IBP1453_13

AIR POLLUTION CONTROL IN DEWAXING STATION OF RISERS

Domenico Capulli[1], Helder Sales Beloto [2]

Abstract

Oil exploration in Brazil has found its "El Dorado" at Campos Bay, in our continental platform sea shelf. The submarine extraction is characterized by the use of a set applied to the head of pipelines manifolds, in depths that can reach up to 3000 meters today.

Valves of these manifolds are connected to flexible tubes built in multilayer called risers, and flowlines operating vertically and horizontally respectively. These tubes are able to withstand high internal and external pressures, corrosion, heavy sea currents, water pressure, at the same time supporting both oil and its own weight.

On the other hand crude oil is characterized by containing 6% weight/ weight of paraffin (C_{20+}) in acyclic chains that over time generates formation of incrustations inside risers, particularly on the initial stage of thermal shock of crude oil with low water temperatures. Knowing that the initial temperature of crystal formation (TIFC) is 20 ° C, when starting the crystallization in the inner walls, it incites the shutting hoses inner space withholding gases such as methane and hydrogen sulfide (H2S). This material deposition on the walls of the riser causes a reduction in the effective diameter of these lines, increasing pumping cost and decreasing production from the well. In the maintenance process of keeping risers and flowlines, some technologies have been developed for removal of scale, among them, the mechanical removal of paraffin deposition. The flexible line is disconnected and removed to bobbin onto the dewaxing unit based on land at Vitoria- Espírito Santo, the flexible inlay is connected to a pressurized water line with PIG, which passes through the entire length of the flexible, removing through fouling by scraping, onto the other end terminal which empties into a tank for collecting the liquid with paraffin wax and gases.

The release of H_2S causes air pollution and risk of explosion in the tank outflow, it requires to exhaust gas by sweeping internal volume of the tank for removal of these gases at levels below the LEL of 4.6%. This stream with H2S has a characteristically low threshold of olfactory perception (0.05 ppm), besides being a corrosive, explosive and poisonous compound. This scenario determines the need for high performance technology use in order to neutralize this gas at levels below the threshold of perception and harmfulness for both applied technology uptake and clearance by Hydrodynamic Precipitators that through spin liquid Multiventuri system is able to neutralize emissions of hydrogen sulfide. This technology is self-aspirant and promotes the exhaustion internal tank outflow subjecting the contaminated air at a synergistic centrifugation with alkaline liquid stimulating chemical neutralization reaction by formation of sodium sulphide, a soluble salt in liquid. When applied a supportive second stage liquid cooled function by fixing H_2S reducing steam pressure favoring its solubilization in chemical reaction, according to Equation 1:

$$H_2S_{(g)} + 2\ NaOH_{(aq)} \rightarrow Na_2S_{(l)}* + 2H_2O_{(l)} \quad (1)$$

This pioneering worldwide application results in eliminating perceptible odors and the absence of pockets of flammable gas ensuring operational safety at last year.

1. Introduction

Oil exploration in Brazil has found its Eldorado in continental sea shelf, turning the country into oil power offshore activity with strong expansion, increased dramatically by the confirmation of large reserves in the pre-salt layers. The submarine extraction is characterized by the use of valve gate set called manifold formed by flow regulators,

[1] Master, Chemical Engineer - CAPMETAL ENVIRONOMENNTAL TECHNOLOGY
[2] Trainee, Chemical Engineer - CAPMETAL ENVIRONOMENNTAL TECHNOLOGY

sensors and nozzles with valve throttling options and flow blockage, which are applied to the head of wells in depths that reach up to 3000 meters. In this environment the water does not freeze due to pressure, but it is at temperatures below 0°C (32°F).

Manifolds valves are connected to flexible tubes built in multilayer called risers, and flowlines operating vertically and horizontally respectively. These tubes are able to withstand high internal and external pressures, corrosion, heavy sea currents, water pressure, at the same time supporting both oil and its own weight; length lines can reach up to 5Km of contact submerged line arrangement until FPSO tank vessel.

On the other hand Brazilian crude oil is characterized by containing 6% weight/ weight of paraffin (C20+) in acyclic chains that over time generates formation of incrustations inside risers, particularly on the initial stage of thermal shock of crude oil, when temperature is about 70°C (158°F), and external deep water environment temperatures about 0°C (32°F), knowing that the initial temperature of crystal formation (TIFC) is 20°C. This low temperature causes the deposition of material on the walls of risers reducing effectiveness of diameter line, increases cost of pumping and drop in well production with serious economic repercussions.

