11's semi crystalline structure brings to the material both the hardness of thermosetting materials and the flexibility of thermoplastics. As a ductile material, it won't chip or crack like epoxy does but its hardness will allow compressions that would damage all polyolefin's based coatings. It results in a high resistance to impact, even at low temperature, that allows pipe transportation and handling before its installation under harsh field conditions as well as a quite remarkable elasticity (>20% elongation at break), which makes possible pipe bending on site up to 30 times its diameter without cracking allowing the coating to follow the deformation of the steel. Moreover, its weathering resistance prevents the coating to chalk as it is observed with currently used Fusion Bonding Epoxy (FBE) coating (picture 4).



Rilsan® coating after 12 months outdoor storage in Australia	FBE coating after 6 months outdoor storage in Australia

Fig. 3. Weathering resistance comparison between FBE and polyamide 11

3.3. Free maintenance coating through an excellent durability

Polyamide 11 coatings systems used for water treatment applications are designed to withstand water and saltwater continuous exposure at temperature up to 50°C, pH from 3 to 10 without limitation considering the pressure (tested with success at 150 bars). In those conditions, it maintains the original designed quality of the piping system thanks to its excellent resistance to wear, chemicals and corrosion. Those are discussed below:

3.3.1. Wear resistance

Erosion tests have been carried out with 450 µm corundum particles. Tests have been performed for several incident angles, particle velocities (5 to 20 m/s) and for several coating types [1]. The graphic 5 shows a much superior resistance to erosion for polyamide 11 coatings compared to solvent based epoxy and FBE powder coatings. Besides, cavitation erosion tests [2], carried according to ASTM G32 (Standard method for determination of cavitation erosion using vibratory apparatus) and reported in the graphic 6, have also demonstrated without surprise that polyamide 11 offers better resistance than FBE coatings, which are eroded to the metal surface. The same experimental work proved that polyamide 11 performs better than the main metals used in water industry like brass, cast iron, carbon steel, stainless steel 316L and even high strength steel alloys (CA-6-MN).

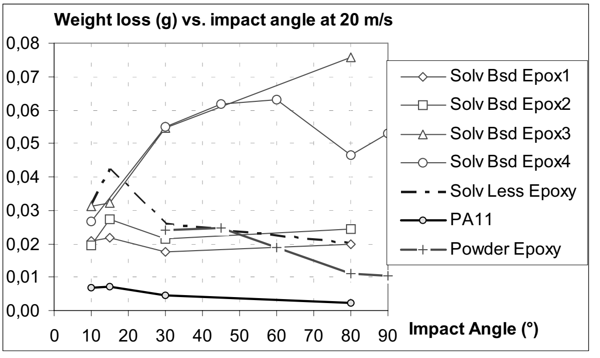


Fig. 4. Comparison of erosion resistance of several coatings

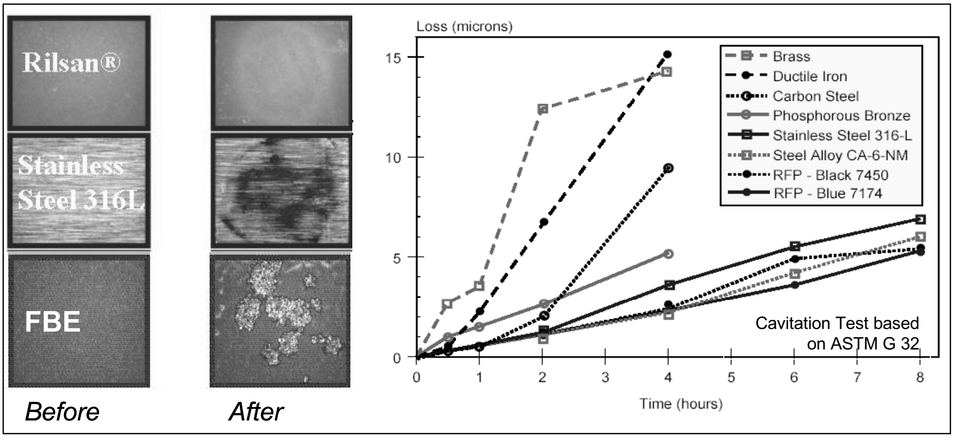


Fig. 5. Cavitation erosion resistance of several materials (loss in µm and optical comparison)

3.3.2. Chemical resistance:

Polyamide 11 coatings resist to most of the chemicals used in water treatment including some that corrode most of stainless steel grades. We can mention disinfectants (chlorine, chlorinated chemicals, ozone…), oxidizing agents (oxygen, potassium permanganate…), flocculants and softening agents (Ferric chloride, aluminium chloride, sulphates) as well as membrane cleaning agents (sodium bisulphite, hydrochloric acid, sodium hydroxide…).

