Operational Safety of the Polymerization Reactors

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RESUMO

Na *SGL Composites, S.A.*, a formação e a constante sensibilização à segurança visam dar a conhecer os procedimentos obrigatórios e indispensáveis, assim como melhorar e adequar o comportamento de todos os funcionários da empresa. No entanto, esta atenção tem de ser acompanhada por uma prévia avaliação de riscos para implementar o controlo específico, de forma a que as possíveis perturbações possam ser corrigidas e, por sua vez, atinjam o estado estacionário o mais rapidamente possível.

No âmbito da *FM Global* tornou-se necessário avaliar a zona dos reatores de polimerização para perceber se, com a instrumentação de controlo já existente, existe alguma possibilidade/probabilidade, ainda que mínima, de explosão ou *runaway*.

Assim sendo, após conhecer a área de polimerização e estudar a reatividade química do sistema de polimerização, desde a cinética à simulação de um sistema adiabático, determinaram-se e analisaram-se, recorrendo ao software *Aspen Plus* e à Instalação Piloto da empresa, os seguintes panoramas (considerados os piores cenários plausíveis de ocorrência no processo de polimerização):

- variação do caudal de alimentação da mistura de monómeros (+20% e -20%): observou-se que a temperatura da mistura reacional diminui com o aumento do caudal da mistura de monómeros visto que, apesar de se formarem mais cadeias, o crescimento de cada uma não é tão grande, libertando menos energia do que o habitual;
- variação do caudal de alimentação de sulfato ferroso (+10% e -10%): observou-se que é possível controlar a temperatura nos 62°C independentemente da variação do caudal de sulfato ferroso;
- variação do caudal de alimentação de persulfato de amónia (+20% e -20%): observou-se que a temperatura da mistura reacional diminui com o aumento do caudal de persulfato de amónia, mas de forma não linear – é necessária uma determinada variação no caudal para variar a temperatura;
- variação do caudal de alimentação de bissulfito de sódio (+20% e -20%): observou-se que a temperatura da mistura reacional diminui com o aumento do caudal de bissulfito de sódio, mas mais uma vez de forma não linear – é necessária uma determinada variação no caudal para variar a temperatura;
- perda de agitação: observou-se que em poucos minutos a temperatura da mistura reacional aumenta abruptamente;
- falta de atmosfera inerte: observou-se que não existe qualquer alteração, sendo que todo o sistema funciona normalmente;

- perda de refrigeração: observou-se que rapidamente a temperatura da mistura reacional começa a aumentar gradualmente;
- variação do pH: observou-se que a temperatura da mistura reacional oscila, mas ronda sempre os 62°C;
- introdução repentina de mistura de monómeros não reagidos: observou-se que a reação deixa de ocorrer e a temperatura da mistura reacional aumenta abruptamente.

Posto isto procedeu-se a uma revisão crítica da instrumentação de controlo e propôs-se que seja ponderada a instalação de alguns aparelhos, como um sensor de nível, um separador de bolhas, um filtro, entre outros. Por fim certificou-se de que a *SGL Composites, S.A.* respeita todos os aspetos relevantes ao *Process Safety Management umbrella*, tendo em atenção a segurança, a qualidade e o ambiente.

Palavras-chave: acrilonitrilo, acetato de vinilo, poliacrilonitrilo, fibras acrílicas, copolimerização radicalar do acrilonitrilo.

ABSTRACT

At SGL Composites, S.A., the formation and constant safety awareness aims to make known the right procedures, as well as to develop and adjust the employees' behavior. However, it is also necessary to conduct a detailed risk analysis to implement the right specific control instrumentation, in order to correct all the possible perturbations so the stationary state can be achieved as soon as possible.

In the scope of *FM Global*, it was found necessary to evaluate the polymerization reactors' zone to comprehend if there is any possibility/probability, even slightly, of explosion or runaway, despite the existing control instrumentation.

Therefore, after studying the polymerization area and the chemical reactivity of the polymerization system – the reaction kinetics and the adiabatic system simulation –, it was determined and analyzed the situations below (considered the worst-case scenarios that are possible to occur in the polymerization process) using the software *Aspen Plus* and the Pilot Unit of the firm:

- variation of monomers bent feeding flow (+20% and -20%): it was concluded that the reactional mixture temperature decreases with the monomers bent flow increasing because, despite forming more chains, each one does not grow as much, releasing less energy than the usual;
- variation of ferrous sulfate feeding flow (+10% and -10%): it was concluded that it is possible to control the temperature around 62°C despite the variation of ferrous sulfate flow;
- variation of ammonium persulfate feeding flow (+20% e -20%): it was concluded that the reactional mixture temperature decreases with the ammonium persulfate flow increasing, but not in a linear way – a certain flow variation is necessary to vary the temperature;
- variation of sodium bisulfite feeding flow (+20% e -20%): it was concluded that the reactional mixture temperature decreases with the sodium bisulfite flow increasing, but once more not in a linear way – a certain flow variation is necessary to vary the temperature;
- loss of agitation: it was concluded that in a few minutes the reactional mixture temperature increases abruptly;
- lack of inert media: it was concluded that there is no variation, thus the whole system works normally;
- loss of cooling: it was concluded that the reactional mixture temperature quickly starts to increase gradually;

- variation of pH: it was concluded that the reactional mixture temperature oscillates, but always around 62°C;
- unexpected introduction of unreacted monomers bent: it was concluded that the reaction stops and the reactional mixture temperature increases abruptly.

Hereupon, a critical review of the control instrumentation was proceeded and it was proposed to be considered the installation of some devices, such as a level sensor, a bubble separator, a filter, among others. Lastly, it was possible to verify that SGL Composites, S.A. respects all the Process Safety Management umbrella relevant aspects, always considering the safety, the quality and the environment.

Keywords: acrylonitrile, vinyl acetate, polyacrylonitrile, acrylic fibers, acrylonitrile free-radical copolymerization

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LIST OF ABBREVIATIONS

AN – Acrylonitrile;

AV – Vinyl Acetate;

CB – Ferrous Sulfate Solution;

CD – Sodium Bisulfite Solution;

CE – Ammonium Persulfate Solution;

CP – Continuous Polymerization;

CSTR – Continuous Stirrer-Tank Reactor;

DCS – Distributed Control System;

DIW2 – Deionized Water;

DSF – Direct Slurry Feed;

EDTA – Ethylenediamine Tetra Acetic Acid;

FMEA – Failure Mode and Effect Analysis;

HAZOP – Hazardous and Operability Study;

HS – Sulfur Acid Solution;

MB – Monomers Bent;

NSP – Internal viscosity control parameter;

PAN – Polyacrylonitrile;

PSM – Process Safety Management;

RTD – Resistance Temperature Detector;

ST – Inhibitor Solution;

TRCA – Temperature Register Controller Alarm;

TW – Cooling Water.

1. OBJECTIVES

The present dissertation can be divided in 3 main objectives. In the first place, it was necessary to study the chemical reactivity and, based on this information, it was possible to proceed to the next step: evaluate the safety risks in different scenarios. As final step, the process instrumentation was critically reviewed with possible recommendation on additional safety instrumentation, besides confirming the Process Safety Management umbrella.

1.1. Scope

The entire work, defined above and developed throughout this dissertation, is based on risky scenarios and on the careful review of the circumstances that may lead to a runaway and/or an explosion. Moreover, it is important to highlight that, either the worst-case scenarios, or all the safety aspects are only focused on the reactors' zone.

2. WORKING PLAN

Due to the objectives of this work, it was applied a strategy of risks identification by the establishment of a cause-effect methodology for each of malfunction possibility. Based on this approach, this thesis dissertation has the following final working plan delineated:

a) Chemical reactivity study
  - Acrylonitrile Copolymerization;
  - Kinetics and mechanism of the re action;
  - Polymerization in adiabatic conditions.

b) Safety risks analysis
  - Determination of the work-case scenarios;
  - Analysis of each scenario (probable cause, estimated probability and preventive measures);
  - Faults and abnormal situations that might lead to uncontrolled polymerization;
  - Faults and abnormal situations that might lead to product out of specification or unusable.

c) Critical review of the process instrumentation to propose additional safety instrumentation, if necessary, just to moderate processual risks. Review of the safety system related to the reactor and its functionality. Intercalate report.

d) Elaborate a *DRAFT* of the Process Safety Management Umbrella.

3. INTRODUCTION

3.1. Acrylonitrile

Acrylonitrile was first synthetized in 1893 by the French Chemist Ch. Moureau, although it had at the time no significant technical or commercial applications until the late 1930s. Just before the second world war, IG Farben industry [1] introduced a synthetic rubber based on a copolymer of butadiene and acrylonitrile and, during the same period, in USA, projects related to nitrile rubber received special support due to their strategic importance. This way, acrylonitrile became recognized as a monomer of commercial importance and, in 1950, the acrylonitrile demand began to increase due to the acrylic fibers. [2, page 3]

Nowadays, all acrylonitrile is produced by direct catalytic conversion of propene, oxygen (as air) and ammonia, and its world production is approximately 5 million tons per year. In addition, acrylonitrile is, today, an industrial intermediate used predominantly in the production of polymeric materials: acrylic fibers accounts for 60%, while the plastics accounts for 25% of world consumption. [2, page 3]

3.2. Polyacrylonitrile

Polyacrylonitrile (PAN) was first synthetized by Dr. º Hans Fikentscher and Dr. º Claus Heuck, in 1930, in the laboratories of IG Farben, in Ludwigshafen, a German company that patented its polymerization method. However, since the polymer was insoluble in most common solvents, the substance was considered to be unusable. Even so, the investigations continued and, in 1931, Dr. º Herbert Rein, also from IG Farben but in Bitterfeld, discovered that PAN, obtained from a sample when visiting the Ludwigshafen plant, could be dissolved in the ionic liquid 1-benzylpyridinium chloride and converted into fibers. Later in 1942, the same chemist discovered a better solvent for the polymer – dimethylformamide, a discovery that allowed to develop the spinning process to produce fibers and films. Due to the second world war, the investigations were interrupted and the polymerization process was not used in an industrial scale. [3]

Despite the interruption, when the war time was over, in 1946, DuPont introduced the large-scale production of PAN to produce the Orlon fibers and patented the wet-spinning process. Later, the Dormagen Bayer company introduced the production of Dralon fibers and patented the dry-spinning process. [3]

Throughout the production of PAN, it was realized that among its main features is the versatility of being able to be chemically modified and thus to produce a wide variety of materials: [3]

- Fibers

Figure 1. Fibers produced from PAN

- Carbon fibers

Figure 2. Carbon fibers produced from PAN

- Adhesives

Figure 3. Adhesives produced from PAN

- Engineering plastics

Figure 4. Engineering components produced from PAN

- Superabsorbent polymers

Figure 5. Superabsorbent polymers produced from PAN

This polymer is essential for textile and high technology applications due to its special properties, such as thermal stability, high strength and modulus of elasticity, UV degradation stability, non-fusible and chemical resistance. Therefore, the main application is in textile industry, while the second one is related to the production of carbon fibers. However, there are other minor applications which use is growing, such as: [3]

- fibers for cement reinforcement;
- filtration membranes;
- awning fabrics and outdoor applications;
- oxidized PAN fibers for thermal and acoustic insulation;
- anti-flame fibers;
- felts’ manufacture for hot air filtration.

3.3. SGL Composites S.A.

SGL Composites, S.A., former FISIPE – Fibras Sintéticas de Portugal S.A., is a producer of acrylic fibers for textile applications and its plant is located in Lavradio, in the county of Barreiro. SGL Composites, S.A. produces a variety of acrylic fibers that can be distinguished mostly by their shine, color, shape, thinness and shrinkage: [4, page 8]

- tow – fiber in a continuous tape

Figure 6. Acrylic fiber – tow

- staple – cut fiber

Figure 7. Acrylic fiber – staple

- top – converted and brushed tow

Figure 8. Acrylic fiber – top

- yarn – Open-End

Figure 9. Acrylic fiber – yarn in a roll

Plus, it is also produced carbon and oxidized precursor fibers.

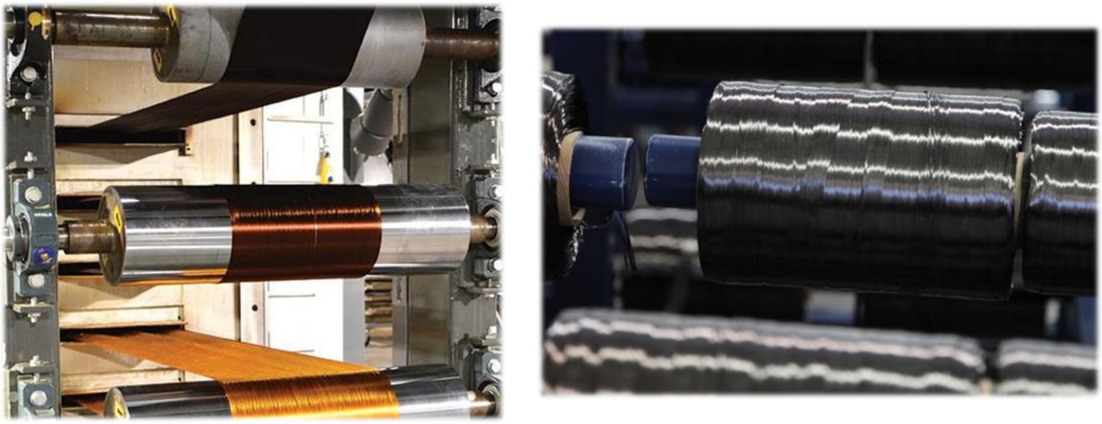

Figure 10. Carbon and oxidized precursor fibers

This firm was set up in September of 1973 as a result of a joint-venture between CUF – Companhia União Fabril and Mitsubishi Rayon Co. and Mitsubishi Corporation, although it started operating in 1976 with a nominal capacity of 12 500 ton/year of acrylic staple and tow. Hereupon, SGL Composites, S.A. always tried to associate the industrial and textile experience with the synthetic fibers production and the Japanese's international knowledge. [4, page 5]

Due to the market expansion, in 1980, the industry's capacity was increased to 23 000 ton/year. Simultaneously, the production of acrylic fibers special types was introduced. Later in 1989, the industrial plant was revamped, increasing the capacity to 36 000 ton/year. [4, page 6]

In 1990, SGL Composites, S.A. began to export and, in 1995, the production of a new product – the black fiber – introduced a new beginning to the industry. [4, page 6]

During its lifetime, SGL Composites, S.A. gradually created conditions to apply its policy and development strategy, so in 1999 the Pilot Unit was planned, where it has been developed some special fibers and new technologies, such as flat fiber and gel dyeing respectively. [4, page 6]

Later in 2003 the capacity reaches 56 000 ton/year, and in the second semester of 2009 the Pilot Unit was built. In February of the same year, it was built FISIGEN, holder of the new cogeneration plant of Barreiro, that provides the necessary steam and started to operate in the end of the year. In July of 2010, the extension of the Pilot Unit was concluded and nowadays it allows to: [4, pages 6, 7]

- test the carbon precursor fibers;
- develop the new carbon fiber;
- establish privileged and trustful relationships with the clients of technical fibers.

Later, in September of 2012, the SGL Group – The Carbon Company, the largest European producer of carbon fibers, concluded the acquisition of 100% of the company's stock capital. For this reason, SGL Composites, S.A. is no longer quoted in Lisbon Stock Exchange. [4, page 7]

Nowadays, SGL Composites, S.A. is an exporter and the firm's priority is directed to quality and sophistication of the commercialized products, rather than to the produced quantity, expecting to gradually abandon the textile industry, dropping the production of commodity fibers with lower margin, and enter in the technical applications sector, where the carbon and oxidized precursor fibers are the future. [4, page 7]

3.3.1. Products

As a result of the advanced characteristics of SGL Composites, S.A. acrylic fibers, a wide range of products supply the textile industry and there are two types: the standard and the special one. [5]

The standard type includes FISIVON standard staple, tow and top. FISIVON fiber is not affected by long exposure to light and it is resistant to aging, mold, moths, to most organic solvents, mineral acids and diluted alkalis. Besides, it is also highly resistant to both dry and wet treatments and it is not affected by normal heat settings carried out at the end of the finishing processes. All FISIVON fibers' answers to all human-ecological requirements related to direct contact to skin were fulfilled, including those for baby clothing. [5] The standard fibers are the second most demanded product, accounting for 31% of the 2017 total sales.[1]

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[1] Numbers withdrawn from an excel file provided by SGL Composites, S.A. on 26/06/2018

The special type has the following range of main products:

Table 1. SGL Composites, S.A. products of special type and the respective percentage of the 2017 total sales

	Fiber type [5]	***Description*** [5]	***% Sold Quantity (2017)***[1]
Colour FISIVON®	Color FISIVON	Colour FISIVON is a fiber dyed by the most advanced technology for on-line dyeing - the Gel Dyeing Process. This is also the most ecological and efficient dyeing process.	44
FISIVON®	FISIVON – Special Tows	FISIVON extrafine, repco, high, medium, low shrinkage, super soft and mixed tow.	7,4
FISIVON®	FISIVON – Special Staples	FISIVON superfine, micro, unrelaxed and mixed fiber. The latter type is also available in gel-dyed colors.	2,5
Flat by FISIPE	Flat by SGL Composites, S.A.	Fiber with flat cross-section, perfectly rectangular, that allows excellent imitations of animal pile with an incredible natural look and very high softness.	2,5

Besides these products, there are others special types in a lower percentage, such as Black FISIVON, Pil Clean and Puma [5], accounting overall for 4% of the 2017 total sold quantity.[1]

In addition, besides the fibers that supply the textile industry, there also are technical fibers and, as a result of the advanced characteristics of SGL Composites, S.A. products as well, they provide advanced solutions in a wide range of applications. [5] This type of fibers accounts for 1% of 2017 total sales and it includes Asphal +, Binder +, Filter +, Pulp + and Paper +.[1]

Lastly, SGL Composites, S.A. also produces pigmented fiber, oxidized precursor fiber and carbon precursor fiber [5], which ones accounts for 2,5%, 3% and 2,6% of the 2017 total sold quantity, respectively.[1]

4. LITERATURE OVERVIEW

4.1. Aqueous Dispersion Polymerization

In the acrylic fibers industry, the aqueous dispersion polymerization is the most used polymerization method [6, page 826], [7, page 11] and, in fact, SGL Composites, S.A. applies this method.

The reaction type in the aqueous dispersion polymerization is the free-radical type, meaning there is a redox system present and the most common one consists of ammonium/potassium persulfate (oxidizer), sodium bisulfite (reducing agent) and ferric or ferrous iron (catalyst) – the one used by SGL Composites, S.A.. Giving this redox system, the radicals are produced from the following two reactions – ferrous iron oxidation by persulfate and ferric iron reduction by SO_2 in the bisulfite form: [6, page 827], [7, page 12]

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{*-}$$

$$HSO_3^- + Fe^{3+} \rightarrow Fe^{2+} + SO_3^* + H^+$$

These radicals, in turn, react with the monomer to initiate a polymeric chain. Concerning termination, it is usually pronounced by radical recombination, although SGL Composites, S.A. uses a chain-transfer agent (sodium bisulfite) – in commercial processes, chain transfer termination is used to control molecular weight with no effect on the overall rate of polymerization: [6, page 827]

$$P_n^* + HSO_3^- \rightarrow P_nH + SO_3^{*-}$$

The initiation step occurs mainly in the aqueous phase, although chain growth is limited since the monomer concentration is normally low and the polymer is insoluble in water. [6, page 826], [7, page 11]

Depending on the conditions, two cases may occur. On one hand, when aqueous chains aggregate or collapse after reaching a certain molecular weight, nucleation may happen – phenomenon favored at low conversion, since the aqueous monomer concentration is high and the existing polymeric particles are low. On the other hand, the aqueous radicals may be captured on the particle surface by an absorption mechanism – phenomenon more likely to happen at high conversion, since the monomer concentration is low and the existing polymeric particles are significant. [6, page 826], [7, page 11] These two events are schematically demonstrated below:

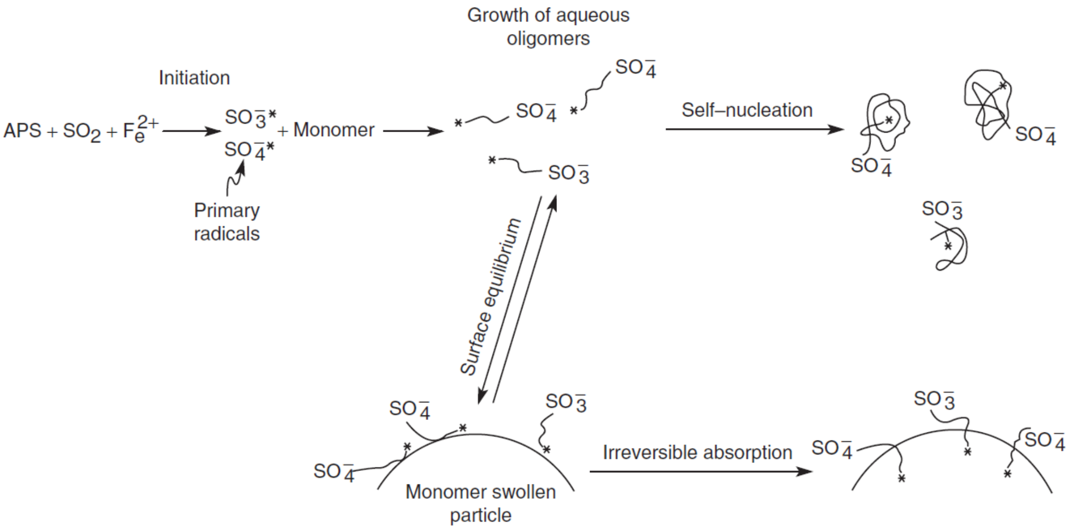


Figure 11. Nucleation and absorption mechanism during the aqueous dispersion polymerization [6, page 826]

As the reaction proceeds, the particle surface gets gradually richer while the aqueous monomer concentration gradually decreases. Therefore, the polymerization continues in this monomer-rich layer and, as it is realized in Figure 11, the sorption becomes irreversible as the chain end grows into the particle. [6, page 826], [7, page 11]

In aqueous dispersion polymerization, the polymeric chains grow by the agglomeration of primary particles because the nucleation is more likely to occur. This is justified by the poor polymer swelling and the significant acrylonitrile water solubility. [6, page 826] The following figure shows the structure of this agglomeration:

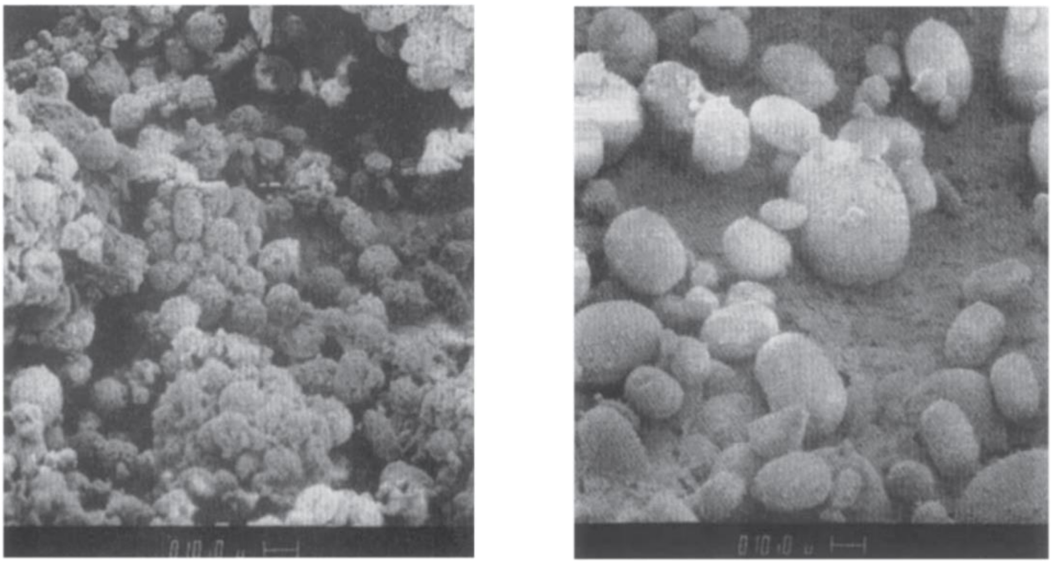


Figure 12. Scanning electron micrograph of a polymer particle formed by aqueous dispersion polymerization: the left one was formed at a 3,5 water/monomer ratio, while the right one was formed at a 2 water/monomer ratio [6, page 823]

The characteristic that differs the images above is the water/monomer ratio – the one used by SGL Composites, S.A. is confidential and it is mentioned in a separate document. In fact, this characteristic allows to manage the process costs: it was already studied that the process costs are significantly reduced at low water/monomer ratios – Mitsubishi Rayon has reported ratios as low as 1,5 to increase the particle density and to improve particle dewatering. This cost reduction comes in the drying step. [6, page 836]

Moreover, and as a matter of curiosity, the use of the redox system mentioned above and the use of a chain-transfer agent benefit the supply of dye sites. [6, pages 826 and 827] Also, the bisulfite/persulfate ratio in the reactional mixture influences the dye site content of the polymer: [6, page 827], [7, page 12]

- if there are no chain transfer reactions, the dye sites are provided by initiator radicals. So, if the termination is based on radical recombination, each polymer chain has a dye site at each chain end; [6, page 827]
- if the termination is based on chain transfer, the reducing agent ends a polymeric chain with a hydrogen atom while initiates another one with a sulfonate radical. On one hand, it is produced polymeric chains with only one dye site. On the other hand, as the polymer molecular weight is reduced, the total polymer dye site content is increased. [6, page 827]

Summing all up, at a given molecular weight, there can be two dye sites per chain at low bisulfite levels or one dye site per chain at high bisulfite levels. [6, page 827], [7, page 12] In CP area of SGL Composites, S.A., the termination type that occurs is the chain transfer one, however the bisulfite/persulfate mass ratio is confidential and it is also mentioned in a separate document.

4.2. Process Control

All process systems consist of three factors: the manipulated variables, the disturbances and the controlled variables. Relating these factors to SGL Composites, S.A. case, and bearing in mind the scope of this work, the manipulated variables are the valve position and the motor speed, while the controlled variables are the flows, the temperature, the level, the pressure, the pH and the NSP. Hereupon, the control system must face the disturbances adjusting the manipulated variables so the controlled variables can return to the set point. [8, page 2] To illustrate this, the following scheme is presented:

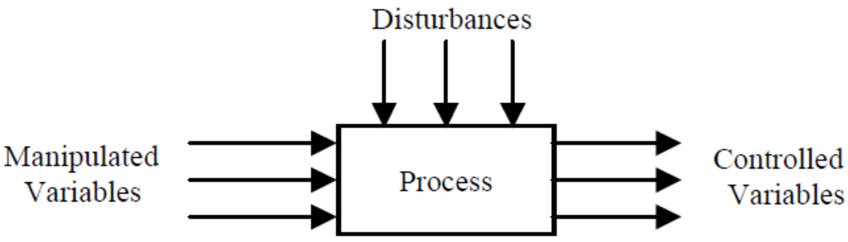


Figure 13. Process control variables [8, page 2]

For each controlled variable there is an associated manipulated variable.

Below some explanations are made, bearing in mind what is used by SGL Composites, S.A. in the polymerization reactors area.

4.2.1. Flow Measurement

4.2.1.1. Magnetic Flowmeters

The magnetic flowmeter is based on a volumetric basis and consists of a nonmagnetic tube surrounded by magnetic coils [8, page 263], as the following figure illustrates:

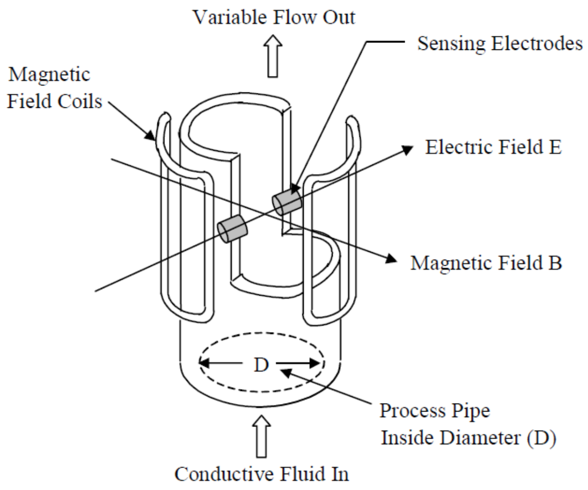


Figure 14. A schematic magnetic flowmeter [8, page 264]

Hereupon, the magnetic coils provide a magnetic field, across the entire tube, when an electric current is applied. Once the fluid must have a minimum conductivity to act like a conductor, when it passes through the magnetic field, a voltage is generated, which value is proportional to the volumetric flow regardless the flow profile. Therefore, this type of flowmeters does not have in count viscosity changes. [8, pages 264 and 265]

4.2.1.2. Coriolis Mass Flowmeters

The Coriolis mass flowmeter is based on the force applied by the fluid's Coriolis acceleration. This type of flowmeter consists of a vibrating tube, where the Coriolis acceleration is created and measured: [8, page 269]

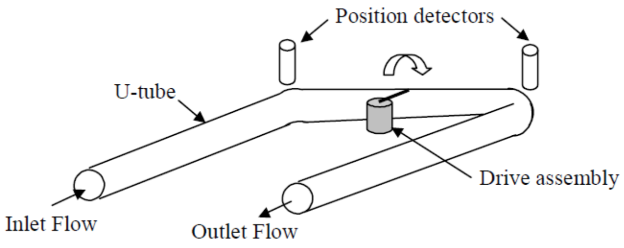


Figure 15. A schematic Coriolis mass flowmeter [8, page 269]

This tube is already designed to have predictable vibration characteristics and it works with any fluid that flows at a enough quantity to operate the Coriolis flow tube. Basically, the drive assembly shown triggers the tube vibration that is sensed by two position detectors, one in each side of the tube. As the vibration frequency depends on the fluid density and the Coriolis acceleration is proportional to the fluid mass, the Coriolis Mass Flowmeter accurately measures the fluid mass flow, density and volumetric flow. [8, page 269]

4.2.2. Temperature Measurement

4.2.2.1. Resistance Temperature Detectors

The RTD designation used at SGL Composites, S.A. is Pt 100: Pt means platinum, the material RTD is made of, and 100 means the resistance measures 100 Ω at 0°C. In order to convert the resistance unit to a temperature unit it is used a function that relates these both measure units. The RTD is used to measure the temperature since it provides a good linear resistance/temperature relation between 0°C and 200°C. Above 200°C, thermocouples are more common to use. In addition, the platinum is the material detectors are made of because it can handle high temperatures and provides a good stability, without losing the good linearity between the temperature and the resistance.

