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ENV-07-133 **Disposal of Spent Caustic at the Repsol YPF
Refinery in La Pampilla, Peru**

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Disposal of Spent Caustic at the Repsol YPF Refinery in La Pampilla, Peru

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Abstract

Repsol YPF's La Pampilla refinery began using a Zimpro® wet air oxidation (WAO) system for the treatment of refinery spent caustic in 2005. The spent caustic comes from a variety of sources including caustic treatment of gasoline, kerosene, and LPG. Prior to installing a WAO system, the refinery was dependent on less satisfactory disposal options. The WAO system allows for on-site treatment without the production of odorous off-gas. System performance includes high chemical oxygen demand (COD) destruction and complete destruction of sulfides and mercaptans to below analytical detection limits. WAO transforms the material from an odorous and toxic feed to a readily biodegradable effluent that is free of noxious odors. The effluent is discharged to the sea.

Introduction

The Repsol YPF refinery in La Pampilla is the largest in Peru. The refinery was purchased from Petroperu in 1996. An overhaul of the refinery was initiated with the new purchase. The spent caustic disposal technique was no longer suitable and this was also updated in the overhaul. After a thorough investigation, WAO was selected as the best option. WAO allowed on-site treatment without producing odorous off-gas. This process was selected because Repsol YPF had reference from another refinery (Refinaria de Petroleos de Mangueiros, Brazil) that was part of the Repsol Group. WAO was compared with several types of spent caustic treatments including:

- Wasted caustic neutralization (with H_2SO_4 or HCl);
- Wasted caustic treatment with $FeSO_4$;
- Oxidation with hydrogen peroxide.

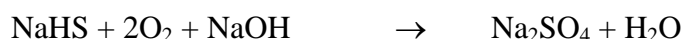
The choice of WAO was based on the fact that many of the other processes would require a large amount of equipment maintenance due to corrosion by acids. The safety in this unit was also important. The added reactants in the WAO process are air and steam (so the personnel protections were normal). The other processes used aggressive chemicals such as H_2SO_4 and H_2O_2 and required special personnel protection. High temperature/pressure wet oxidation was selected in order to control foaming. This would be an operational problem at lower operating conditions due to the naphthenics present. For additional background information, refer to Carlos and Maugans, 2002; Grover and Gomaa, 1993; and Maugans and Ellis, 2002.

Technology description

Wet oxidation is an aqueous phase process that operates at elevated temperature and pressure. Dissolved or entrained contaminants are oxidized in the liquid phase water. The process relies on the liquid water molecules to catalyze the oxidation. Oxygen is used as the oxidant and is supplied by mixing air with the spent caustic. For refinery spent caustic, the design operating temperature was 260 °C (500 °F), which is well above the normal boiling point. System pressure is 88 kg/cm² (1250 psi). The pressure keeps most of the water in the liquid phase, which also minimizes the energy consumption.

The typical reactions occurring during WAO of refinery spent caustic include the following:

Sulfide oxidation:



Mercaptan oxidation:



Naphthenics and cresylics oxidation:



Where R' is an organic chain, typically acetate or oxalate in the oxidized compounds.

Description of wastewater

The spent caustic comes from multiple streams and includes sulfidic, naphthenic, and cresylic spent caustics. Sulfidic spent caustics come from the caustic scrubbing of liquefied petroleum gas (LPG) and pentane from fluidize catalytic cracker (FCC) and continuous distillation unit (CDU). Naphthenic spent caustics come from the Merox® type treatment of kerosene. Cresylic spent caustics come from the Merox® type treatment of visbreaker gasoline. The compositions are shown in Table 1.

Table 1. Spent Caustics Composition

	Reported as (g/L)	Sulfidic spent caustics	Naphthenic spent caustics	Cresylic spent caustics
COD	O ₂	7 – 110	50 – 100	165 – 230
TOC	C	0.02 – 4	11 – 25	23 – 60
DIC	C	0.15 – 5	0 – 0.16	0.33 – 0.35
Sulfide	S	2 – 53	<0.001	0 – 64
Sulfite	S	0.002 – 0.48	0.004 – 0.009	0.8 – 1.6
Mercaptans	CH ₃ SH	0 – 28	<0.03	0 – 5.4
Thiosulfate	S ₂ O ₃	0 – 3.7	0.07 – 0.13	10 – 12
Total phenols	C ₆ H ₆ O	0.003 – 0.02	2 – 10	14 – 20

(Values reported as <# represent non-detection, with # being the analytical detection limit.)

