The Use of Wet Oxidation and PACT® for the Treatment of Propylene Oxide/Styrene Monomer (PO/SM) Industrial Wastewaters at the Repsol PO/SM Plant in Tarragona, Spain

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In 1999 Repsol YPF constructed a sophisticated industrial wastewater treatment plant in Tarragona, Spain to accommodate the new 678,000 tons per year propylene oxide/styrene monomer (PO/SM) and derivatives chemical production plants. The high strength aromatic and polyol compounds in the PO/SM wastewater are unaffected by conventional biological treatment processes and a more sophisticated wastewater treatment approach was necessary. To achieve the goal of a liquid effluent dischargable directly to the Mediterranean, wet oxidation is employed to pre-treat the high strength PO/SM wastewater. The wet oxidation effluent, along with all other production facility wastewaters, is then treated in a large two stage Powdered Activated Carbon Treatment (PACT®) system in which a homogeneous mixture of powdered activated carbon and biological solids treat the wastewater in a synergistic fashion. The waste solids (spent carbon and biomass) are treated in a separate wet oxidation reactor that simultaneously regenerates the activated carbon for reuse in the PACT system while destroying the biological fraction of the sludge. The PACT effluent is sand filtered and discharged, through an undersea sewer, into the Mediterranean Sea. The final effluent quality is excellent and the average value of effluent COD during the first year of operation was only 15% of the effluent specification limit. This paper describes the wastewater treatment plant in detail.

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INTRODUCTION

The treatment of the liquid effluents coming from the production of propylene oxide/styrene monomer (PO/SM) and its derivatives, flexible/polymeric polyols and propylene glycols, requires special technical considerations because of the characteristics of the wastewater generated. Of the multiple wastewater streams, some have a high content of aromatic and polyolic components which are difficult to degrade by a biological treatment system. This makes conventional biological treatment of these wastewaters an unsuitable option.

The wastewater treatment of the PO/SM and derivatives wastewater at the Repsol YPF plant in Tarragona, Spain applies wet oxidation combined with biological treatment using powdered activated carbon (PACT). The entire grassroots production facility, including the wastewater plant, was commissioned in 2000.

At the beginning of the project, the Repsol YPF Technology Center considered various wastewater treatment options and initially favored solvent extraction or incineration as the best available technologies for the more difficult to treat wastewaters. Conventional biological treatment was favored for the treatment of the remainder of the production facility wastewater. However, test work with these technologies provided unsatisfactory results. Tests with solvent extraction showed high losses of solvent, insufficient extraction, and a final effluent with a high solids content, a high coloration, and a high chemical oxygen demand (COD) value. So this technology was rejected. Tests with incineration showed insufficient energy content in the wastewater for economical operation and the high salt content of the wastewater further complicated incineration operation, so this technology was rejected.

After a reevaluation, Repsol YPF chose the wet oxidation process combined with a non-conventional biological treatment as the best wastewater treatment option. The main advantage to wet oxidation, which is a liquid phase oxidation, is that there is sufficient heat of reaction to maintain the reaction conditions without any additional fuel (autothermal).

Repsol YPF contacted USFilter's Zimpro Products group (Zimpro), because Zimpro has several industrial references of this kind and is the established leader in the wet oxidation and PACT technologies. Zimpro also has the capabilities to test a variety of processes in their pilot plants. After the preliminary basis of the project was established, pilot tests were performed at the Zimpro facility in Wisconsin, USA. For the pilot test work, it was necessary to send 20000 kg of actual wastewater samples from another Repsol YPF PO/SM site in Puertollano, Spain. The first tests were performed in December of 1996 and confirmed that wet oxidation followed by PACT was a feasible treatment train. PACT was chosen as the biological treatment technology because PACT provides greater treatment performance in a smaller footprint than conventional biological treatment. A wet air regeneration (WAR) unit was added to regenerate the spent powdered activated carbon from the PACT unit. This was done in order to reduce activated carbon consumption and to eliminate a problematic sludge disposal issue. Additional verification tests were also performed in April and May of 1997, again with positive results.