A typical RTD is shown below:

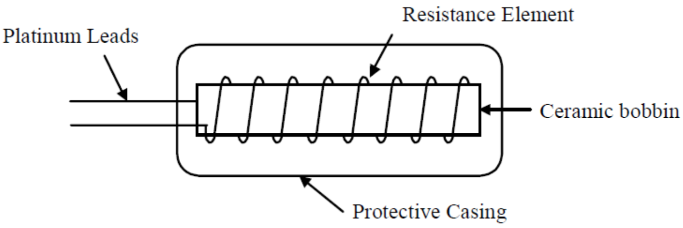


Figure 16. A schematic typical RTD [8, page 189]

The resistance of an RTD is measured using a Wheatstone bridge circuit. Supposedly, it would be enough to measure the RTD resistance locally. However, despite the RTD is located directly on the equipment, the measurement is done in the control room that can be at any distance. Therefore, wires are used to connect the RTD amplifier and the Wheatstone bridge measurement circuit. The wire itself has an associated resistance (called lead resistance) that leads to a significant error while measuring the temperature. [8, pages 190 and 191] To avoid this problem, SGL Composites, S.A. uses the arrangement of three-wire RTD bridge:

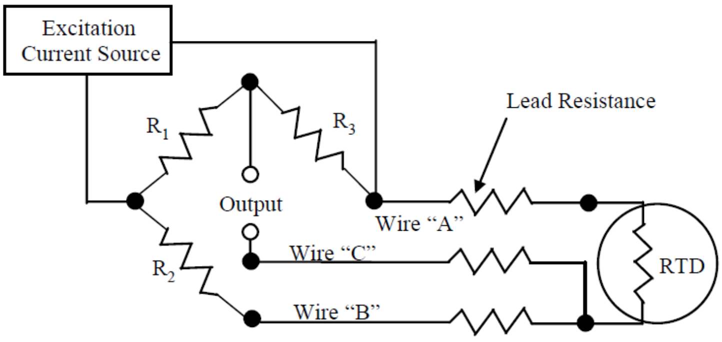


Figure 17. Three-wire RTD bridge circuit [8, page 191]

This way, two wires are in opposite sides of the bridge (A and B, in this case), which means their resistance is canceled, while the third wire (C, in this case) is the sense lead and allows to precisely measure the temperature. [8, page 192]

In addition, the pH and the NSP are also measured at SGL Composites, S.A. – not in a continuous way, but according to an established routine because, since the reactional mixture is a suspension, if a device is used to obtain a continuous measure, as it was already done in the past, a polymeric lay starts forming around the measurement apparatus, making it impossible to get a correct measure. These two variables are used to intermediately control the products' quality.

4.2.3. Controllers

In industrial processes, it is expected to witness disturbances upon the stationary state of the process. However, it is possible to manage them by using controllers that use transfer functions to reduce or even to eliminate the error.

Therefore, the goal is to reduce the error between the process output and the respective set point. To do so, the value of the measured variable is first sent to a transducer that produces a current output. This current enters the controller where it is compared to the set point and an error signal is produced and converted to an output signal. The latter enters the converter which produces another output signal that, in turn, is sent to the final control element, which actuates depending on the information received. [9, page 188] The following illustration resumes what was described:

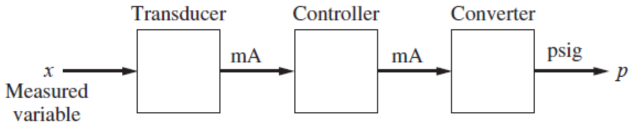


Figure 18. Block diagram of the control process that goes from the input (measured variable) to the output (manipulated variable) [9, page 190]

The controller is capable of producing an output signal because of the control algorithm. [9, page 188] Below, the mode of the control algorithm used by SGL Composites, S.A. is explained.

4.2.3.1. Proportional-Integral-Derivative Control

All the controllers at SGL Composites, S.A. uses the three control modes: proportional, integral and derivative mode.

The proportional control reduces the error by leading the system to a new steady-state value [9, page 192] (the difference between the new stationary state and the original one is called offset [9, page 198]). The integral control integrates the offset, eliminating it, so the system returns to the original steady-state value. [9, page 198] Although in an oscillatory way. [9, page 198] The derivative control derives the offset, eliminating it as well, so the system returns to the original steady-state value but with no oscillations. [9, page 198]

Gathering the three control modes, the proportional-integral-derivative control has an improved response: the error is reduced quicker, meaning there is a stabilizer action of the proportional mode, the controlled variable returns to the original steady-state value, meaning the offset is eliminated by the integral mode, and it happens with little or no oscillations, meaning the stabilization is quicker and the error amplitude is reduced/eliminated by the derivative mode. [9, pages 197 and 198]

The following figure shows the response of the control types:

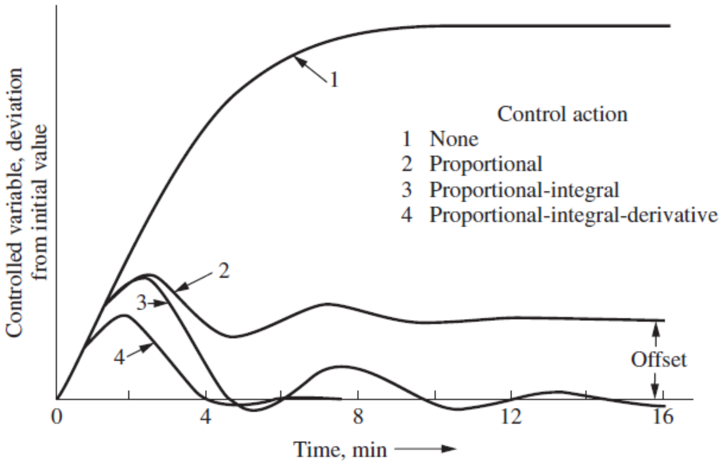


Figure 19. Typical response of each control action [9, page 198]

4.2.4. Types of Control

In CP area, SGL Composites, S.A. has implemented the three following control types.

4.2.4.1. Ratio Control

The ratio control is usually used when keeping a certain proportion between two flows of two different streams is important/necessary. [9, page 370] The actuator is placed only in one of the streams and, after the two flows are read, it operates to keep the required ratio. [9, page 371] Though there is no direct control over the magnitude of the controlled variable, which may lead to instability of the system. Hereupon, the ratio control may be ineffective.

4.2.4.2. Feedback Control

The feedback control is the normal/basic type – the transmitter reads the controlled variable and sends a signal to the controller. After comparing the read value and the setpoint, the controller sends a signal to the actuator, which adjusts the manipulated variable to correct the controlled variable. [9, page 361] However, if the indicator response time is slow or if the indicator is located far from the disturbances zone, the actuator response may lead to instability of the system. Hereupon, the feedback control may also be ineffective.

4.2.4.3. Cascade Control

The cascade control measures two variables – the master one that is the controlled variable, and the slave/secondary one that is used to reduce the response time – and has two controllers. Basically, the primary controller controls the master variable and adjusts the set point of the secondary controller that, in turn, controls the secondary variable. Hereupon, the secondary control loop acts quickly to maintain the secondary variable close to the set point adjusted by the primary controller by measuring the master variable. [9, page 354]

4.2.5. Final Control Elements

The final control devices convert the control signal into the correct action to control the system, having a direct influence on the process. [8, page 275] The final control devices that are mentioned below are control valves and pumps. Despite on/off valves do not control any variable, this type is also mentioned here.

4.2.5.1. Control Valves

A control valve is an apparatus used to regulate the flow of fluids by varying the area of the existing orifice. [10, page 639] It basically consists of an actuator and a valve that, in turn, is divided into the body and the trim. [9, page 423] The following figure shows the existing control valves classification:

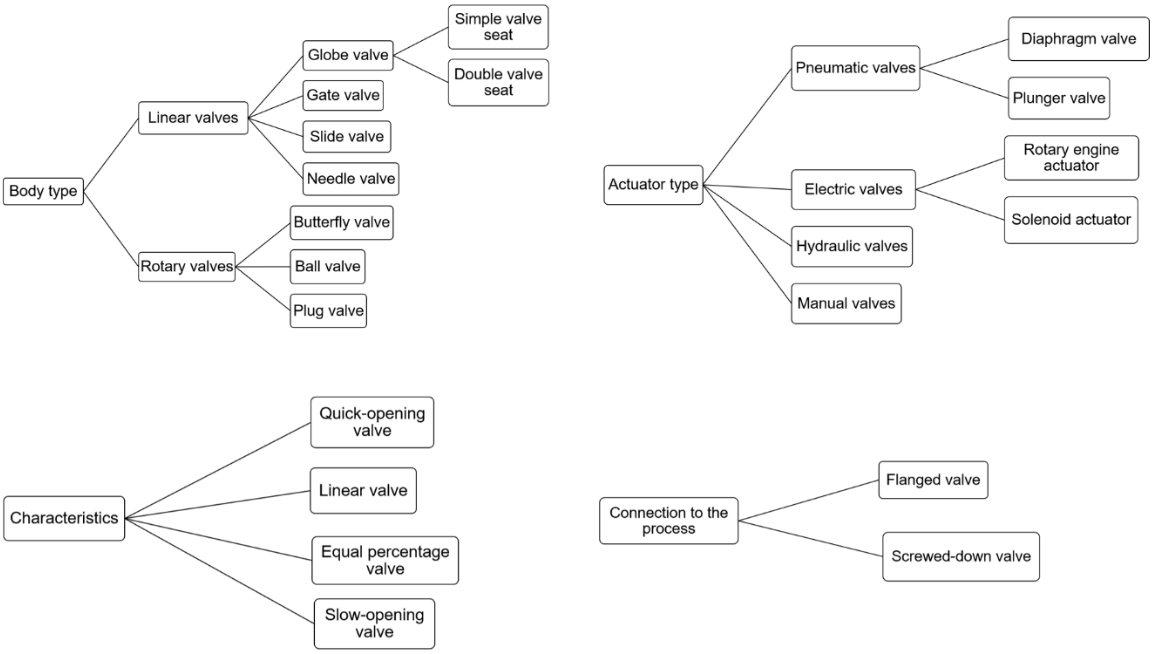


Figure 20. Classification of valves [10, page 640]

The area of the valve orifice is changed by an actuator depending on the required flow – here, it will only be described the type of actuator SGL Composites, S.A. uses in the CP area.

The actuator designation depends on the energy used and, as it can be realized by Figure 20, there are pneumatic, electric, hydraulic and manual actuators – the pneumatic one is the most used. In fact, in the CP area of SGL Composites, S.A., all the actuators are pneumatic since the valves are diaphragm valves. This actuator type positions the stem according to the air pressure, existing the air-to-close valve and the air-to-open valve. These valves are based on a linear movement. [10, page 657] As the air pressure increases, in the air-to-close valve the plug moves downward and restricts the fluid flow that passes through the valve, while in the air-to-open valve the plug moves upward and allows greater fluid flow to pass through the valve. [9, page 187]

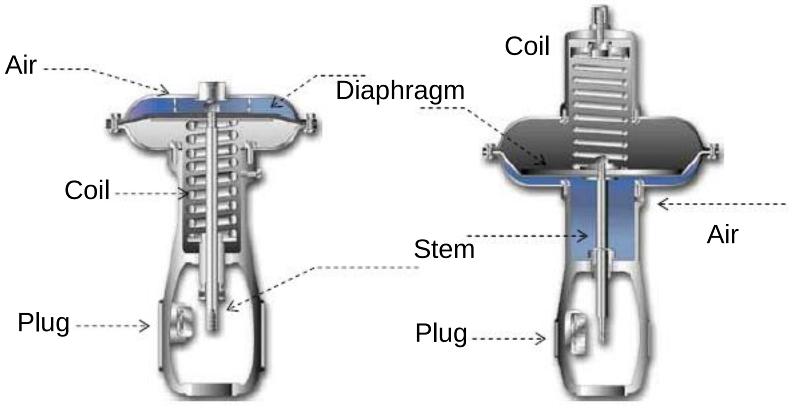


Figure 21. A schematic diaphragm actuator: the left valve is an air-to-close one, while the right valve is an air-to-open one [10, page 657]

A pneumatic signal is sent to the pneumatic actuator, which is received by the positioner. Depending on the required stem position, the sent pressure signal changes. [10, page 657]

4.2.5.2. On/Off Valves

This type of valves is either fully open (on) or fully closed (off), but it does not control any variable. Thus, even if the process deviates only slightly from the set point, the valve moves from one extreme position to the other one. [9, page 194]

4.2.5.3. Pumps

Other final control device are pumps, which are used to move fluids from one place to the other by mechanical action. This device is simple to operate, energy efficient and can provide both flow and pressure control in a single piece of equipment. [8, pages 302 and 303]

In the CP area of SGL Composites, S.A., the pumps used are the centrifugal ones. These pumps are dynamic, meaning the fluid velocity and the resulting momentum are used to move the fluid through the piping system. Therefore, a centrifugal pump imparts velocity to the process fluid and, as it leaves the pump, the velocity is converted into pressure energy. [8, page 303] A scheme is shown below:

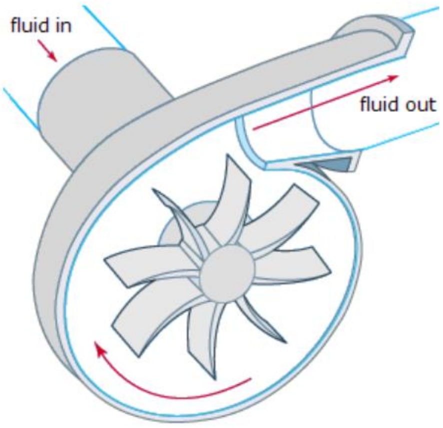


Figure 22. A schematic centrifugal pump

Usually, centrifugal pumps operate at a fixed speed but, if a control valve is used in the discharge line, as it is an energy-consuming device, the pump operates at a variable-speed to compensate the energy loss. [8, page 303]

Although centrifugal pumps are the most common, there are other types as shown below:

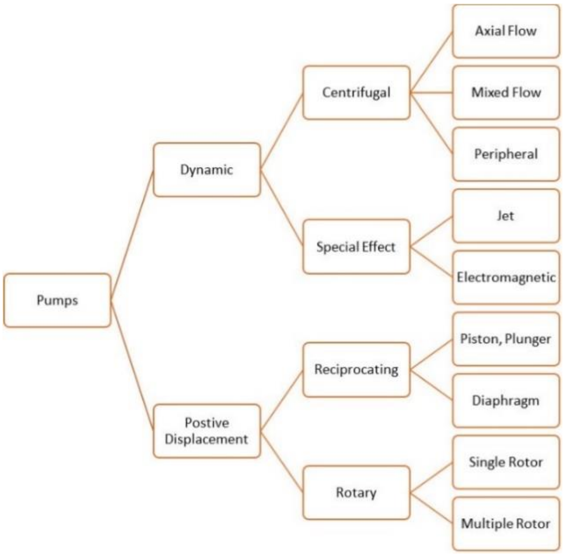


Figure 23. Classification of pumps

4.3. Distributed Control System

DCS is a design concept that distributes the process control to computer modules, and each of them controls one to four instrument loops. Therefore, the operator is able to monitor the operation of each local process. [8, page 315]

Microprocessor-based controllers perform loop controls and apply logic functions, collect and analyze process data and finally transfer it to the rest of the system. The process control and monitoring (through a screen) are possible due to controllers, input/output systems and their associated field devices, but the attention goes to the communication of input and output signals between the process and the DCS. Basically, the input/output systems consist of signal conversions, using control functions, required by measurement devices and control elements. Regarding the operators in the control room, it is only necessary to provide information about the inputs and outputs to be controlled, since the DCS internal software performs the control functions. [8, pages 316 and 317]

Summing all up, the DCS console allows the operators to control and monitor either an area of the plant or a specific zone. Moreover, DCS software stores long-term data and it is possible to obtain graphics that change colors, level and messages. [8, page 318] These graphics are as a function of time and can show dynamic detail or long-term trends (the time segment can be selected to be a few minutes to a few hours). [9, page 587]

4.3.1. Alarms

Giving the importance of being aware of the problems that are possible to occur in a process, it is necessary that the control software is able to detect and report them – this is usually done by an alarm. At SGL Composites, S.A., all the alarms are based on a visual and an audible signal. During the configuration of the alarms, their limits and type of annunciation are specified, as well as their priority rate (the alarms of the most critical variables have a highest priority, while the alarms of less critical variables have a lower priority). [9, page 587]

In the polymerization area of SGL Composites, S.A., all the flows, the temperature, the pressure and the motor sign of all the reactors have an alarm associated – a higher and a lower alarm, depending if the value is higher or lower than the set point, respectively.

5. ACRYLONITRILE POLYMERIZATION AT SGL COMPOSITES, S.A.

The acrylonitrile polymerization at SGL Composites, S.A. is based on a free-radical reaction of the acrylonitrile and the vinyl acetate. [11]

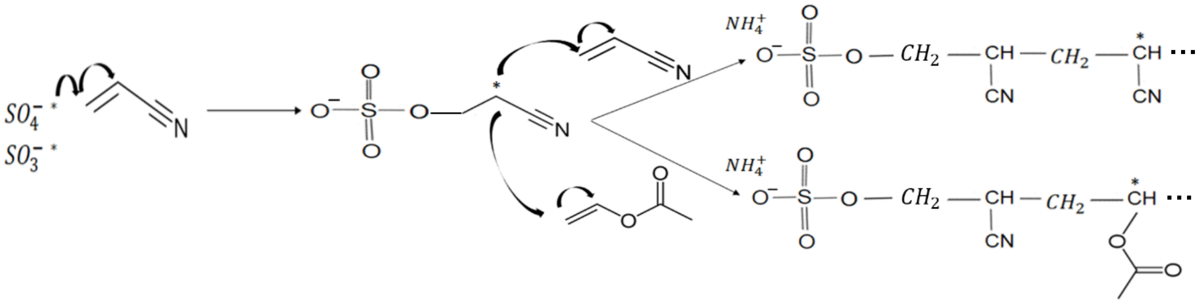
This exothermic reaction takes place in an aqueous medium and occurs continuously under quasi steady state conditions with an 88% conversion. The reaction is performed in 3 of 4 CSTR reactors, in order to vary the production regime of this area, and the redox system consists of aqueous solutions previously prepared of ferrous sulfate, sodium bisulfite and ammonium persulfate. The first one works as a catalyst of the reaction, while the latter is an oxidizer and the main initiator. Concerning sodium bisulfite, it is a chain-transfer agent that also regenerates the oxidized form of the ferrous ion and, hence, acts simultaneously as an initiator. [12, page 1] The initiation and propagation reactional mechanisms are as follows: [7, page 12]

<u>Initiation</u>

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + SO_4^{-*} + Fe^{3+}$$

$$HSO_3^{-} + Fe^{3+} \rightarrow SO_3^{-*} + Fe^{2+} + H^{+}$$

<u>Propagation</u> [2]



Concerning the termination step, free-radical polymer chains can terminate by three mechanisms:

<u>Chain Transfer</u> (more likely to happen) [7, page 11]

$$SO_4(CH_2CHCN^{*})_n{}^{-} + HSO_3^{-} \rightarrow SO_4(CH_2CHCN)_nH^{-} + SO_3^{-*}$$

<u>Radical Recombination</u> [2]

$$SO_4CH_2CHCN^{*-} + SO_4(CH_2CHCN^{*})_{n-1}{}^{-} \rightarrow SO_4(CH_2CHCN)_nSO_4{}^{2-}$$

<u>Disproportionation</u> [2]

$$SO_4CH_2CHCN^{*-} + SO_4CH_2CHCN^{*-} \rightarrow SO_4CH = CHCN^{-} + SO_4CH_2CH_2CN^{-}$$

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[2] Mechanisms shown and explained in a presentation at SGL Composites, S.A. on 04/2018

As it can be confirmed, sodium bisulfite is both a reducing agent and a chain-transfer agent. Besides all the solutions mentioned above, a sulfur acid filtered solution is also applied to keep a constant pH, which value is confidential and is mentioned in a separate document. [12, page 1]

On the one hand, the monomers bent, previously prepared, is fed continuously in each reactor by direct discharge in the reactional mass, as well as the deionized water and CE. The latter is fed separately so the reaction does not initiate earlier. On the other hand, the solutions of CB, CD and HS are fed through the DIW2 admission stream, at such distance that it is possible to uniformly mix them before entering the reactors. All the feedings mentioned above are completed in the top of the reactors. Moreover, the reactional mixture is continuously agitated by a propeller-type stirrer, describing an axial movement. While the reaction occurs, the polymer suspension is expelled out of the respective reactor by overflow. However, since this discharge is not uninterrupted giving the nature of the product, the direct slurry feed – a little column – is used to receive the reactor's overflow and to feed the next equipment direct and continuously.

The inhibitor solution is added in the reactors discharge tube to prevent the reaction to last. [12, pages 1 and 2] This is possible because this solution is composed by: [12, page 2]

- oxalic acid, which is an antioxidizer;
- EDTA, to complex the iron and prevent it from starting the reaction;
- sodium bicarbonate, which increases the pH of the suspension and consequently disfavors the reaction by neutralization.

The reactional temperature value is confidential and it is also mentioned in a separate document. Nevertheless, the temperature is controlled by the cooling water that circulates in the cooling jackets of the reactors, in a closed circuit and with a high flow. Its admission is found in the low zone of the respective jacket and its discharge is in the superior side zone. The TW water comes from the cooling tower, where it is cooled along with the posterior tubular heat exchanger that uses chilled water. TW is cooled in the end to 18°C, as well as MB and DIW2 feeding streams, but in a plate heat exchanger, to avoid an overload of the cooling system. [12, page 1] A scheme of the cooling circuit and the respective control is exposed below:

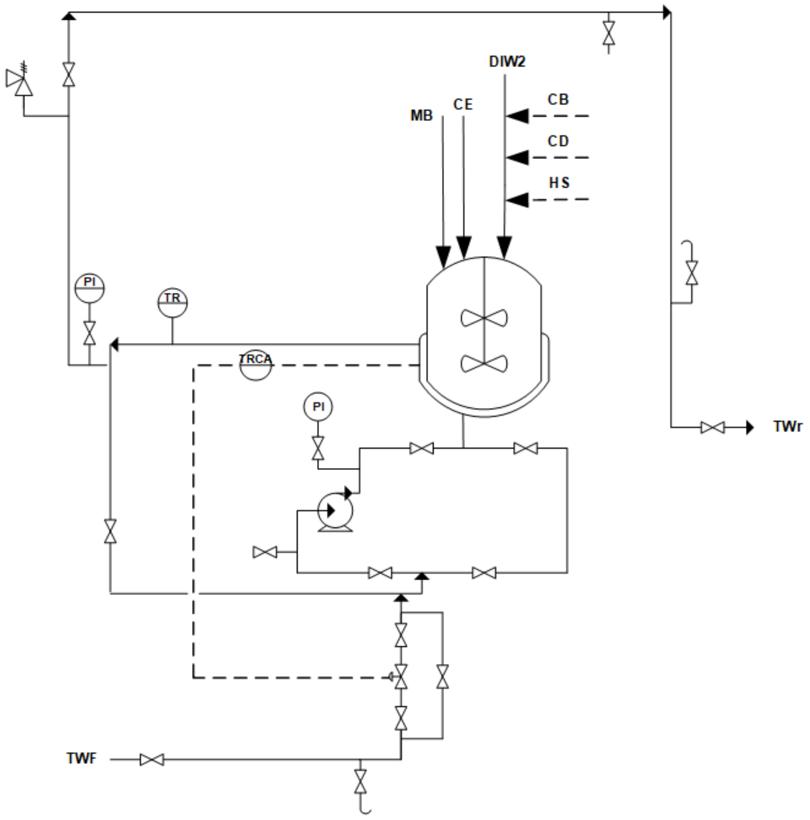

Figure 24. Cooling control scheme

The cooling control scheme above confirms the cooling water comes from the cooling tower, and enters the cooling jacket with the help of the centrifugal pump. This scheme also confirms the TW flows in a closed loop, although only a small portion. The major quantity returns to the cooling tower to proceed to the cooling process once more. Besides monitoring the pressure, by pressure indicators, the temperature is also monitored by a temperature register. Now, regarding the reactional mixture temperature, it is controlled by a temperature register controller with an associated alarm and its value is indicated on the panel. This TRCA is connected to a diaphragm valve, which receives a pneumatic signal from the controller and actuates depending on the information – bearing in mind the reaction is exothermic, if the reactor inner temperature increases, the valve opens so more TW flow can circulate in reactor's jacket and decrease the temperature in question; and vice-versa. In addition, to realize if all malfunctions possibilities were considered, the inlet and outlet streams' pressure were known: 2 bar and 1 bar, respectively. This way, if the centrifugal pump stops working, the pressure difference is enough for TW to flow.

A picture of a 12 m^3 reactor is presented below: [3]

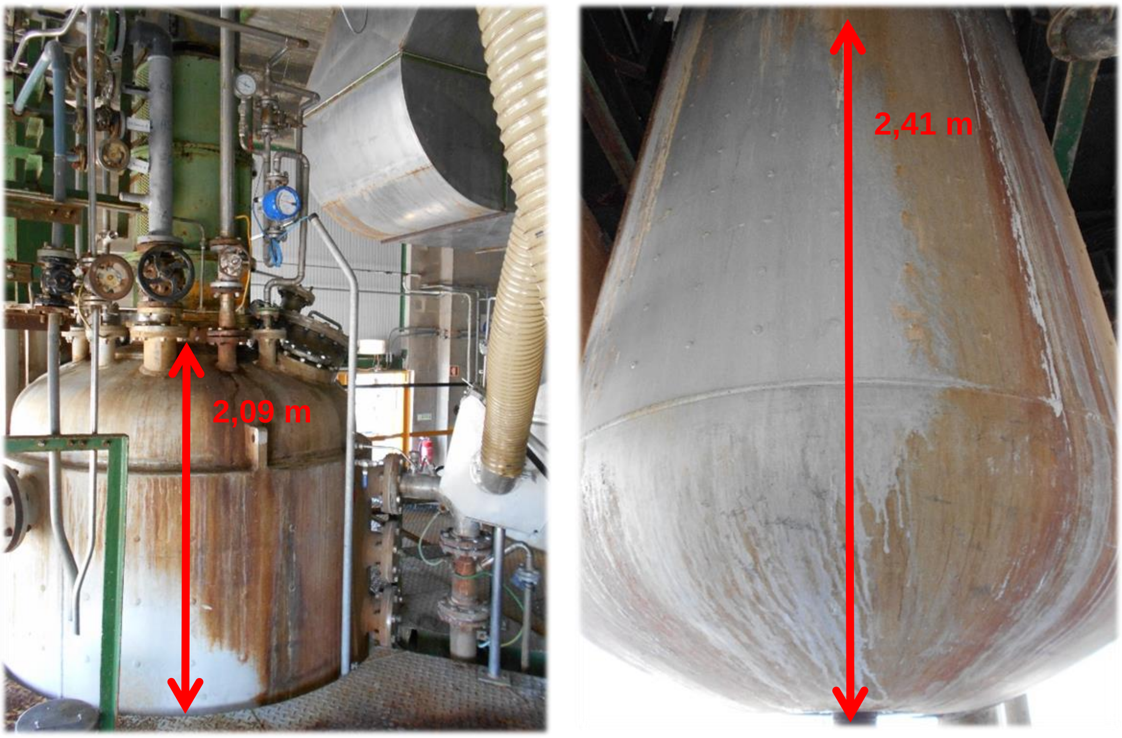

Figure 25. Pictures of a 12 m^3 polymerization reactor with the real measures: on the left, it is the upper zone; on the right, it is the lower zone. Its diameter is 1,86 m

as well as its scheme:

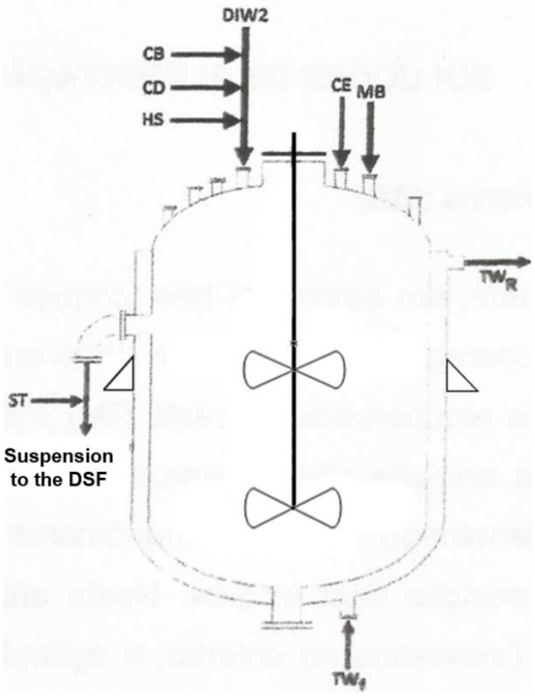

Figure 26. Scheme of the polymerization reactor [12, page 2]

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[3] Pictures taken on the spot on 18/06/2018

About the construction materials of the equipment and their surrounding pipes, these are corrosion resistant to not contaminate the reactional mixture with metallic ions – copper, iron or mercury – that might catalyze the reaction – these ions influence, not only the polymerization reaction, but also the thermal stability of the polymer color. Therefore, all the pipelines and equipment are made of stainless steel, except for the ones HS and CD solutions cross which are made of PVC. In the reactors case, except for the stirrers shafts that are also made of stainless steel, these are constructed in aluminum, not only to avoid the reaction catalysis since this material is not composed by iron, but also because of its high heat transfer coefficient and its low tendency to form inlays. [12, page 2]

Given the importance of not losing heat and protecting people from burns, aluminum isolation is used in steam, condensates and some process pipes.

In addition, after the reaction step, the slurry proceeds to a column so the unreacted monomers can be separated. This is followed by filtration and washing steps and, after that, the polymer is pelletized, dried, ground and finally stored for later spinning. [6, page 836] To produce PAN fibers after obtaining the polymer, there are those who apply the dry-spinning process, but SGL Composites, S.A. follows the Mitsubishi Rayon example and applies the wet-spinning process using dimethylacetamide as solvent.

6. CHEMICAL REACTIVITY

The chemical reactivity study was divided in kinetics research and in an adiabatic system simulation. The kinetics research helped to understand the role each monomer performs during copolymerization and to embrace the system as three different parts, in order to understand their different energetic behavior. The adiabatic system simulation allowed to understand how the system reacts under adiabatic conditions.

6.1. Kinetics

As implicitly mentioned, PAN is a copolymer, and the distribution of both monomers is the great importance and curiosity. Such parameter is described by the respective reactivity ratios that, for this case, were withdrawn from [13]. The reactivity ratio is the ratio of the rate constant for adding to the chain the same monomer at the chain end to the rate constant for adding the other monomer. Assuming that monomer 1 is AN and monomer 2 is AV, the values are: $r_1 = 4{,}05$ [13] and $r_2 = 0{,}04$ [13]. This is a limiting case and means that, in the initial stage of copolymerization, AN is incorporated faster and PAN is rich in AN but, when it gets depleted, more AV segments are added.

During software handling (*Aspen Plus)*, the required kinetic information was related to Arrhenius parameters – the activation energy, being the energy required for the reaction to occur, and the pre-exponential factor, being related to collision of molecules and their orientation. Such information, withdrawn from [13], is therefore presented in Arrhenius equation form:

$$k = Ae^{-E_A/RT} \tag{1}$$

and, according to [13], the parameters' values of the initiation, propagation and termination are included in the following table:

Table 2. Initiation constant and activation energy at 40°C. Propagation and termination constants and the respective activation energy at 25°C [13, pages 68, 81 and 417]

	***E_A* (kcal/mol)**	***k_x* ($Lmol^{-1}s^{-1}$)**
Initiation	20,0	$1{,}65 \times 10^{-2}$
Propagation	4,1	$1{,}54 \times 10^{4}$
Termination	5,4	$2{,}70 \times 10^{9}$

With the information above and giving the fact the initiation constants were determined at 40°C [13, page 68] and the propagation and termination ones were determined at 25°C [13, page 81], each pre-exponential factor was calculated. Hereupon, the stages that complete a polymerization reaction are defined by the following equations:

$$k_i = 1{,}50 \times 10^{12}\, e^{-20{,}0/RT} \text{ (L/mol.s)} \tag{2}$$

$$k_p = 1{,}56 \times 10^7 \, e^{-4{,}1/RT} \text{ (L/mol.s)} \quad (3)$$

$$k_t = 2{,}45 \times 10^{13} \, e^{-5{,}4/RT} \text{ (L/mol.s)} \quad (4)$$

About the initiation, it is important to mention that the values found are related to the initiator potassium persulfate [13, page 68] but, as this component is a good substitute for ammonium persulfate, assuming the values above is reasonable.