Approximately 85% (by volume) of the spent caustic is produced continuously in the treatment of kerosene. The remaining 15% of the flow is produced in batches of varying quantities and compositions. Two storage tanks are used as equalization tanks. One large batch of sulfidic spent caustic is segregated into one storage tank. The remaining spent caustics (sulfidic, naphthenic and cresylic) are combined and held in the other storage tank. The partial segregation is done so that the sulfide concentration fed to the WAO unit can be better regulated. This is done to control oxygen uptake and corrosion that can result from uncontrolled sulfide concentration spikes.

Metering pumps are used to control the flow rate of spent caustic from the two storage tanks and the fresh caustic. Dilution water is added to control the heat release from the oxidation. The water is added using a centrifugal pump. Caustic is consumed by the oxidation products. If there is insufficient caustic, the pH of the oxidized effluent will become acidic, which can damage the nickel alloys used in the high temperature portion of the WAO system. Fresh caustic is added to the feed to maintain the discharge pH above 8.

Description of the oxidation system

The process flow diagram of the wet oxidation system is shown in Figure 1 and photographs of the system are shown in Figures 2 and 3. The operating conditions for the system are shown in Table 2.

Table 2. Operating conditions for the wet oxidation system

Sulfidic caustic feed rate	0.04 m ³ /hr (0.2 gpm)
Combined naphthenic/cresylic spent caustic feed rate	0.31 m ³ /hr (1.4 gpm)
Fresh caustic feed rate (20 °Be)	0.21 m ³ /hr (0.9 gpm)
Dilution water feed rate	0.08 m ³ /hr (0.4 gpm)
Reactor temperature	250 °C (482 °F)
Reactor pressure	88 kg/cm ² (1250 psi)

The four feed streams are combined and pass through the high pressure feed pump. Compressed air is added to the feed and the mixture is heated in the feed/effluent heat exchanger (F/E HX). The F/E HX is a concentric tube exchanger with the feed passing through the inner tubes and the hot reactor effluent through the annular space of the outer tube. The feed is heated further in the trim heat exchanger. The system operating temperature is regulated by the steam flow to the trim heat exchanger. The oxidation reactions begin with the heat addition in the heat exchangers. The hot fluid enters the bottom of the reactor. The exothermic reaction heats the fluid to the final operating temperature in the reactor.

The reactor is a bubble column, with the gas bubbles rising through the liquid phase. The reactor is sized to provide the retention time necessary to achieve the desired degree of treatment. The fluid exits the top of the reactor and passes through the shell of the F/E

HX for heat recovery. After partial cooling in the F/E HX, the oxidized effluent passes through the process cooler and then to the process separator. The off-gas is separated from the oxidized liquor by gravity in the separator. The liquid effluent is discharged to the sea. The off-gas is scrubbed and is sent to a burner used to fire a distillation column.