According to Felix (2011), the Brazilian petroleum presents typical concentrations of paraffin ranging from 25% p/p at Recôncavo to 6% p/p at Campos Bay reservoir with temperature ranging from 60°C to 80°C with an initial crystal formation (TIFC) temperature of 35°C and 20°C respectively.

As the inner walls crystallization incrustation of the hoses starts, paraffin cloisters in its gaps, light fractions and gases such as methane and hydrogen sulfide, being the initial anchor fouling for lifting the thickness and increase the length, given the fact that these have a deep thermal stabilization that cools the oil at levels below the TIFC. At a certain stage of disposal losses occur in the ability to transfer the oil due to high pressure drop in order to operate within the "balanced diameter" threshold pressure reached by the shaft that prevents greater decrease or blockage of the line.

In the process of maintaining risers and flowlines, some technologies have been developed since paraffin deposition occurs also in other transfer operations and petroleum refining processes. Techniques such as the use of chemical inhibitors, injection of heated solvents, thermochemical reactions, magnetic field application and mechanical removal are known. This last is accomplished by applying a plunger called PIG piston inside the duct with high pressure water inducing the displacement duct incrustations with inlays that are removed by the mechanical action of PIG structures embedded in the crystallized flexible.

For cleaning, the flexible line typical show in “Figure 1. Riser is disconnected from the well, and removed to reel in the dewaxing ashore unit”. The reel containing the inlay flexible hose is connected to a pressurized water line with SGA for removing fouling over the entire length of flexible, to the other end of the terminal, which empties into a tank for collecting the liquid with paraffin wax and waste included.

Dewaxing operation releases gases withheld in the interstices of scale, such as methane and hydrogen sulfide (H_2S) from 20 to 400 ppm occurrences, which has reduced threshold for odor perception. Hydrogen sulfide compound is corrosive, explosive, poisonous, and it is determined that all activities should be shut down when there is a concentration greater than 8 ppm in the local atmosphere, which defines the need of high performance application technology to capture and control these gaseous emissions polluting of flexible pipes carrying oil.

Figure1. Riser Terminal - In preparation for pigging process of removing incrustations

These are empirical foundations dewaxing operational information growing with enough time experience developed in Espírito Santo, Brazil. Where we have pioneering operation of a worldwide dewaxing base, with about 14 years activity, it has promoted the cleanup and recovery through PIG application of risers with circulating water flow, accumulated experience, a large number of quite variable records that reflects how diverse is the deposition of wax on the inner walls of these hoses that enables subsea oil exploration.

Totally random factors determine the greater or lesser deposition of hydrogen sulfide in the cavities of the reservoir, in the same way that we have wells reservoir with presence of gas in the interstices of paraffin embedded in flexible extraction and not in others, based on experience, record in lines of 1200 meters x 6 "(21.7 m³ internal volume) with 50% of paraffin volume + sand with hydrogen sulfide included, while the largest diameter in (63 m³) encrustations rows, sometimes reaching just 10-20% of the volume of the line.

And, if the activity is new, the control of pollutant emissions is an innovation solution that will be presented here through technology approach of capture and purification by net centrifugation multiventuri to be engaged in the application of offsetting unit emissions of hydrogen sulfide generated by the process of internal cleansing of flexible pipelines used to transport oil in offshore platforms.

2. Characteristics of Gases Present in Crude Oil

The crude compound is, in addition to oil, composed by gases in considerable concentrations. The gaseous compounds which are present in higher light fractions are hydrocarbons (which contains from 1 to 4 carbon atoms in its composition), such as methane and ethane, hydrogen sulfide, nitrogen and carbon dioxide. The forecasts of large production in Brazil from subsea exploration in the pre-salt rocks accumulating below the salt layer of 2000 meters, which can total up to 7000m distance from product to surface. The pre-salt oil is located between the States of Santa Catarina and Espírito Santo, in Santos Basin oil is found with a specific gravity of 28.5 ° API, low acidity and low sulfur, characteristic of a high quality oil and higher market value.