3.3.3. Corrosion resistance

The corrosion resistance of the polyamide 11 coating system has been proven throughout laboratory evaluations, on field trials and confirmed by 40 years track records. The table 7 gathers the most relevant information. This outstanding behavior is due to the low gas and vapor permeability combined with the excellent adhesion retention of the system avoiding the creation microscopic gaps or lack of intimate contact, which favor the condensation or the enrichment of corrosive agents on the metal. Actually, there is o corrosion in the absence of any gaps or failure of adhesion at the metal/coating interface, so demonstrating the importance of adhesion. More over the primer limits the propagation of the rust in case of coating damage due to inappropriate manipulation giving to the plant operators or constructors the chance to repair the damage on site with a touch up.

Tab. 2. Information regarding the corrosion resistance polyamide 11 system

Laboratory results	On site trials	
No loss of adhesion or corrosion propagation after 2000 hours salt spray	 External and internal coating of a water pipeline used for the water injection assisted extraction of crude oil (Algeria)	Temperature: -6→45°C Pressure: 15bars Water quality: - 41g/l of NaCl, - 6ppm of H_2S - 150ppm of CO_2 Conclusion [3]: No coating degradation, no loss of adhesion or blistering after five years and a half.
No loss of adhesion or corrosion propagation after ten years immersion in seawater		
Resist to cathodic disbondment WIS 4- 52-01 EN 10310		

3.4. Energy saving

Polyamide 11 coating has a very smooth and low friction surface. This benefits to keep the pressure loss of the piping system and the pumps low and thus optimise the energy consumption. Measurements have demonstrated a reduction of pipe pressure loss by 50% compared to cement coated pipes and a lower friction parameter of PA 11 coatings compared to epoxy based ones (1). This low factor of friction lasts, as the coating does not support bio-film formation, scaling and resists to erosion

3.5. References throughout the whole water cycle

Polyamide 11 has been used in water industry for coating pipes, pumps, valves and fittings since 1967. We can find references all along the water cycle.

3.5.1. Pumping station

The French company Les Eaux du Nord uses Polyamide-11 coated drilling pipes to pump abrasive underground water. Many pumping stations in Europe are using this coating. We can observe an example on Picture 8.

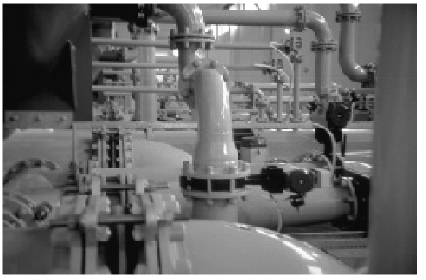


Fig. 6. Pumping station

3.5.2. Water treatment

In 1967, Polyamide 11 coated mild steel piping system was first used in a potable water production plant at Looksbroek operated by Waterleidingmaatschappij Oost-Brabant N.V. in Holland. Kersten B.V. at Brummen, Holland was the coating applicator. This plant is still in operation 40 years after its construction and the piping system hasn't required any renovation yet. Now, around 70% of the Dutch potable water treatment plants and more than 50% of the German one have been using polyamide-11 coated pipes.

3.5.3. Water transportation

Since 1980, the Japanese water utility has adopted polyamide 11 coating for the water storage tank panel and the pipes along bridges to transport water from mainland to the nearby islands. The coated pipes resists to earthquakes due to their flexibility. Its usage in Europe in the domain of drinking water transport started in 1986. In Turin, as in several other localities in Italy, several hundred of kilometers of pipelines (with a diameter ranging from 10" to 50") have been laid. The clients are not only impressed by the physical and chemical properties but also by the ease of installing the pipeline.