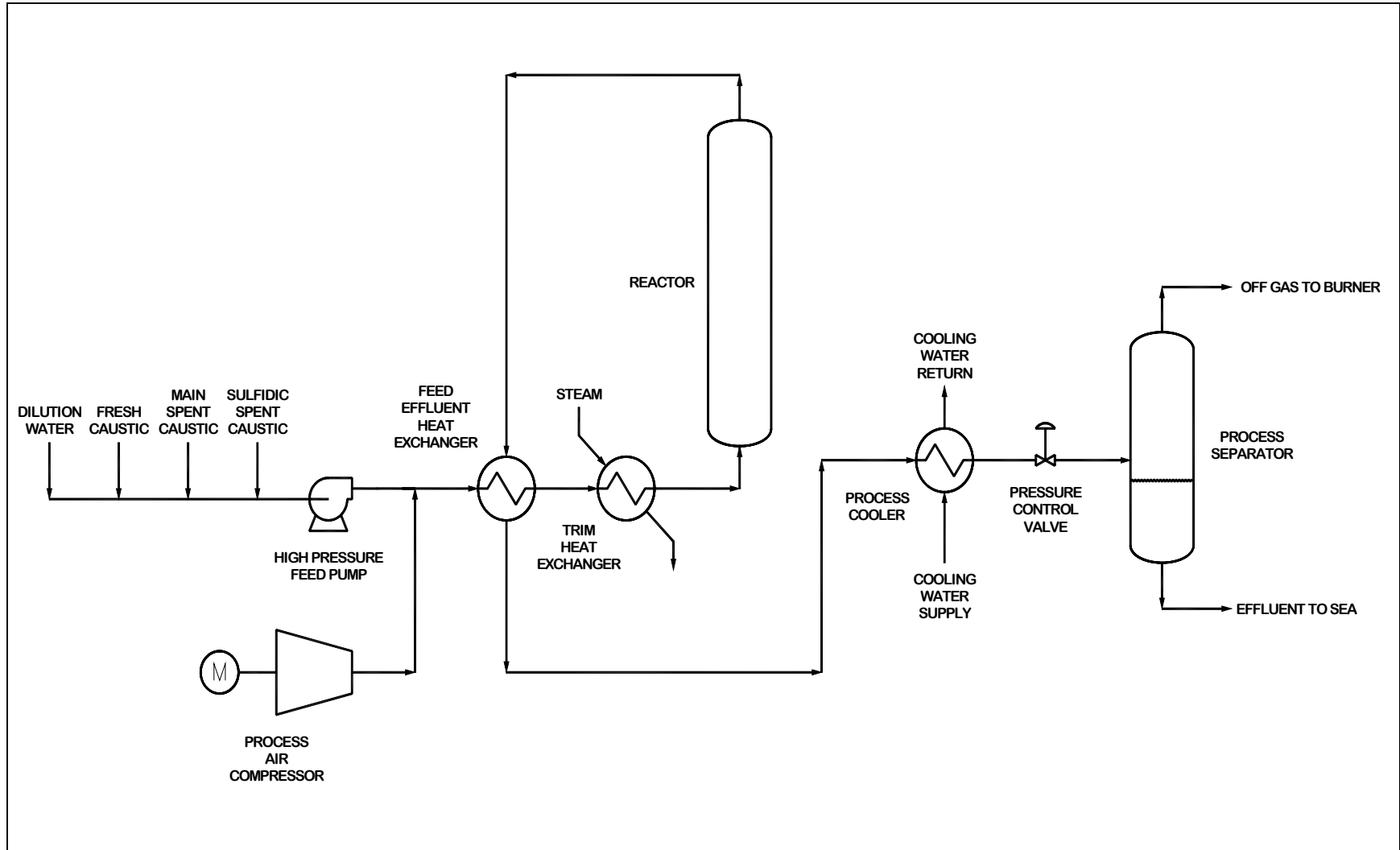


Figure 1. WAO system process flow diagram



Figure 2. Overview of WAO system.



Figure 3. WAO system oxidation tower.

Performance

The performance of the system is shown in Table 3. The combined spent caustic and fresh caustic composition is reported in the feed column of Table 3. Dilution water is added to the feed after the feed sample point. Additionally, scrubber water is added to the oxidized effluent in the process separator. These water streams dilute the oxidized effluent to approximately 60% strength, which is reflected in the effluent column in Table 3. After correcting for the dilution effect, the WAO system destroyed 85% of the COD, 73% of the TOC, and >99.97% of the sulfide. Figure 4 is a photograph showing the sulfidic spent caustic, the main spent caustic (naphthenic and cresylic), and the oxidized effluent.

Table 3. WAO system performance at 250 °C

	Reported as (mg/L)	Feed	Effluent (as measured, after dilution)
COD	O ₂	73,000	6,300
TOC	C	15,000	2,400
DIC	C	1,200	5,600
Sodium	Na	41,000	24,000
pH	-	13.2	8.9
Sulfide	S	8,500	<1
Sulfite	S	100	<2
Mercaptans	CH ₃ SH	1,500	<30
Thiosulfate	S ₂ O ₃	1,500	<30
Total phenols	C ₆ H ₆ O	6,500	36
Flow rate	m ³ /hr	0.67	1.14

(Values reported as <# represent non-detection, with # being the analytical detection limit.)