The main types of oil worldwide are classified as:

- Brent oil: North Sea oil produced, from the system for oil exploration Brent and Ninian. It is the oil in its crude form (raw) before going through the refining system.
- Light Oil: Without impurities, this already passed the refining system.
- Naphthenic oil: oil with loads cycle paraffinic hydrocarbons, naphthenic series, typical occurrence of Caucasus (Russian).
- Oil Paraffinic: oil with a high concentration of paraffinic hydrocarbons series of alkanes, typical occurrence in the Americas (USA and BRAZIL).
- Aromatic Oil: with high concentrations of benzene hydrocarbons, aromatic range of typical Indonesian (BORNEO).

If we consider the components derived from aromatics and hetero-atomic oil contained in their separation, virtually impossible for a reference, see table 1, the number of paraffinic isomers found in the number of chain carbons and also the boiling temperature clearly shows that the origin of the fouling problem be related to the low temperatures at depths of oil extraction on the continental shelf of Brazil.

Table1. Paraffin and boiling point

Carbon Number	Boiling Point (° C)	Number of Isomers
5	36	3
10	174	75
15	271	4.347
20	344	366.319
25	402	36.797.588
30	450	4.111.846.763
40	525	62.491.178.805.831

It is almost impossible to separate paraffin components individually. If we consider the components derived aromatics and hetero-atomic, even considering limiting the number of isomers by maturation processes, yet the number of possible components is extraordinarily high.

Sulfur is the third most abundant element found in oil, Ribeiro e Silva (2009) indicates that its medium concentration is 0.65% by mass, with values between 0.02 and 4.00%. Oils with concentration above 0.5% sulfur are termed "acid" or "sour" and require more processing, since compounds which form acids may damage equipment, and can even be found in the final products if untreated. In gaseous form, is in the form of hydrogen sulfide (H2S) mainly in the lighter fractions of oil due to its low molecular weight.

Hydrogen sulfide is characterized by a low threshold of perception, i.e., fractions of 0.05 ppm are noticeable and causes revulsion; high performance technologies should be implemented to ensure the clearance at levels below the threshold of perception, which is the main focus of this study. Because it is a gas and can form an explosive atmosphere/ environment, including toxic gases such as methane that can cause long eye irritation, damage to the respiratory and central nervous system and even death within minutes in cases of high concentrations exposure.

The H_2S has a characteristic odor and unpleasant, but at concentrations above 150ppm, it causes fatigue of the olfactory system, meaning you cannot detect its presence increase concentration. It features more of a risk, an operator may be in a medium containing the gas unknowingly causing him serious harm, which reinforces the need for an efficient exhaust system that eliminates the risk of explosion and poisoning.

With respect to methane, is not considered a toxic gas, if maintained the minimum concentration of oxygen in the atmosphere of 18 vol. %. It is considered asphyxia, however, is a highly flammable gas, so there should also be control so that its concentration does not reach values that could provide risk.

The American Conference of Governmental Industrial Hygienists (ACGIH) recommended exposure limits (TLVs) that can undergo "most workers, repeatedly, day after day for a lifetime of work without suffering adverse health effects." Table 2 displays below the exposure limit values of concentration considering a time-weighted average (TWA) for an ordinary working day of 8 hours daily and 40 weekly hours, the limit of short-term exposure (STEL) considers that a concentration weighted average of 15 minutes, which should not be exceeded at any time.

Table 2. Exposure limits – 2012 adopted values

Substance	**TWA (ppm)**	**STEL (ppm)**	**Molecular Weight (g/mol)**	**TLV Base**
Hydrogen Sulfide	1	5	34,08	Upper respiratory tract irritation, central nervous system involvement
Methane	1000	-	16,04	Cardiac sensitization, central nervous system involvement
Carbon Dioxide	5000	30000	44,01	Asphyxia

Regarding the composition of the gas mixture, of one or more components explosive mixture, characteristics are introduced the concepts of lower explosive limit (LEL) and upper explosive limit (UEL). The LEL is the minimum concentration of gas in air for an explosion to occur and UEL is the maximum concentration of gas present in the air so that the explosion occurs, i.e., an explosion only occurs if the concentration of the gas is between these two values. In Table 3 below, these limit values have to methane and hydrogen sulfide.