In addition, and to support the above-mentioned results, the kinetic parameters related to propagation and termination were found as well in an article. [14, page 221] The following table compares the results from both references:

Table 3. Propagation and termination Arrhenius parameters from an article [14] and from a polymer handbook [13]

	Article		***Polymer Handbook***	
	E_A (kcal/mol)	***k_0 ($Lmol^{-1}s^{-1}$)***	***E_A (kcal/mol)***	***k_0 ($Lmol^{-1}s^{-1}$)***
Propagation	4,1	3×10^7	4,1	$1{,}56 \times 10^7$
Termination	5,4 (radical recombination) 2,3 (chain transfer)	$3{,}3 \times 10^{13}$ (radical recombination) $6{,}7 \times 10^5$ (chain transfer)	5,4	$2{,}45 \times 10^{13}$

As it can be seen, the propagation and termination Arrhenius parameters are quite similar between both references, although the article specifies two different types of termination – radical recombination and chain transfer. Comparing both references, it can be concluded that the termination values withdrawn from the polymer handbook are related to radical recombination, giving the similarity. In fact, theoretically, termination is usually pronounced by radical recombination (chain transfer is more likely to happen during SGL Composites, S.A. process because of a chain-transfer agent existence). If there is a chain-transfer agent, a polymeric chain can terminate by chain transfer and, analyzing Table 3, it is more likely to happen since the activation energy is lower than the activation energy of radical recombination (which means the energy required for the chain transfer reaction to occur is lower, then more probable).

Despite the similarity, the values withdrawn from the polymer handbook were used in the future work, since the article is not recent (from 1959), there are no initiation parameters' values in it and the method used (dilatometric method) to determine the values on Table 3 is not precise.

6.2. Adiabatic System

Bearing in mind the estimation of the maximum temperature the polymerization reactor can reach without any exchange of heat, during the experiments in the Pilot Unit (a topic later explained on this dissertation) it was simulated an adiabatic system by leaking the cooling jacket out. Although it is not a 100% isolated, that experiment led us to a realistic idea of what could happen on the industrial polymerization reactor. The result is presented below:

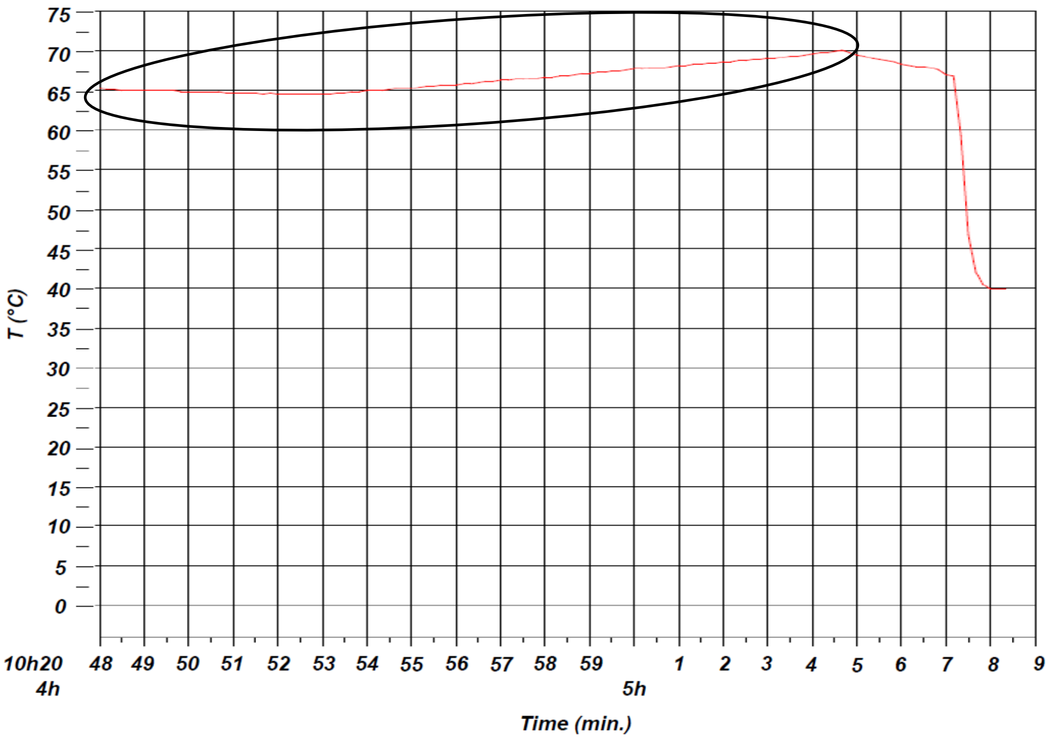

Figure 27. Impact of an adiabatic system on the reactional mixture temperature

As it was expected, the reactional mixture temperature increased abruptly due to no cooling. Despite the agitation, since the heat could not be exchanged with any cooling liquid, the reaction exotherm was not regulated and the reactional mixture started hardening. Although this test was stopped around 70°C, it was observed that the temperature does not stabilize, therefore it would increase infinitely until the reactional mass solidifies completely.

Moreover, this experiment had a setback: initially, instead of leaking the cooling jacket out, a greater quantity of cooling water was circulating inside of it – that is why there is a temperature drop in Figure 27.

In case this scenario happens industrially, due to a pipe rupture for example, in the first place the alarm associated to the reactional mixture temperature is triggered. However, many reasons can be behind this rise: in this case, it is noticed by the TW outlet temperature indicator. The response to this possible scenario, in case the system is not recovered, is to stop and clean the reactor out, as the operators well know.

7. PROCESS HAZARD ANALYSIS

In order to diagnose the probability of runaway or explosion at the polymerization reactor, the worst-case scenarios were analyzed. To do so, the software *Aspen Plus* was used to understand the behavior of the reactional mixture towards the flow variation of the feeding solutions, while in the Pilot Unit it was studied the behavior of the reactional mixture towards the cooling and agitation loss, the lack of inert media, the pH variation and the unexpected introduction of unreacted MB. These deviations were evaluated through the reactional mixture temperature.

7.1. Software Aspen Plus (Polymers)

The software used for the first simulations was *Aspen Plus*, but more specifically the *Polymers* template.

The *Polymers* template is a general-purpose process modeling system for the simulation of polymer manufacturing processes. The modeling system includes modules to estimate thermophysical properties, to perform polymerization kinetic calculations and associated mass and energy balances. [15, page 5] After establishing the stationary state, there is a module of sensibility analysis, in which the simulations are based on, where it is possible to understand how a manipulated variable impacts the variable to be studied.

So, to proceed to the sensibility analysis, first each component present in the feeding solutions was defined, and then the following flowsheet that resumes the reactor zone was prepared:

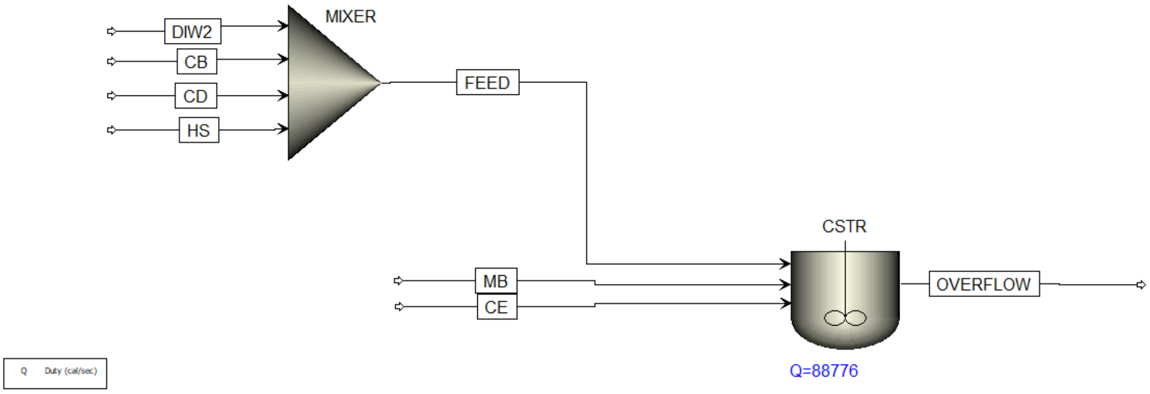

Figure 28. The acrylonitrile copolymerization process schematically

Then, the polymerization reaction was described, as well as its kinetics, and lastly the inlet conditions of each stream and working conditions of each block were defined. These conditions are the ones used industrially (Appendix I). The reactor here simulated was a 12 m^3 one and, after running the known stationary state, it was obtained an overflow temperature of 62,03°C. Meanwhile, the simulations began and the reactional mixture temperature was measured at the overflow.

7.1.1. Results of the Simulations

7.1.1.1. MB

The first scenario being analyzed is the variation of MB solution's flow. The table below describes the sensitivity analysis in question and the deviation here employed was between less 20% and more 20%.

Table 4. Impact of the variation of MB feeding flow on the reactional mixture temperature

Q_{MB} (L/h)	$T_{reactional\ mixture}$ (°C)
2986	63,91
3135	63,52
3285	63,13
3434	62,75
3584	62,37
3733	62,00
3882	61,64
4032	61,28
4181	60,93
4331	60,59
4480	60,25

The red numbers indicate the standard conditions of this solution. In order to facilitate the results conception and its comprehension, the following graphic was drawn:

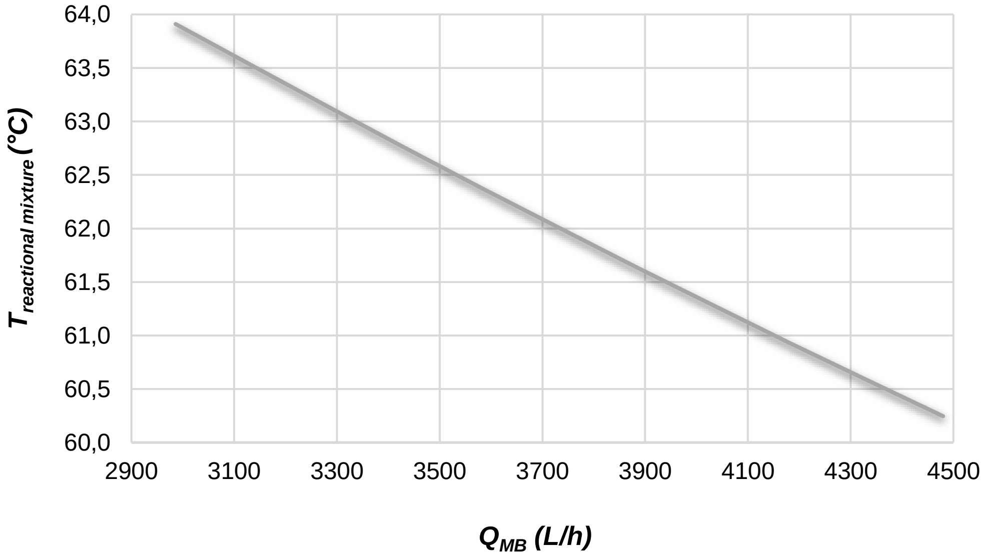

Figure 29. Reactional mixture temperature dependence on MB feeding flow

In MB case, the temperature of the reactional mixture linearly decreases with its feeding flow increasing and vice-versa. In fact, if there are more monomers reacting, there are more radicals forming, which means that more chains are growing at the same time. However, the residence time remains, so each chain does not grow as much and, thus, the final polymer chains are smaller. This results in polymeric chains with lower molecular weight and that is why the energy released is lower than the usual and, consequently, the temperature decreases. However, to a large variation of flow corresponds a low variation of temperature (the maximum temperature indicated by Figure 29 is 63,91°C).

7.1.1.2. CB

The next scenario to analyze is the variation of the catalyst solution's flow. Table 5 resumes the results of this simulation and the deviation here employed was between less 10% and more 10%.

Table 5. Impact of the variation of CB feeding flow on the reactional mixture temperature

Q_{CB} (L/min)	$T_{reactional\ mixture}$ (°C)
0,757	62,03
0,774	62,03
0,791	62,03
0,807	62,03
0,824	62,03
0,841	62,03
0,858	62,03
0,875	62,03
0,891	62,03
0,908	62,03
0,925	62,03
0,757	62,03

Yet again, the red numbers indicate the standard conditions of this solution and the data is gathered in the following graphic:

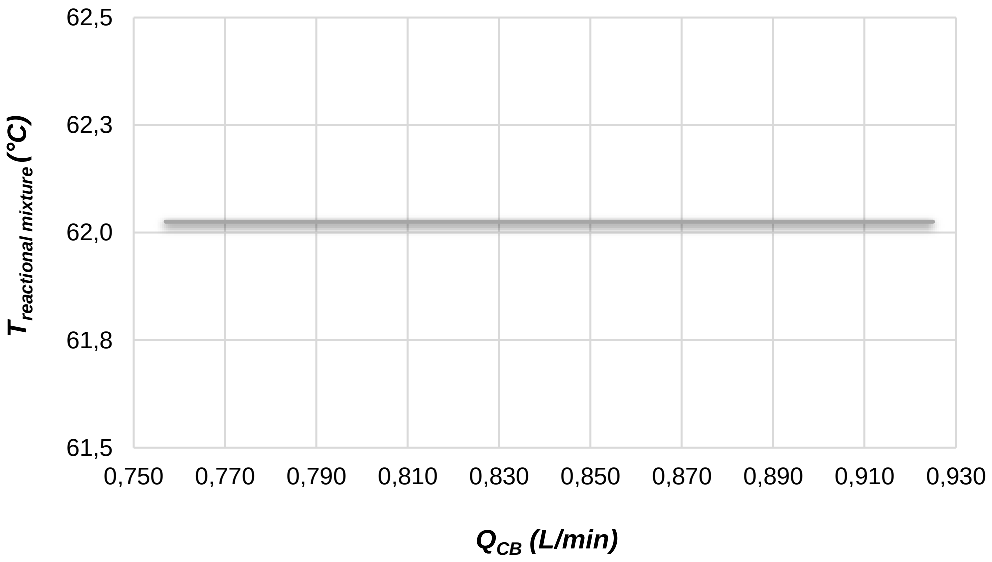

Figure 30. Reactional mixture temperature dependence on CB feeding flow

In CB solution case, there is enough cooling water flow to answer the released heat deviation due to the flow variation, so the reactional mixture temperature is controlled around 62,03°C, maintaining its stationary state value.

7.1.1.3. CE

This scenario is related to the variation of the initiator solution's flow. Table 6 summarizes the results of this simulation and the deviation here employed was between less 20% and more 20%.

Table 6. Impact of the variation of CE feeding flow on the reactional mixture temperature

Q_{CE} (L/min)	$T_{reactional\ mixture}$ (°C)
4,54	62,38
4,77	62,38
5,00	62,38
5,22	62,38
5,45	62,08
5,68	62,08
5,91	62,08
6,14	62,08
6,36	61,78
6,59	61,78
6,82	61,78

Once more, the red numbers indicate the standard conditions of this solution, which temperature is different from the stationary state temperature (62,03°C). This difference was not expected, however the RTD only measures up to the tenth, so this difference is not detectable. The data above is represented in the graphic below:

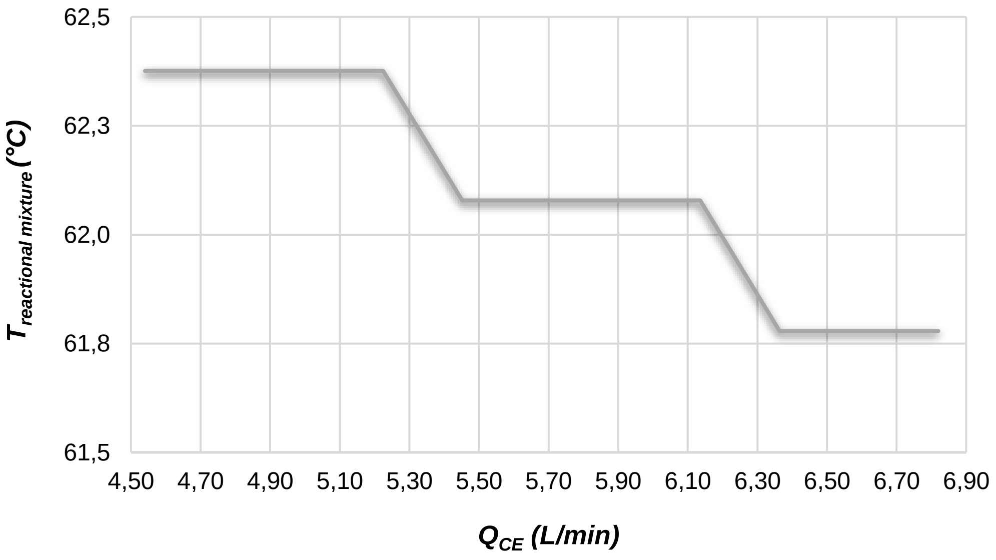

Figure 31. Reactional mixture temperature dependence on CE feeding flow

In CE case, the reactional mixture temperature decreases with CE feeding flow increasing, although not in a linear way: contrary to what happens in MB case, here the temperature does not change along any flow variation (that is why the graphic has the shape of a stair). Curiously, the temperature always varies 0,30°C. Hereupon, there is enough cooling water flow to answer the released heat deviation, and so to control the reactional mixture temperature around 62°C, but only for a narrow range of CE flow. Despite the temperature variations, the values above and below the standard one are within the alert limits (62±1,5)°C.

Additionally, the feeding flow of the initiator solution must be carefully controlled, since its increase leads to polymeric chains with lower molecular weight, resulting from more chains growing up at the same time during the same residence time of the stationary state, which consequently leads to a reactional mixture temperature decrease that in turn leads to a slow reaction that may even stop.

7.1.1.4. CD

The last scenario is related to the variation of the transfer agent solution's flow. The table below resumes the results of this simulation and the deviation here employed was between less 20% and more 20%.

Table 7. Impact of the variation of CD feeding flow on the reactional mixture temperature

Q_{CD} (L/min)	$T_{\text{reactional mixture}}$ (°C)
5,47	62,44
5,74	62,44
6,02	62,44
6,29	62,44
6,57	62,09
6,84	62,09
7,11	62,09
7,39	62,09
7,66	61,74
7,94	61,74
8,21	61,74

Again, the red numbers indicate the standard conditions of this solution, which temperature is different from the stationary state temperature (62,03°C). This difference was once more not expected, however the RTD only measures up to the tenth, so this difference is not detectable. The data above is presented in the graphic below:

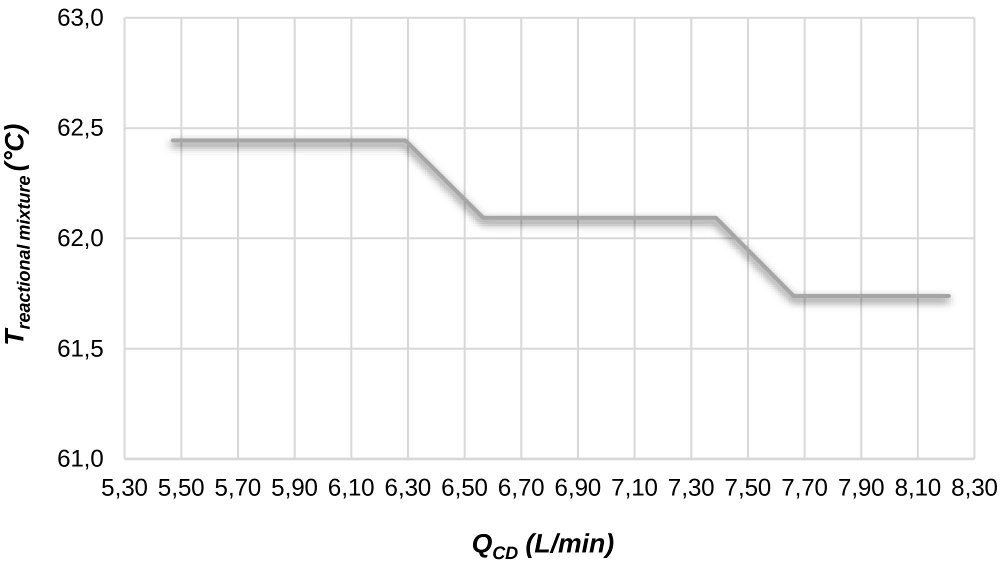

Figure 32. Reactional mixture temperature dependence on CD feeding flow

Like the previous case, the reactional mixture temperature decreases with CD feeding flow increasing, although not in a linear way: once more, the temperature does not change along any flow variation (that is why this graphic also has the shape of a stair). Comparing CE and CD simulation results, the slope between the different temperatures is softer in this case, since it is necessary a bigger flow variation for temperature to vary – the system is more sensitive to CE variations. Despite this difference, it is also concluded there is enough cooling water flow to answer the released heat deviation, and so to control the reactional mixture temperature around 62°C, but only for a narrow range of CD flow. Besides, despite the temperature variations, the values above and below the standard one are as well within the alert limits (62±1,5)°C.

As it is important to control MB, CB and/or CE feeding flow, the CD feeding flow is no exception since its increase leads to polymeric chains with lower molecular weight, but in this case it results, not only from more chains growing up at the same time during the same residence time of the stationary state, but also from chain termination, which consequently leads to a reactional mixture temperature decrease that in turn leads to a slow reaction that may even stop.

In spite of the results obtained with *Aspen*, in reality the impact of any reagent flow variation might not be exactly as shown in the graphics above. The difference may be the fact that in reality there is a controller response which may be slow, probably due to its own lag or due to the controller good stability that leads to a slower response. Consequently, the intervention of operators must be needed and the human factor is also not considered by *Aspen* – the response time of a software is clearly faster than the response time of a human. Industrially, the same deviation can be handled differently and can have different results, unlike *Aspen* that is not influenced by any of these external and uncontrollable factors.

Additionally, in case any of the deviations above happens industrially, and bearing in mind today's control system at SGL Composites, S.A., the alarm associated to the reactional mixture temperature is triggered. However, many reasons can be behind this deviation: in this case, it is noticed by the feeding flows indicators, which each of them also has an alarm associated. The response to this possible scenario, in case the system is not recovered, is to stop and clean the reactor out.

7.2. Pilot Unit

The Pilot Unit is an infrastructure where the following processes are simulated in a pilot scale: [4]

- polymerization;
- dope preparation;
- spinning;
- cutting and baling.

Thus, the process in the Pilot Unit goes from the acrylonitrile to the fiber production. Moreover, the aim of these simulations is to develop new products and processes, as well as optimizing the existing ones. [4]

Nowadays, as SGL Composites, S.A. belongs to the SGL group, the Pilot Unit utilizes the oxidized and carbon fiber precursors for new developments. To do so, the infrastructures used (the processes mentioned above) had to be updated. [4]

In 2010, the Pilot Unit was revamped to install a conversion unit of precursors into carbon fibers. Now, the process goes from the acrylonitrile to the carbon fiber production. [4]

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[4] Information provided by SGL Composites, S.A. via e-mail on 04/07/2018

Now, concerning the polymerization experiments, the experimental setup is presented below: [5]

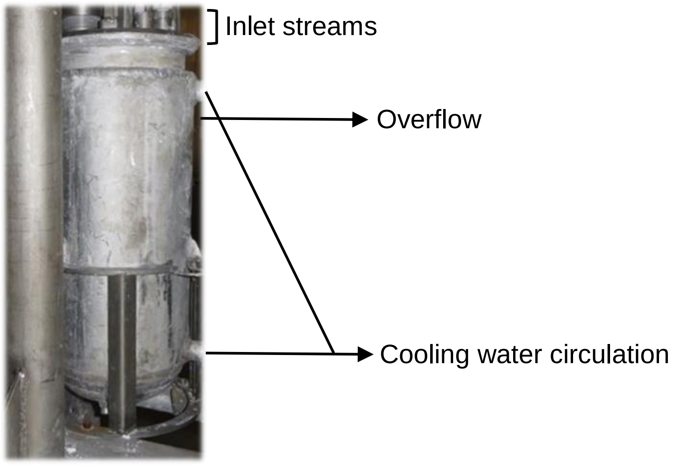

Figure 33. Experimental setup used in the Pilot Unit

and so, the installation where the experimental setup was: [5]

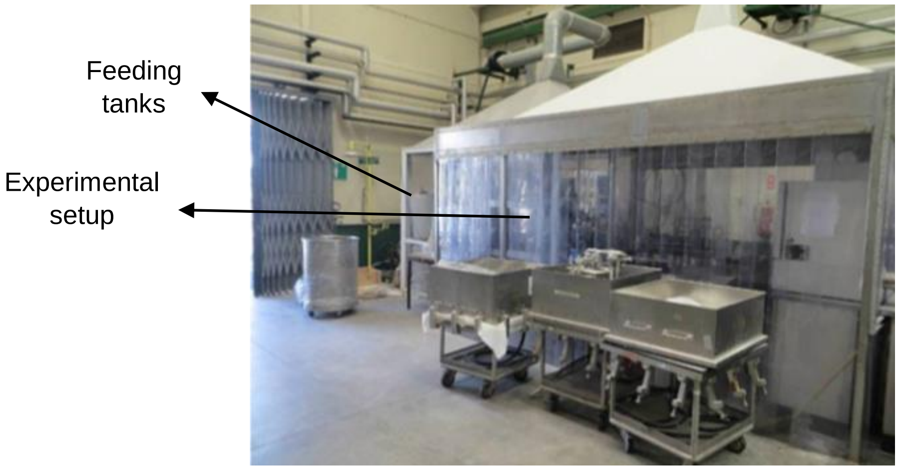

Figure 34. Pilot Unit installation for the polymerization experiments

While in *Aspen Plus* a 12 m^3 reactor could be defined, in the Pilot Unit the experiments were carried out in a 5,7 L reactor (consequently, the industrial conditions had to be adjusted to this volume). Once the experimental setup was prepared, there was a check-list for the polymerization tests to be completed (Appendix II).

Furthermore, the registration sheet of each experiment (the calibration of the flows and the data that was punctually obtained during the tests) is presented in the Appendix III. Below, during results presentation, what all the graphics illustrate after the tests results (marked with a black circle) is the reactor stoppage and its cleaning.

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[5] Picture provided by SGL Composites, S.A. on 04/09/2018

7.2.1. Materials

Before starting the experiments of the worst-case scenarios, it was necessary to prepare the required solutions, bearing in mind the following quantities:

Table 8. Necessary quantities to prepare the feeding solutions

	m_{solid} (g)	Total (g)
CD	1592	80000
CE	404	80000
CB	1800	80000
HS	200	19000
AN+AV	11383 (AN) 1013 (AV)	14376

Concerning the monomers bent, it was supposed to use the one continuously and already prepared in the processual area. As it was not possible, the MB was prepared in the Pilot Unit, even though the AN came from its storage tank. At the end of these preparations, the solutions were agitated with nitrogen during 5 to 10 minutes.

As it is discriminated in the check-list (Appendix II), during the reactor's pre-start there were two steps involving the addition of CB and HS, each one in its right time. These solutions are from the previous preparations, but only the following quantities are added:

Table 9. Required quantities of CB and HS solutions for the reactor's pre-start

	m_{liquid} (g)
CB (1:1000)	103
HS	26
DIW2	3975

Hereupon, together with the other steps completed, it was all set to start the tests.

7.2.2. Results of the Experiments

7.2.2.1. Loss of Agitation

As first experiment, it was studied the impact of the agitation loss on the reactional mixture temperature. The result is presented below:

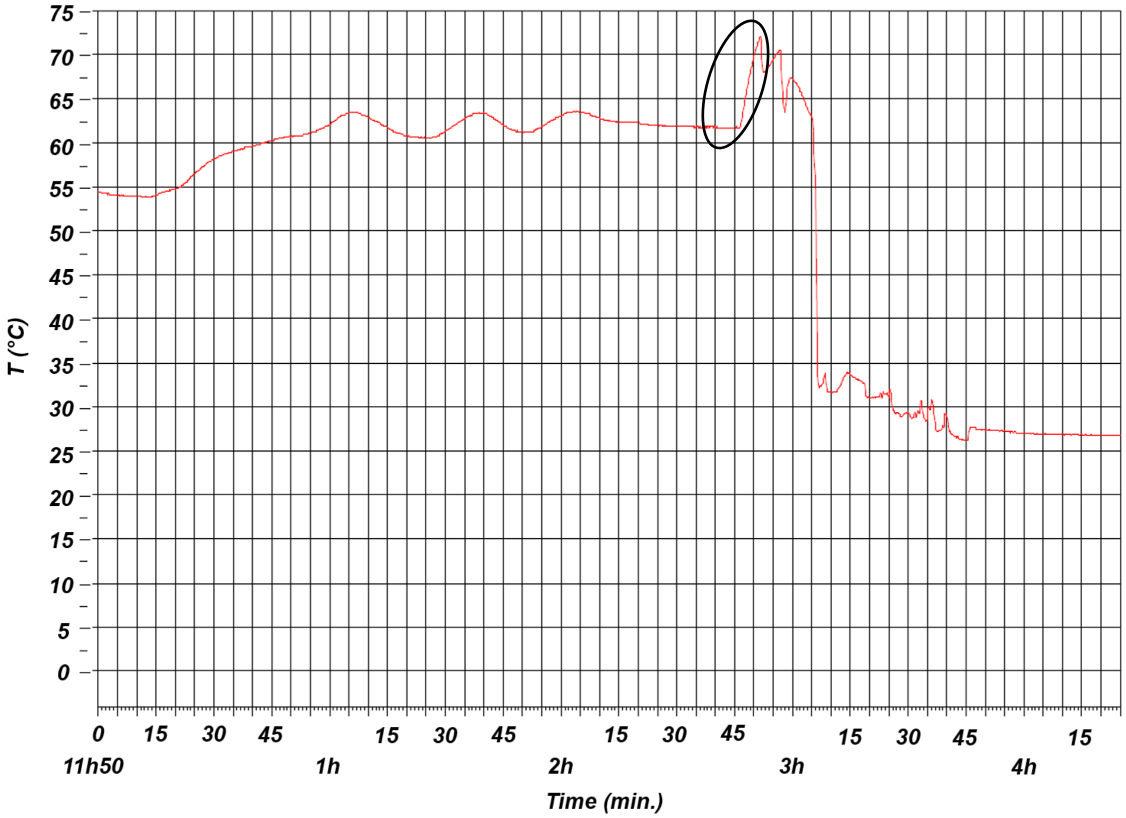

Figure 35. Impact of agitation loss on the reactional mixture temperature

As it can be realized, once the agitation stopped the reaction continued and its respective heat concentrated instead of dispersing. Naturally, the reactional mixture temperature increased abruptly and uncontrollably and the reactional mass started solidifying.

In case this scenario happens industrially, the reactional mixture temperature alarm is triggered so the operators can be aware. When it happens, it all the variables that can cause such effect must be checked – in this case, there are two possibilities since the stirrer can stop for two reasons: either there is a problem in its coupling or an electrical problem.