HISTORY

The new Repsol PO/SM and derivatives production facility in Tarragona, Spain has a global production of 678,000 tons per year and represents a growth of approximately 20% in the total sales volume for Repsol Quimica, the petrochemical division of Repsol YPF. From the total 500 million euros of anticipated investment in this project, 40 million euros were budgeted for the wastewater treatment plant.

The Repsol YPF Technology Center and Engineering Central Unit developed the basic engineering of the Tarragona facility. The detailed engineering, construction, and erection of the production, utility, and wastewater plants were performed by INTEIN, a temporary joint venture of three engineering companies: Initec, Tecnicas Reunidas, and Intecsa. The facility was engineered and constructed in a record 29 months.

The start-up of the PO/SM and derivatives production plants took place in June, 2000. The commissioning and start-up of the wastewater treatment plant, planta de Tratamiento de Aguas Residuales (TAR), was performed previously in April, so that it was operational before the start-up of the production plants.

The selected wastewater biological treatment technology, PACT, is a technology developed by both Zimpro and DuPont separately in the early 1970s. The first commercial PACT system was built in 1975. Zimpro has owned the license to the PACT process since 1982 and over 100 facilities are now in operation worldwide. The wet oxidation technology was commercialized by Zimpro beginning in the 1950s and over 200 commercial and municipal wet oxidation facilities have been constructed by Zimpro. Zimpro developed the WAR process as an extension of the wet oxidation process in the 1960s and has installed approximately 20 WAR systems worldwide. The Repsol YPF Tarragona plant is the only plant combining all three technologies: wet oxidation, PACT, and WAR, resulting in the TAR plant.

WASTEWATER TREATMENT PLANT (TAR) DESCRIPTION

All liquid wastes and rainwater from the Repsol YPF Tarragona facility first pass through the TAR prior to discharge. There are four wastewater streams that are fed to the TAR and shown in Table 1.

Table 1. TAR Feed Stream Description

Stream	Description	Strength and Flow
ACC	PO/SM combined wastewater	Strong COD, high flow
POE	polyol ether wastewater	Mild COD, high flow
AP	PO/SM acid purge	Strong COD, low flow
BCC	mixed low strength wastewaters	Low COD, high flow

The TAR uses three treatment processes:

- Wet Oxidation
- PACT
- WAR

Wet oxidation is used to treat the high COD ACC stream and the biologically untreatable POE stream. Even though the COD is reduced significantly, the wet oxidation effluent does not have a sufficient quality to be discharged, so it must be biologically treated using the PACT system. The AP stream and other facility wastewater, BCC, are also treated in the PACT system. The sludge from PACT is treated by WAR for regeneration of the activated carbon and destruction of the biomass. The effluent from the PACT process is filtered using a HydroClear® sand filter and discharged along with the rest of the complex effluent waters into the Mediterranean Sea through an undersea sewer. The TAR system process flow diagram (PFD) is shown in Figure 1. Each of the three technologies is described in greater detail below.