Table 3. Explosive limits

Substance	**LEL (%)**	**UEL (%)**
Hydrogen Sulfide	4,3	46
Methane	5	15

In order to maintain a non-explosive atmosphere environment and without risks of intoxication for operators, it is necessary that the concentration of gas is kept below LEL, and not above UEL. As safety measure, it is recommended that the atmosphere is maintained with concentrations of explosive gases to 10% of LEL, so that the value of the LEL is never actually reached.

The density of the gas is also a factor which must be taken into account in confined work, in order to know on which point the gas is more concentrated, that is, if it will rise or be deposited on the ground. It's important information,

which determines the points of entry and exit of exhaust ducts. As in this case have the hydrogen sulfide with relative density of 1.19 and 0.55 methane with the exhaust system must encompass the entire environment so as to leave no gas fractions at the top or bottom

3. Risers Dewaxing System

The economically feasible use period of the risers depends on the type and depth of oil extraction. The large volumes of light oil from pre-salt brings a new concern for operation in deep water, where there is no collected know-how, and because we are the new frontier of exploration with high quality oil that has relevant rates of paraffin, specifically the typical Brazilian and American oil.

It is necessary to do maintenance to recover the flowability thereof, since the paraffin deposition occurs continuously during the oil extraction process which reduces the effective diameter of the line. We have reported layers fouling rate of 3 mm/ day in lines 10" transferring 22,000 barrels/ day to reach equilibrium diameter according to Shecaira, Barros et al.

When riser reaches the diameter of equilibrium, which is not possible due to the over flow charge loss caused or even before that diameter is reached, which is collected by a vessel-type PLSV (Pipe Laying Support Vessel) which are responsible for launching pipes to connect the platforms to the systems of oil production. In “Figure 2 we can see a riser with advanced paraffin deposition”, with its flow ability impaired, with serious maintenance required.

Figure 2. Diameter flow compromised by the deposition of paraffin.
Photo by Mokhatab and Towler.

The operating arrangement on shore, which is usually, performed off-shore gives up the position of a spool containing the flexible removed. The flexible tip that operated submerged tank is positioned on locks in a specific sealed off cabin, with clamped fixing exhaust system, connected by pipelines laid on the upper side of the tank to promote negative pressure in the cabin and in the cracks opening cap flexible. The other end, also making use of mobile remote sensor receives the SGA and the connection to the pressurized water line which will cause the displacement of PIG through the entire length of the riser, promoting the mechanical removal of scale. On the tip over the tank occurs the discharging of the pasty mass, characterized by containing oil, water, sand, paraffin wax and pollutant gases. It is on this removal that we have the release of volatile fractions of gases included in the interstices of embedded paraffin. The tank which now functions as a lung outflow occurs where great agitation of the mass collected, which further increases the emission of combustible gases and pollutants. In “Figure 3 you can see the large amount of mass removed paraffin by this process”.

Figure 3. Removing paraffin by pigging
Photo by Mokhatab and Towler

4. Air Purification Technology

Once the gaseous released on riser by pigging dewaxing process, it must be removed continuously so as to avoid the formation of explosive atmosphere and intoxication operation when inspection, maintenance and / or operation are to be performed by the end pipe. Precisely these gases are to be processed in air purification unit before being released to the external environment.

The route chemical neutralization is applied by the equation: acid + base = salt + water. Hydrogen sulfide is transformed into hydrogen sulfide when dissolved in water, and in the presence of strong alkalies becomes salt according to the reaction equation 2 below:

$$H_2S_{(g)} + NaOH_{(aq.)} \Rightarrow Na_2S_{(l)} + H_2O_{(l)} \quad (2)$$

Since the sodium sulfite and hydrate thereof (Na2S.9H2O), the most common version, which appears as a soluble salt colorless and strongly alkaline.

The harmfulness of this poisonous and inflammable gas, which mainly attacks the central nervous system, and it can lead to the need of artificial respiration death within two minutes exposure to concentrations above 700 ppm, added to its low odor threshold of perception from 0, 05 ppm, determines the use of technologies BADCT ("Best Available Demonstrated Control Technology"), i.e. the best available control technology proven, which encouraged us to develop and apply technology spin multiventuri in uptake and clearance by chemical reaction neutralization of acid contaminants.