3.5.4. Wastewater treatment

The first waste water treatment plant using polyamide-11 was built in 1980. Since that, we have referenced more than 16 wastewater plants using this coating for the piping system. The picture 9 shows a wastewater treatment plant using flanged pipes and fittings coated with polyamide 11, which was built in 1990 at Bocholt in Germany.

Fig. 7. Waste water treatment plant at Bocholt in Germany

4. PA 11 coatings: A cost effective alternative in membrane treatment plants

Membrane filtration market has been growing very fast last years as membranes provide unique solutions to current water industry challenges. Actually, Salt Water Reverse Osmosis gives new possibilities to combat the lack of water caused by the climate change. Nano-filtration, ultra-filtration and micro-filtration provide responses to the problem of the pollution of river and underground water and play also major roles in regards to the challenges raised by the strengthening of wastewater regulations. This makes this sector very dynamic and highly innovative. But even if many problems have already been solved, water companies have to produce water at competitive cost so they are still looking for innovations that make the use of membranes in water treatment plant more affordable. Actually the use of this technology induces indirect costs that impact both capital expenditure and operating expenditure. The major ones are listed below:

- The materials cost because of the sharp increase in price of precious metal, like Ni, which are essential components in stainless steel and the expensiveness of complex Glass Reinforced Plastics (GRP) parts
- The energy cost because of the pressure required by those processes
- The maintenance costs due to the replacement of the membranes and the aggressive environments that degrade current materials

In order to decrease those costs, some innovative companies involved in membrane filtration technology, including ultra-filtration, salt water and brackish water reverse osmosis, have specified polyamide 11 coated piping system to replace 316L and super duplex stainless steel. We will discuss why among the piping systems currently available for water treatment plant, polyamide-11 coated piping system appears to be one of the best solution to fulfill the objective to deliver high quality treated water at optimum CAPEX and OPEX.

4.1. Material costs

The piping system represents nowadays a very high percentage of the capital cost of a water treatment plant. The graphic 10 based on 2007 data [4] shows that piping based on high alloy materials contributes in 15% of the capital cost for Salt Water Reverse Osmosis desalination plants. So the choice of the material for the water treatment plant piping system appears to be key in order to save CAPEX. This is more and more the case since the sharp rise of stainless steel prices due to the combination of the exponential rise in consumption for the last 10 years (+14% in 2006) and the strong increase of alloy surcharges. Stainless steel prices rose by a factor 2.5 between January 2006 and May 2006 mainly due to the skyrocketing nickel price. We are going toward stabilization but at high prices because of the demand that should remain high.

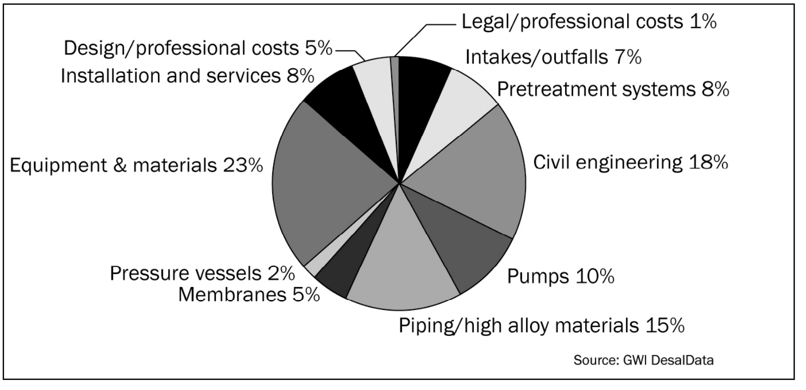


Fig. 8. Segmental SWRO capital costs

Obviously, the cost of the full installed piping system in a water treatment plant depends not only on the material costs (pipes and fittings) but also on the shop fabrication, the field installation costs as well as the equipment and contractor fees. To get an accurate estimation of the cost comparison between different piping, we need to consider each cost segments as they vary materials from materials. For instance:

- Welding stainless steel will be more expensive than welding steel, increasing the costs for shop fabrication and field installation.
- GRP parts cannot be shop fabricated like steel. So their price from the spool manufacturer will be more expensive especially for complex parts but they won't require further shop fabrication.
- Coated pipes cannot be welded on site. So more prefabrication works are required but this cost is balanced by the quicker assembly time of flanged pipes compared to welded pipe reducing contractor fees.