On the one hand, if the problem is in the stirrer's coupling, the engine sign remains on, but the stirrer power decreases, whose value is indicated on the panel. Hereupon, the reactor must be stopped and cleaned out.

On the other hand, if the problem is electrical, the engine sign is off, so its alarm is triggered. In this case, the operators try to start the engine up again and, if it does not respond, the stirrer must be fixed. As the stirrer cannot be stopped for more than 5 minutes, when it does the reactor must be stopped and cleaned out.

As a curiosity, if there is an energy cut, the stirrer is connected to the emergency generator, which actuates within seconds. Furthermore, on the first business day of every month the generator is checked so that possible problems can be fixed.

7.2.2.2. Lack of Inert Media

Another worst-case scenario was related to the reactor start up with no inert media. The following graphic resumes the data:

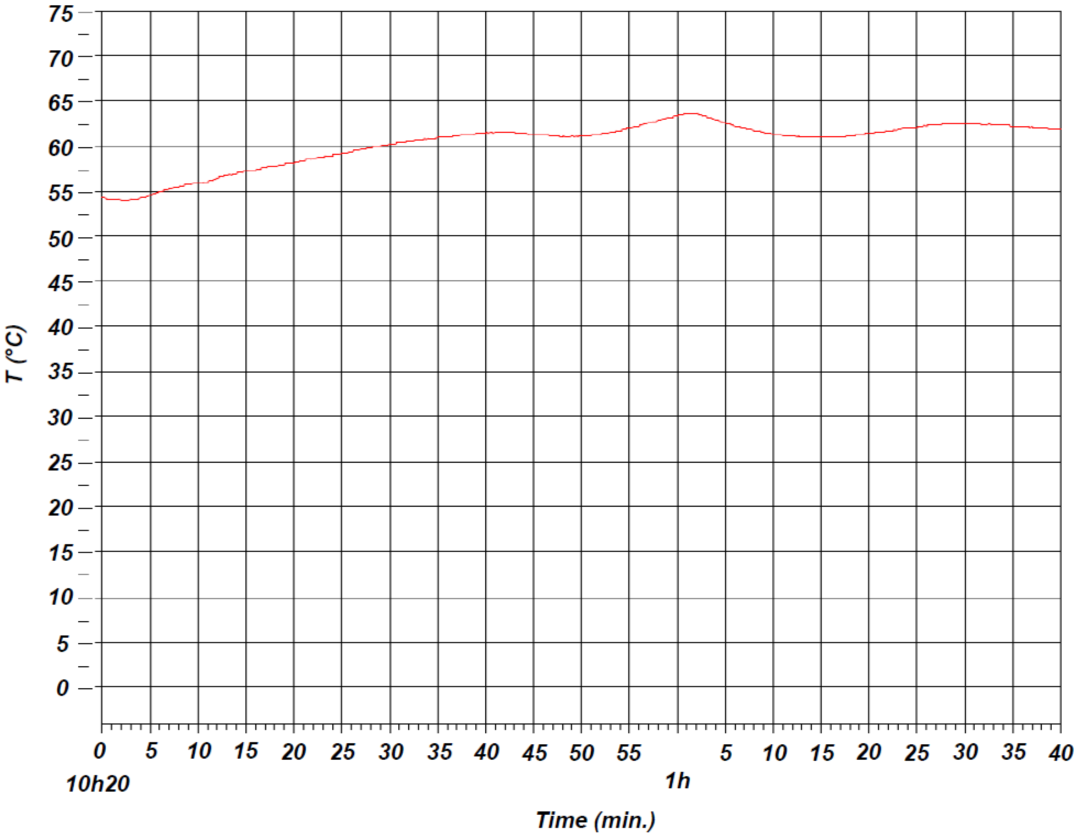

Figure 36. Impact of inert media on the reactional mixture temperature

As the aim of the inert media is to suppress the reactive atmosphere, this circumstance does not influence the reactor operation. Therefore, it is expected to start and to work normally with no impact on the reactional mixture temperature, as it is shown by Figure 36.

7.2.2.3. Loss of cooling

Regarding the cooling loss scenario, the graphic below sums it up:

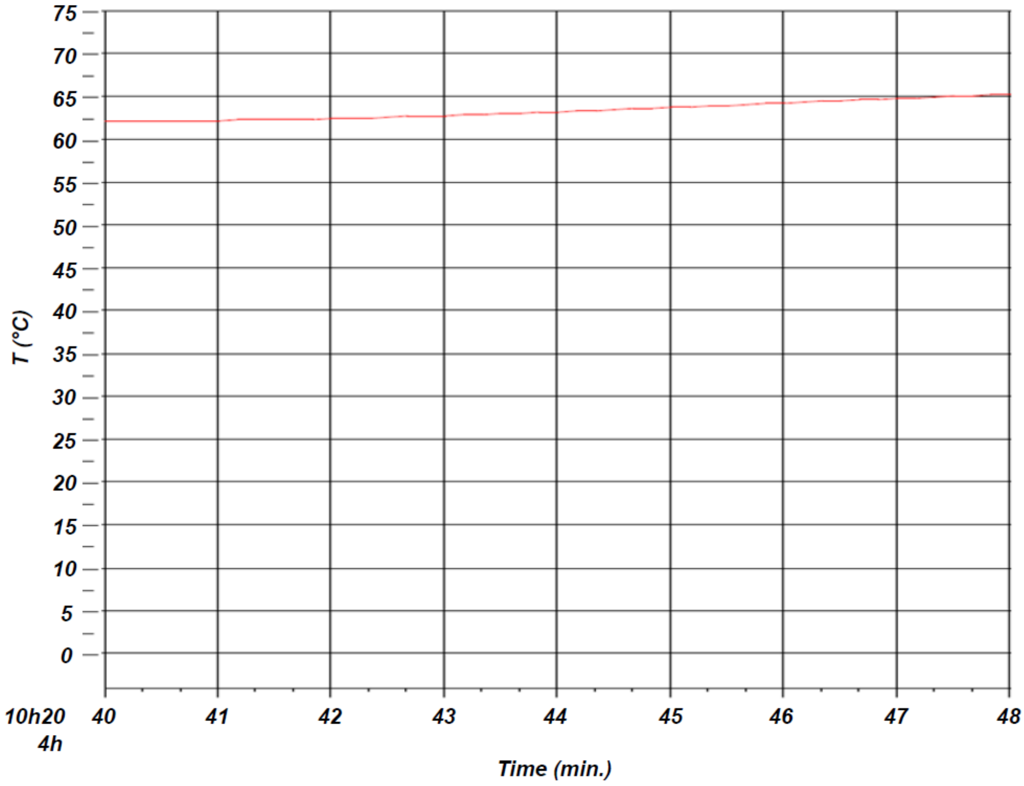

Figure 37. Impact of cooling loss on the reactional mixture temperature

The difference between this experiment and the adiabatic system simulation is that, in this case, the cooling water remained still inside the jacket. Therefore, as it was expected, the reactional mixture temperature increased markedly due to the cooling loss and again the reactional mixture started hardening.

In case this scenario happens industrially, in the first place the reactional mixture temperature alarm is triggered. When it happens, the operators must check all the variables that can cause such effect – this situation is noticed by the TW inlet flow indicator, whose value would be lower, and whose variable has an alarm associated. The response to this possible scenario, in case the system is not recovered, is to stop and clean the reactor out.

Additionally, at 3:08 pm (4 hours and 48 minutes after), the cooling water was drained to simulate the adiabatic system clarified above.

7.2.2.4. pH increasing

The pH experiment started with its intentional increase. Both data (reactional mixture temperature and pH) are presented below:

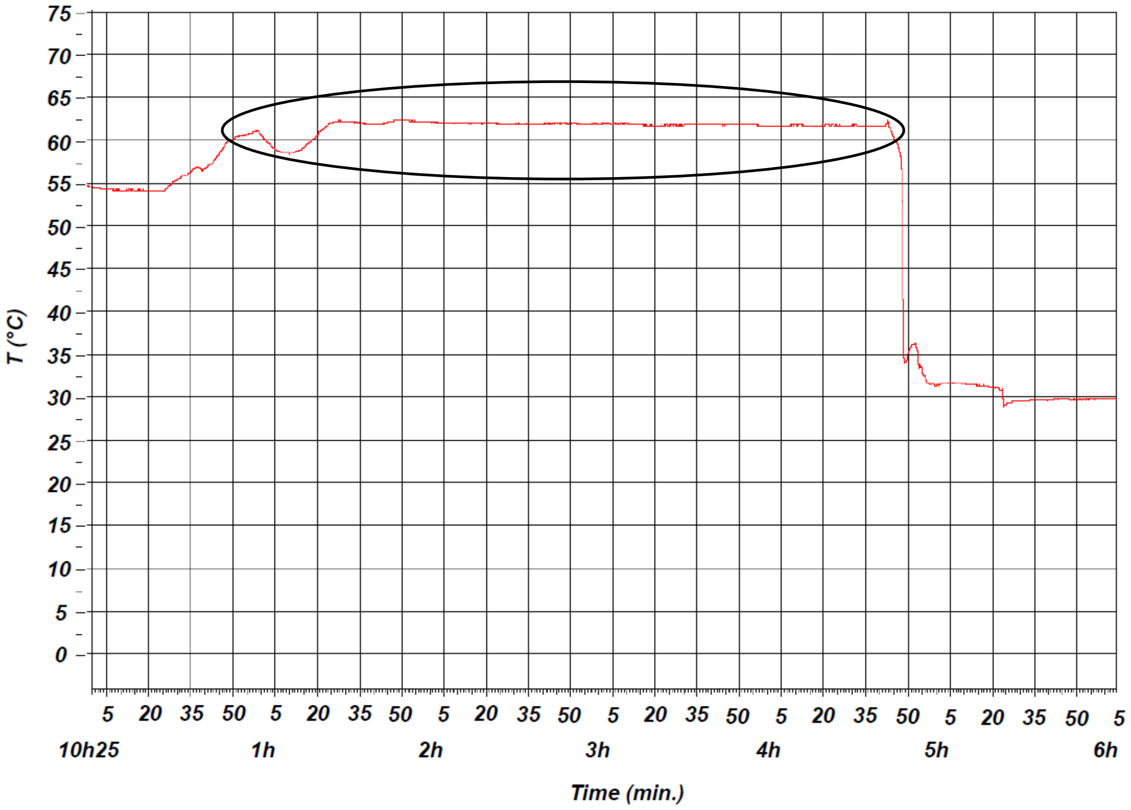

Figure 38. Impact of pH intentional increasing on the reactional mixture temperature

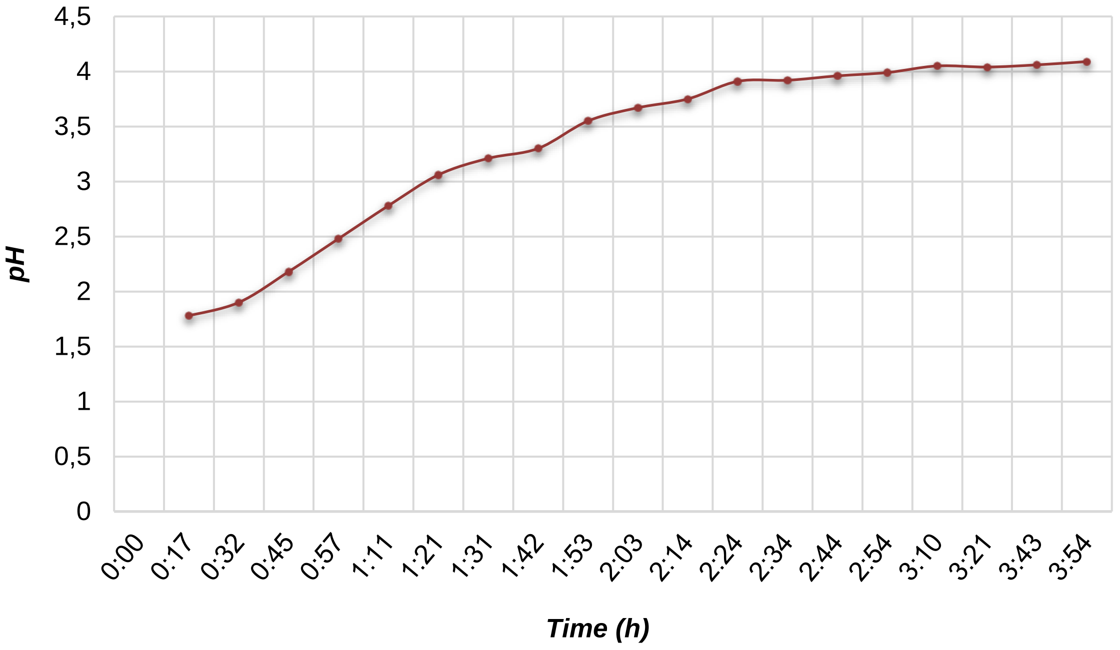

Figure 39. pH evolution during the pH increasing experiment

Regarding pH variation, it was regulated with the acid flow and surprisingly the pH value increased gradually stabilizing around 4, while the reactional mixture temperature poorly oscillated around 62°C.

Concerning safety matters there is no problem associated with pH variation, since the reactional mixture temperature remains constant. However, as a curiosity, the NSP value was measured to register that this scenario influences the product quality. Moreover, as polymerization experiments with CE in the Pilot Unit were never done at the time, the NSP value was also measured under right industrial conditions with the system stabilized (standard value). The result obtained was 0,164 comparing to the central value – 0,175.

Since the temperature in question remains constant, this scenario is harder to notice if it happens industrially. Yet, if this happens, the operator realizes it mainly by the pH measurement routine (every 8 hours) and, although it looks not enough, because something can happen during the time pH is not measured, such circumstance can be possibly controlled by the acid inlet flow as well, whose indicator has an alarm associated.

7.2.2.5. pH decreasing

To complete the pH variation experiment it was intentionally decreased as well. Again, both data (reactional mixture temperature and pH) are presented in the figures below:

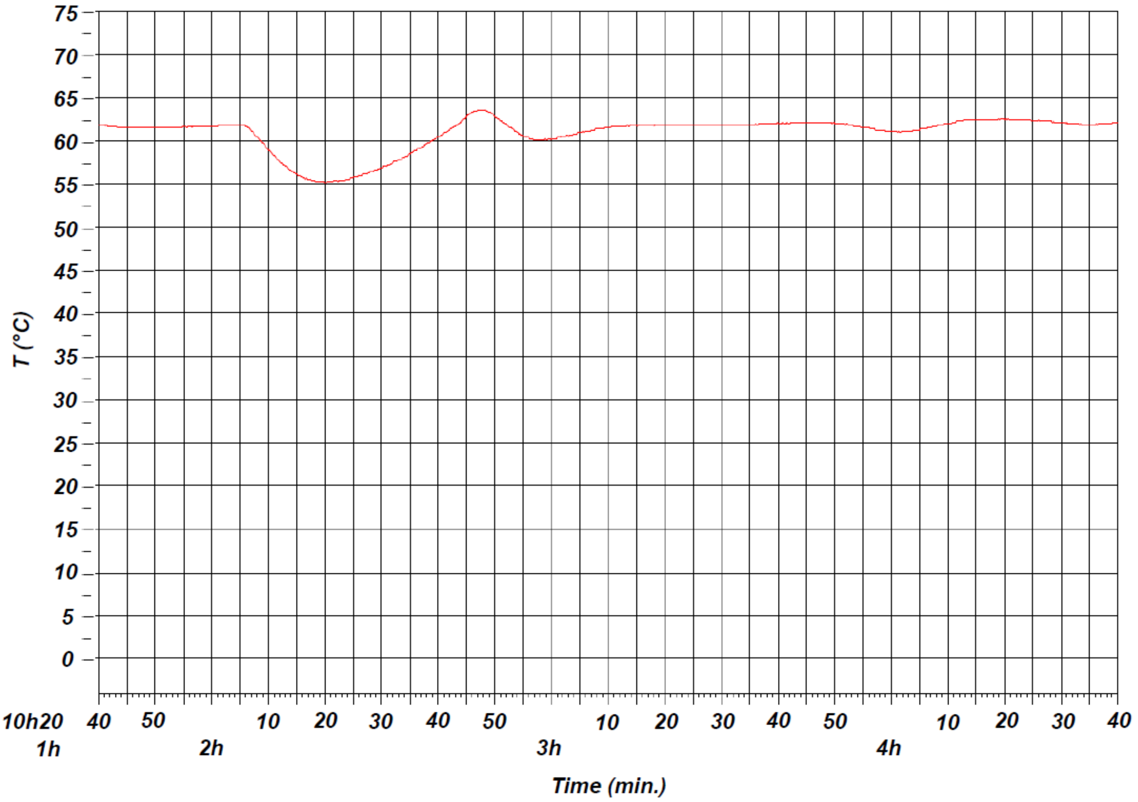

Figure 40. Impact of pH intentional decreasing on the reactional mixture temperature

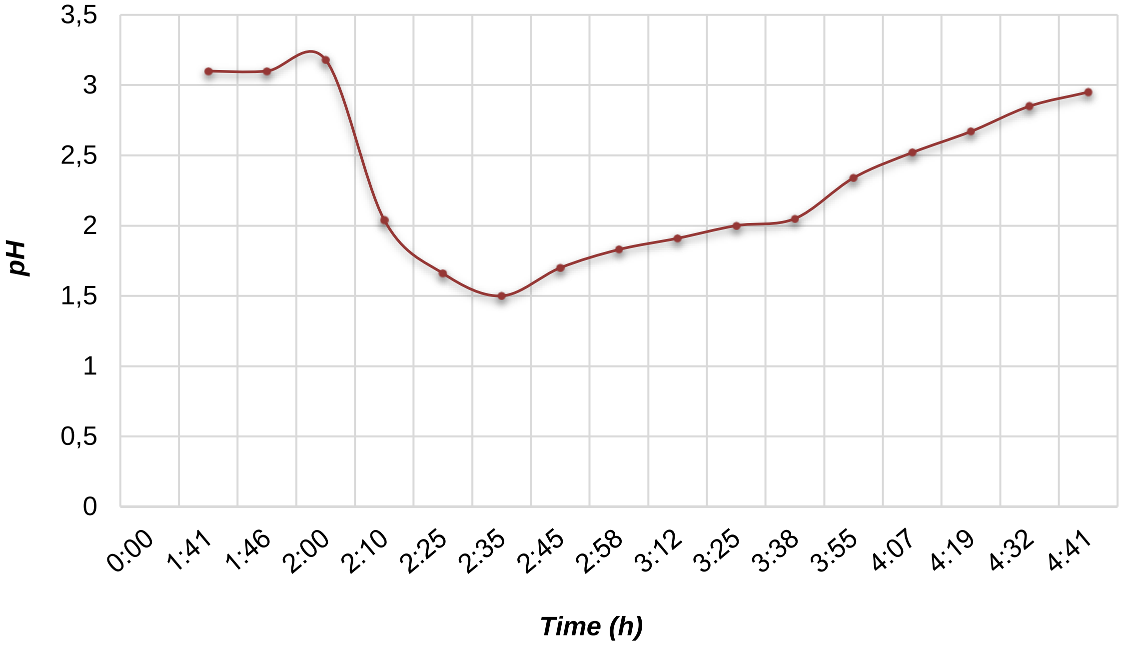

Figure 41. pH evolution during the pH decreasing experiment

The variation in question here was also regulated with the acid flow. When it was increased, the pH value oddly increased as well until it was noticed the HS tube was broken (zero flow). Meanwhile, the tube was replaced and the increased HS flow was established, which resulted in an instantaneous and sudden pH decrease (therefore, the increased HS flow was adjusted because the one established was too much). The pH reduction was accompanied by an abruptly reactional mixture temperature decrease, since a significant quantity of a cold stream was introduced. During this experiment, it was necessary to increase the cooling jacket temperature so the activation energy was enough to stimulate the reaction. Once the reaction started to release heat, the cooling jacket temperature was gradually adjusted until returning to the stationary point.

Similar to the prior scenario, if this happens industrially, it may be hard to notice, but again the operator realizes it mainly by the pH measurement routine (every 8 hours) and possibly by the acid inlet flow as well, whose indicator has an alarm associated, as mentioned above.

7.2.2.6. Unexpected introduction of unreacted monomers bent

The last worst-case scenario to be tested was the sudden introduction of unreacted monomers bent, as the figure below well illustrates:

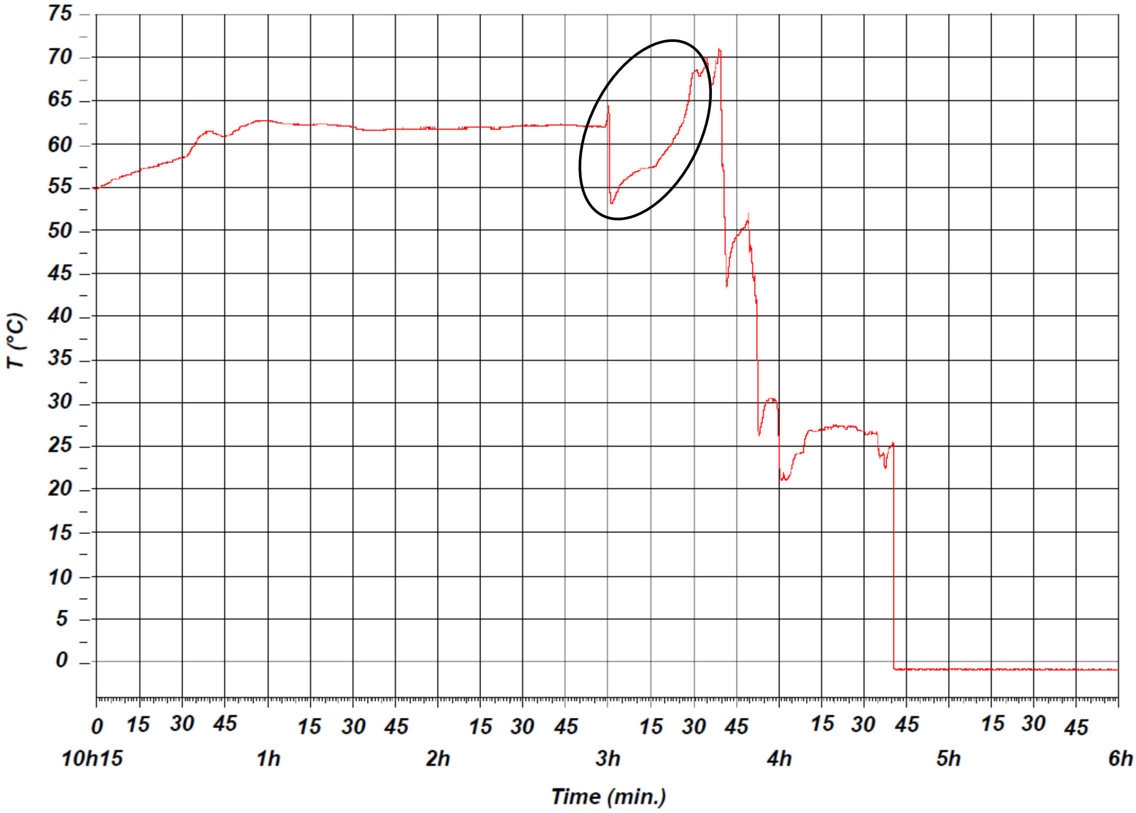

Figure 42. Impact of the unexpected introduction of unreacted MB on the reactional mixture temperature

To test this possibility, half of the reactional mixture was first drained out of the reactor and then the same quantity of MB was suddenly introduced in it, while the stirrer was off – that is why there is a temperature peak. As a significant amount of a cold stream was introduced, when the stirrer was rebooted, the reactional mixture temperature decreased instantly and abruptly. Nevertheless, while MB reacted, the reactional mass temperature increased.

Meanwhile, the cooling jacket temperature was reduced to recover the reactor standard temperature. The reactor inner temperature discreetly decreased, but then it started to rise again to the point there was no longer an overflow – the reactional mixture had solidified.

Concerning safety matters, if this happens industrially, the temperature alarm is obviously triggered and the operator is aware of this scenario by the MB flow indicator, which also has an alarm associated. Due to the fact this scenario originates a harder solidification, probably the system would be uncontrolled and lost. The response to this situation, as always, is to stop and clean the reactor out.

8. PROCESS INSTRUMENTATION ANALYSIS

Before doing a critical process instrumentation review, some relevant information was collected. After analyzing the previous worst-case scenarios, the most common non-conformities related to the reactors' zone were gathered and are detailed in the graphic below: [6]

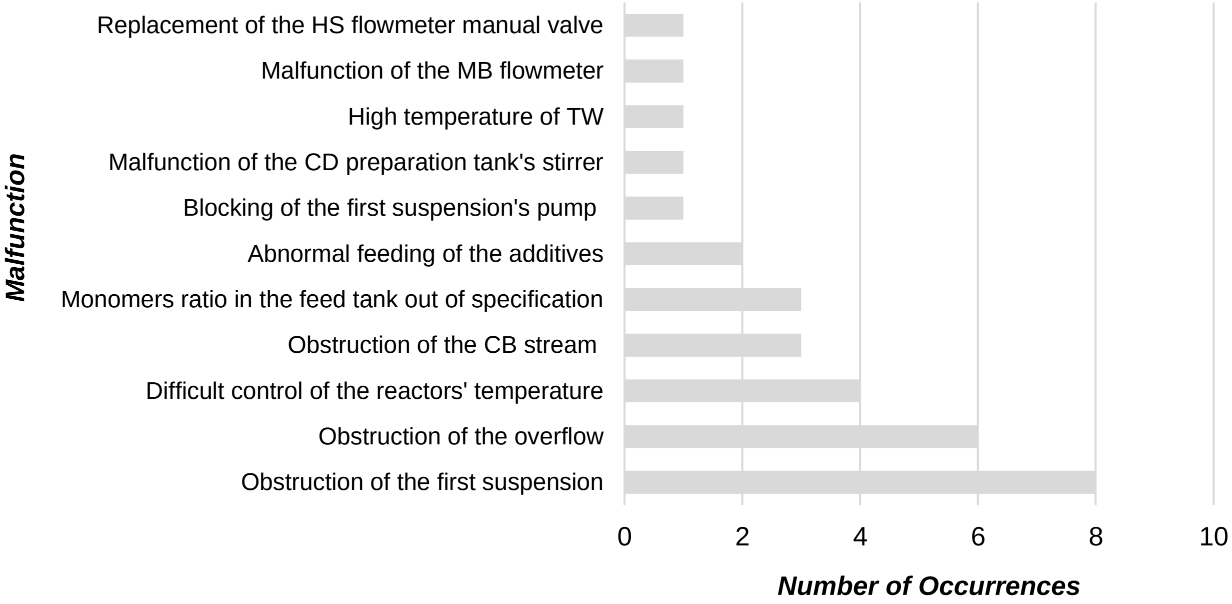

Figure 43. Number of occurrences of the most common malfunctions throughout the last 3 years (2015 – 2018)

Obviously, more attention was given to the first three malfunctions, whereas the first suspension is basically the overflow but, while the obstruction of the overflow is related to the reactor's exit, the obstruction of the first suspension is related to the DSF's entrance.