The core technology of Hydrodynamic Precipitators, operating by multiventuri centrifugation net is based on the theory of convergence of the vibration amplitude of molecular fluids according to their physical condition and temperature. With the synergy of mechanical contact through the spinning rotor simultaneous fluid phases with gas and liquid flow lines of the fluid mixture in the hundreds of portions which are subdivided in the cross perforations that multiventuri contains within the perimeter of the rotor.

Following technology functional fluids ejected by the rotor spinning liquid, receive a complementary external liquid flow which contributes to the rotor entrainment of contaminants in the mixture being ejected to the opposed lobe, which has the function of phase separation by cyclonic acceleration and the large difference density between air and liquid (1:1000), returning it to the tank of circulating liquid air treated and released to the atmosphere.

The conception suction gas through rotor technology, with innovative simultaneous mixture of these gases with liquid in turbulent regime and synergistic with in “Figure 4. showed sequential passage in multiple venturi perforations type”, achieves e neutralization efficiency of will level parts per million (ppm) as required by the critical pollutant hydrogen sulfide, which that threshold of very low olfactory perception.

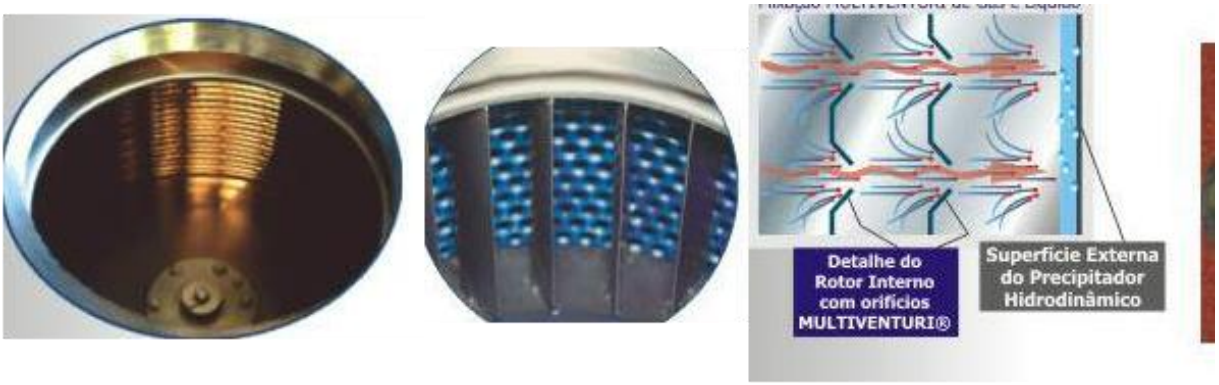

Figure 4. Details rotor Multiventuri spins where reactions occurs neutralizing gases.

In this conception of projected application the use of two stages of Multiventuri centrifugation, the second stage being represented by Hydrodynamic Precipitator operating system with refrigerated liquid, capable of cooling the streams and reduce the vapor pressure of fluids, rising the synergy and efficiency of the system. Through the use of liquid centrifugation technology you can cool by Multiventuri the rebate, by chemical reaction of sulfuric gas with an alkaline solution of sodium hydroxide, adopting the cooling to reduce the vapor pressure of H2S favoring its presence in the aqueous medium reaction.

Hydrodynamic Precipitators are based on the unique combination of centrifugal force with Multiventuri effect acting simultaneously in the gases emitted by the process of cleaning and alkaline cooled circulating liquid. The use of the refrigeration circuit as condensers are connected to Hydrodynamic Precipitator, cool the circulating fluid working in the transfer of energy by centrifugation, promotes cooling air by direct contact at lower temperature (18°C), favoring stabilization of residual fractions of unreacted hydrogen sulfide in the liquid so as to maintain the pollutant in the reaction medium alkaline.

