A SOLUTION FOR DRINKING WATER NETWORKS: EMERGING NEW GENERATION PE100 PIPES WITH HIGHER CHLORINE RESISTANCE

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Abstract
(Polyethylene, Lifetime, Disinfectant, PE 100)

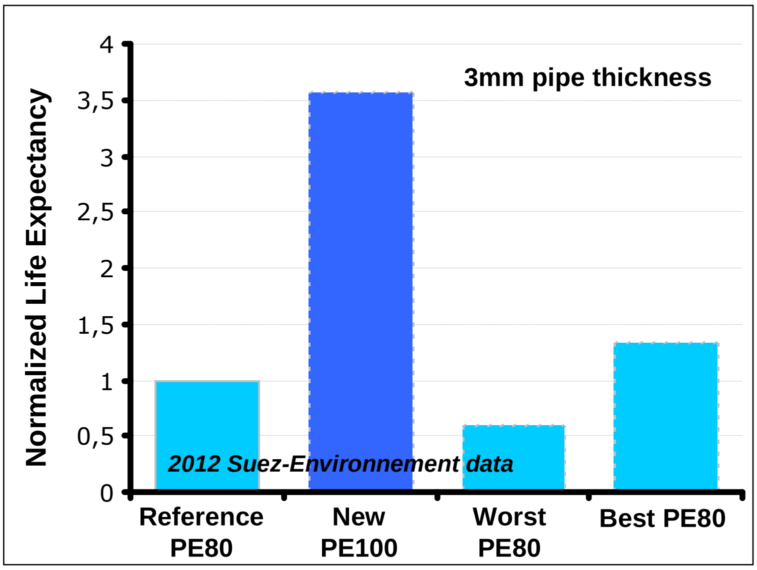
Polyethylene is sensitive to chemical oxidation through the action of disinfectants used in drinking water, as explained in previous works. Based on accelerated ageing tests (high water temperature, chlorination, high pressure level), SUEZ-ENVIRONNEMENT defined a testing methodology to benchmark plastic pipes according to their resistance to chlorine in drinking water. After 6 years of pipe testing, a new generation of PE100 is emerging. However, chlorine resistance is not the only property required for approving the material's suitability to drinking water networks. Indeed, antioxidant stability within PE, resistance to UV and temperature during outdoor storage, suitability for welding to other PE materials, resistance to slow crack growth and resistance to notch penetration are also very important factors to investigate for operational validation. This paper illustrates the results on one PE100 pipe modified for higher chlorine resistance, called hereafter "PE100-NEW". However, as good as this new product is, the key point for operators is its suitability works and the ease in which it can be installed (welding, flexibility, handling, laying conditions). Trials in 3 different areas (South West, South East of France and Paris area) were performed in order to test different field conditions and techniques. Feedback obtained from the pipe fitters is described here.

INTRODUCTION

For implementing its internal asset management policy, THE POLYETHYLENE SUSTAINABLE LIFE-CYCLE©, SUEZ ENVIRONNEMENT focuses particularly on the properties of the PE resin used for PE water service pipelines and mains. As illustrated in previous works, not all PE is the same and the lifetime could vary from 1 to 3 depending upon the resin chosen. A promising PE100 was identified thanks to the accelerated ageing performed on Suez-Environnement's bench test. *Rozental-Evesque (1).* The experiment was conducted up to failure point in extreme water network conditions (40°C, 6 bar, 1 mg/L Chlorine Dioxide) in order to assess the benefit of this resin compared to the standard ones (PE80 and PE100). The results are shown in Figure I. The new formulation of the studied PE100-NEW provides higher resistance towards chlorine dioxide and it could be assumed towards chlorine too. Indeed, chlorine dioxide is much more aggressive than chlorine towards polyethylene.