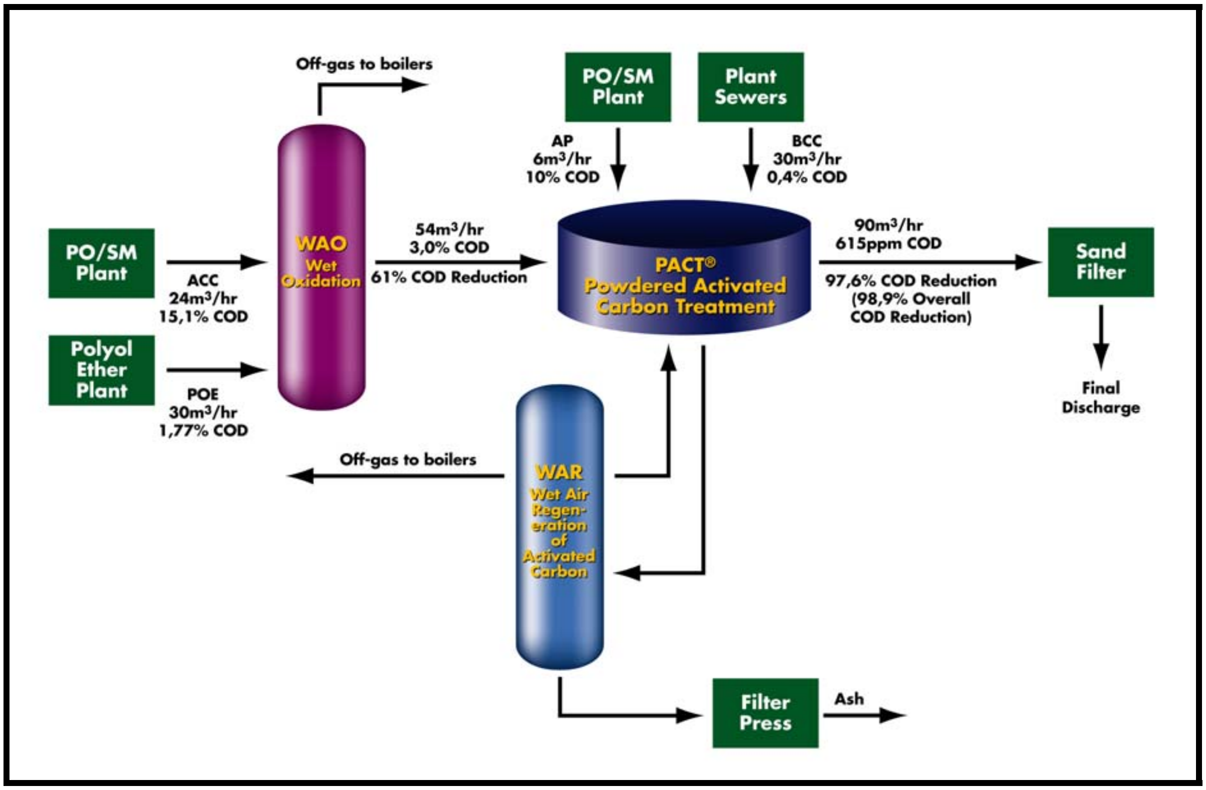

Figure 1. Repsol Tarragona wastewater treatment plant (TAR) process flow diagram and design conditions.

Wet Oxidation

The wet oxidation process is an oxidation reaction that occurs in liquid water. The chemistry of wet oxidation is such that large molecules which are difficult to treat biologically, readily break apart and spontaneously oxidize with dissolved oxygen at an elevated temperature. The reactions occur at much lower temperatures than incineration and the water is an important component of the reaction process. Wet oxidation reactions do not occur in the gas phase and elevated pressure is required to maintain water in the liquid phase. Because the liquid is not vaporized, wet oxidation requires less energy for autothermal operation than incineration. Nitrogen and sulfur, when present, are not released as gaseous NO_x or SO_x but remain in solution as environmentally acceptable nitrate and sulfate. The hydrocarbons are converted to CO_2 and water. Oxidation is rarely complete so a portion of the organic COD remains as readily biologically treatable organic acids, such as acetic acid. The wet oxidized effluent is readily biodegraded and typically exhibits a BOD:COD ratio of 0.6 - 0.7.

The operating conditions for the stainless steel lined wet oxidation bubble reactor are 295°C at 95 bar and a 1.5 hour reaction time using compressed oxygen gas as the oxidant. Air could also have been used, but the larger compressor cost, higher pressure rated equipment, and heat loss to the nitrogen component in air made the choice of pure oxygen the more attractive option.

The purpose of the wet oxidation process is two-fold. First, it is to destroy the biologically untreatable high molecular weight branched molecules in the POE stream. The second function is to reduce the high organic loading going to the PACT biological system from the ACC stream by first destroying most of that COD content. Combining the ACC and POE streams in the wet oxidation process allows the high COD loading of the ACC stream to provide autothermal operation for the treatment of the POE stream.