All these malfunctions might lead to a feed cut, or to a reaction temperature out of specification, or to an NSP out of specification or, lastly, to an area stop. The following fishbone diagrams resume these cause-effect relations: [6]

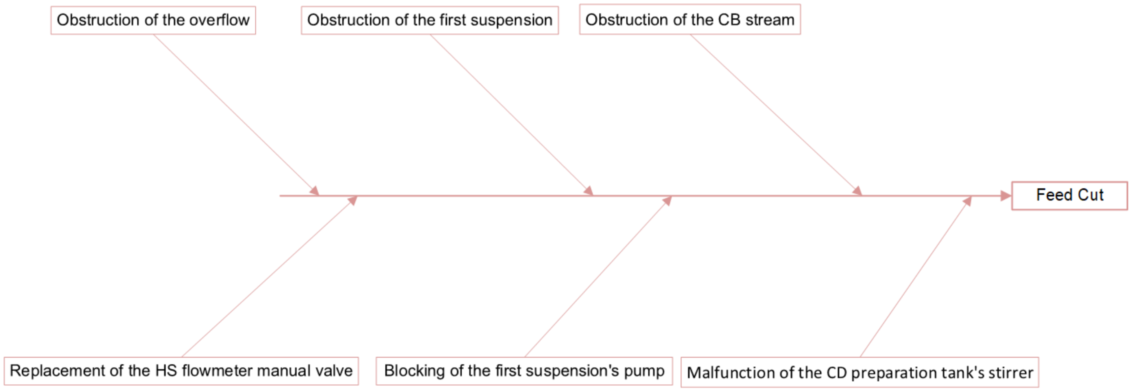

Figure 44. Cause-effect diagram regarding feed cut

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[6] Information provided in an excel file by SGL Composites, S.A. on 08/05/2018

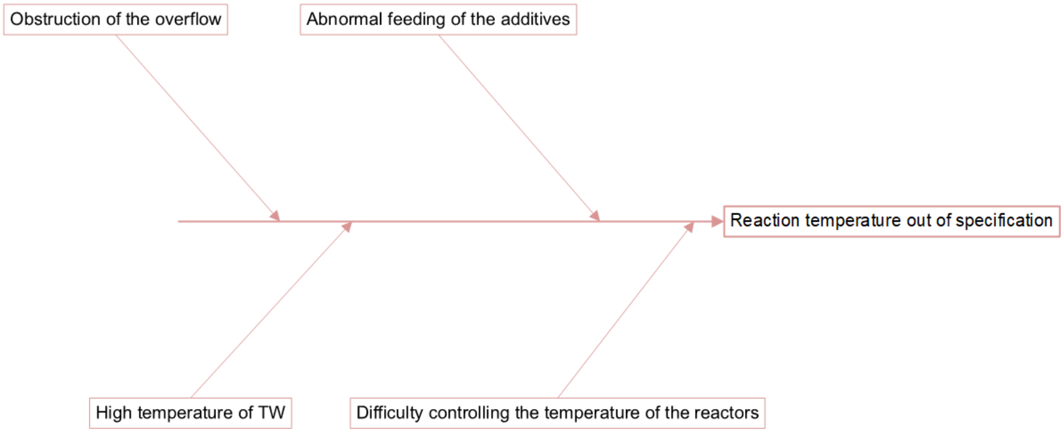


Figure 45. Cause-effect diagram regarding reaction temperature out of specification

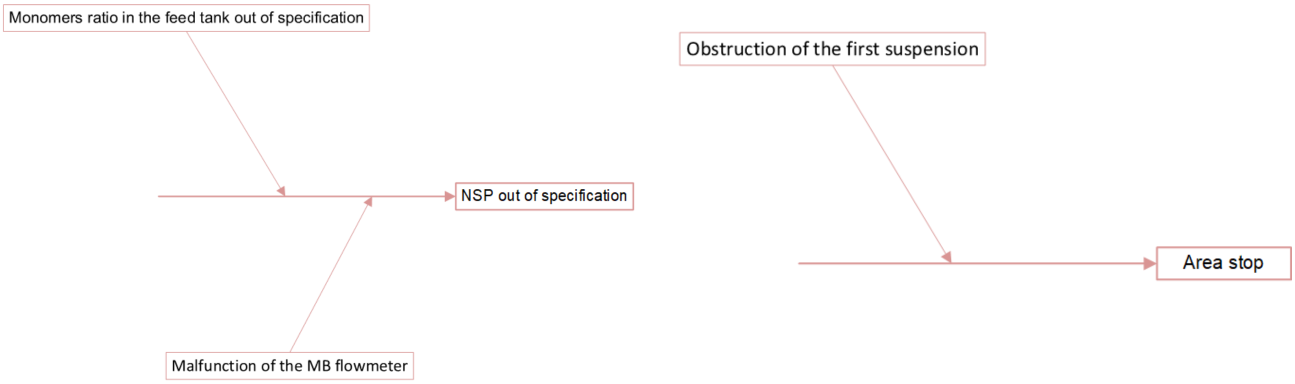
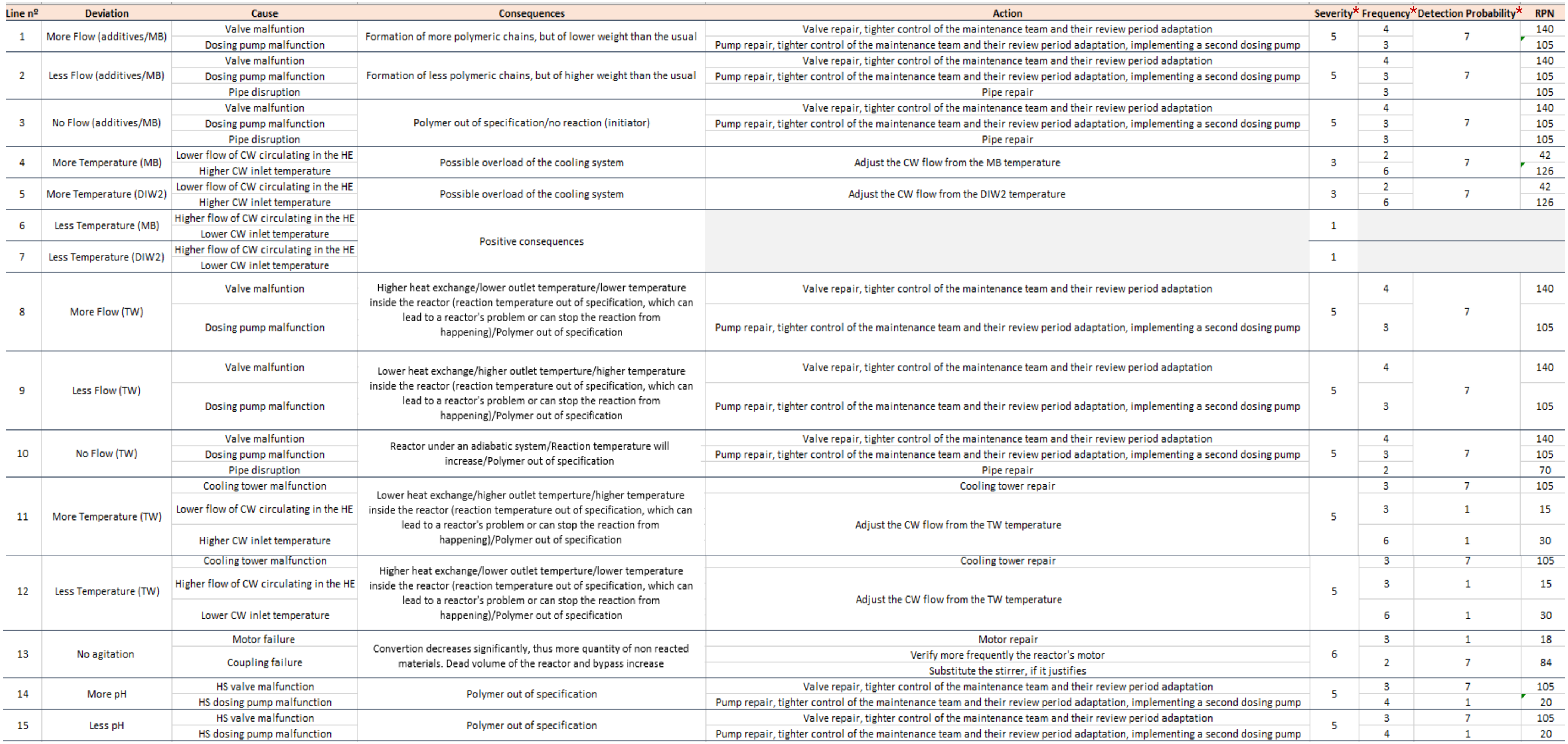


Figure 46. On the left: cause-effect diagram regarding NSP out of specification; on the right: cause-effect diagram regarding area stop

Furthermore, just to ensure all major failures were considered, the following HAZOP was proceeded:



Line nº	Deviation	Cause	Consequences	Action	Severity*	Frequency*	Detection Probability*	RPN
1	More Flow (additives/MB)	Valve malfuntion	Formation of more polymeric chains, but of lower weight than the usual	Valve repair, tighter control of the maintenance team and their review period adaptation	5	4	7	140
		Dosing pump malfunction		Pump repair, tighter control of the maintenance team and their review period adaptation, implementing a second dosing pump		3		105
2	Less Flow (additives/MB)	Valve malfuntion	Formation of less polymeric chains, but of higher weight than the usual	Valve repair, tighter control of the maintenance team and their review period adaptation	5	4	7	140
		Dosing pump malfunction		Pump repair, tighter control of the maintenance team and their review period adaptation, implementing a second dosing pump		3		105
		Pipe disruption		Pipe repair		3		105
3	No Flow (additives/MB)	Valve malfuntion	Polymer out of specification/no reaction (initiator)	Valve repair, tighter control of the maintenance team and their review period adaptation	5	4	7	140
		Dosing pump malfunction		Pump repair, tighter control of the maintenance team and their review period adaptation, implementing a second dosing pump		3		105
		Pipe disruption		Pipe repair		3		105
4	More Temperature (MB)	Lower flow of CW circulating in the HE	Possible overload of the cooling system	Adjust the CW flow from the MB temperature	3	2	7	42
		Higher CW inlet temperature				6		126
5	More Temperature (DIW2)	Lower flow of CW circulating in the HE	Possible overload of the cooling system	Adjust the CW flow from the DIW2 temperature	3	2	7	42
		Higher CW inlet temperature				6		126
6	Less Temperature (MB)	Higher flow of CW circulating in the HE	Positive consequences		1			
		Lower CW inlet temperature						
7	Less Temperature (DIW2)	Higher flow of CW circulating in the HE			1			
		Lower CW inlet temperature						
8	More Flow (TW)	Valve malfuntion	Higher heat exchange/lower outlet temperature/lower temperature inside the reactor (reaction temperature out of specification, which can lead to a reactor's problem or can stop the reaction from happening)/Polymer out of specification	Valve repair, tighter control of the maintenance team and their review period adaptation	5	4	7	140
		Dosing pump malfunction		Pump repair, tighter control of the maintenance team and their review period adaptation, implementing a second dosing pump		3		105
9	Less Flow (TW)	Valve malfuntion	Lower heat exchange/higher outlet temperture/higher temperature inside the reactor (reaction temperature out of specification, which can lead to a reactor's problem or can stop the reaction from happening)/Polymer out of specification	Valve repair, tighter control of the maintenance team and their review period adaptation	5	4	7	140
		Dosing pump malfunction		Pump repair, tighter control of the maintenance team and their review period adaptation, implementing a second dosing pump		3		105
10	No Flow (TW)	Valve malfuntion	Reactor under an adiabatic system/Reaction temperature will increase/Polymer out of specification	Valve repair, tighter control of the maintenance team and their review period adaptation	5	4	7	140
		Dosing pump malfunction		Pump repair, tighter control of the maintenance team and their review period adaptation, implementing a second dosing pump		3		105
		Pipe disruption		Pipe repair		2		70
11	More Temperature (TW)	Cooling tower malfunction	Lower heat exchange/higher outlet temperture/higher temperature inside the reactor (reaction temperature out of specification, which can lead to a reactor's problem or can stop the reaction from happening)/Polymer out of specification	Cooling tower repair	5	3	7	105
		Lower flow of CW circulating in the HE		Adjust the CW flow from the TW temperature		3	1	15
		Higher CW inlet temperature				6	1	30
12	Less Temperature (TW)	Cooling tower malfunction	Higher heat exchange/lower outlet temperture/lower temperature inside the reactor (reaction temperature out of specification, which can lead to a reactor's problem or can stop the reaction from happening)/Polymer out of specification	Cooling tower repair	5	3	7	105
		Higher flow of CW circulating in the HE		Adjust the CW flow from the TW temperature		3	1	15
		Lower CW inlet temperature				6	1	30
13	No agitation	Motor failure	Convertion decreases significantly, thus more quantity of non reacted materials. Dead volume of the reactor and bypass increase	Motor repair	6	3	1	18
		Coupling failure		Verify more frequently the reactor's motor		2	7	84
				Substitute the stirrer, if it justifies				
14	More pH	HS valve malfunction	Polymer out of specification	Valve repair, tighter control of the maintenance team and their review period adaptation	5	3	7	105
		HS dosing pump malfunction		Pump repair, tighter control of the maintenance team and their review period adaptation, implementing a second dosing pump		4	1	20
15	Less pH	HS valve malfunction	Polymer out of specification	Valve repair, tighter control of the maintenance team and their review period adaptation	5	3	7	105
		HS dosing pump malfunction		Pump repair, tighter control of the maintenance team and their review period adaptation, implementing a second dosing pump		4	1	20

*Figure 45. HAZOP of the polymerization reactor (the rating scales signed here by * are detailed in the Appendix IV)*

Concerning lines nº 6 and 7 (Figure 45), bearing in mind that the MB and DIW2 streams are normally cooled to avoid the overload of the cooling system, the positive consequences are due to the lower probability of that overload given the lower temperature of MB and DIW2 streams.

This data helped understand the deviations that might happen more frequently, the respective causes and the right actions.

8.1. Improvements made the last 3 years

Nevertheless, over time some improvements were made:

i. regarding the obstruction of the CB stream, the answer was to acidify the solution. This malfunction was a consequence of the iron precipitation, that in turn was hindering the passage of the CB solution. Reducing its pH makes the precipitation more difficult and, thus, avoids the pipe blocking. Therefore, bearing in mind the pH of the reactional mass, it had to be adjusted with the HS solution.

ii. regarding the abnormal feeding of the additives, the answer was to implement Coriolis flowmeters. This malfunction was a consequence of electromagnetic flowmeters' use, which measure the volumetric flow and convert it to mass flow by using a defined density. However, the density is always changing, so the flows indicated had errors associated. The new flowmeters measure the mass flows and the respective instant density, so the volumetric flows are correctly calculated;

iii. regarding the monomers ratio out of specification in the feed tank, an automatic system was constructed to avoid the contamination of the solution ready to feed the reactor, when a new one is being prepared. To do so, it was settled a condition that only allows the preparation of a new solution when the valve that fills the feed tank is closed.

Based on the information above, there are in fact some proposals that would improve the process efficiency and increase the operational safety:

8.2. Instrumentation Proposals (for discussion)

8.2.1. Implementation of a Rupture Disk in the Polymerization Reactors

While the reactors are operating, the pressure may increase, so it is usual to implement a relief valve (vent stream). However, in polymerization reactors, solid polymer frequently adheres to the seat of the valve and glues all the periphery. When the pressure increases, the valve may not open and that is why it is a common safety practice to install a rupture disk for an overpressure slightly higher than the spring of the valve. Plus, since froth is formed, an oversize duct is necessary to lead it to an appropriate size container.

Figure 46. Rupture disk [16, page 2]

It is factual that the pressure can be also relieved through the overflow, but this airway is usually obstructed as well, when the pressure increases.

Objective: to relieve the pressure when the relief valve cannot, with no worries concerning possible obstructions.

Advantages:

- there is a way to release the pressure, when and while the relief valve is obstructed or when the seat of the valve is glued with polymer;
- there is a way to release higher pressures than the usual.

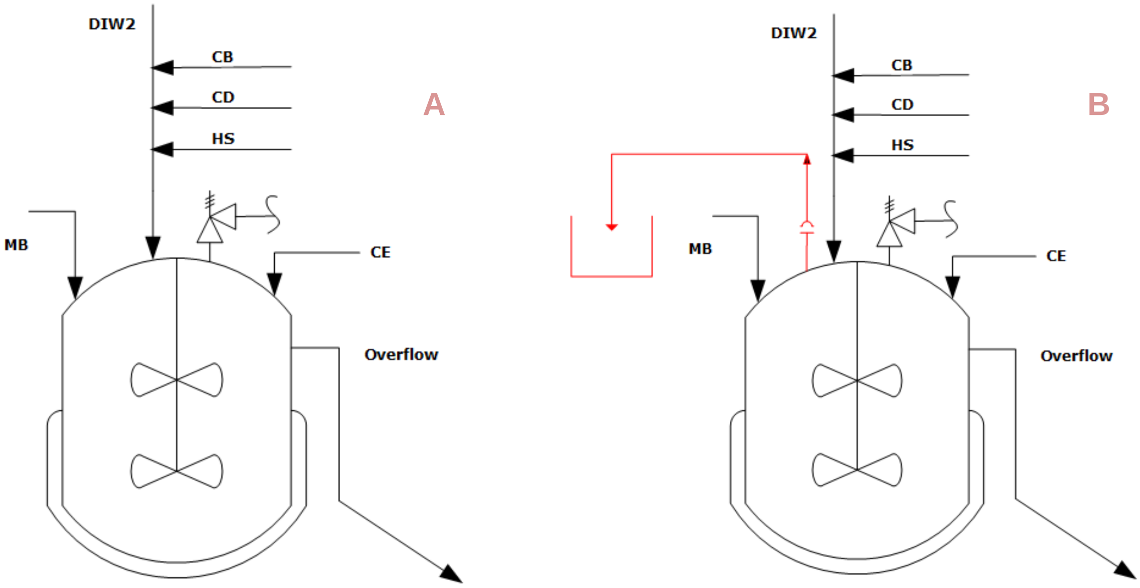


Figure 47. Schematic drawing of the rupture disk implementation: A – scheme as it currently is, B – scheme after the rupture disk implementation

8.2.2. Implementation of a Manual Self-Cleaning Filter connected to the Overflow

As it can be seen in Figure 43, one of the most common deviation is the obstruction of the overflow, which leads to parameters out of specification and to malfunction of pumps and valves. In order to avoid the repeat feed cut or the probable need to shut the area down, a possible suggestion is to implement a manual self-cleaning filter in the overflow: [7]

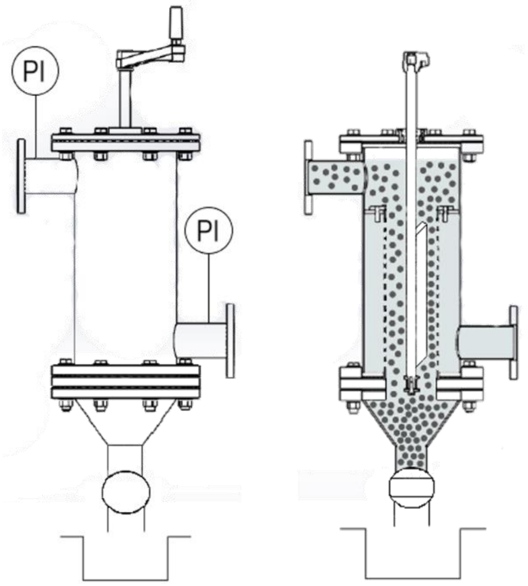


Figure 48. Manual self-cleaning filter with a scrapper

The idea is for the polymeric suspension to enter the screen (the lateral zones are closed on the top) and trap the debris inside it, while the cleaned polymeric suspension passes through the filter's tiny holes and continues its way. When the filter saturates, the inlet pressure rises exceeding the outlet pressure (atmospheric pressure) and an operator must rotate the scrapper to clean the filter. Now, to warn the operators about the pressure difference, there are two pressure indicators – one in the inlet stream and other in the outlet stream.

In case this proposal is implemented, an expansion of the overflow pipe would probably be necessary.

<u>Objective:</u> to remove the inlays and, thus, mitigate its accumulation.

<u>Advantages:</u>

- no need to interrupt the process flow during filter cleaning and inlays removing;
- less problems in adjacent pumps and valves;
- DSF's obstruction is not so frequent;
- the basket filters' baskets near to DSF do not have to be cleaned or replaced as frequently;
- no operator contact with liquid during cleaning operation; [17, page 2]

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[7] Manual self-cleaning filter designed by Secil and constructed to its own use – document provided by Professor João Bordado on 22/06/2018

- minimized product loss – during both process production and system cleaning; [17, page 2]
- increased quality output – minimum disruption to product flow; [17, page 2]
- reduced contamination – less possibility of accidents or operator exposure to the fluid. [17, page 2]

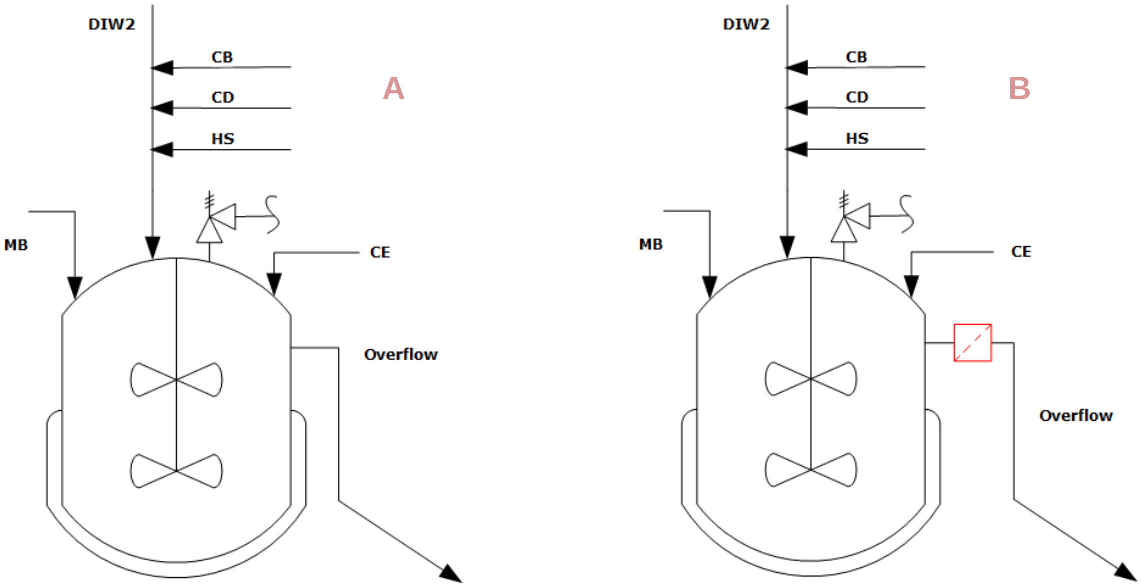

Figure 49. Schematic drawing of the self-cleaning filter implementation: A – scheme as it currently is, B – scheme after the filter implementation

8.2.3. Implementation of an Obstruction Detector in the Overflow

Still regarding the most common deviation mentioned above, a different suggestion is to implement a distance meter, which measures the distance between the overflow and the reactor's wall (set point distance). Therefore, in case an obstacle appears, the distance will be different, which certainly indicates, in this case, there are inlays.

Objective: this suggestion aims to preliminarily warn the operators of any accumulation in the overflow, as soon as possible.

Advantages:

- the operators are warned in advance of any accumulation problem in the overflow;
- the response to the problem is faster and can be prevented.

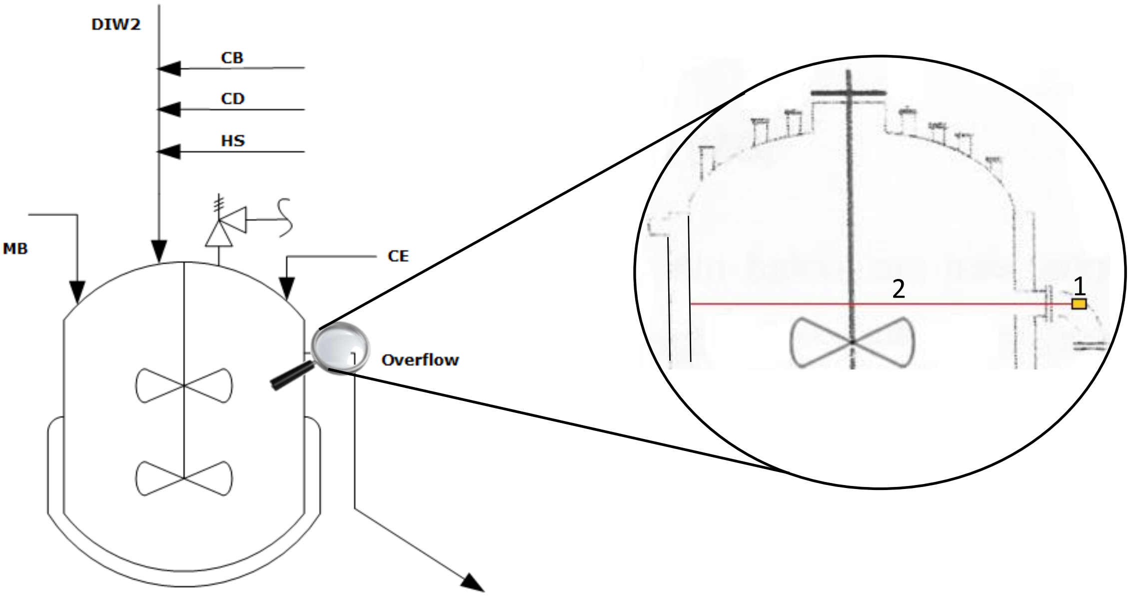

Figure 50. Schematic drawing of the distance meter implementation with a zooming: 1 – distance meter instrument, 2 – laser that measures the distance marked

8.2.4. Implementation of a Level Sensor near to DSF entrance

Still concerning the problem of lumps' accumulation, it can also happen in the DSF entrance, where, if so, a column of polymeric material begins to form and must be controlled with a level sensor:

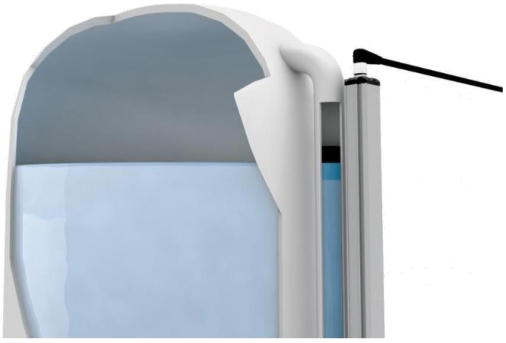

Figure 51. Level Sensor [18, page 3]

Objective: this suggestion aims to preliminarily warn the operators of any accumulation in the DSF, as soon as possible.

Advantages:

- the operators are warned in advance of any accumulation problem in the DSF;
- the response to the problem is faster and can be prevented.

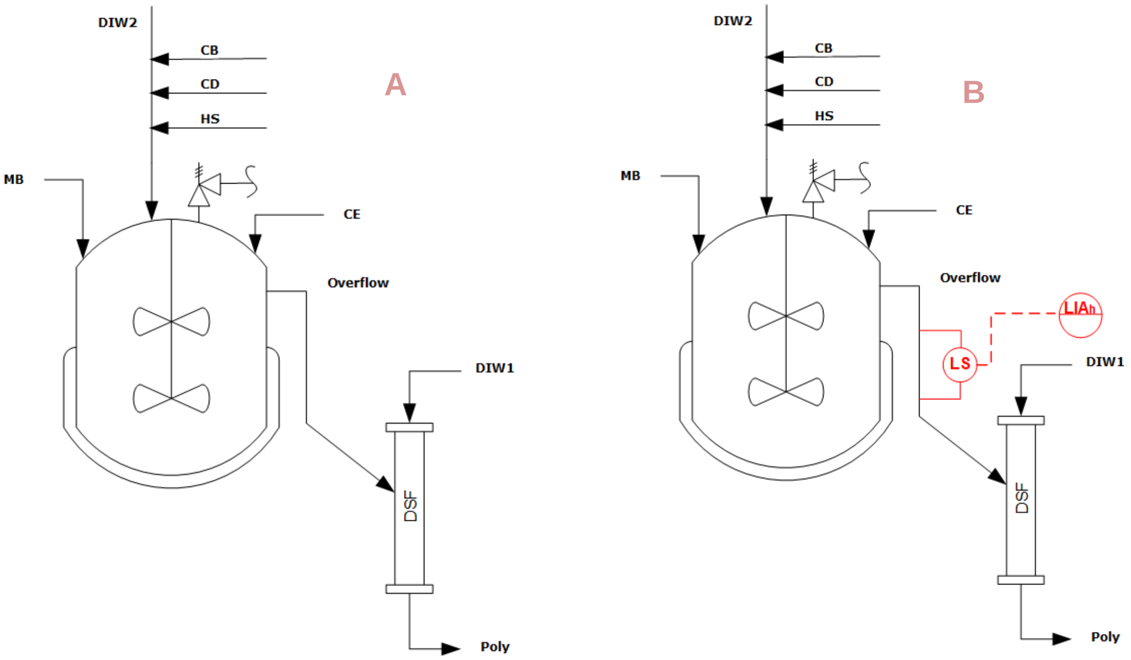

Figure 52. Schematic drawing of the level sensor implementation: A – scheme as it currently is, B – scheme after the level sensor implementation

8.2.5. Implementation of a Bubble Separator before the Flowmeters of the Reactors Feeding Streams

While preparing the solutions/mixtures and racking them to the feeding tanks by gravity, bubbles can be formed. Despite having no weight, the bubbles take up some volume, fact that might lead to wrong measures in the volumetric flowmeters. Therefore, when they are used, the bubbles must be eliminated by implementing a bubble separator – in this case, it would only be implemented in the MB stream, since it is the only stream that still has a volumetric flowmeter.

Objective: to eliminate possible bubbles that might be formed while the feeding solutions go to the reactors.

Advantages:

- flowmeters correct indication of the flow values;
- unnecessary corrections/interventions are avoided.

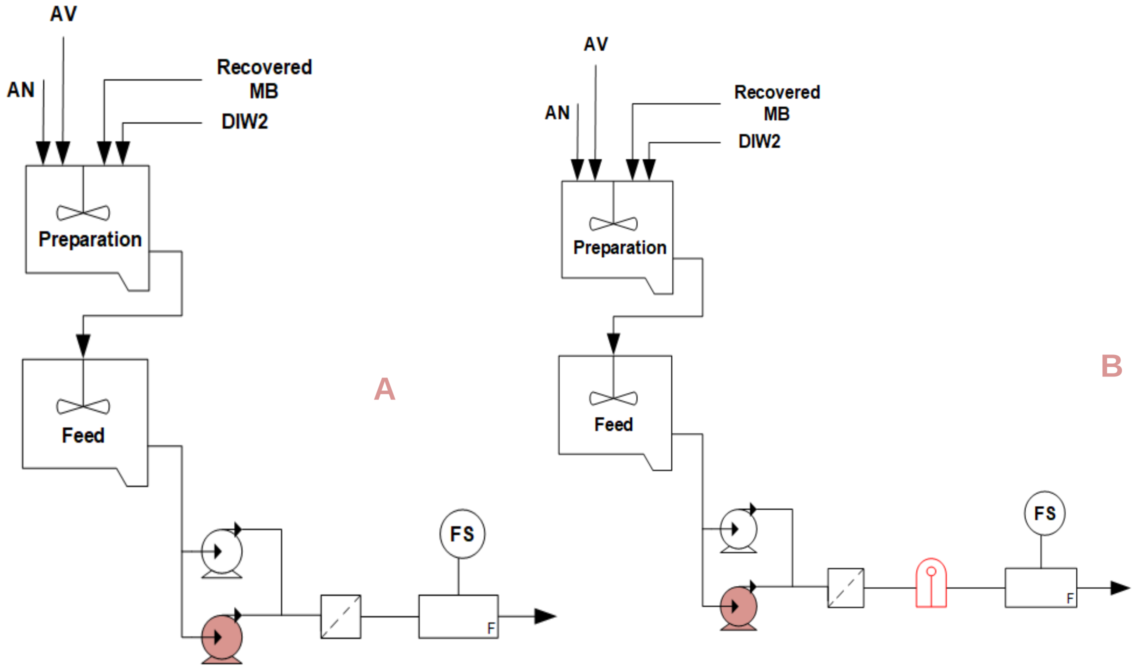

Figure 53. Schematic drawing of the bubble separator implementation (the colored pump is the one working): A – scheme as it currently is, B – scheme after the bubble separator implementation

8.2.6. Implementation of another Measurement System (Redundancy)

This suggestion is a case of redundancy due to the possibility of implementing another measurement system, despite the existing one. Even so, applying the measurement devices only in key points is probably better. Moreover, this instrumentation is, almost certain, stored, so it is not really an investment.

Objective: to ensure all the values are correctly indicated so the processual system works the best way.

Advantages:

- no doubts of all values in the reactors zone;
- any calibration needed is instantly noticed;
- any malfunction due to a device damage is instantly noticed;
- unnecessary corrections/interventions are avoided.

9. PROCESS SAFETY MANAGEMENT UMBRELLA

Process Safety Management provides the whole firm a structured guidance on how to manage numerous hazards. [19] Therefore, the Environmental, Health and Safety Management are top priority, allowing SGL Composites, S.A. to be responsible, sustainable and build trust with employees and society. [20, page 2] SGL Composites, S.A. includes all elements PSM Umbrella should contain:

i. Document Policy;
ii. Objectives;
iii. Accountability;
iv. Risk Assessment;
v. Risk Management;
vi. Mechanical Integrity;
vii. Management of Change;
viii. Incident Investigation;
ix. Emergency Response;
x. Contractor Oversight;
xi. Employee Selection;
xii. Competency;
xiii. Training;
xiv. Auditing.

Accountability is clear at SGL Composites, S.A. everyday work, as it can be seen in Appendix V. Whenever a new employee starts working at SGL Composites, S.A., the first weeks are reserved for the training program – the employee must know how to overview the process and its operating procedures – and for the worker evaluation. From time to time, a new training program is provided and the employee is once more evaluated. Likewise, if a contractor is needed, the firm must guarantee the new member is trained and evaluated. The documentation acknowledging that is mandatory and whenever necessary a new evaluation must be acquired. Besides, a suitable employee must oversight him. In Appendix VI, the questionnaire provided to everyone, either a firm's employee or a contractor, is presented. In addition, the employees are trained to be able to respond towards an emergency with proper actions. Every time an incident occurs, an investigation begins (Appendix VIII) so the causes can be identified, and a corrective measure can be developed and implemented. Furthermore, SGL Composites, S.A. makes a risk assessment, like a HAZOP and/or a FMEA (Appendix IX – Figure 55 and Figure 56, respectively), so each possible deviation is evaluated, the consequences are known and correct changes are made for the system to be able to answer to the nonconformities.

9.1. SGL Composites, S.A. Policy

The quality management and organization principles at SGL Composites, S.A. are based on an existing policy, which states important orientational ethics concerning the firm's proceeding. This policy is implemented and operated by the directors, the leaders, the departments, the functional areas and processes, through objectives identification, goals, indicators and consequent monitorization and control of execution. [4, page 12]

9.2. Management of Change

Over time, the technology improves and better equipment is constructed. Consequently, the firm feels the need to update the industry technology so its functionality does not get retarded. In addition, through a risk assessment, some irregularities are noticed. Either case, some changes are necessary through years and, in fact, some proposals were made in the previous chapter. In case SGL Composites, S.A. decides to implement any of them, the procedures regarding process changes must be written – the chemicals and/or the technology and/or the equipment. Likewise, any relevant information is updated in the same document. This is the usual way SGL Composites, S.A. practices management of change.