Finally, depending on piping system design (straight run piping or complex piping system), the importance of each cost segment will be different. The cost of pipes and fittings will have a greater share in a straight run piping whereas shop fabrication costs will be higher for complex piping systems.

Taking into account the above considerations, we have tried to compare the full installed cost of piping systems using carbon steel coated with polyamide 11, stainless steel 316L and GRP. We did this exercise for both a straight run piping and a complex piping system. We based our work on a study published by Lindley & Floyd [5] and updated the 1993 results to get an estimation of what could be achieved in 2007. We proceeded as explained below:

- We updated the pipes and fittings costs with the French construction price evolution index (provided by INSEE), which consider raw materials as 65% of the costs and 35% for manpower costs.
- Field installation costs were updated at 110% of the French inflation rate to take into account the price increase of oil.
- Other costs were updated at 90% of the French inflation rate taking into account the evolution of the technology

The graphics 12 and 13 showed the costs comparison obtained for a 4” Diameter 500 feet Straight Run Piping System and a 4” Diameter 400 feet Complex Piping System. We achieved with those particular designs a cost reduction around 50% over stainless steel 316L for both straight and complex piping systems. Although this calculation has to be determined design by design, we can note the huge savings that may be achieved switching from stainless steel 316L to polyamide-11 coated steel. This cost reduction would be even higher considering more expensive stainless steels like the super duplex grades, which are used in SWRO desalination plants