Figure 4. Sulfidic spent caustic (left), main spent caustic (center), and oxidized effluent (right)

Safety

The oxygen supply is limited by the capacity of the compressor. This prevents excessive temperature increase in the event of a COD excursion in the feed. The liquid water and air in the reactor is an energy sink to further dampen temperature excursions. The pressure in the reactor is regulated, so an excessive energy release in the reactor creates more steam at the process temperature, rather than excessively increasing the temperature or pressure.

The off-gas may contain between 5 and 21% O₂ and some volatile organic compounds. To prevent an explosion hazard in a flare system (due to the oxygen) a dedicated off-gas line is used to take this gas to the firebox of a burner.

The system processes spent caustic at elevated temperature and pressure. Typical spray and spill protections are used to protect personnel and the environment. There have been no safety incidents with the WAO system.

Reliability

Since unit start-up in 2005, the WAO system has proved to be reliable. The only item of note is fouling in the heat transfer equipment. After approximately 12 months of operation the tubes of the heater exchangers became fouled. This caused an increase in pressure drop and a loss of heat transfer efficiency. The scale was found to be mostly iron and is formed from iron in the feed. The scale was partially cleaned using steam. The scale is not completely removed and more cleaning is needed. Recent tests show the scale may also have an organic component. Heat exchanger fouling will be managed by conducting a solvent wash of the equipment when needed.

Economics

The system operates at elevated temperature and pressure using nickel components. Capital components include the air compressor, heater transfer equipment, pumps, tanks, separators, and the reactor. The technology was licensed from Siemens Water Technologies (formerly USFilter). The exact cost of this project is propriety. In general terms, the capital expense was several million US dollars. Operating costs are staffing (18 man hrs/day), chemicals, and utilities. Most of the heat for operation is produced by the oxidation reactions. The F/E HX is used to recover this heat, therefore only a relatively small amount of steam is needed.

Conclusions

The WAO system is an effective approach for treating the spent caustic. Sulfides and mercaptans are destroyed to below analytical detection limits. TOC and COD are greatly diminished and the oxidation products neutralize the pH to between 8 and 10. The gaseous and liquid effluents are not malodorous. The oxidized spent caustic is discharged to a holding tank, and then directly to the sea. The off-gas is of sufficient quality that it is directed to a burner to destroy the volatile compounds. System operation has proven reliable. After a year of operation an iron/organic scale has accumulated in the heat transfer equipment. This scale accumulation will be removed.

References

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Author biographies

Felix Davila is a mechanical engineer in Process Unit of Pampilla Refinery (REPSOL YPF, Peru). His responsibilities since joining the group in 1999 have included projects management, energetic optimization and supervision of WAO Unit, Sour Water treatment and Amines Plants.

Nicolás Villar Márquez graduated as petrochemical engineer (Engineering National University – Perú), he works for Repsol YPF at La Pampilla Refinery (Perú) since 1997. His works include engineering process in Distillation, Catalytic Cracking and Reforming, Hydrotreating, Visbreaking, Waste Caustic Treatment, etc. He works in researching and development proposals for new units or modifications for existing units, troubleshooting, operator training, unit startups, risk assessments and standards, Solomon coordinator in the refinery, etc.

Chad Felch has worked as a chemist at Siemens Water Technologies (formerly USFilter) since 1999. He focuses on research and development of new applications of the WAO technology. He is the chief materials and construction specialist for hydrothermal applications. He holds a BS in chemistry from University of Wisconsin, Stevens Point.

Clay Maugans has worked as a chemical engineer at Siemens Water Technologies since 1999. He focuses on research and development of new applications for the WAO technology. He field support to existing WAO facilities. He holds a Ph.D. in chemical engineering from Texas A & M University.

Steve Olsen has worked as a process engineer at Siemens Water Technologies since 1996. He has designed and assisted with the commissioning of several wet air oxidation units treating refinery and ethylene/chemical plant waste streams. He holds a BS in chemical engineering from the Univ. of Wisconsin-Madison.