9.3. Mechanical Integrity

As it is clear, controlling the mechanical integrity is essential in every industry to ensure the process equipment is correctly installed and operates properly.

The employees involved in maintaining the mechanical integrity are trained and, despite respecting the verification plan, they must have a critical spirit and adjust the checking frequency every time an equipment does not operate as expected.

An example of a failure is in Figure 43, regarding the replacement of the HS flowmeter manual valve. If its operation had been better controlled and the verification period had been adapted, maybe the operators could have prepared the process for the situation, instead being obliged to produce polymer out of specification. If it gets more frequent, another option is to isolate the manual valve, creating a bypass around it.

Appendix X and XI show the 2018 calibration plan of monitorization and measurement instruments and its management procedure, respectively.

Besides the 14 topics mentioned above, it is important to refer SGL Composites, S.A. position towards the client:

9.4. Client Importance

The main objective is the satisfaction of the clients and other relevant interested parts. To reach this goal, SGL Composites, S.A. established a set of processes and working procedures, which purpose is the identification of the clients' requests and the continuous improvement of their satisfaction. [4, page 12]

The performance of these procedures, directly connected to the fulfillment of the clients' requests, is revised in audits and through the specific indicators defined, besides being communicated and monitored by the Administration in usual meetings. [4, page 12]

In addition, in today's extremely competitive world, due to increased legislative and regulation requirements and in order to respond to Community and National Policies on Security and Environment, it is important to refer the implemented Management Systems that are in harmony with such issues as Quality, Environment, Security and Health. [21]

9.5. Quality Standards

9.5.1. ISO9001 Certification

As its matrix, Management System has adopted the Quality Management System in compliance with the ISO 9001:2008 standard, in which are integrated the following sub-categories: Environmental Management and Occupational Health and Safety, aiming to satisfy all parties. [21]

9.5.2. ÖKO-TEX Certification

The Öko-Tex Standard 100 appeared in 1992, due to the consciousness emerged in Europe regarding a possible textile-allergies relation, and since then it has become the threshold of certification for the textile and clothing industry. This standard label placed on textile products and accessories guarantees the absence of substances harmful to anyone's health. [21]

Presently, SGL Composites, S.A. certificate covers the tow, the staple, the yarn as ecru and gel dyed, and the top as ecru, blanched, pigmented, gel dyed and anti-bacterial. [21]

10. CONCLUSIONS

SGL Composites, S.A. is an acrylic fiber producer and the production process follows the one created by the Japanese (Mitsubishi Rayon) – wet spinning process, with several punctual improvements made along the time since the construction.

In the scope of FM Global, this dissertation was directed to the polymerization reactors in order to study the occurrence probability of explosion or runaway. This part of the thesis was based on computational simulations and experimental work.

Regarding the computational simulations, the software used was *Aspen Plus*, *Polymers* template, and the deviations triggered were just related to the variation of the reagents feeding flow. By these results, it was witnessed the temperature varies with the variation of any reagent feeding flow, but CB. However, the variation of MB feeding flow has a different impact on the reactional mixture temperature than the variation of CD and CE feeding flows: in MB case the temperature variation is linear, while in CD and CE cases the temperature does not change with any flow variation. This impact difference might be related to the fact that CD and CE are present in faster reactions (initiation and/or termination), while MB is the principal reagent during propagation (a reaction that takes up almost all the free-radical reaction time). Nonetheless, it cannot be forgotten that, although in reality the adjustment of the manipulated variables is automatic, the possible controller slow response and the possible intervention of an operator are not considered, therefore the differences between the results returned by the software and the real-life results are to be expected. Even though it was confirmed that, so far, the existing control loops and the used controllers, as well as the room operators' training and experience, have proved to be able to prevent a nefarious occurrence, such as a runaway, the controller response can be improved to avoid the "human error". Returning to the results, despite changing, almost all temperature variations are within the alert limits – bigger MB feeding flow variations might result in unacceptable temperatures; however, that MB feeding flow values are unlikely. Summarizing the computational simulations, there is no reason to be threaten by any variation of reagents feeding flow. There is no probability of explosion or runaway: no result was alarming and it was confirmed that SGL Composites, S.A. has the necessary control instrumentation to a correct automatic adjustment and the required equipment to alert the operators of the anomalies that are occurring at the time.

Concerning the experimental work, it could be concluded that the pH increasing, pH decreasing and the lack of inert media do not affect the reactor safety. But, the pH variation scenarios affect the product specification. Actually, during the pH increasing experiment, the NSP was sent to measure: 0,164, while the central value is 0,175. Concerning the agitation loss, cooling loss, adiabatic system and the unexpected introduction of unreacted MB scenarios, these affect the reactor safety and are hard to control since the reactional mixture solidifies in minutes and its temperature increases infinitely. Even so, accidents are avoided because, meanwhile, the reactor is immediately stopped and cleaned out – no one lets the reactor to reach its maximum. Additionally, and regarding the existing instrumentation, it was once more confirmed that SGL Composites, S.A. has the necessary control instrumentation to a correct automatic adjustment and the required equipment to alert the operators of the anomalies that are occurring at the time. Summarizing the experimental work, it is necessary to be vigilant of any system alteration but still, nefarious occurrences are prevented, at least any of those triggered by the scenarios here simulated.

The process instrumentation was critically reviewed and some proposals were made to contribute to the overall process safety and to increase the “intrinsically safe” components.

Summing all up, there is no need to be threaten about a possible explosion or runaway, at least considering the operating procedures, the operators’ training and experience and the existing control instrumentation. However, a progress that can be made gradually over time is the improvement of the controllers’ response, decreasing its slowness that sometimes may require the intervention of an operator.

11. PROSPECTS

Once completed this description of the performed work, it is time to propose a future work.

In the CP area of SGL Composites, S.A., after the reaction step, it is necessary to filter the polymeric suspension and to dry the pellets meanwhile formed, as it was already mentioned. Although the low water/monomer ratio provides a wet cake moisture level of 100% or less, instead of 200% for conventional ratios (3-5), [6, page 836] in the drying zone there still is a 12 sections dryer – a problematic, longstanding and elaborated system.

Hereupon, a possible future work is to study the feasibility of the replacement of the actual dryer by a spray dryer, a more recent technology. This equipment consists in a chamber connected to a hot air system to eliminate the existing humidity in the product, by atomization. The product is atomized inside the chamber, while is submitted to an air stream at an appropriate temperature, in order to remove the solvent (water in this case) by quick vaporization. [22]

The spray dryer revolutionized the drying process, once it is one of the most versatile and flexible drying systems in the market. Besides, it is expected an extremely fast and efficient drying, so the processual time is reduced, an excellent operation yield and low operation costs. Using a spray dryer, there is no product degradation, as well as a homogeneous residual humidity during all process and a low energy consumption. It is an apparatus easy to install and to operate, which reduces the manpower time in the drying sector. Lastly, the occupied space is significantly reduced, the dried product obtained is of a high quality and the quality-price relation is the greatest – it is an advantageous equipment. [22]

To operate this "major modification" of the drying process, it is important to perform several tests in a small pilot spray dryer, with a complete range of polymer suspensions. The main objective of these trials in a pilot unit is to get information for the design of the drying process, such as:

- adjust the atomizing head to the rheology of the suspension;
- optimize droplet size to assure the complete drying of the droplets;
- fine tuning of the characteristics of the final dried powder (average size, porosity, hardness and other important characteristics for the subsequent solution preparation).

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APPENDIXES

I. OPERATIONAL CONDITIONS OF THE PROCESS AT SGL COMPOSITES, S.A.

Due to confidential reasons, the operational conditions of the process are not disclosed. Nevertheless, such information is mentioned in a separate document.

CHECK-LIST PARA ENSAIOS DE POLIMERIZAÇÃO – E83A

1 - Véspera do ensaio:

☐ Verificar na tampa do reactor a posição das cânulas de alimentação segundo o esquema fornecido.

☐ Colocar a tampa no reactor com o alinhamento correcto.

☐ Passivação do reactor

- o Encher até cerca de metade o reactor. Adicionar ~260 mL de HS e DIW2 até o reactor transbordar. Medir o pH (pH~2 a 3). 2,16
- o Deixar agitar durante cerca de 20 minutos.
- o Desligar o agitador

☐ Preparação de soluções de CB, CD, CE, HS e ST segundo as quantidades na folha de ensaio, agitando no final com azoto durante 5 a 10 min.

☑ Ir buscar MB ao CP.

☐ Selecção dos tubos e bombas.

☐ Verificação das tubagens (bolhas de ar / estrangulamento) e ajuste de caudais com DIW2 das bombas de CB, CD, CE, HS e ST.

2 - Dia do ensaio:

2.1 – Pré-Arranque

☑ Termostatização da camisa do reactor.

☑ Adição ao reactor de DIW2 sob IG e agitação.

☑ Iniciar a gravação no registador de temperatura.

☑ Obtenção de temperatura de arranque. $T_{arranque} = (55,0 \pm 0,5)$ºC.

☑ Ligar IG ao tanque de MB e do CD

☑ Calibração de caudais mássicos iniciais de CB, CD, CE, HS, ST e MB (Purgar todas as tubagens, sendo que a do MB deve ser em maior quantidade devido a dilatação do tubo da bomba peristáltica)

☐ Recolha de amostras iniciais de CB, CD, CE, MB e ST.

☑ ~30 min antes do arranque: Adição ao reactor de HS (pH = 2,5±0,2) sob IG e agitação. 11:04

☑ ~10 min antes do arranque: Adição ao reactor de CB sob IG e agitação.

2.2 – Arranque

☑ Arranque a 2/3 do caudal nominal até transbordo. Ligar todas as bombas excepto a do MB.

☑ Ligar bomba do MB após 5 min e arranque do cronómetro (t=0).

☐ Medição de temperatura da mistura reaccional e do banho de água de 15 em 15 min ou sempre que necessário.

2.3 – Após transbordo

☐ Reposição de caudais nominais.

☐ Adição de ST no transbordo. Pretende-se habitualmente pH=(4,2±0,2).

☐ Ligar sistema de Vácuo

☐ Corte de IG 15 minutos após o transbordo.

☐ Medição de temperatura e pH da mistura reaccional (pH=3,0±0,2) e também do pH do transbordo (pH=4,2±0,2) de 15 em 15 min ou sempre que necessário.

☐ Amostragem da suspensão para NSP de 1 h em 1 h para um frasco com 70 ml de ST.

2.4 – Final do ensaio

☐ Desligar todas as bombas excepto a da água de arrefecimento da camisa e a do ST (só desligar quando já não houver descarga do reactor para o filtro).

☐ Fechar o azoto

☐ Descarga do reactor

        - Adicionar o conteúdo do reactor ao tambor de recolha de suspensão.

☐ Desligar equipamentos

  - Banho de água e respectiva Bomba
  - Fechar a CW
  - Bomba de vácuo e respectiva água do anel líquido
  - Paragem de gravação no registador de temperatura.

☐ Lavar reactor com mais duas cargas de DIW2

☐ Tirar as pás do reactor, lavar e colocar no suporte com CR

☐ Calibração de caudais mássicos finais de CB, CD, CE, HS, AV e ST e recolha das amostras correspondentes, excepto o HS.

3 - Dia(s) seguinte(s):

☐ Limpeza da instalação e controlo analítico.

4 – Nota(s) específica(s) do ensaio - Efeitos a estudar:

1. Falha de IG; ✓
2. Falha de água de refrigeração; ✓
3. Variação de pH (subida, descida); ✓
4. Perda de agitação; ✓
5. Acumulação de monómeros não reagidos. ✓

III. FLOWS' CALIBRATION AND DATA FROM THE TESTS DONE IN THE PILOT UNIT

✓ AGITATION LOSS EXPERIMENT

Table 10. Flows' calibration

	Required values		Initial calibration		Final calibration	
	Q (g/min)	**rpm**	**Q (g/min)**	**rpm**	**Q (g/min)**	**rpm**
MB (B6)	20,39	15,3	20,59 (water) 20,73 (solution)	16,7	21,45 21,45	16,7
CB (B1)	15,86	36,0	15,09 (water) 15,59 (solution) 15,93 (solution)	36,8	16,36 16,69	36,8
CD (B3)	15,16	34,8	15,28 (water) 15,03 (solution) 15,21 (solution)	34,8	14,88 14,92	34,8
CE (B7)	15,48	36,5	15,07 (water) 15,76 (solution)	36,5	14,82 15,08 15,12	36,5
HS (B10)	4,29	67,9	4,00 (water) 4,45 (solution)	25	1,30 1,64 1,53	25
ST (B5)	2,26	30,6	3,77 (water) 4,00 (solution)	15	3,92 4,02	15

Table 11. Punctual data

t	$T_{reactor}$ (°C)	T_{jacket} (°C)	$pH_{reactor}$	Observations
11h04	54,98	57,50		HS addition
11h24	54,95	58,00		CB addition
11h34	54,99	58,00		Start up on 2/3 of the flow
11h39 (t=0)	54,55	57,90		Start up on 2/3 of the MB flow
5'	54,10	58,00		
15'	54,03	59,90		
22'	55,56	64,20		
36'	59,33	64,90		
45'	60,59	65,80	2,15	Overflow
50'	60,91	65,80		
53'	61,00	65,80		↓ HS to 50 rpm
1h03	63,30	62,80		
1h07	63,65	59,50	2,28	↓ HS to 30 rpm
1h17	61,28	59,80		↓ Cooling flow from 220 to 180 rpm
1h22	60,79	59,70	2,43	
1h35	63,17	62,90	2,70	
1h50	61,46	63,20	2,73	↓ HS to 25 rpm
2h	63,10	62,90	2,87	
2h10	63,16	61,10	2,84	↓ HS to 20 rpm
2h20	62,42	60,90	2,93	↑ HS to 25 rpm
2h37	61,92	60,70	2,91	Stirrer off
2h46	61,20	63,78		
2h49	68,00			
2h50	69,00			
2h54	68,00			End of test

✓ LACK OF INERT MEDIA, COOLING LOSS AND pH DECREASING EXPERIMENTS

*Table 12. Flows' calibration (the * sign is to indicate there was a change due to the broken tube)*

	Required values		**Initial calibration**		**Final calibration**	
	Q (g/min)	**rpm**	**Q (g/min)**	**rpm**	**Q (g/min)**	**rpm**
MB (B6)	20,39	16,7	21,50 20,67 →	16,4	20,63 20,58	16,4
CB (B1)	15,86	36,8	15,89	35,3	15,85 16,16 16,22	35,3
CD (B3)	15,16	34,8	15,09	34,8	14,82 14,92	34,8
CE (B7)	15,48	36,5	15,05 15,38 →	37	15,10 15,13	37
HS (B10)		25	1,66 1,63	25	3,23* 3,29*	13*
ST (B5)		15				15

Table 13. Punctual data

t	**$T_{reactor}$ (°C)**	**T_{jacket} (°C)**	**$pH_{reactor}$**	**Observations**
9h30	55,04	58,00		HS addition
9h50	55,05	58,10		CB addition
10h05	54,77	58,30		Start up on 2/3 of the flow
10h10 (t=0)	54,36	58,00		Start up on 2/3 of the MB flow
10’	56,13	64,30		
20’	58,14	66,10		
30’	60,32	66,70		
40’	61,63	65,80		
45’	61,43	65,00		Overflow/Return to the standard flows
50’	61,27	65,20	2,56	↓ HS to 24 rpm
1h00	61,31	61,30	2,96	
1h20	61,92	62,50	2,93	
1h30	62,57	61,80		
1h38	62,50	61,50	3,10	
1h41	61,92	61,50		Test: ↑ HS to 100 rpm
1h46	61,70	61,80	3,20	
1h48	61,67	61,70		↑ HS to 200 rpm
2h00	61,97	61,50	3,18	Broken HS tube (Q=0)
2h05	61,90	61,60		Return HS to 200 rpm
2h10	59,48	61,50	2,04	↓ HS to 100 rpm
2h15	55,74	64,50	1,66	
2h35	58,35	64,60	1,50	
2h45	63,37	55,80	1,70	
2h48	63,39	55,60		
2h58	60,28	61,00	1,83	
3h12	61,94	61,50	1,91	
3h11	61,93	61,60		↓ HS to 18 rpm
3h25	61,99	61,50	2,00	
3h31	62,00	61,80		↓ HS to 13 rpm
3h38	62,15	61,50	2,05	
3h41	62,22	61,70		↓ HS to 0 rpm
3h46	61,77	60,20		↑ HS to 13 rpm
3h55	61,60	60,50	2,34	
3h57				↓ HS to 0 rpm
4h07	61,82	61,60	2,52	

4h19	62,51	60,70	2,67	
4h32	62,16	60,20	2,85	
4h41	62,43	60,60	2,95	The cooling water circulation was stopped
4h44	63,40	60,50		
4h45	63,85			
4h46	64,30			
4h46,40	64,69			
4h47	64,80			
4h47,07	65,00			Attempt to drain the cooling jacket
4h49	65,15			
4h50	65,04			
4h51	64,92			
4h52	64,73			
4h53	64,70			The cooling jacket was drained (adiabatic system simulation)
4h54	65,30			
4h56	65,76			
4h57	66,27			
4h58	66,80			
4h59	67,29			
5h00	68,06			
5h01	68,32			
5h02	68,67			
5h03	69,12			End of test

✓ pH INCREASING EXPERIMENT

Table 14. Flows' calibration

	Required values		**Initial calibration**		**Final calibration**	
	Q (g/min)	**rpm**	**Q (g/min)**	**rpm**	**Q (g/min)**	**rpm**
MB (B6)	20,39	16,7	20,32	16,4	20,47	16,4
CB (B1)	15,86	36,8	16,16 15,54 16,03	35	16,16 16,31	35
CD (B3)	15,16	34,8	14,88 15,15	35,1	14,92 14,95	34,8
CE (B7)	15,48	36,5	14,47 15,08	37,3	15,60 15,63	37,3
HS (B10)		25	2,20 1,48 1,61	75	1,60	75
ST (B5)		15				15

Table 15. Punctual data

t	**$T_{reactor}$ (°C)**	**T_{jacket} (°C)**	**$pH_{reactor}$**	**Observations**
9h40	54,87	57,60		HS addition
10h00				CB addition
10h10				Start up on 2/3 of the flow
10h15 (t=0)				Start up on 2/3 of the MB flow
45’	58,93	65,60		Overflow
49’	60,21	65,60		Return to the standard flows
52’	60,59	65,70	1,75	
1h02	59,69	61,50	1,78	HS flow cut-off
1h17	60,08	62,90	1,90	
1h30	62,21	61,00	2,18	
1h42	61,97	61,70	2,48	
1h56	62,31	61,40	2,78	
2h06	62,09	61,50	3,06	
2h16	62,10	61,40	3,21	
2h27	61,97	61,50	3,30	
2h38	61,99	61,40	3,55	
2h49	62,06	61,60	3,67	
3h00	62,03	61,30	3,75	
3h10	62,01	61,30	3,91	
3h20	61,87	61,50	3,92	
3h30	61,97	61,50	3,96	
3h40	62,01	61,40	3,99	
3h53	62,01	61,40		
3h56	61,95	61,30	4,05	
4h07	61,86	61,40	4,04	
4h19	61,89	61,60	4,30	
4h29	61,93	61,40	4,06	
4h40	61,85	61,30	4,09	End of test

✓ UNEXPECTED INTRODUCTION OF UNREACTED MB EXPERIMENT

Table 16. Flows' calibration

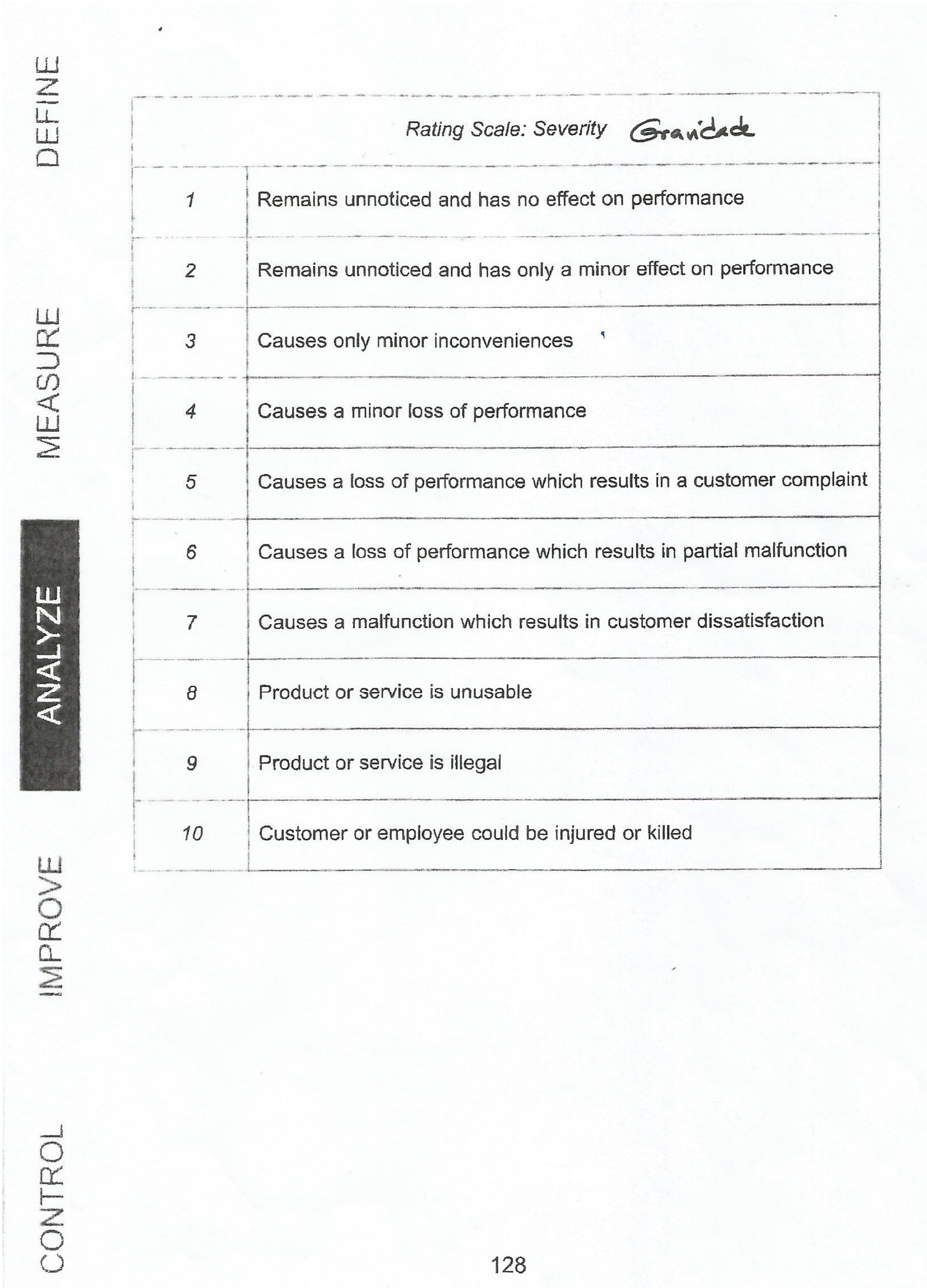
	Required values		***Initial calibration***		***Final calibration***	
	Q (g/min)	***rpm***	***Q (g/min)***	***rpm***	***Q (g/min)***	***rpm***
MB (B6)	20,39	16,4	20,24	16,6	21,30 20,90	16,6
CB (B1)	15,86	35,0	16,01	35	16,17	35
CD (B3)	15,16	34,8	15,16	34,8	14,70 14,80	34,8
CE (B7)	15,48	37,3	15,30 15,41	→ 37,5	15,37	37,5
HS (B10)		75	5,10 1,62	→ 24	2,65 2,61	40
ST (B5)		15				15

Table 17. Punctual data

t	**$T_{reactor}$ (°C)**	**T_{jacket} (°C)**	**$pH_{reactor}$**	**Observations**
9h30	54,74	58,10		HS addition
9h50	55,40	58,10		CB addition
10h00	55,13	58,00		Start up on 2/3 of the flow
10h05 (t=0)	54,93	59,80		Start up on 2/3 of the MB flow
5’	55,97	61,00		
30’	58,76	66,20		
37’	61,49	64,50		Start up on 100% flow
40’	61,34	64,00		Overflow
45’	61,25	65,30	3,08	
50’	62,22	65,10	3,10	
1h03	62,42	63,30	3,14	
1h17	62,35	62,50	3,30	↑ HS to 35 rpm (1h25)
1h35	61,64	62,70	3,20	↑ HS to 45 rpm (1h37)
1h48	61,83	62,90	2,97	
1h59	61,85	62,80	2,95	
2h15	61,90	62,90	2,87	↓ HS to 40 rpm
2h30	62,19	63,00	2,91	
2h40	62,29	63,30	2,94	
2h55				The reactor was drained/The stirrer was stopped
2h58				Fresh MB addition
2h59	64,77	63,10		Stirrer rebooted
3h10	57,40	62,90	1,94	
3h20	59,72	66,00	1,86	
3h30	68,26	60,60	2,63	End of test

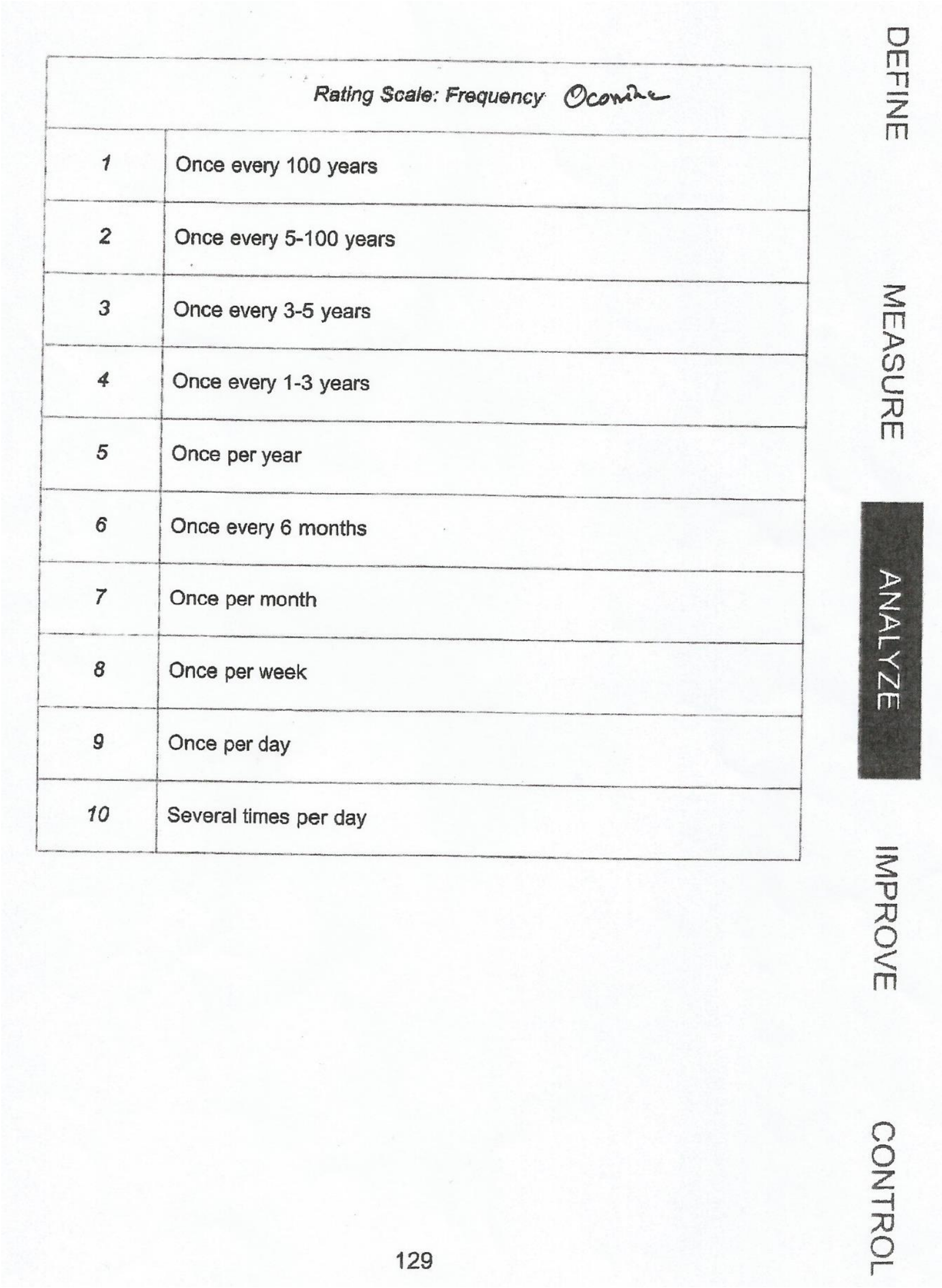
IV. RATING SCALES USED IN HAZOPS

✓ **SEVERITY**



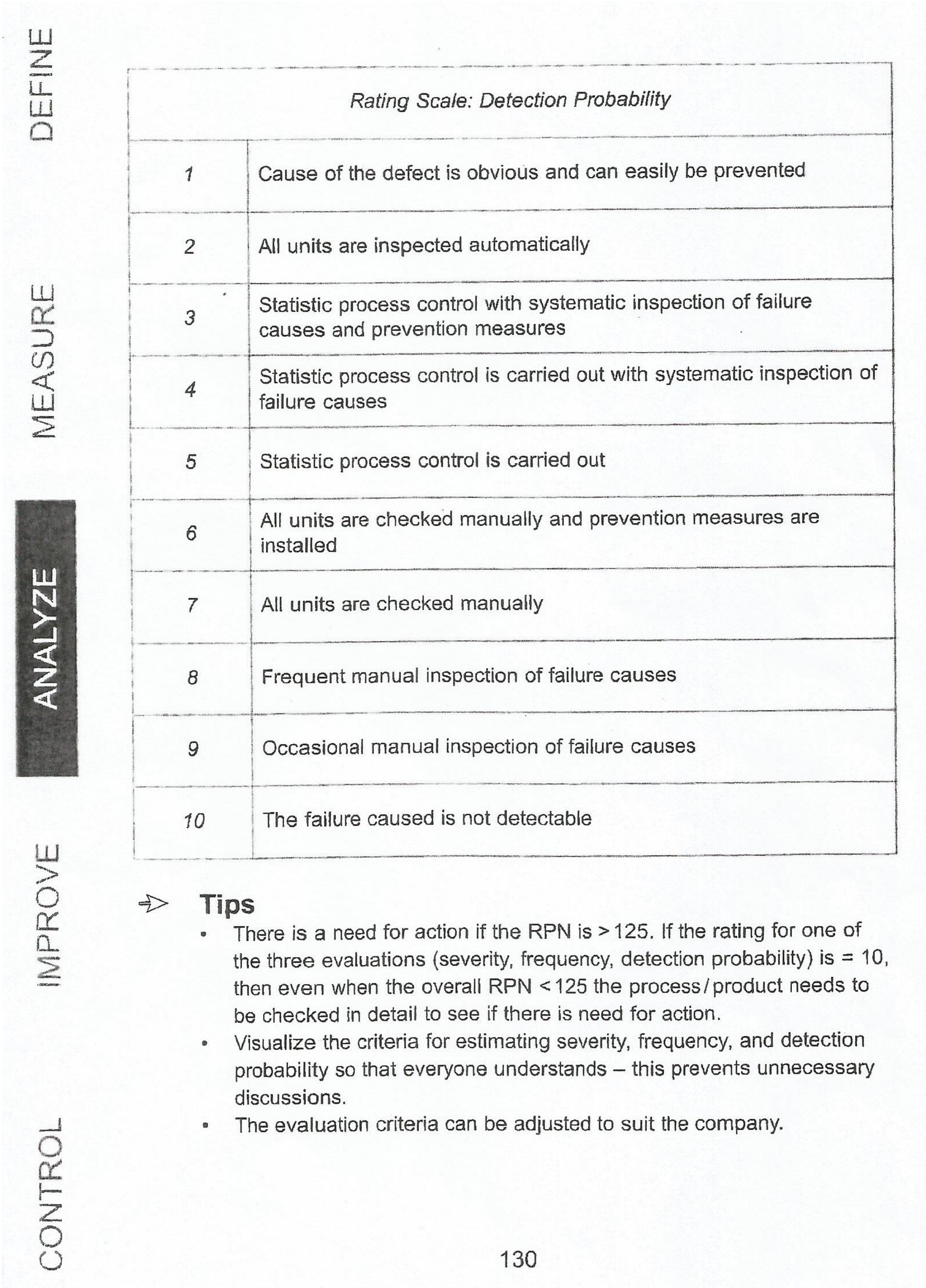
Rating Scale: Severity Gravidade	
1	Remains unnoticed and has no effect on performance
2	Remains unnoticed and has only a minor effect on performance
3	Causes only minor inconveniences
4	Causes a minor loss of performance
5	Causes a loss of performance which results in a customer complaint
6	Causes a loss of performance which results in partial malfunction
7	Causes a malfunction which results in customer dissatisfaction
8	Product or service is unusable
9	Product or service is illegal
10	Customer or employee could be injured or killed