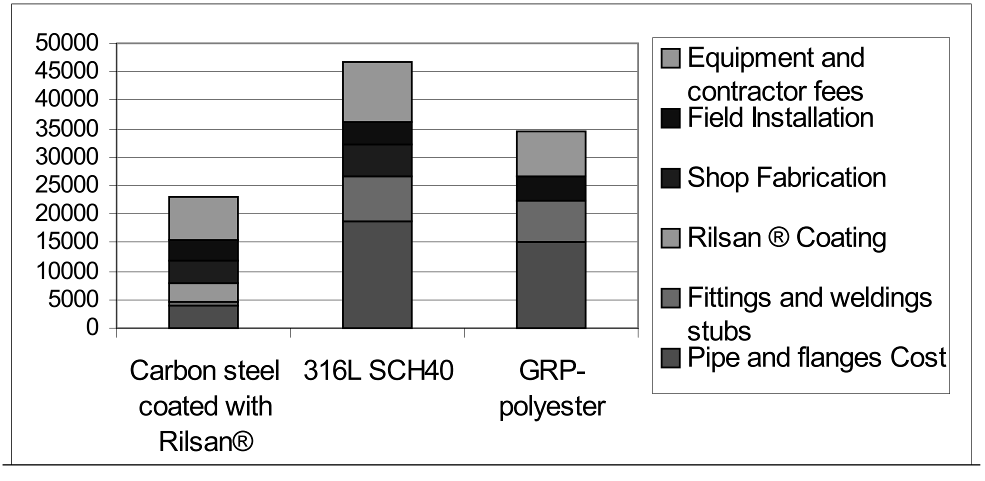


Fig. 9. Cost comparison for a 4” Diameter, 400 ft Complex Piping System

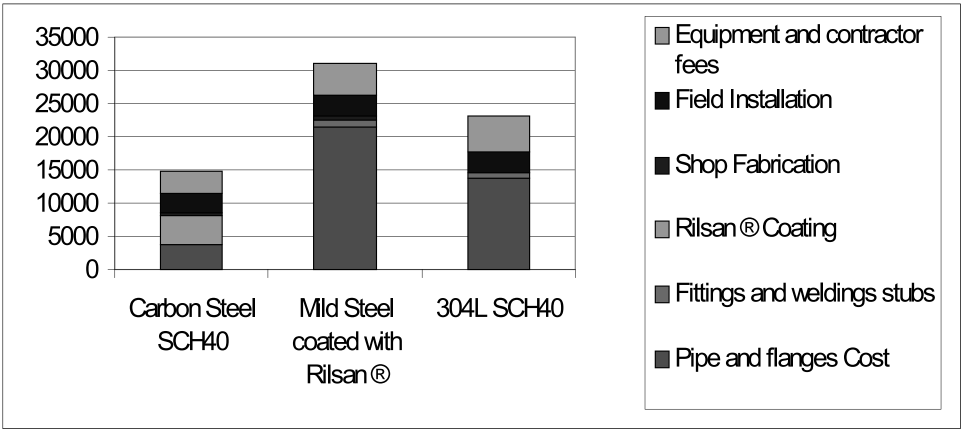


Fig. 10. Cost comparison for a 4” Diameter 500 feet Straight Run Piping System

4.2. Energy costs

Energy represents one the largest expenditure for SWRO desalination plants with a typical 30% share. Actually, standard energy consumptions are around 3.8 KWh/m^3 of produced water considering energy recovery. So here again, there are possibilities for major savings. Most of the work done to reduce the energy costs focused on developing technologies for energy recovery (Pelton wheel, Pressure exchanger…) or to optimize pumps efficiencies through new designs. Materials through their friction factor have also an impact on energy consumption. Optimizing pressure losses of the piping system in using materials having smooth surfaces may lead to OPEX savings. Those needs to be calculated for each piping system as they are highly design dependent.

The figure 13 shows roughness profiles of both Polyamide 11 coating and stainless steel 316L. Both surfaces lead to the same Ra (0.5-0.9µm) but the density of peak of the polyamide 11 coating is 3.5 times lower than stainless steel 316L, which benefits to lower the pressure losses.

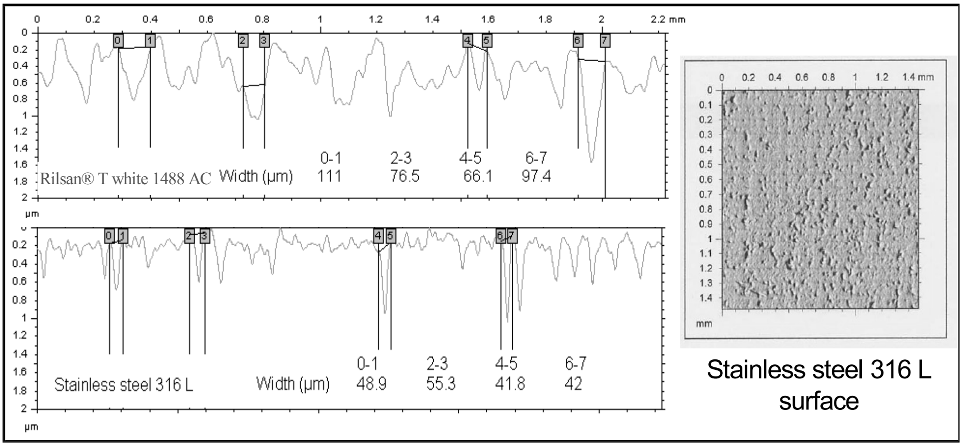


Fig. 11. Roughness profile comparison between Polyamide 11 coating and stainless steel 316L

4.3. Maintenance costs

Membrane filtration technologies still require high maintenance cost primarily to take care of the membranes itself. Actually the membranes are prone to bio fouling, scaling and accidental damage. In order to limit the maintenance, companies have set up cleaning procedures that consist in backwashing the membrane with specific solutions. But those chemicals lead to pitting corrosion for most of stainless steel grades, especially when they consist in chlorinated chemicals in acidic medium, and thus cause further maintenance problems on the piping and the pumps.