Previous works have already analysed and compared the aggressiveness and kinetics of chlorine dioxide and chlorine on PE. *Colin (2-4).*

Figure I: Performance of the PE100-NEW resin in chlorinated water



Before approving this new PE100, several other mechanical and chemical properties must be checked to ensure the long-term performance and the suitability of the PE100-NEW material for field applications. Two project phases were performed:

- analyses of material properties, carried out by CRIGEN, the GDF-SUEZ Group's Gas Research Centre. The results were compared to standard PE100, also used for applications in gas industry.
- trials under different field conditions and using different techniques, conducted by LYONNAISE DES EAUX, the French subsidiary of SUEZ-ENVIRONNEMENT, in 3 different operational sites (respectively in South West France, South East France and the Paris area).

VALIDATION OF PE MATERIAL PROPERTIES

The performance of a new type of PE is strongly linked to its application. This concerns overall chemical, physical and mechanical properties. For drinking water, resistance to chlorinated disinfectants has only really been taken into account since 2003. Consequently, specific developments were required based on the current generation of polyethylene resins, those designed for gas performance during the previous decades.

Testing methodology

For assessing the performance of new PE material for use in drinking water, the first step is to ensure the resistance to chlorine. SUEZ ENVIRONNEMENT's accelerated ageing test bench of provides this validation. *Rozental-Evesque (5).*
Secondly, chemical properties must be checked such as the melt flow index (extrusion performance) and the stability of additives during outdoor storage (UV exposure). Then, for ensuring the product's performance during installation, slow crack growth resistance,

material weldability and notched pipe resistance tests are required. This testing protocol was defined jointly with the CRIGEN, based on the knowledge of the gas industry, for comparing the PE100-NEW material properties to other PE resins used for water or gas application.

Reference materials

All of the tested materials are approved by the French National Quality Mark (NF114 approval). Taken as a reference, PE1 is a PE100 resin with the same polymer structure as PE100-NEW but without the specific additives for chlorine resistance. PE2 is a PE100 RC resin with very good properties towards slow crack growth resistance. PE3 is a PE100 resin currently used for the manufacture of fittings, with good mould injection characteristics. PE4 is a former PE80 resin used for fitting applications during the 1990s.

Extrusion performance

The analytical protocol for measuring the melt flow index (MFI) is based on the NF EN ISO 1133 standard widening the range of thermo-mechanical stresses at high loads. *Gueugnaut (6)*. Testing was conducted at 190℃ by means of the Melt Indexer DAVENPORT 3/81 bench with oven temperature regulation adjusted to ± 2℃. The results are shown in Table I .

Table I: Melt flow indexes at 190℃ (unit: g/10min)

Samples	MFI 190℃ 5kg	MFI 190℃ 10kg	MFI 190℃ 21,6 kg
PE100-NEW Resin	0.232 ± 0.001	0.983 ± 0.004	7.040 ± 0.27
PE100-NEW DN25 pipe	0.234 ± 0.001	0.986 ± 0.006	6.830 ± 0.143
PE100-NEW DN110 pipe	0.240 ± 0.003	0.978 ± 0.007	6.725 ± 0.208
PE1 DN200 pipe	0.209 ± 0.003	0.820 ± 0.010	6.380 ± 0.430
PE2 DN63 pipe	0.326 ± 0.004	1.486 ± 0.016	11.567 ± 0.717

For the lowest load (5kg), i.e. the lowest shear gradient, the PE100-NEW fluidity is about 0.23 g/10min that is twice lower than standard PE100 resin for which value is around 0.45 g/10min. This new PE can be considered as a low sagging (LS) material. This property is very useful for manufacturing large diameter pipes with a thick pipe wall. For higher loads (10kg and 21.6kg), the fluidity of PE100-NEW materials increases more slowly than that of the PE2 pipe. Therefore the viscosity of PE100-NEW is significantly higher than the PE100RC reference and this is true for a large range of shear rates.