- ✓ **FREQUENCY**



Rating Scale: Frequency Ocorrência	
1	Once every 100 years
2	Once every 5-100 years
3	Once every 3-5 years
4	Once every 1-3 years
5	Once per year
6	Once every 6 months
7	Once per month
8	Once per week
9	Once per day
10	Several times per day

✓ **PROBABILITY**

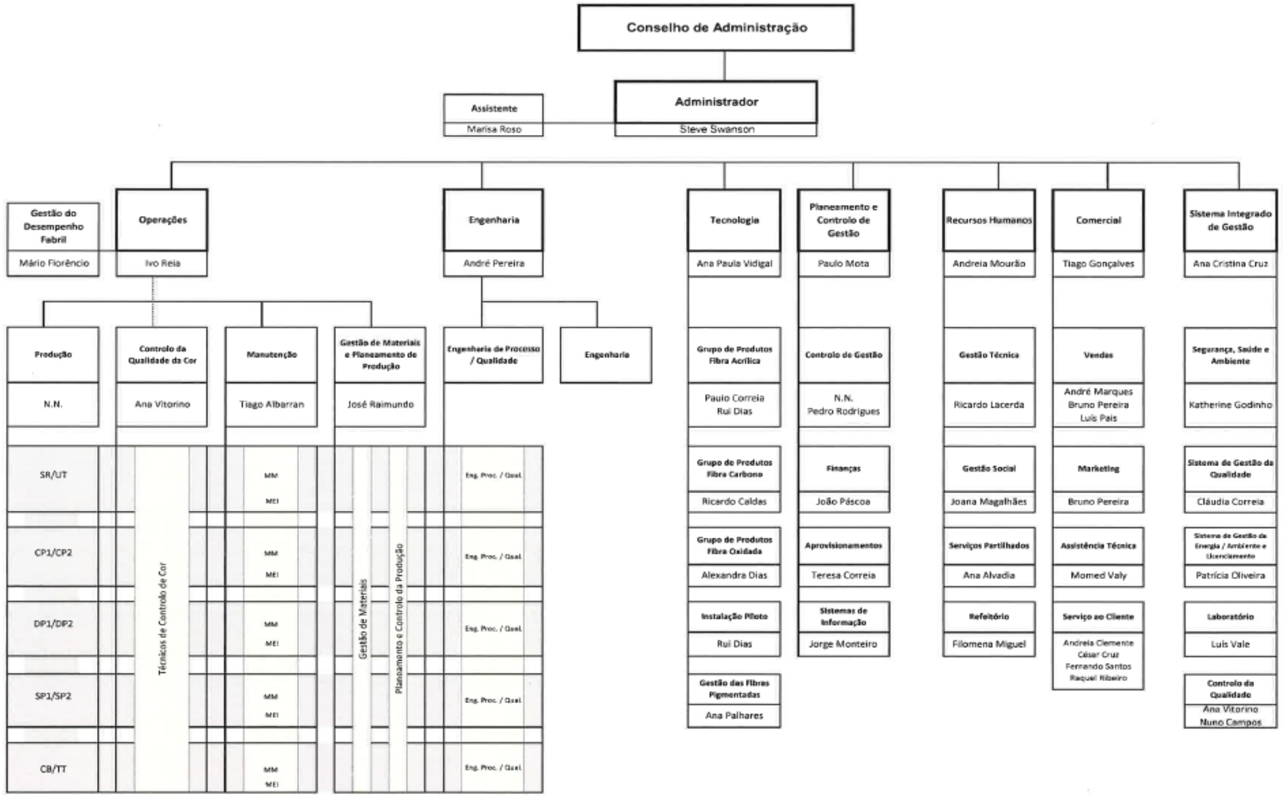


Rating Scale: Detection Probability	
1	Cause of the defect is obvious and can easily be prevented
2	All units are inspected automatically
3	Statistic process control with systematic inspection of failure causes and prevention measures
4	Statistic process control is carried out with systematic inspection of failure causes
5	Statistic process control is carried out
6	All units are checked manually and prevention measures are installed
7	All units are checked manually
8	Frequent manual inspection of failure causes
9	Occasional manual inspection of failure causes
10	The failure caused is not detectable

➢ Tips

- There is a need for action if the RPN is > 125. If the rating for one of the three evaluations (severity, frequency, detection probability) is = 10, then even when the overall RPN < 125 the process/product needs to be checked in detail to see if there is need for action.
- Visualize the criteria for estimating severity, frequency, and detection probability so that everyone understands – this prevents unnecessary discussions.
- The evaluation criteria can be adjusted to suit the company.

V. *ACCOUNTABILITY*



Acrónimos:
SR/UT: Recuperação de Solvente / Utilidades
CP: Polimerização Contínua
DP: Preparação de Xarope
SP: Spinning
CB/TT: Corte e Embalagem / Tow-to-Top
MM: Manutenção Mecânica
MEI: Manutenção Eléctrica e Instrumentos
Eng. Proc./Qualidade: Engenharia de Processo / Qualidade
N.N.: Not nominated (vaga)

Outras responsabilidades:
Diretor Geral a partir de 01/06/2018 Andreas Witte
Local Compliance Representative: Paulo Mota
Site Data Protection Officer: Patrícia Oliveira

Legenda:
.... Liderança funcional

APROVADO: Swanson

EM VIGOR: **14-05-2018**

Figure 54. Firm's departments organization

VI. WORKERS QUESTIONNAIRE

FISIPE
YOUR CREATIVE PARTNER
IN ACRYLIC FIBRES

FR-SSA-06

WORKERS QUESTIONNAIRE

1. Does FISIPE have a Security Policy and an Accident Prevention?

   Yes ☐ No ☐

2. Is it mandatory to wear the working outfit (identified clothes, shoes and helmet)?

   Yes ☐ No ☐

3. Is it allowed to have the mobile phone with you, as long as it is switched off?

   Yes ☐ No ☐

4. In noisy areas, is it mandatory to wear protector ear plugs?

   Yes ☐ No ☐

5. In FISIPE, there are areas with explosion/fire risk. In those zones, is it necessary additional security measures?

   Yes ☐ No ☐

6. When the emergency bell rings, every work must be immediately and safely interrupted?

   Yes ☐ No ☐

7. The meeting point is near to the field and the gate?

   Yes ☐ No ☐

8. Is 4415 the emergency number in case of accident?

   Yes ☐ No ☐

9. Before executing any fire work (cuts, welds, others) do you must have in your possession the "Special Work Authorization" document?

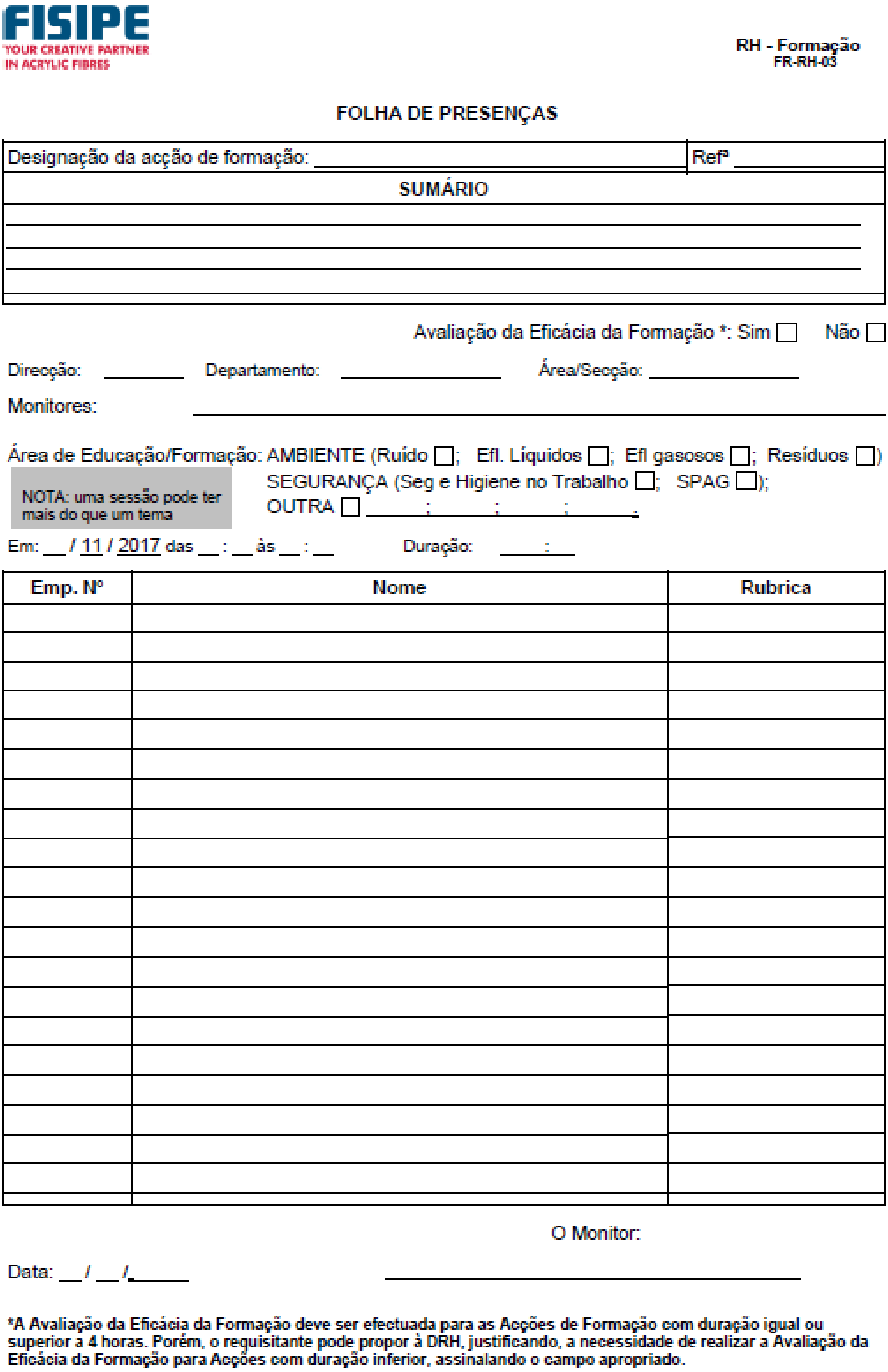
   Yes ☐ No ☐

Company: ____

Employee Name: _________________________________ Signature: ________________

Date: ___/____/______

VII. APPEARANCE SHEET



FISIPE
YOUR CREATIVE PARTNER
IN ACRYLIC FIBRES

RH - Formação
FR-RH-03

FOLHA DE PRESENÇAS

Designação da acção de formação: ____________________ Refª ________

SUMÁRIO

____

____

____

____

Avaliação da Eficácia da Formação *: Sim ☐ Não ☐

Direcção: ________ Departamento: ______________ Área/Secção: ______________

Monitores: ______________________________

Área de Educação/Formação: AMBIENTE (Ruído ☐; Efl. Líquidos ☐; Efl gasosos ☐; Resíduos ☐)
SEGURANÇA (Seg e Higiene no Trabalho ☐; SPAG ☐);
OUTRA ☐ _____;_____;_____;_____.

NOTA: uma sessão pode ter mais do que um tema

Em: __ / 11 / 2017 das __ : __ às __ : __ Duração: ___:___

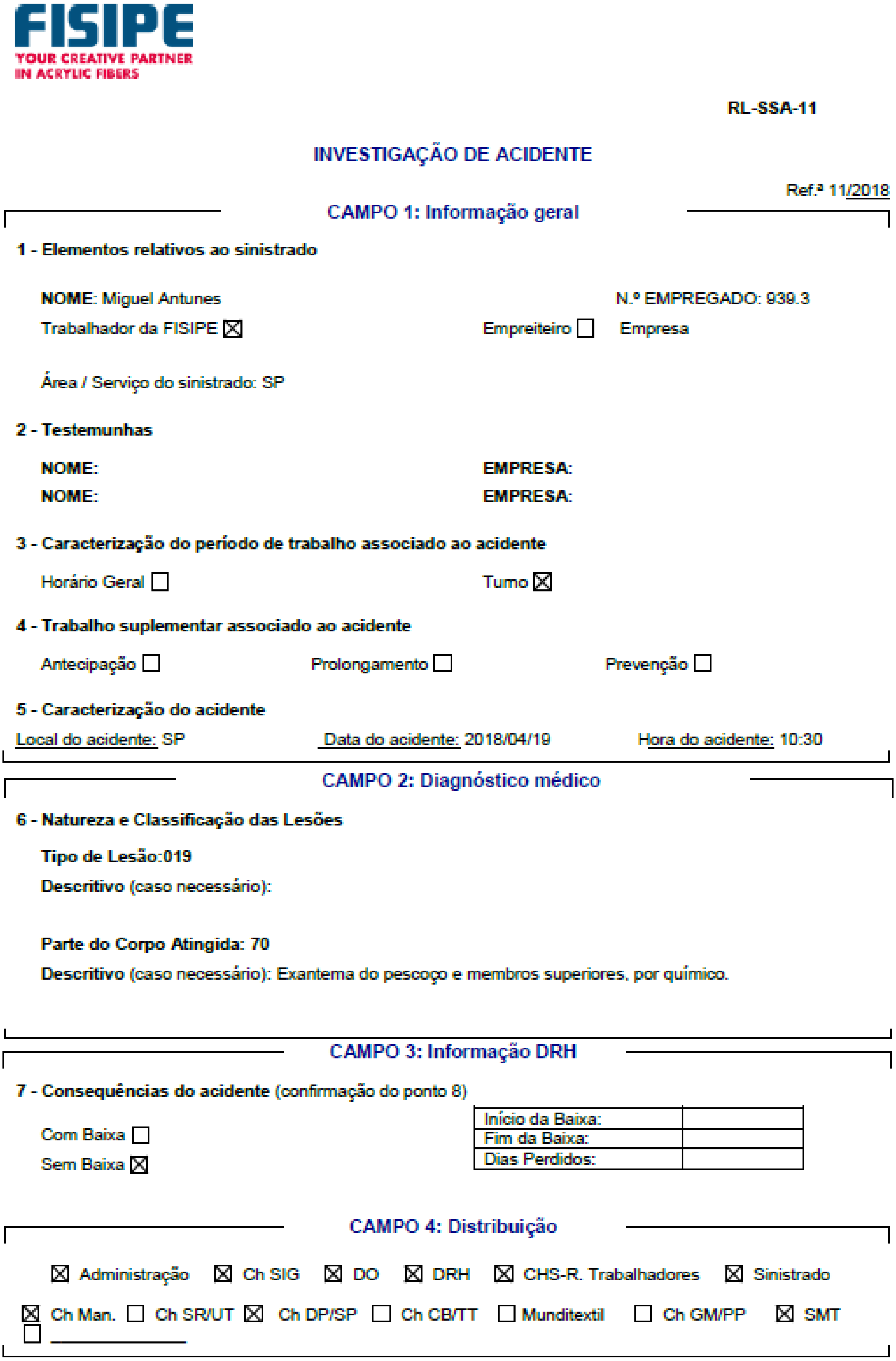
Emp. Nº	Nome	Rubrica

O Monitor:

Data: __ / __ /_____ ______________________________

*A Avaliação da Eficácia da Formação deve ser efectuada para as Acções de Formação com duração igual ou superior a 4 horas. Porém, o requisitante pode propor à DRH, justificando, a necessidade de realizar a Avaliação da Eficácia da Formação para Acções com duração inferior, assinalando o campo apropriado.

VIII. INCIDENT INVESTIGATION



FISIPE
YOUR CREATIVE PARTNER
IN ACRYLIC FIBERS

RL-SSA-11

INVESTIGAÇÃO DE ACIDENTE

Ref.ª 11/2018

CAMPO 1: Informação geral

1 - Elementos relativos ao sinistrado

NOME: Miguel Antunes N.º EMPREGADO: 939.3

Trabalhador da FISIPE ☒ Empreiteiro ☐ Empresa

Área / Serviço do sinistrado: SP

2 - Testemunhas

NOME: **EMPRESA:**

NOME: **EMPRESA:**

3 - Caracterização do período de trabalho associado ao acidente

Horário Geral ☐ Turno ☒

4 - Trabalho suplementar associado ao acidente

Antecipação ☐ Prolongamento ☐ Prevenção ☐

5 - Caracterização do acidente

Local do acidente: SP Data do acidente: 2018/04/19 Hora do acidente: 10:30

CAMPO 2: Diagnóstico médico

6 - Natureza e Classificação das Lesões

Tipo de Lesão:019

Descritivo (caso necessário):

Parte do Corpo Atingida: 70

Descritivo (caso necessário): Exantema do pescoço e membros superiores, por químico.

CAMPO 3: Informação DRH

7 - Consequências do acidente (confirmação do ponto 8)

Com Baixa ☐

Sem Baixa ☒

Início da Baixa:	
Fim da Baixa:	
Dias Perdidos:	

CAMPO 4: Distribuição

☒ Administração ☒ Ch SIG ☒ DO ☒ DRH ☒ CHS-R. Trabalhadores ☒ Sinistrado

☒ Ch Man. ☐ Ch SR/UT ☒ Ch DP/SP ☐ Ch CB/TT ☐ Munditextil ☐ Ch GM/PP ☒ SMT

☐ ____________

FISIPE
YOUR CREATIVE PARTNER
IN ACRYLIC FIBERS

FICHA DE INVESTIGAÇÃO DE ACIDENTE

SERVIÇO DE SEGURANÇA, HIGIENE E AMBIENTE

Ref.ª 11/2018

1. Descrição do Acidente

Quando o operador se encontrava a pressurizar o recipiente de limpeza de rolos, a junta da tampa saltou com a pressão, tendo o operador sido atingido com salpicos de base.

2. Dados Complementares:

A – Formação para o Trabalho ☒ Sim ☐ Não
B – Experiência anterior do Acidentado no Trabalho ☒Sim ☐Não
C – Supervisão Directa ☐ Sim ☒ Não
D – Supervisão Indirecta ☒ Sim ☐Não
E – Acidentes semelhantes na Área ☐Sim ☒Não
F – Outros acidentes do sinistrado ☐Sim ☒Não

3. Causas do Acidente:

A junta de vedação é inadequada para o equipamento, com a abertura e fecho do equipamento faz com que sofra movimentação da junta não vedando eficazmente o equipamento.

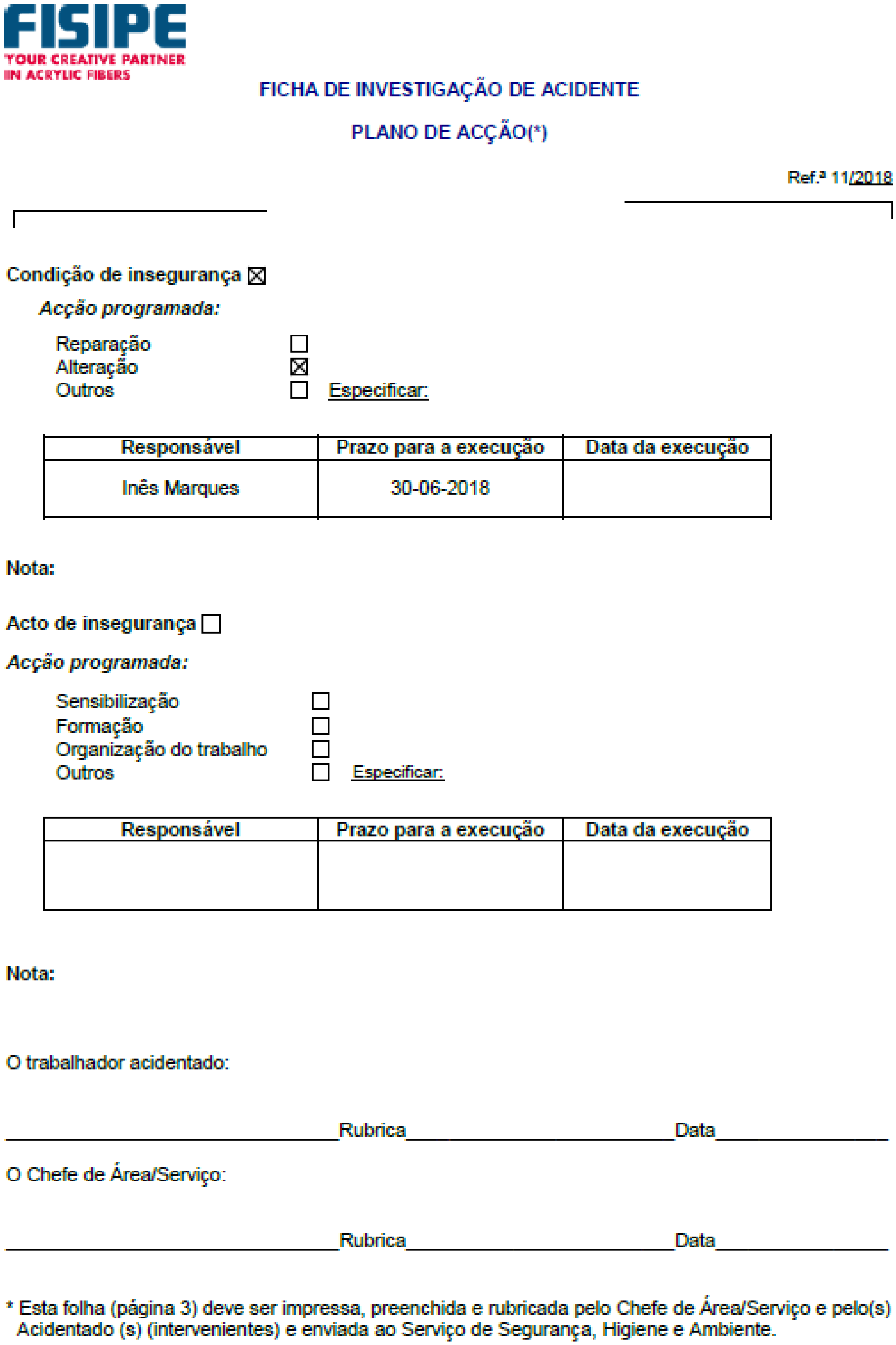
4. Medidas corretivas propostas:

Substituição da junta por uma que garanta o trabalho em segurança do equipamento com uma resistência a pressões superiores a 3bar.

Utilização de fato de proteção química (Tyvec) para além dos outros EPI's já utilizados (protecção mãos e face)

5. Elaborado por: Katherine Godinho, Luís Zuna, Sandro Nobre **Data:** 10/05/2018

6. Equipa de investigação (SSHA): Katherine Godinho, Luís Zuna e Sandro Nobre



FISIPE
YOUR CREATIVE PARTNER
IN ACRYLIC FIBERS

FICHA DE INVESTIGAÇÃO DE ACIDENTE

PLANO DE ACÇÃO(*)

Ref.ª 11/2018

Condição de insegurança ☒

Acção programada:

Reparação ☐
Alteração ☒
Outros ☐ Especificar:

Responsável	Prazo para a execução	Data da execução
Inês Marques	30-06-2018	

Nota:

Acto de insegurança ☐

Acção programada:

Sensibilização ☐
Formação ☐
Organização do trabalho ☐
Outros ☐ Especificar:

Responsável	Prazo para a execução	Data da execução

Nota:

O trabalhador acidentado:

____________________________Rubrica_______________________Data_______________

O Chefe de Área/Serviço:

____________________________Rubrica_______________________Data_______________

* Esta folha (página 3) deve ser impressa, preenchida e rubricada pelo Chefe de Área/Serviço e pelo(s) Acidentado (s) (intervenientes) e enviada ao Serviço de Segurança, Higiene e Ambiente.

IX. RISK ASSESSMENT

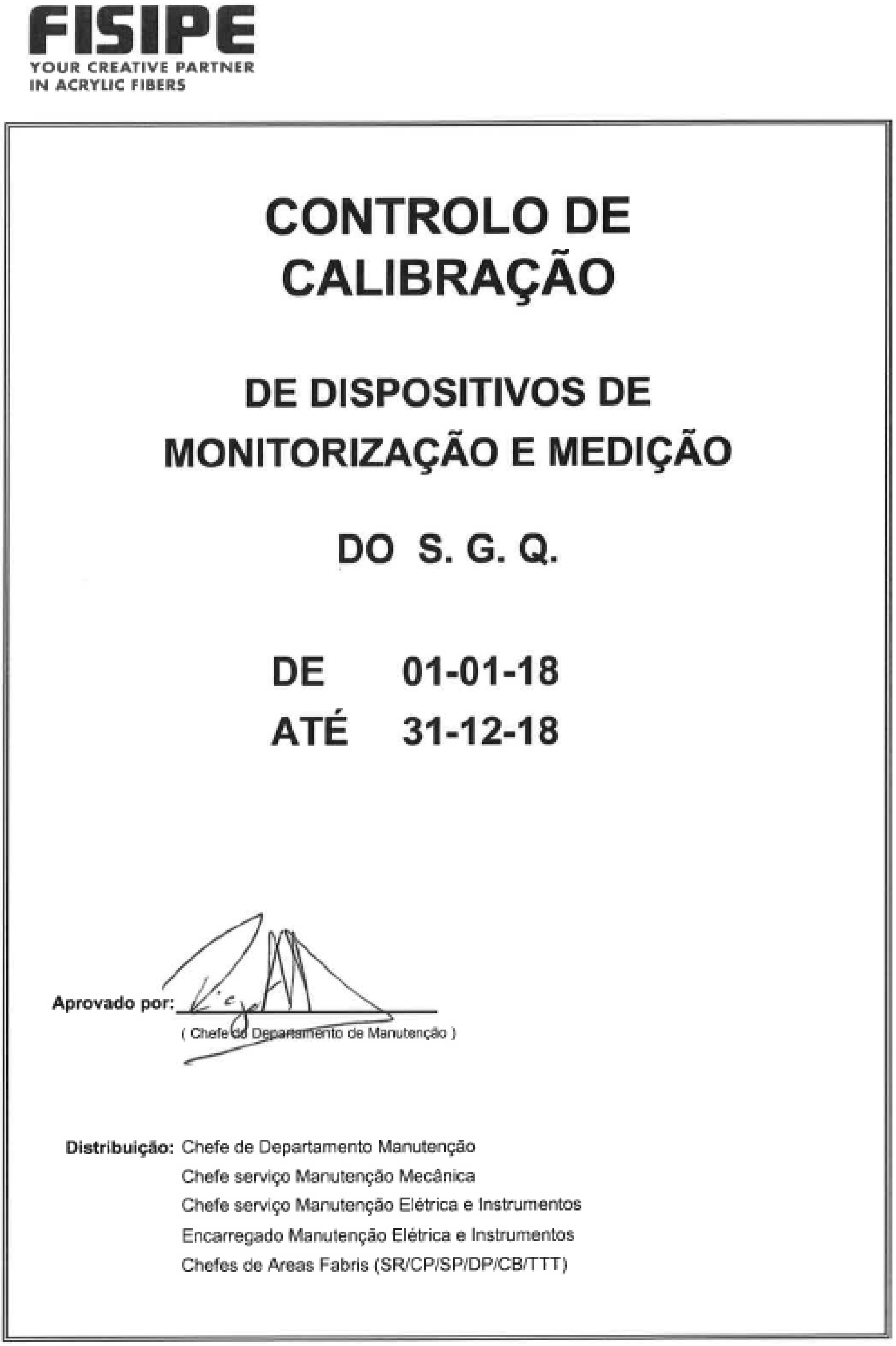
Node	Line numbe	Description	Parameter	Drawings	Guidewor	Deviation	Causes	Consequences	Severity	Likelihood	Safeguards	Rec No	Recommendations
5	23	Preparation tanks	Level	1130145A	More	Higher Level	Programming bug.	Cross-contamination to other tanks	serious	unlikely	comissioning and system test	19	Rigorous testing with a comprehensive plan and enough time
5	24	Preparation tanks	Level	1130145A	More	Higher Level	Valves failure	Cross-contamination to other tanks	serious	unlikely		20	See lines 10, 11 and 12
5	25	Preparation tanks	Level	1130145A	More	Higher Level	Level transmitter failure	Cross-contamination to other tanks	serious	unlikely		21	Install a high level switch to prevent overflow
5	27	Preparation tanks	Level	1130145A	Less	Lower Level	Failure of feeding valves	Long waiting time	moderate	unlikely	local level	22	Time out alarm local level check routine
5	28	Preparation tanks	Pressure	1130145A	More	Higher Pressure	Overfill of all tanks	High pressure in the system	moderate	unlikely		23	High level switches
5	29	Preparation tanks	Pressure	1130145A	More	Higher Pressure	Failure of breather system (breather valve failure or pipe clogging)	High pressure in the system. Wrong level indications	serious	unlikely	preventive maintenance	39	Revise preventive Maintenance schedule
5	30	Preparation tanks	Pressure	1130145A	Less	Lower Pressure	Failure of breather system (breather valve failure or pipe clogging)	Low pressure in the system. Wrong level indications. Tanks collapsing	serious	unlikely	preventive maintenance	40	Revise preventive Maintenance schedule
5	31	Preparation tanks	Mixing	1130145A	Incorrect	Incorrect Composition	Agitator / its parts mechanical & electrical failure	Offspec batch.	serious	unlikely	DCS alarm for agitator motor failure	24	Current alarm for high/low motor current
5	34	Preparation tanks	Flow	1130145A	No	Out of sequence	Blockage or malfunction in the automatic discharge	Batch sequence interrupted. No flow to CP-	moderate	unlikely		25	Create alarm linking valve opening with decrease of level.
5	35	Preparation tanks	Contamination	1130145A	Incorrect	Incorrect Composition	Leakage through discharge valves	Contamination of feed tank	serious	unlikely	Analysis of feed tank	26	Preventive maintenance
6	36	Vent system	Pressure	1130145A	More/Less				moderate	rare		27	See lines 29 and 30
7	37	Transfer to CP-104	Flow	1130145A	No	No Flow	closed valve in the line	possible polymerization inside the pumps	moderate	unlikely		28	Detect no change in tank levels Stop pumps automatically
7	38	Transfer to CP-104	Flow	1130145A	Less	Less Flow	Filter clogging	transfer time	moderate	likely	change over to spare filter	29	Install PD connected to DCS with an alarm
8	42	Feed tank	Level	1130145A	More	Higher Level	Programming bug.	Cross-contamination to other tanks through the vent lines	moderate	unlikely	comissioning and system test	30	Rigorous testing with a comprehensive plan and enough time
8	44	Feed tank	Level	1130145A	More	Higher Level	Level transmitter failure	Cross-contamination to other tanks	moderate	unlikely		31	Install a high level switch to prevent overflow
8	46	Feed tank	Level	1130145A	Less	Lower Level	Leakage through flange/valves seal	Stop CP Area	serious	unlikely		32	create a minimum alarm to prepare/transfer a batch in due time (20% as low low level alarm)
8	52	Feed tank	Pressure	1130145A	More	Higher Pressure	Failure of breather system (breather valve failure or pipe clogging)	High pressure in the system. Wrong level indications	serious	unlikely	preventive maintenance	41	Revise preventive Maintenance schedule
8	53	Feed tank	Pressure	1130145A	Less	Lower Pressure	Failure of breather system (breather valve failure or pipe clogging)	Low pressure in the system. Wrong level indications. Tanks collapsing	serious	unlikely	preventive maintenance	42	Revise preventive Maintenance schedule
9	55	Feed from CP-104	Flow	1130145A	No	No Flow	closed valve in the line	possible polymerization inside the pumps. Reactors feed cut. B-Grade production.	moderate	unlikely	DCS alarm for no flow	33	Stop pumps automatically
9	56	Feed from CP-104	Flow	1130145A	Less	Less Flow	Filter clogging	Decreased flow to reactors	moderate	likely	change over to spare filter	34	Install PD connected to DCS with an alarm
9	58	Feed from CP-104	Pressure	1130145A	Less	Lower Pressure	malfunctioning of the pressure control valve	Decreased flow to reactors	moderate	unlikely	controller alarms in the DCS	35	Define minimum pressure set point for the control loop Check operating current conditions in order to design the pressure control loop Install PT before and after the filter connected to DCS Create automatic switch for the feed pumps in the DCS
10	60	Utility / Electricity	Power		No	No Current	Various Causes	<2h - Reactors Feed Cut > 2h - Plant Shutdown	serious	likely		37	Adapt failure emergency procedure
10	61	Utility / DCS	Service Failure		No	Off	UPS malfunction	Control/Indication	serious	unlikely		38	Link DCS to the emergency power generation