As shown in Figure 2 the ACC and POE feed streams are pumped by a high pressure pump and are then combined with a small amount of compressed air. This air is provided by a small air compressor. Only a small amount of air is required in order to prevent fouling of the feed / effluent heat exchangers (F/E HX) which are used to heat the cold feed. A steam trim heater is also included for system start-up. The hot feed is injected into the base of a bubble reactor that is 2 m diameter and 30 m tall. Compressed oxygen is injected separately into the base of the reactor. Compressed oxygen is used rather than air in order to minimize the cost of the compressor, which is only 1/5 the size of an equivalent air compressor. Twenty-five bar gaseous oxygen is available because it is also used in other production processes at the complex, meaning that only an oxygen booster compressor is needed for the wet oxidation system. A photograph of the wet oxidation system is shown in Figure 3.

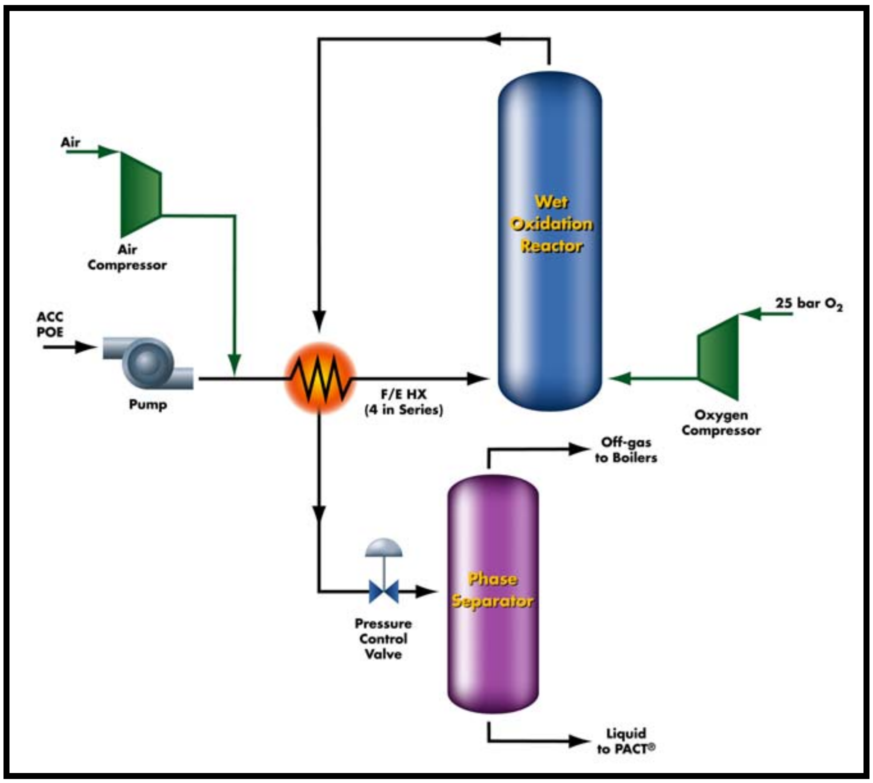

Figure 2. Repsol Tarragona wet oxidation system process flow diagram.

The oxidation reaction occurs in the reactor, which has a nominal 1.5 hour retention time. As the reaction progresses heat is released, increasing the reactor temperature 15°C to the 295°C operating temperature. The wet oxidation system was designed to destroy approximately 61% of the feed COD.