Additive stability

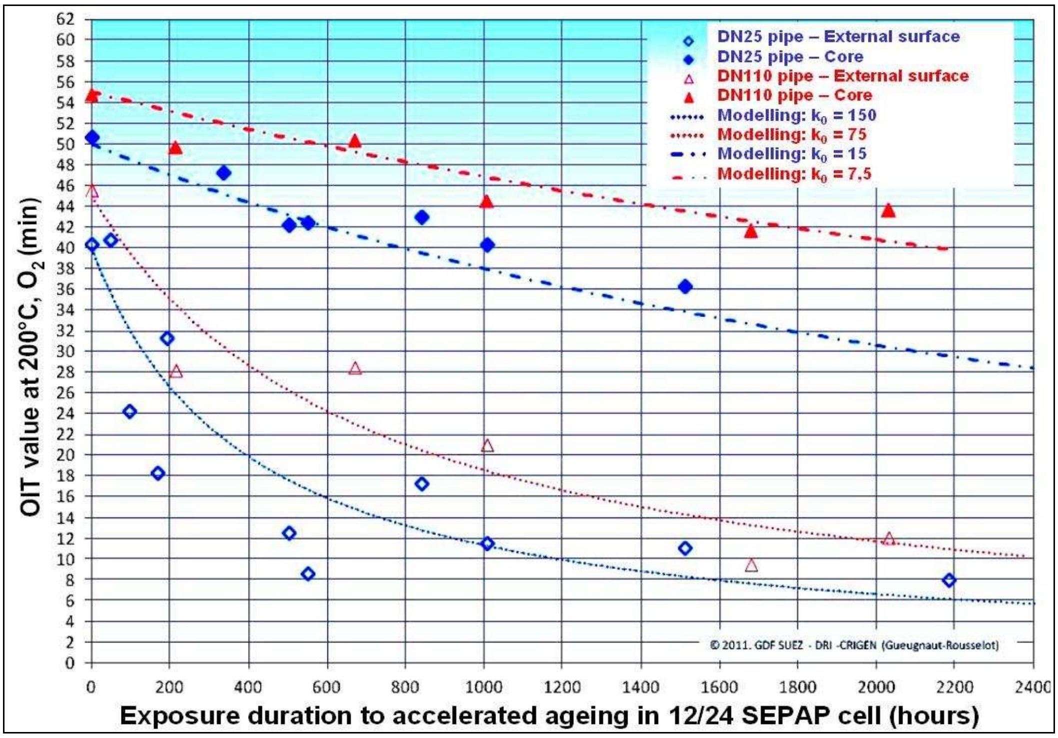
A CRIGEN accelerated ageing test protocol, called 12/24 SEPAP method, was used for determining the additive stability within PE100-NEW pipes. Two different diameters, DN25 and DN110 pipes, were studied for identifying a potential reservoir effect of stabilizers within the pipe thickness, respectively 3 mm and 10 mm for those diameters. Figure II illustrates the experimental apparatus.

Accelerated ageing is performed at 60℃ under UV exposure. This accelerated photo-thermal oxidation provides information relative to the PE degradation when it is exposed to heat (during extrusion) or outdoor exposure (storage before laying). The maximum exposure time is fixed at 2200h per sample. The experiment was carried out over 10 months. Oxidation induction time at 200℃ under oxygen is measured by differential scanning calorimetry with a DSC30 METTLER TOLEDO TDD197 cell. Samples (10 mg ± 0,5 mg) were collected every 11 days at the core and at the inner surface of each analysed pipe following different exposure times in the 12/24 SEPAP cell.

Figure II: 12/24 SEPAP cell, photo-thermo-oxidative accelerated ageing

It is recalled here that stabilizer consumption results from a chemical reaction (blocking oxidation reactions of PE matrix) and physical phenomena (migration and evaporation). Figure III shows, respectively, the OIT results for both DN25 and DN110 pipes according to the ageing exposure time.