Figure 55. Example of a HAZOP of the continuous polymerization area

Item nº	Item / Função	Modo Potencial de falha	Efeito da Falha Potencial	GRAV	OCO	Controlo(s) actual (ais)	DET	NR	Acção(ões) Recomendadas
1	Reator CP-524-C	Rutura da parede do reactor C junto à camisa de arrefecimento	Contaminação da TW e da massa reaccional	5	2	Controlo da temperatura, pH, caudal de refrigeração, NSP, teste hidraulico à camisa do reactor	3	30	Alarme no caudal de TW à camisa do reator
2	Reator CP-524-C	Rutura na tubagem de descarga de fundo do reator	Diminuição da temperatura, diminuição do caudal de saída do reator, derrame de produto, formação de atmosfera inflamável / tóxica	1	2	Controlo de temperatura do reator	1	2	Contenção e encaminhamento de fugas
3	Reator CP-524-C	Rutura na linha de alimentação de MB	Eventual diminuição de temperatura, diminuição de caudal de overflow, derrame de produto, formação de atmosfera inflamável / tóxica, eventual inflamação da mistura	4	2	Controlo de temperatura do reator	1	8	
4	Reator CP-524-C	Rutura na linha do overlfow do reator	Diminuição do caudal do overflow, derrame do produto, formação de atmosfera inflamável / tóxica	1	2	Indicação de caudal à coluna SS, controlo visual	1	2	
5	Reator CP-524-C	Obstrução da linha do overlfow do reator	Eventual aumento de temperatura, diminuição de caudal, aumento de pressão, possível contaminação da linha de vents	2	4	Limpeza do overflow 1xturno, caudal de alimentação à coluna SS	1	8	
6	Reator CP-524-C	Polimerização violenta, aumento do pH da reação, redução do caudal de HS	Eventual explosão no reator	5	1	Controlo de temperatura do reator, controlo do pH da reação	1	5	
7	Reator CP-524-C	Falha nas bombas de TW de refrigeração à camisa do reator por falha de energia elétrica	Produto mal processado	5	4	Controlo de temperatura do reator, controlo do pH da reação, indicação do funcionamento das bombas em DCS	1	20	Ligar bombas ao sistema de corrente de emergência.
8	Reator CP-524-C	Falha nas bombas de TW de refrigeração à camisa do reator por falha mecânica	Produto mal processado	3	2	Existem spares, controlo de temperatura do reator, caudal de alimentação de TW à camisa do reator, indicação do funcionamento em DCS.	1	6	
9	Reator CP-524-C	Falha no sistema de agitação por falha de energia elétrica	Produto mal processado	5	3	Controlo de temperatura do reator, indicação do funcionamento do agitador em DCS	1	15	
10	Reator CP-524-C	Falha no sistema de agitação por falha mecânica	Produto mal processado	3	2	Controlo do funcionamento do motor do agitador, indicação da amperagem do motor	1	6	Controlo de alarme por amperagem do motor do agitador
12	Reator CP-524-C	Falha da válvula de controlo de TW, fechando demasiado ou não abrindo quando solicitada	Produto mal processado	4	4	Controlo de caudal de TW para a camisa do reator, controlo de temperatura do reator	1	16	

Figure 56. Example of a FMEA of the continuous polymerization area

X. CALIBRATION CONTROL OF MONITORIZATION AND MEASUREMENT EQUIPMENT



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CONTROLO DE CALIBRAÇÃO

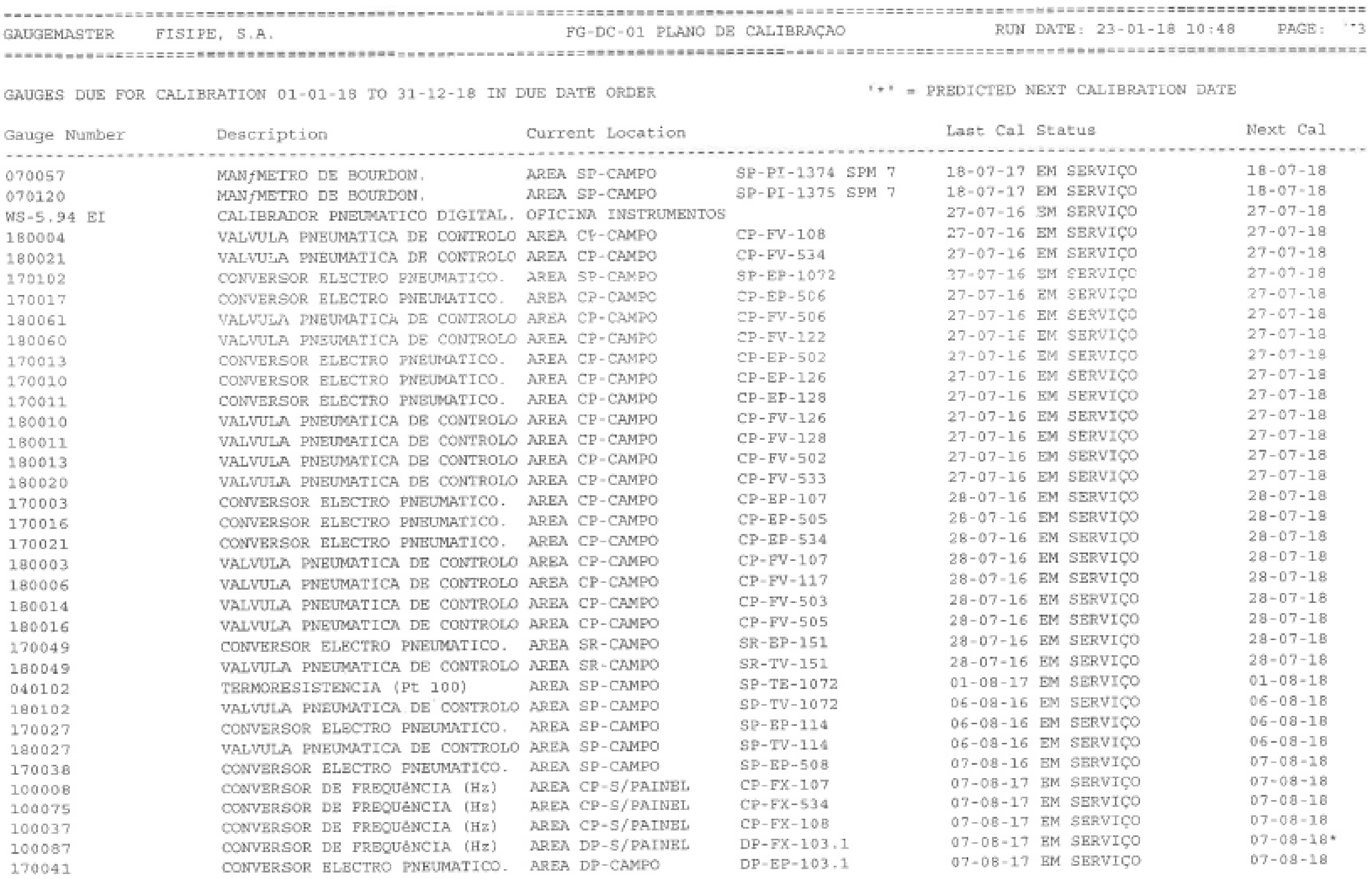
DE DISPOSITIVOS DE MONITORIZAÇÃO E MEDIÇÃO

DO S. G. Q.

DE 01-01-18
ATÉ 31-12-18

Aprovado por: ____________________
(Chefe do Departamento de Manutenção)

Distribuição: Chefe de Departamento Manutenção
Chefe serviço Manutenção Mecânica
Chefe serviço Manutenção Elétrica e Instrumentos
Encarregado Manutenção Elétrica e Instrumentos
Chefes de Areas Fabris (SR/CP/SP/DP/CB/TTT)



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=====================================================================================================================================================
GAUGEMASTER    FISIPE, S.A.                               FG-DC-01 PLANO DE CALIBRAÇAO               RUN DATE: 23-01-18 10:48     PAGE: [illegible]3
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GAUGES DUE FOR CALIBRATION 01-01-18 TO 31-12-18 IN DUE DATE ORDER                      '*' = PREDICTED NEXT CALIBRATION DATE

Gauge Number        Description                      Current Location                         Last Cal Status                   Next Cal
-----------------------------------------------------------------------------------------------------------------------------------------------------
070057              MANƒMETRO DE BOURDON.            AREA SP-CAMPO        SP-PI-1374 SPM 7    18-07-17 EM SERVIÇO              18-07-18
070120              MANƒMETRO DE BOURDON.            AREA SP-CAMPO        SP-PI-1375 SPM 7    18-07-17 EM SERVIÇO              18-07-18
WS-5.94 EI          CALIBRADOR PNEUMATICO DIGITAL.   OFICINA INSTRUMENTOS                     27-07-16 EM SERVIÇO              27-07-18
180004              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-108           27-07-16 EM SERVIÇO              27-07-18
180021              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-534           27-07-16 EM SERVIÇO              27-07-18
170102              CONVERSOR ELECTRO PNEUMATICO.    AREA SP-CAMPO        SP-EP-1072          27-07-16 EM SERVIÇO              27-07-18
170017              CONVERSOR ELECTRO PNEUMATICO.    AREA CP-CAMPO        CP-EP-506           27-07-16 EM SERVIÇO              27-07-18
180061              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-506           27-07-16 EM SERVIÇO              27-07-18
180060              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-122           27-07-16 EM SERVIÇO              27-07-18
170013              CONVERSOR ELECTRO PNEUMATICO.    AREA CP-CAMPO        CP-EP-502           27-07-16 EM SERVIÇO              27-07-18
170010              CONVERSOR ELECTRO PNEUMATICO.    AREA CP-CAMPO        CP-EP-126           27-07-16 EM SERVIÇO              27-07-18
170011              CONVERSOR ELECTRO PNEUMATICO.    AREA CP-CAMPO        CP-EP-128           27-07-16 EM SERVIÇO              27-07-18
180010              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-126           27-07-16 EM SERVIÇO              27-07-18
180011              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-128           27-07-16 EM SERVIÇO              27-07-18
180013              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-502           27-07-16 EM SERVIÇO              27-07-18
180020              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-533           27-07-16 EM SERVIÇO              27-07-18
170003              CONVERSOR ELECTRO PNEUMATICO.    AREA CP-CAMPO        CP-EP-107           28-07-16 EM SERVIÇO              28-07-18
170016              CONVERSOR ELECTRO PNEUMATICO.    AREA CP-CAMPO        CP-EP-505           28-07-16 EM SERVIÇO              28-07-18
170021              CONVERSOR ELECTRO PNEUMATICO.    AREA CP-CAMPO        CP-EP-534           28-07-16 EM SERVIÇO              28-07-18
180003              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-107           28-07-16 EM SERVIÇO              28-07-18
180006              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-117           28-07-16 EM SERVIÇO              28-07-18
180014              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-503           28-07-16 EM SERVIÇO              28-07-18
180016              VALVULA PNEUMATICA DE CONTROLO   AREA CP-CAMPO        CP-FV-505           28-07-16 EM SERVIÇO              28-07-18
170049              CONVERSOR ELECTRO PNEUMATICO.    AREA SR-CAMPO        SR-EP-151           28-07-16 EM SERVIÇO              28-07-18
180049              VALVULA PNEUMATICA DE CONTROLO   AREA SR-CAMPO        SR-TV-151           28-07-16 EM SERVIÇO              28-07-18
040102              TERMORESISTENCIA (Pt 100)        AREA SP-CAMPO        SP-TE-1072          01-08-17 EM SERVIÇO              01-08-18
180102              VALVULA PNEUMATICA DE CONTROLO   AREA SP-CAMPO        SP-TV-1072          06-08-16 EM SERVIÇO              06-08-18
170027              CONVERSOR ELECTRO PNEUMATICO.    AREA SP-CAMPO        SP-EP-114           06-08-16 EM SERVIÇO              06-08-18
180027              VALVULA PNEUMATICA DE CONTROLO   AREA SP-CAMPO        SP-TV-114           06-08-16 EM SERVIÇO              06-08-18
170038              CONVERSOR ELECTRO PNEUMATICO.    AREA SP-CAMPO        SP-EP-508           07-08-16 EM SERVIÇO              07-08-18
100008              CONVERSOR DE FREQUêNCIA (Hz)     AREA CP-S/PAINEL     CP-FX-107           07-08-17 EM SERVIÇO              07-08-18
100075              CONVERSOR DE FREQUêNCIA (Hz)     AREA CP-S/PAINEL     CP-FX-534           07-08-17 EM SERVIÇO              07-08-18
100037              CONVERSOR DE FREQUêNCIA (Hz)     AREA CP-S/PAINEL     CP-FX-108           07-08-17 EM SERVIÇO              07-08-18
100087              CONVERSOR DE FREQUêNCIA (Hz)     AREA DP-S/PAINEL     DP-FX-103.1         07-08-17 EM SERVIÇO              07-08-18*
170041              CONVERSOR ELECTRO PNEUMATICO.    AREA DP-CAMPO        DP-EP-103.1         07-08-17 EM SERVIÇO              07-08-18
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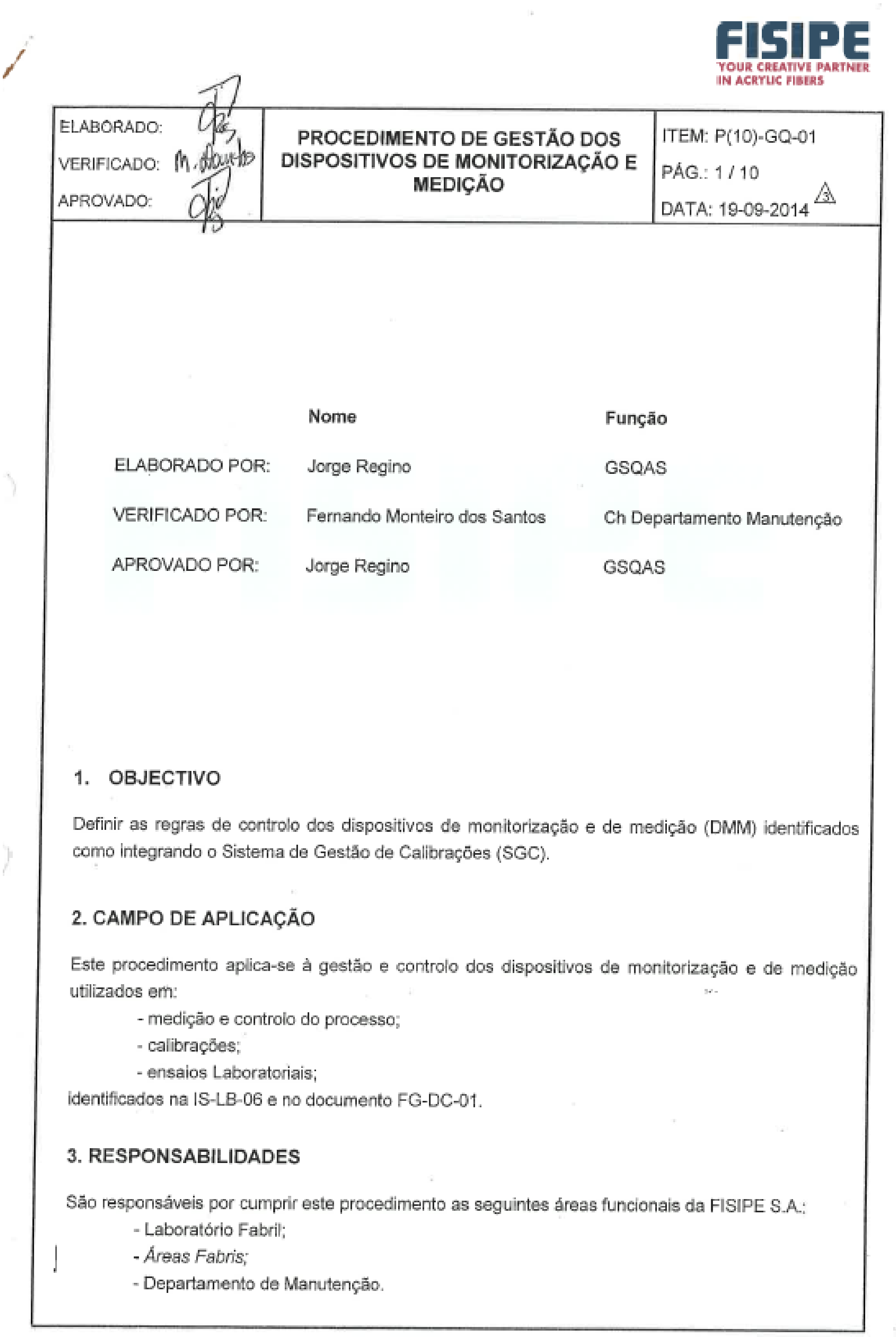
XI. *Management Procedure of the Monitorization and Measurement Equipment*



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ELABORADO: VERIFICADO: APROVADO:	**PROCEDIMENTO DE GESTÃO DOS DISPOSITIVOS DE MONITORIZAÇÃO E MEDIÇÃO**	ITEM: P(10)-GQ-01 PÁG.: 1 / 10 DATA: 19-09-2014 △3

	Nome	**Função**
ELABORADO POR:	Jorge Regino	GSQAS
VERIFICADO POR:	Fernando Monteiro dos Santos	Ch Departamento Manutenção
APROVADO POR:	Jorge Regino	GSQAS

1. OBJECTIVO

Definir as regras de controlo dos dispositivos de monitorização e de medição (DMM) identificados como integrando o Sistema de Gestão de Calibrações (SGC).

2. CAMPO DE APLICAÇÃO

Este procedimento aplica-se à gestão e controlo dos dispositivos de monitorização e de medição utilizados em:

- medição e controlo do processo;
- calibrações;
- ensaios Laboratoriais;

identificados na IS-LB-06 e no documento FG-DC-01.

3. RESPONSABILIDADES

São responsáveis por cumprir este procedimento as seguintes áreas funcionais da FISIPE S.A.:

- Laboratório Fabril;
- *Áreas Fabris;*
- Departamento de Manutenção.

6. GESTÃO E CONTROLO DOS DMM

As actividades inerentes à gestão dos DMM estão descritas nos processos de gestão:

- Análise e Controlo Laboratorial;
- Manutenção;

envolvendo transversalmente várias Áreas funcionais e processos a que estão atribuídas diferentes responsabilidades:

ÁREAS FUNCIONAIS	RESPONSABILIDADES
- Gestão da Qualidade, Ambiente e Segurança	- *Zelar pelo* cumprimento do descrito neste procedimento.
- *Áreas Fabris*	- Seleccionar os pontos de processo a monitorizar, medir e/ou controlar. - Seleccionar os equipamentos que integram o Sistema de Gestão de Calibrações.
- Laboratório Fabril	- Seleccionar o equipamento que integra o Sistema de Gestão de Calibrações; - Elaborar e gerir o Plano de Calibração dos equipamentos que integram ao Sistema de Gestão de Calibrações; - Executar o plano de calibração utilizando as instruções de calibração aplicáveis a cada equipamento.
- Manutenção	- Gerir a calibração dos equipamentos de processo e outros tais como padrões de referência que integram o Sistema de Gestão de Calibrações; - Elaborar os Planos de Calibração para os equipamentos do processo e para os padrões de referência da Manutenção de Instrumentos; - Executar o plano de calibração utilizando as instruções de calibração aplicáveis a cada equipamento.

6.1. AQUISIÇÃO DE NOVOS DMM

A responsabilidade pela especificação (nomeadamente das características metrológicas) e selecção dos DMM é de:

- Chefe *de Departamento* da Manutenção para os equipamentos de processo;
- Chefe de Laboratório Fabril para os equipamentos de Laboratório.

Os responsáveis referidos garantem que a incerteza dos equipamentos de monitorização do processo incluídos no SGC é melhor do que 1/3 da especificação do processo / produto.

Os DMM adquiridos ao exterior para utilização em pontos de processo podem:

- ser colocados em armazém a aguardar utilização e decisão posterior;
- directamente na linha de produção se possuírem certificado de calibração e as suas características metrológicas forem adequadas às medições a realizar no ponto de processo em causa.

Os equipamentos comprados com destino ao Laboratório, que integram o SGC, são calibrados antes da entrada em serviço, se não tiverem sido adquiridos com Certificado de Calibração. Este equipamento, enquanto aguarda a respectiva calibração, *mantém-se* marcado com etiqueta de "NÃO CALIBRADO".

6.2. PLANEAMENTO DAS CALIBRAÇÕES

6.2.1. Critérios de Selecção dos DMM a Calibrar

A selecção dos DMM a calibrar é feita de acordo com os seguintes critérios:

- dispositivos utilizados para fazer a calibração dos dispositivos que integram o SGC;
- equipamentos utilizados para demonstrar a conformidade do produto com os requisitos especificados;
- equipamentos que se destinam a efectuar medições que suportem decisões ou acções que requeiram um nível de confiança elevado.

6.2.2. Selecção dos DMM a Calibrar

No caso de DMMs instalados no processo fabril, os chefes das Áreas Fabris, com base nos critérios referidos no item 6.2.1, informam o Chefe de Departamento de Manutenção dos equipamentos que consideram preencher os critérios para serem incluídos no SGC. Para isso utilizam o documento FG-SIG-01 (Anexo 1). Após discussão do assunto entre as partes interessadas, o Chefe de Departamento de Manutenção compila os DMMs a serem incluídos no SGC no documento FG-DM-01 (Anexo 2).

No caso de preparações ou produtos intermédios, os chefes das Áreas Fabris, com base nos critérios referidos no item 6.2.1, informam o Chefe de Laboratório das especificações dos produtos referidos. Para isso utilizam o documento FG-SIG-01 (Anexo 1).

As informações referidas são elaboradas quando são efectuadas alterações ao processo ou às suas especificações.

No caso de matérias-primas e de produtos finais, o Chefe de Laboratório avalia a capacidade dos métodos de ensaio para fazer o controlo dos produtos referidos.

6.2.3. Periodicidade da Calibração

Os critérios utilizados para definir os intervalos entre calibrações são:

- Recomendação 4/99 do CNQ;
- Directiva 19/90 do CNQ;
- Importância do parâmetro ou variável de processo a controlar;
- Experiência acumulada sobre o equipamento em causa;
- Evolução do estado do equipamento.

A responsabilidade pela definição ou ajuste das periodicidades cabe ao Chefe *de Departamento* da Manutenção e ao Chefe do Laboratório Fabril.

6.2.4. Planos de Calibração

Na FISIPE S.A. são elaborados Planos de Calibração Anual. As entradas para a elaboração dos Planos de Calibração são:

- as recomendações e directivas aplicáveis mencionadas *no item* **Erro! A origem da referência não foi encontrada.**;
- conhecimento real do estado dos equipamentos (regime de funcionamento, importância relativa na cadeia produtiva, alterações introduzidas, ...);
- a informação recolhida junto dos fornecedores dos equipamentos;
- as datas de paragem das fábricas e/ou equipamentos fabris;

- as datas reais de calibração dos equipamentos;
- informações obtidas doutros parceiros com equipamentos semelhantes.

Os Planos de calibração contêm a seguinte informação:

- Número do instrumento / equipamento;
- Descrição do dispositivo;
- Local actual;
- Data da última calibração;
- Estado de calibração;
- Tipo de calibração (interna ou externa);
- Data da próxima calibração.

Os Planos de Calibração Anual são aprovados por:

- Chefe *de Departamento* da Manutenção Operacional para os equipamentos de processo;
- Chefe de Laboratório Fabril para os equipamentos de Laboratório.

Os Planos de Calibração Anual são distribuídos a:

Plano gerido pela Manutenção de Instrumentos	Plano gerido pelo Laboratório
- Chefe Departamento de Manutenção;	- *Chefe do Laboratório*;
- Chefe da Manutenção *Mecânica*;	- Analista Principal Coordenador;
- *Encarregado da Manutenção Eléctrica e Instrumentos;*	
- Responsáveis das Áreas funcionais onde existem dispositivos integrados no Sistema de Gestão de Calibrações.	

O Plano da Calibração é permanentemente actualizado com base nos dados gerados através do seu cumprimento e das intervenções desenvolvidas sobre os dispositivos. Esta actualização tem como objectivo garantir que os dispositivos se mantêm permanentemente aptos a realizar as medições previstas.

O software de controlo dos DMM permite a elaboração de planos parcelares numa janela temporal mais estreita para facilitar a gestão operacional do Plano de Calibração.

6.2.5. Padrões de Calibração e Dispositivos de Referência

Os padrões de trabalho estão claramente caracterizados quanto a:

- designação;
- número do instrumento / equipamento;
- intervalo de calibração;
- padrão de nível superior utilizado na calibração;

- relação entre a incerteza do padrão e do a equipamento *a calibrar*.

Os padrões de trabalho são calibrados no exterior, excepto nos casos em que esses dispositivos são fixos.

A responsabilidade pela manutenção e apresentação dos DMM para calibração é de:

- Chefe *de Departamento* da Manutenção para os equipamentos de processo;
- Chefe de Laboratório Fabril para os equipamentos de Laboratório.

6.2.6. Calibração Interna e Externa

As calibrações podem ser executadas internamente ou externamente consoante:

- o tipo de equipamento;
- o número de equipamentos idênticos;
- os custos inerentes à realização da calibração;

Sempre que é feita calibração interna o Responsável da Área Funcional que assegura a gestão do dispositivo deve garantir:

- as competências necessárias para a realização da calibração;
- que existam padrões/equipamentos de referência calibrados por entidades reconhecidas;
- que existam instruções de calibração;
- que a execução da calibração cumpra o descrito nas instruções da calibração respectivas.

Sempre que é feita calibração externa, é seleccionada uma entidade acreditada para o efeito. Neste caso, os Certificados de Calibração são recepcionados pelo Responsável da Área Funcional que assegura a gestão do dispositivo a que corresponde o certificado.

A recepção */ aceitação dos* Certificados de Calibração é efectuada de acordo com:

- *IS-CEI-32 - no caso de dispositivos da Manutenção;*
- *IS-LB-06 - no caso de dispositivos do Laboratório.*

e evidenciado através do preenchimento *dos documentos:*

- *FR-CEI-01 - no caso de dispositivos da Manutenção;*
- *FR-LB-60 - no caso de dispositivos do Laboratório.*

6.2.7. Estado de Calibração

Após a realização das calibrações os equipamentos são marcados com uma etiqueta que indica:

- o número de identificação do DMM;
- data da última calibração;
- data da próxima calibração;
- responsável pela calibração.

6.4.2. Manutenção Curativa

Em qualquer DMM pertencente a pontos de processo integrados no SGC em que seja detectada uma avaria e cuja reparação e posterior calibração não possa ser efectuada de imediato os procedimentos a efectuar serão os seguintes:

- Marcação com etiqueta "NÃO CALIBRADO";
- Informação ao Chefe de Produção da área funcional respectiva que toma as medidas adequadas;
- A gestão e controlo da manutenção segue o Procedimento de Manutenção - P(8)-GQ-02.

Quando um elemento / instrumento de um anel de controlo estiver avariado considera-se que todo o anel de controlo está "NÃO CALIBRADO".

6.5. REGISTOS

Após a execução de calibração, os resultados das mesmas são tratados e registadas no software de Gestão da Calibração, bem como as conclusões e observações efectuadas durante as mesmas.

O sistema de registos permite assegurar a rastreabilidade.

6.6. ARQUIVO

Os registos de calibração são arquivados de acordo com o Procedimento P(4)-GQ-01.

7. ANEXOS

Anexo 1 - FG-SIG-01 - Solicitação de integração de DMMs no SGC;

Anexo 2 - FG-DM-01 - DMMs a integrar no SGC.

8. NATUREZA DAS ALTERAÇÕES

As linhas verticais na margem esquerda e o texto em itálico indicam alterações relativamente à versão anterior.

ANEXO 1

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FG-SIG-01

SISTEMA DE GESTÃO DA QUALIDADE
GESTÃO DOS DMMs

Solicitação de integração de DMMs no SGC

ÁREA	IDENTIFICAÇÃO DO CONJUNTO	TOLERÂNCIA DO PROCESSO	NÍVEIS DE ALERTA	LOCALIZAÇÃO DO CONJUNTO	FUNÇÃO	OBS

ANEXO 2

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FG-DM-01

DEPARTAMENTO DE MANUTENÇÃO
GESTÃO DOS DMMs

DMMs a integrar no SGC

ÁREA	IDENTIFICAÇÃO DO CONJUNTO	RESOLUÇÃO	TOLERÂNCIA DO PROCESSO	NÍVEIS DE ALERTA	CRITÉRIO DE ACEITAÇÃO	LOCALIZAÇÃO DO CONJUNTO	FUNÇÃO	OBS