The hot effluent and off-gas pass through the F/E HX to heat the incoming feed and are further cooled using a water cooler. The cool effluent is then depressurized using an erosion resistant valve and is separated from non-condensable gases in a gas/liquid separator. The off-gas has approximately 5-15% oxygen content and is routed to the PO/SM boilers. The liquid effluent contains 20000 - 30000 mg/L of COD and is routed to the PACT system for further treatment. The parameters for the wet oxidation reactor are shown below:

- Cylindrical vertical vessel, 30 m tall and 2 m in diameter
- Operating pressure of 95 bar
- Feed temperature of 280°C
- Exit temperature of 295°C
- Nominal residence time of 1.5 hour
- Nominal feed rate of 60 m^3/hr
- Nominal oxygen feed rate of 3100 kg/hr
- Nominal feed COD rate of 4750 kg COD/hr
- Nominal COD reduction of 61%

Figure 3. Wet oxidation system. Feed effluent heat exchangers on left, reactor on right, phase separator on far right.

PACT®

Powdered activated carbon treatment (PACT) is an enhanced biological treatment process that allows enhanced performance in a shorter hydraulic retention time than can be achieved by conventional or by high rate activated sludge treatment systems. This enhanced treatment is achieved by use of powdered activated carbon within the treatment system itself. Operating in this manner increases and improves:

- Organics removal
- VOC / odor control
- color removal
- resistance to shock loads
- metals removal
- sludge settling / thickening

There is a synergism within the PACT system that is not possible when the biomass and the carbon are kept separate. Unlike waste activated sludge, where organics are only acted upon by the biomass for the hydraulic retention time within the aeration tank, in PACT organics remain within the treatment zone for the hydraulic retention time and for the sludge residence time of the system and thereby undergo both adsorptive and biological treatments.

Because there is both biological growth and adsorption of organic components occurring in the PACT system, wasting of excess solids ("spent carbon") is required. This wasted spent carbon is regenerated using WAR, described further below, and then returned to the PACT system.

To meet the stringent discharge requirement, 2-stage PACT is used in the TAR. The first stage (PACT-1) is a 30,000 m^3 concrete aeration tank (shown in Figure 4) using specially designed USFilter Jet Tech jet aerators and a 17 m diameter clarifier. To give a perspective of scale, the 65 m diameter PACT-1 aeration tank is believed to be the largest concrete tank in Europe. The hydraulic retention time in PACT-1 is 14 days and the sludge retention time is 12 days. The jet aeration system in PACT-1 is operated to maintain a minimum dissolved oxygen concentration of 2 ppm. The clarifier is a rapid pick-up Envirex TOW-BRO® unit. The PACT-1 clarifier separates the mixed liquor solids/sludge from the treated water. The treated water (effluent) passes to the second stage, PACT-2. The excess sludge from PACT-1 is removed from the bottom of the clarifier, is thickened to ~5% solids content, and is then

Figure 4. 65 m diameter PACT-1 aeration basin.

fed to the WAR system for regeneration of the activated carbon, which is then recycled back to PACT-1. PACT-1 was designed to achieve 87% COD removal from the combined BCC, AP, and WAO effluent streams.

PACT-2 consists of a smaller aeration tank than the PACT-1 aeration tank and a 17 m diameter clarifier. The 30 m diameter PACT-2 aeration tank has a hydraulic retention time of 3 days and a sludge retention time of 20 days. PACT-2 was designed to achieve a 71% COD reduction. Aeration is provided by a separate Jet Tech jet aeration system, which can separately adjust both mixing intensity and oxygen transfer ability by regulating blower and/or pump outputs. The mixed liquor from the PACT-2 aeration tank passes to the clarifier where the solids (carbon and biomass) in the mixed liquor readily settle out of suspension and are recycled back to the PACT-2 aeration tank. The clarifier effluent passes through a Hydro-Clear® sand filter, which is a final polishing filter to remove suspended solids and any carbon fines. A photograph of the sand filter is shown in Figure 5. After filtration the liquid effluent is mixed with the rest of effluent waters of the complex and is discharged into the Mediterranean Sea through an undersea sewer. Spent carbon from PACT-2 is only partially spent and is periodically wasted to PACT-1. The process flow diagram for the PACT system is shown below in Figure 6 and a photograph of the PACT system is shown in Figure 7.