Figure III: OIT measurements and modelling of additive consumption kinetics



Values are spread out due to the heterogeneous distribution of additives within the pipe thickness and the location where the sample was collected. High initial OIT values are noticed at around 40 mins (DN25) and 45 mins (DN110) at the outer surface and

50 mins (DN25) and 55 mins (DN110) at the core. This is between twice and three times the required level of ISO 1555-3 standard (20 mins). The stabilisation level reduces slowly at the core with respective OIT values around 30 mins for the DN25 pipe and 40 mins for the DN110 pipe after 2000h of exposure. Conversely, additives are consumed quickly at the external surface and OIT values decrease to 10 mins for the DN25 pipe and 12 mins for the DN110 pipe. Under accelerated ageing conditions, the reservoir effect, i.e. the migration of the additive from the core to the external surface, is not present.

Modelling of additive consumption kinetics is calculated by a theoretical law expressed by the following equation:

$$(\frac{1}{OIT})-(\frac{1}{OIT_0})=\int_0^t k_0.h.\exp(\frac{-E}{RT}).I^{\alpha}.du \qquad \textbf{(I)}$$

Where OIT = oxidation induction time at t and t_0; k_0 = proportional parameter of stabilizer consumption (chemical reaction and evaporation); h = constant of leaching by rain;
E = activation energy; R = 8,314 $J.mol^{-1}.K^{-1}$; T = the absolute temperature (in Kelvin);
I = maximum UV energy component and α = attenuation factor

Compared to standard water and gas pipes with classical stabilizing systems (2 or 3 antioxidants), the obtained k_0 values are lower, indicating slow consumption in the new stabilizing system for the PE100-NEW resin. *Gueugnaut (7).* k_0 values are about ten times higher at the outer surface than at the core for both pipes and double for the DN25 pipe when it is compared to the DN110 pipe. This therefore confirms the relative low migration of additives and the higher stability of the additive package for large diameters.
Based on these results, it is possible to determine the storage time limit for the material before critical consumption of additives, considered for an OIT value of 5 mins. Previous works defined a multiplying factor of 50 between the 12/24 SEPAP method and natural ageing induced by outdoor storage in the site of Bandol (South of France). *Gueugnaut and Rousselot (8).* Table II summarizes the results.

Table II: estimation of maximum exposure time to reach an OIT = 5 min

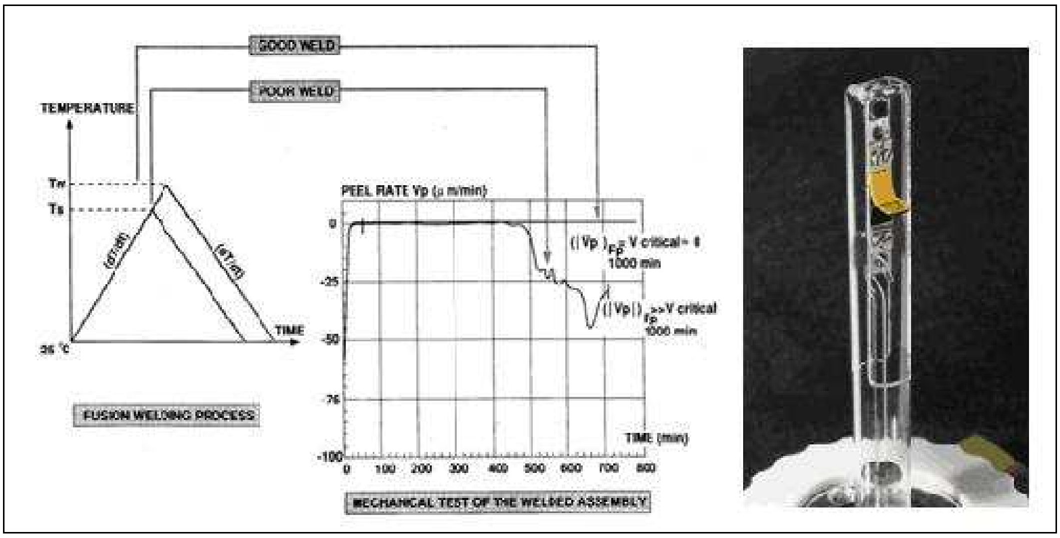
Samples	By 12/24 SEPAP method	In natural ageing (Bandol)
PE100-NEW DN25 pipe	≅ 2750 hours	≅ 15 – 16 years
PE100-NEW DN110 pipe	≅ 5600 hours	≅ 32 years