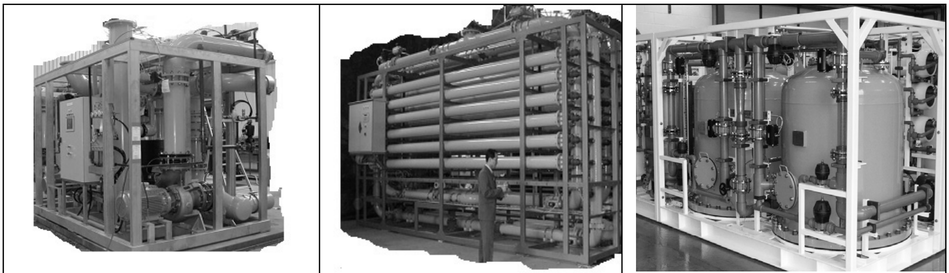
Besides the problems related to the maintenance of the membrane, SWRO desalination plants face major corrosion challenges for their piping. Actually, only very expensive grades of stainless steel like super duplex can resist to seawater and even more to brines. Even using those very specific grades, problems occur because of the difficulty to weld the pipes onsite without creating potential corrosion sites.

Polyamide-11 coated piping systems do not face this corrosion issue, as the coating system is inert to seawater, brine and membrane cleaning agents. More over, plants using coatings are engineered for flanges pipes. The simple design adjustments required are greatly balanced by avoiding the risks of corrosion due to welding onsite.

4.4. Reference in water membrane technology

Keeping in mind their objective of delivering good quality water without interruption at competitive cost, some companies already use polyamide 11 coated piping system to replace 316L and super duplex in order to decrease operating and capital expenditure in some of their water treatment plants using membrane technologies. We can mention the following references:

- The coating of the piping system and vessels in membrane filtration skids (see picture 14). Those are in operation in several water and wastewater treatment plants in France, Russia, China and on-board ships.



Vertical ultra filtration skid (internal and external coating of the piping)	Horizontal ultra filtration skid (internal and exter-nal coating of the piping)	SWRO skid (internal and external coating of the vessel)

Fig. 12. Membrane filtration skids using polyamide 11 coatings

- The coating of the piping system (joining the skids) of the ultra filtration water treatment plant of Roetgen in Germany (144 000 m3/day)

- The coating of piping systems, valves and fittings in the Okinawa reverse osmosis seawater desalination plant of 40 000 m3/day in Japan (see picture 15). There hasn't been any maintenance with the polyamide 11 coating since its installation in 1997.

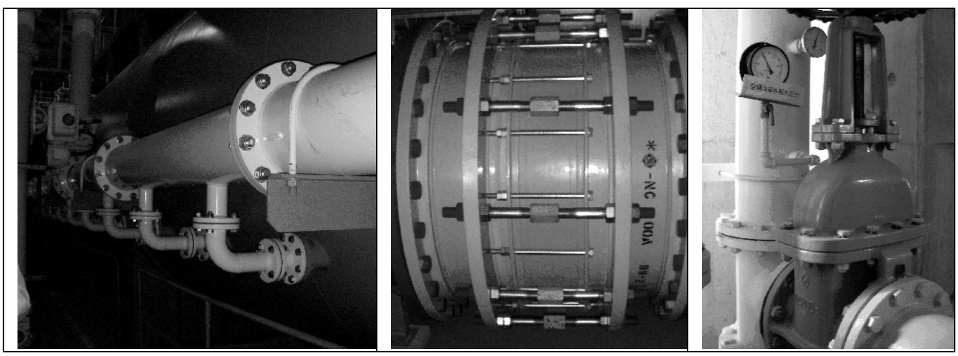


Fig. 13. Polyamide coated parts in the SWRO Okinawa desalination plant

- The coating of split case pumps and impellers up to 7 tons for salt water injection or brackish water pumping

5. Conclusion

Polyamide 11 has been used in water industry for coating pipes, pumps, valves and fittings since 1967. Its unique properties bring to the water companies, the municipalities and the industries numerous benefits including the preservation of the water quality, the protection of the parts during handling and storage, the decrease of maintenance cost as well as the saving of energy. Those benefits have been proven through relevant usage references in the water industry.

Besides, polyamide 11 coating appears to be an alternative to stainless steel to decrease operating and capital expenditure in water treatment plants using membrane technologies. Actually we showed that it may bring savings up to 50% on the high alloy piping system, may save maintenance costs due its better corrosion resistance to membrane cleaning agents, seawater and brines and could allow to save energy decreasing pressure losses. Those benefits are already used by companies involved in membrane filtration technology, which have specified polyamide 11 coated piping system to replace 316L and super duplex.

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