Figure 5. Effluent passing through a Hydro-Clear® sand filter.

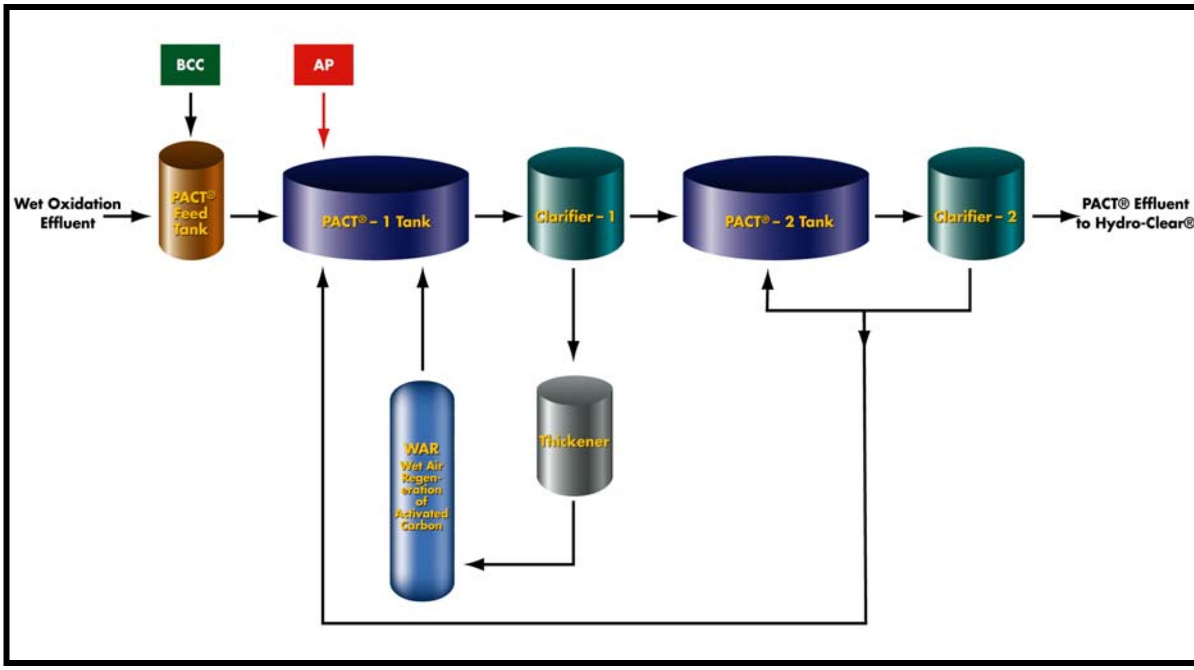

Figure 6. Repsol PACT® system process flow diagram.

To get some perspective of the organics load that is treated in the PACT system, the capacity of this PACT system is large enough to treat all of the typical municipal wastewater from a city that contains one million persons. The overall PACT system was designed to treat a flowrate of 90 m^3/hr with an average feed COD of 26000 mg/L. The design effluent COD is 615 ppm, representing 97.6% COD removal in the PACT system. System parameters are shown below:

- PACT system throughput of 90 m^3/hr
- PACT-1 hydraulic residence time of 14 days
- PACT-1 sludge residence time of 12 days
- PACT-2 hydraulic residence time of 3 days
- PACT-2 sludge residence time of 20 days
- PACT system design COD removal of 97.6%

Figure 7. Repsol PACT® system. Tanks (clockwise from lower left), PACT-1 aeration tank, PACT-2 clarifier, PACT-2 aeration tank (top), PACT-1 clarifier, spent carbon feed tank (far right), and sludge thickener (center). Note black color of liquor, due to the powdered carbon.

WAR

The wet air regeneration system (WAR) is used to regenerate the spent carbon from the PACT system. WAR simultaneously recovers the powdered activated carbon for reuse in the PACT system and destroys adsorbed organics and biomass.