For standard PE pipes, it is estimated that additive consumption is complete after 2 years of outdoor storage due to photo-thermal oxidation. Thus, the new stabilizing system for PE100-NEW resin is excellent regarding the stability of additives and even better for large diameter pipes.

Material weldability
The intrinsic weldability of PE100-NEW with other standard PE100 resins, here PE3, was determined by a peel decohesion test on a small lamellar micro-assembling unit (10 mm x 6 mm x 0,35-0,40 mm for each sample) at 80℃ under a fixed load. The

welding is performed by means of an infra-red oven with 2 heating rates at 200℃/min and 300℃/min directly at the sub-outer pipe surface (350 – 400 µm) for simulating a scraped pipe. These conditions were selected so as to allow a comparison to be made with previous experiments on PE2 and PE4 resins, carried out by the CRIGEN. This testing consists in determining the minimum temperature to be reached per heating rate at which decohesion no longer occurs, as illustrated in Figure IV.

Figure IV: welding cycle and peel decohesion test for the micro-assembling



Samples before and after accelerated ageing (SEPAP method, UV, 60℃, 0, 20 and 40 days) were tested for assessing the impact of outdoor storage on material weldability. Experiments were conducted with DN110 pipes. Typical speed rate for DN110 (SDR11) pipes are currently below 150℃/min. The results are shown in Table III.

Table III: minimum temperature for good welding per heating rate

Micro-assembling samples	200℃/min cycle	300℃/min cycle
PE100-NEW + PE3, without ageing	≅ 165℃	≅ 170℃
PE100-NEW + PE3, after 1032 hours of exposure	≅ 170℃	≅ 180℃
PE100-NEW + PE3, after 2032 hours of exposure	≅ 170℃	≅ 180℃
PE2 + PE2, DN63 pipe, without ageing	≅ 165℃	≅ 170℃
PE4 + PE4, DN63 pipe, without ageing	≅190℃	≅ 205℃

After 2000 hours of accelerated ageing, only a slight increase in the welding minimum temperature was noticed, close to the new sample value, reflecting the absence of any barrier or lubricant effect from the stabilizing system. Moreover, even under these aggressive conditions (2000 hours, UV, 60℃), the welding minimum temperature for PE100-NEW resin remains better than that of the PE4 resin, used over the last few decades, and this without any ageing. Compared to the PE100 RC resin, PE100-NEW and PE2 resins have the same intrinsic weldability.

These results were also confirmed by crushing decohesion tests carried out on electrofusion couplings (ISO 13956 standard) and connector sockets (modified ISO 13955 standard) on DN63 (SDR 9) pipes made from PE100-NEW resin and PE2 resin, used as reference samples. From the operator point of view, the material weldability is excellent.

Slow crack growth resistance

An optimised cone test was performed. The pipe thickness was notched by a mechanical cone. Then the sample is artificially aged applying a high temperature (80℃) in the presence of an aggressive surfactant, 3% F-Teepol (dodecylbenzensulfonate) for 40 days (1000 hours). The use of F-Teepol instead of Arkopal® is recommended to avoid its premature chemical ageing. The experiment by the CRIGEN lab showed that this optimised methodology can provide reliable results for pipes with a thickness of 2mm to 15mm. The notch propagation is performed every 100 hours. The crack initiation time is determined by tangent method and the crack propagation rate is obtained by linear regression. The results are shown in Table IV.