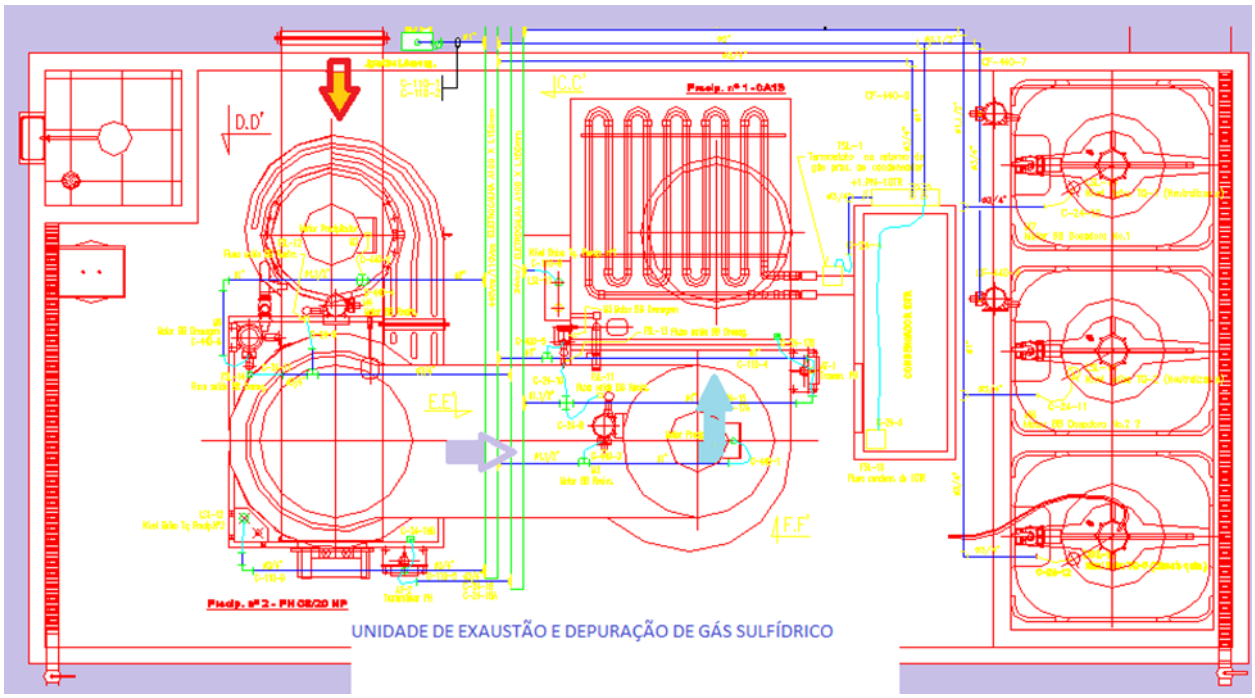

Figure 5. Sulfide hydrogen gas debugging suction line by hydrodynamic precipitator

In "Figure 5 the flowchart of the cleansing of hydrogen sulfide", in its functional flow we have the air volume inside receiving tank muck contaminated, which will undergo a permanent negative pressure, while there contaminant sludge inside the same, i.e., the tank should have nozzles with damper sub-pressure to allow air to enter, where there are no cleaning operation and the roof covers of the tank are closed, while there is still collected material within the pond. The control may be a level detector or hydrogen sulfide and / or methane with two types of equipment, a network of six

fixed XGARD-General detectors in the range of 0-50 ppm and multi-gaseous portable detectors ORION - BO-43465 and SÍRIUS - A3-3898 with an accuracy of 1 ppm connected to the command of Hydrodynamic Precipitators.

The air aspirated by the depression generated by Hydrodynamic Precipitators through nozzle damper sub-scanning will create pressure within the internal gas volume of the tank outflow of liquid paraffin and its removal, carrying gaseous emissions emitted even potentiated by mechanical stirring of the liquid containing the waste mass collected. Attention should be paid to the need for permanent operation of the exhaust system due to the risk of forming an explosive atmosphere by the emission of methane and hydrogen sulfide, both flammable, requiring the tank all elements of security to be activated, as the lower limit sensors explosiveness for H_2S and its security seal.

The exhausted gaseous stream containing hydrogen sulfide will be transported by pipeline network rectangular, as seeing on the foreground of the photo in Figure 6 is subjected to circulating centrifugation liquid in the rotor Multiventuri hydrodynamic precipitator, in which kinetic energy is added to the liquid in abduction cooled, with subsequent division into hundreds of portions with high surface contact provided by Venturis' perforations around the perimeter of the rotor of the machine. Being that the actual mixture obtained by centrifugation Multiventuri ensures a high degree of conversion reactions of the gaseous acidic neutralization of fractions, and refrigerated operation allows greater solubility in the reaction medium by reduction of vapor pressure of the pollutants. The arrangement is complemented by the refrigerant condensers, pH meters, flow and level sensors, pump diaphragm metering alkaline solution, drain pump and control panel with programmable logical controller-PLC with about 45 digital and analogic inputs for automatic control of the whole operation of the peripheral in matters of fundamental safety and environmental compliance facilities dewaxing flowlines and risers used in subsea oil exploration.