Operation of the WAR unit is similar to the main TAR wet oxidation system, however compressed air is used instead of oxygen. The PACT sludge is first thickened to ~5% solids content. This is done to obtain sufficient COD content for autothermal operation. The sludge is then pumped using a hydraulic exchange pump and then compressed air is added to the sludge before the stream passes through an F/E HX. The hot stream is injected into the bottom of a 1.8 m diameter bubble reactor. The stainless steel lined bubble reactor is 13 m high and the exothermal heat of reaction increases the fluid temperature from 210°C inlet to the 243°C reactor exit temperature. The effluent passes through the F/E HX and a cooler. The cooled fluid is depressurized using an erosion resistant valve and then phase separated. The off-gas passes to the PO/SM plant boilers and the regenerated activated carbon slurry returns to the PACT-1 aeration tank. Inert ash collects in the bottom of the WAR reactor and is periodically purged to a storage drum, from where it is sent to a filter press to be dewatered prior to disposal. The WAR system process flow diagram is shown in Figure 8 and a photograph of the WAR system is shown in Figure 9.

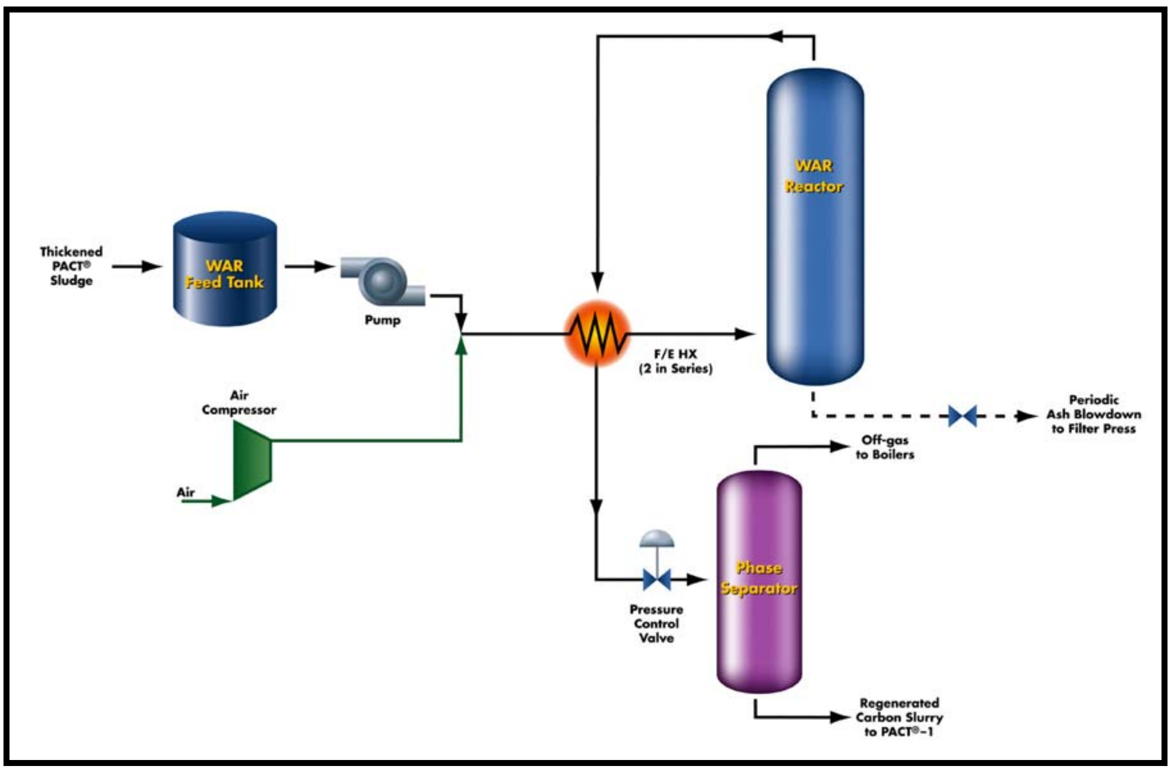

Figure 8. Repsol wet air regeneration (WAR) system process flow diagram.