Table IV: cone test results, assessment of slow crack growth resistance

SCG resistance	PE100-NEW (25 mm)	PE100-NEW (110 mm)	PE2 (63 mm)
Crack initiation time	between 1h – 47h	690h – 3400 h	260 h – 510 h
Crack propagation rate	3 – 3.7 mm/day	2.4 – 2.9 mm/day	0.7 – 1.3 mm/day

As expected, crack initiation starts around the notched area and near the external surface, a consequence of high stress content. A very short initiation time (<50h) was recorded for the small diameter (DN25) contrary to larger diameter. For large diameters the NF EN ISO 13479 standard requires an initiation time value higher than 500 hours. It is estimated that the PE100 polymer structure of PE100-NEW was targeted for larger diameters.

The ISO13480 standard requires a crack propagation of less than 10 mm/day. However this standard is not very restrictive. For current PE materials, it is estimated that a good PE80 resin should have a crack propagation rate of around 4 mm/day whereas that of poor quality resin would be around 10 mm/day. The presence of two crack propagation rates between DN25 and DN110 pipes highlights a crystalline heterogeneity at the pipe wall.

The shorter initiation time and higher propagation rate for the DN25 pipe indicate that service pipelines are more sensitive to slow crack growth than mains. Compared to PE2, the results allow the PE100-NEW resin to be classified as a very good PE80 resin but not as resistant as good PE100 RC material.

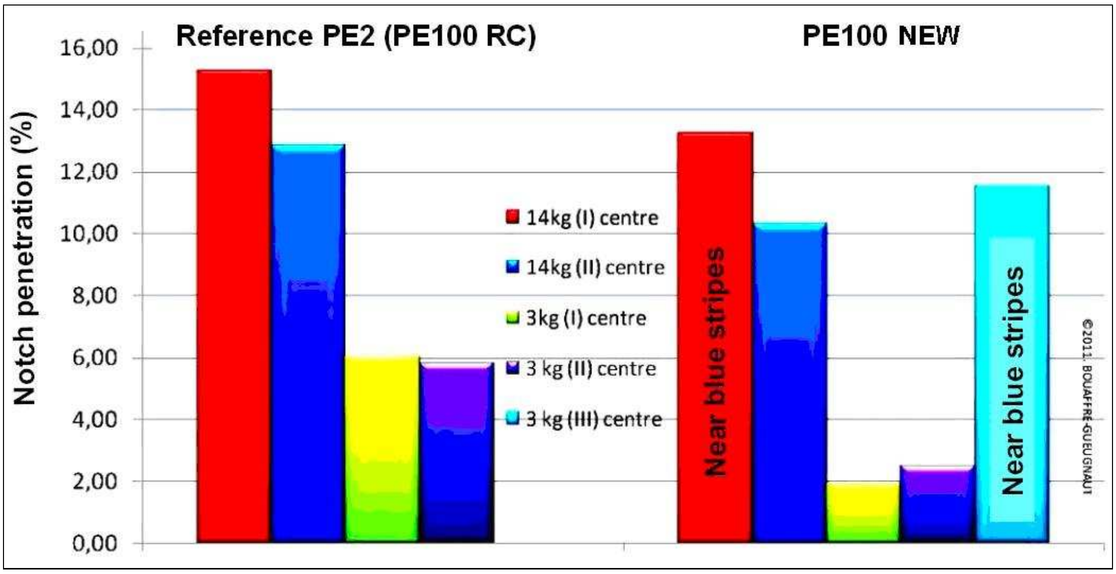
Notched pipe test

This test estimates the pipe resistance towards scratches and notches induced by installation. This characteristic is required by PAS 1075 (2009) for PE100 RC materials.