Figure 6. Arrangement with the suction line of gases, hydrodynamic precipitator cooling and condensing the bottom containers of alkaline and waste sludge.

The results in these 15 months of operation recorded values between 7 and 2500 ppm in aspiration of gases emitted during the dewaxing operation, and zero discharge of treated air by the system, as shown below.

Table 4. Concentration of H2S onto dewaxing operation

N° flexible	Date	Diameter of Riser (inch)	Concentration of H_2S at bobbin (ppm) internal	external	concentration of H_2S from depuration system (ppm)
C475XXA	11/01/2013	6	135	2500	0
C475XXB	13/01/2013	6	14	7	0
TR5041	16/03/2013	6	146	75	0
TR5141	24/04/2013	4	29	149	0

The above results demonstrates close to 100% effectiveness of this technology, confirmed by the absence of complaints in the heavily populated neighborhood where applied.

5. Conclusion

Aging lines operating in Brazil has generated a greater necessity to have this service for in a way that developments in the operations that faces the demand, of severe safety-proof explosion in confined spaces and occupational health, coupled with environmental legislation more effective and environmental awareness have made the business system and exhaust gas cleaning a peripheral device indispensable to the operation of dewaxing foundation.

Fifteen months operation of installation gathers all the know-how accumulated by the operator carries a wide range of security sensors and firefighting that are integrated with system debugging and gas treatment operates autonomously, even in aspects of chemical neutralization of circulating liquid to drain and waste container class IIA effluent operation. This deployment location with extremely close proximity enables operation in shifts of 24 hours without neighborhood odor impact or detection of explosive atmospheres having certain security procedures.

Out of this experience it is evident the functional efficiency of the centrifugation liquid multiventuri technology in control of hydrogen sulfide gas through alkaline blanketing chilled, groundbreaking technology worldwide, and has been developed from the specific characteristics and problems of domestic oil extracted in deep water, that is innovation occurs through technical need and demand contributing to the consolidation of the Brazilian expertise in the oil segment, starting from our base specificities of exploratory deep-water pioneer oil manipulation, that now will require innovation for new frontiers to reach deep in the pre-salt fields, being that our main challenge which stimulates our creativity in the development of efficient innovative technology.

7. Acknowledgements

Our thanks the information and guidance provided by the Thomasi Antonio about cleaning system risers, and Louise Passalacqua for translating this work.

8. References

AMARAL, L. H. R., TAVARES, J. H. S., OLIVEIRA, P. P. P., O gás sulfídrico, perfuração do sudeste, engenharia de segurança e meio ambiente Petrobras, 1994.

FÉLIX, M. M., Petróleo: história, prospecção, perfuração, refino, derivados, pré-sal. Available at: www.marciofelix2011.xpg.com.br/ciencias/petroleo/petroleo.html**.** 2011. Access: November 2012.

MOKHATAB, S., TOWLER, B., Wax prevention and remediation in subsea pipelines and flowlines. Available at: http://coretan-intern-arres.blogspot.com.br/2010_04_01_archive.html. 2010. Access: November 2012.

RIBEIRO, M. P., SILVA, E. F. B., ARAUJO, A. S., FERNANDES JR, V. J., IORIO, S. M. B. M., SANTOS, M. F. P., Evolução de gás sulfídrico em petróleos por TG-MS, 5º Congresso Brasileiro de pesquisa e desenvolvimento em petróleo e gás- UFRN, 2009.

SHECAIRA, F., BARROS, D., RAMACHANDRAN, K., BONIN, G., WALTRICH, P., JENNINGS, D., NEWBERRY, M., ZIGLIO, C., The Cottonwood Field Case History: The Pig/Paraffin Obstruction of remediated in a deepwater subsea tieback of the Gulf of Mexico's Cottonwood field. Available at: www.onepetro.org/.../SPE-146156-MS-P.pdf**.** Access: November 2012.