While the bulk of the activated carbon is regenerated in the WAR system, there is approximately 10% loss of the activated carbon from WAR oxidation, effluent losses, and ash control, which must be compensated for. Fresh carbon is added to the PACT-2 aeration tank using a USFilter WHM carbon silo and feed system to make-up for this loss. WAR system parameters are shown below:

- Cylindrical vertical vessel, 13 m high and 1.8 m diameter
- Design operating pressure of 63 bar
- Feed temperature of 210°C
- Operating temperature of 243°C

Figure 9. Repsol WAR system. PACT® system on far left. Sludge feed tank on left (back), vertical U-bend heat exchangers in back, WAR reactor on far right. WAR system ash blowdown tank (right corner) for feeding the filter press.

RESULTS

The design conditions of the TAR are for a total of 90 m^3/hr; 60 m^3/hr through the wet oxidation unit, plus 30 m^3/hr combined with the wet oxidation effluent and fed through the PACT unit. The design COD removal was for 61% in the wet oxidation unit and 97.6% in the 2 stage PACT system, to give a final effluent of 615 ppm COD and overall reduction of 98.9%.

The results obtained during the first year of operation have been excellent. The COD values in the sand filter effluent have been around 100 ppm COD and at times daily averages are around 50 ppm. This performance has been achieved while always keeping the process flowrate to the TAR plant at 90 m^3/hr at strengths with the feed COD concentrations that were equal to or greater than the design conditions. The overall COD reduction is between 99.85% and 99.99%.

The average value of COD obtained in the TAR effluent during the first year of operation is just 15% of the specification limit. Table 2 shows the results obtained from the operation of the TAR facility.

Table 2. System Performance

	Design Value	Actual Value
WAO System Flowrate	60 m^3/hr	60 m^3/hr
PACT System Flowrate	90 m^3/hr	90 m^3/hr
WAO % COD Removal	61%	55-75%
PACT % COD Removal	97%	98.5 - 99.9%
TAR Overall % Removal	98.85%	99.85 - 99.99%

CONCLUSION

During the first year of operation, not only were the guaranteed treatment values achieved, but the TAR plant exceeded the expected performance results. As with any major project of this scale, unforeseen contingencies and difficulties were encountered during the commissioning and start-up; all of which were smoothly solved with good cooperation between Zimpro, the Technology Center, the Central Engineering Unit, and the Repsol YPF Start-up Team. The excellent spirit of cooperation and dedication allowed for the construction, commission, and start-up of the TAR plant with better than design performance and on schedule.

Frequently an exception is given to the discharge permit of a new petrochemical facility for the first few months of operation during the highly unsteady start-up period. However such an exception was not necessary at the Repsol YPF Tarragona facility due to the impressive reliability and resilience of the Zimpro wet oxidation, PACT, and WAR processes. At no time during start-up or operations has Repsol YPF failed the discharge permit requirements.

In summary, the selection of wet oxidation, together with PACT biological treatment and WAR regeneration of the PACT activated carbon, all through USFilter's Zimpro Products, has demonstrated to be the most suitable process for the wastewater treatment of streams coming from the PO/SM and derivatives plants of the Repsol YPF Tarragona facility. The actual performance exceeds the performance that is required by administration authorities. This TAR plant represents a milestone for the environmental commitments of the Repsol YPF group.

ABBREVIATIONS

ACC...........Mixed PO/SM wastewater
AP..............Acid purge. A PO/SM wastewater
BCC...........A mixture of miscellaneous facility wastewaters
COD ....Chemical oxygen demand
F/E HX ......Feed effluent heat exchanger
POE ....Polyol ether wastewater
PACT.........Powdered Activated Carbon Treatment
WAR ....Wet air regeneration
TAR...........Repsol YPF's Tarragona wastewater treatment plant
Zimpro.......USFilter's Zimpro Products