The CRIGEN developed in the early 2000s its own methodology to benchmark plastic materials for scratch resistance. The experimental setup comprised a test bench with a calibrated and loaded blade tool and tested over 40cm on a DN63 pipe sample with an average rate of 2m/min. The notch penetration was adjusted to a depth of 10% for a 3kg

load and to a depth of 20% for a 14kg load on a pipe sample made from a PE80 resin, well-known for its efficiency in gas applications. During testing, 2 notches were made with a 30° tool inclination associated with a 3kg load and 2 other notches with a 90° tool inclination and a 14kg load and were performed on the 4 sides of the pipe. Then the notch depth was measured by an impression kit, specially defined by the company SOPROGA.
For assessing PE100-NEW performance, PE2 is taken as a reference. Figure V gives the depth results taken at the centre of the notch for both materials.

Figure V: average notch penetration for both materials



Both materials have very good performance towards notch penetration compared to the standard PE80 (respectively 10% for 30°/3kg and 20% for 90°/14kg). Indeed, for the 90°/14kg couple, the notch penetration fluctuates between 10-13% for PE100-NEW and between 13-15% for PE2. For the second couple, PE100-NEW exhibits only a 2% notch depth compared to 6% for the reference.
So, PE100-NEW appears more resistant to notch penetration than the PE100 RC taken as a reference. However, near the blue stripes, notch penetration is abnormally high. This anomaly, if confirmed, can reveal a heterogeneous crystalline microstructure at this specific location and extrusion conditions should be monitored.

PE100-NEW INSTALLATION

Several different nominal diameter and nominal pressure pipes were industrially manufactured by a French pipe manufacturer using the PE100-NEW resin (See Table V). As the PE100-NEW complies with the French Health Acceptance Certification (ACS), the produced pipes were installed as usual within current pipe renewal programmes.
A total of 131 house connection pipes were installed using different operational techniques: open cut trench, pipe extraction for lead pipe renewal, pipe splitting, welding by electrofusion. Amongst them, 30 service pipelines were laid by a works company in order to obtain the opinion of our subcontractor.

Table V: pipe production specifications for the trials

Nominal Diameter	Nominal Pressure (bar)	Conditioning	Produced length
DN25 (25 mm)	PN25 and PN20	Coils	600 m for each PN
DN32 (32 mm)	PN25 and PN20	Coils	300 m for each PN
DN50 (50 mm)	PN20	Coils	150 m
DN63 (63 mm)	PN16	Coils	300 m
DN110 (110 mm)	PN16	Straight lines	50 m
DN125 (125 mm)	PN16	Drums	200 m
= 6 diameters	**= 3 nominal pressures**	**= 3 types**	**= 2 500 m of pipes**

A DN125 PE100-NEW pipe was used to renew an asbestos-cement pipe in an open trench due to the presence of a gas network close by the AC pipe. The trials were performed over 5 months from January to May 2011 and assessed the influence of the external temperature on pipe flexibility during its installation. Figure VI illustrates a few examples of pipe installation.

Figure VI: Examples of pipe installation during the trials

Globally, the results are satisfactory as illustrated within Table VI.

Table VI: opinions of pipe fitters on PE100-NEW pipes

Pipe specifications	Installation technique	Number*	Opinions
DN25 PN25	Open cut trench	30	Good
DN25 PN25	Trenchless techniques	23	Not suitable
DN25 PN20	Open cut trench	38	Good
DN25 PN20	Trenchless techniques + Electrofusion	23	Good
DN32 PN25 & PN20	Open cut trench + Electrofusion	17	Good
DN125 PN16	Open cut trench + Butt fusion	1	Good

** number of installations carried out*

From a qualitative point of view, pipe fitters agree that:

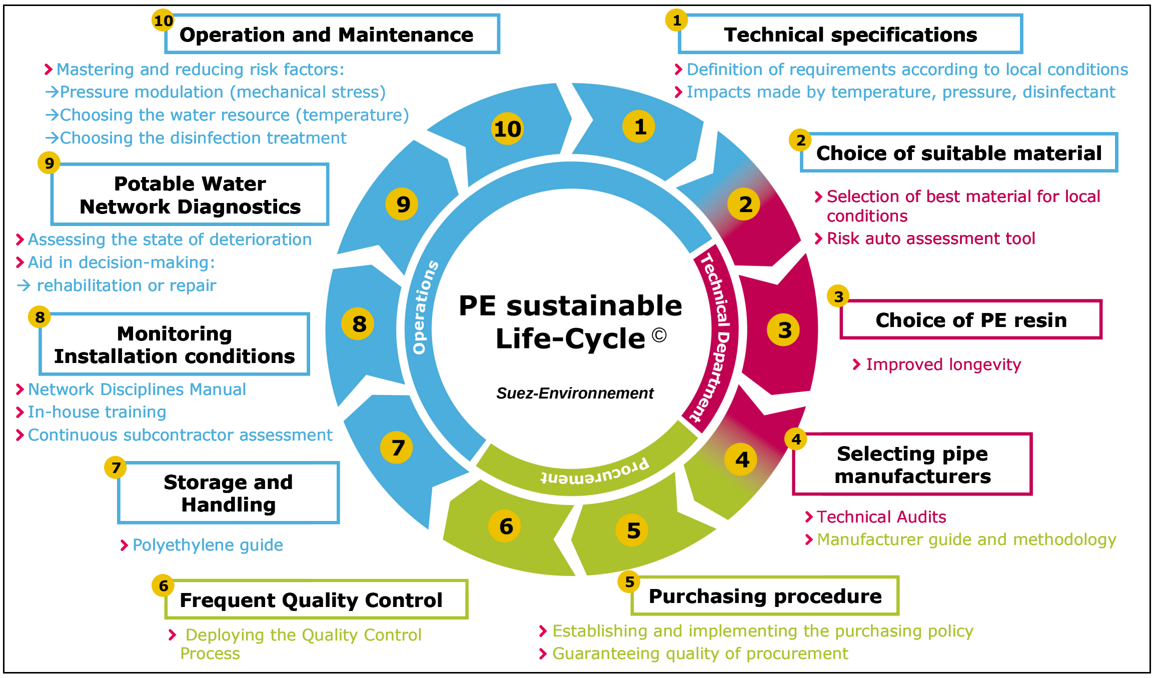
- handling and installation for DN25 pipes are more difficult, but manageable, due to the lower flexibility of PE100-NEW compared to PE80 currently used for service pipelines. This happens particularly during winter when temperatures are the coldest.

- Less easy for connecting push-fit fittings for DN25 pipes for the same reason as above.
- DN25 PN25 is unsuitable for trenchless techniques due to the reduction of the internal diameter making it impossible to connect the cutting tool.
- Good suitability for DN25 PN20 in all conditions. The PN20 pipe thickness is 3mm instead of 3.5 mm for PN25.
- Good compliance with all types of fittings (mechanical, electrofusion and push-fit fittings) except for DN25 PN25 for push-fit fittings.
- Good handling and installation with PE pipes having been coiled around a drum
- No particular issue for using plastic covers for service pipelines
- No particular issues according to the type of works to be performed

The lower flexibility of the PE100 resin is not judged as an issue for its implementation. The use of PN20 DN25 is recommended to enable trenchless techniques to be implemented.

CONCLUSION

The PE100-NEW resin was already promising due to its lifetime in chlorinated water which is three times higher than that of other resins. The overall chemical, physical and mechanical lab tests now complete the positive evaluation of this product which fully complies with the requested specifications for drinking water application. The trials performed validate its performance for field installation with the same use as standard PE pipes. Consequently, LYONNAISE DES EAUX has decided to move towards to this new material which brings strong added value, especially to all service pipelines due to its higher lifetime. After 8 years of intensive work, SUEZ-ENVIRONNEMENT can provide its customers with the best asset management by implementing Sustainable Life-Cycle© of Polyethylene.



This methodology ensures best material quality through a full spectrum of skills and tools to provide a tailor-made solution for each network.
This new generation of product is perfectly in line with the sustainable development policy of water companies. All producers should be encouraged to develop similar products that can meet drinking water networks specifications.

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