

**WET AIR OXIDATION OF
ETHYLENE PLANT SPENT CAUSTIC**

by

Claude E. Ellis
Director of Wet Air Oxidation Marketing

Robert J. Lawson
Director of Industrial Sales

and

Bruce L. Brandenburg
Manager, Field Services

Zimpro Environmental, Inc.
301 West Military Road
Rothschild, WI 54474

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I. Introduction

In an olefin plant, hydrocarbon feed stocks are cracked to manufacture products including ethylene and propylene. The cracked gas from the cracking furnace is scrubbed in a caustic wash tower to remove carbon dioxide, hydrogen sulfide, and mercaptans prior to further processing in the plant's cold section. The spent caustic is purged from the wash tower and is laden with sulfidic constituents plus organics such as condensed oils and benzene.

This spent caustic scrubbing liquor (spent caustic) is commonly the most problematic waste stream generated by an olefin plant. This is due primarily to the sulfide concentrations which can range as high as 6 percent (expressed as NaHS), depending on the cracking furnace feed stock and wash tower operation. High levels of sulfides can create odor and safety problems when liberated as a gas. Operational problems associated with discharge to a plant's wastewater treatment plant can also occur.

The most effective means for on-site treatment of spent caustic is wet air oxidation which can achieve the oxidation of reactive sulfide to soluble thiosulfate, sulfite and sulfate. This treated stream is then suitable for biotreatment in the plant's wastewater treatment system. Wet air oxidation is a proven technology currently being used by numerous olefin plants. On a worldwide basis, most newly constructed grassroots facilities use wet air oxidation for spent caustic treatment.

The purpose of this paper is to provide insight into the design of a wet air oxidation system as it is applied on a full scale basis for spent caustic treatment. There are numerous design parameters, including temperature and pressure. The variations in spent caustic characteristics and treatment objectives must be carefully considered prior to choosing the optimal design. These issues can have a significant impact on the critical design parameters including the materials of construction. The information included herein is based on the experience of Zimpro Environmental, Inc. in designing twelve full scale wet air oxidation systems for treating spent caustic from the production of ethylene.

II. Wet Air Oxidation Process Description

Wet air oxidation is an aqueous phase oxidation process using molecular oxygen contained in air (or any other oxygen containing gas) as an oxidant. The process operates at elevated temperatures and pressures ranging from 120°C (248°F) to 320°C (608°F) and 760 kPa (110 psig) to 21000 kPa (3000 psig), respectively.

The basic flow scheme for a typical wet air oxidation system is illustrated in FIGURE 1. The wastewater or feed liquor is pumped up to pressure by a high pressure feed pump. A gas stream, in this case air, containing sufficient oxygen to meet the oxygen demand requirements of the waste stream is injected into the pressurized waste stream, and the air/liquid mixture is preheated to the required reactor inlet temperature.

The reactor provides sufficient retention time to allow the oxidation to approach the design reduction in chemical oxygen demand (COD). Oxidation reactions, being exothermic, produce a temperature rise in the reactor making the reactor outlet temperature higher than the inlet temperature. This temperature differential allows for the recovery of heat from the hot reactor effluent by preheating the feed to the reactor.

Generally, sufficient preheat can be added by cooling the hot reactor effluent in a feed/effluent heat exchanger to make the process thermally self-sustaining. Autothermal operation can be attained with a heat release of as little as 210 kJ/liter (750 BTU/gal) of liquid. The thermal efficiency of the system is the result of operating at an elevated pressure where the heat of vaporization can be recovered when steam recondenses during cooling of the hot reaction products.

In most cases, there is more thermal energy available than is required for preheating the reactor feed. After heating the reactor feed, the reactor effluent usually requires further cooling before discharge.

After cooling, the final step is to reduce the pressure of the reactor effluent stream and separate the vapor and liquid. The liquid is typically discharged to a biological treatment plant for final polishing.

III. Spent Caustic Characteristics

Spent caustic derived from scrubbing ethylene gas typically contains a range of various components, as shown in TABLE 1. The exact composition of the spent caustic liquor will depend on the contaminants in the ethylene gas being scrubbed which, of course, is dependent on a number of factors such as feed stock, furnace operating condition, etc.

TABLE 1 - Typical Olefin Spent Caustic Components

NaHS	0.5% - 6%
Na ₂ CO ₃	1% - 5%
NaOH	1% - 4%
NaSR	0% - 0.2%
Soluble Oil	50 - 200 ppm
Benzene	20 - 100 ppm

In addition to soluble components, insoluble polymers resulting from the condensation of olefins during scrubbing are present in the liquor. These insoluble polymers have a lower specific gravity than the spent caustic and can be removed from the spent caustic stream by gravity separation and decanting from a quiescent tank or separator.

IV. Wet Air Oxidation Design Variables

The primary variables considered in the design of a wet air oxidation system are as follows:

- * reactor temperature
- * reactor pressure (function of reactor temperature)
- * hydraulic detention time
- * oxygen partial pressure

Of these variables, the degree of oxidation is most sensitive to temperature. A higher degree of oxidation is achieved as the temperature is increased.

The system pressure is directly related to the system temperature and the air rate. The system is pressurized to control evaporation. As temperature and/or air rate increase, the required system operating pressure will increase.

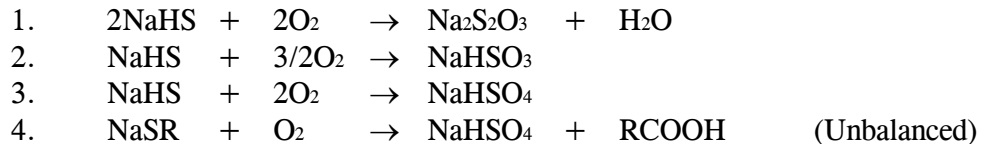
The hydraulic retention times of between 45 and 90 minutes are typical of wet air oxidation system designs with operating temperatures above 150°C (302°F). At lower operating temperatures, longer retention times are typically required. Under these conditions, only sulfide oxidation can reasonably be achieved, and the retention time will be dependent on the total sulfur oxygen demand. Increasing retention time will positively affect the degree of sulfide destruction (oxidation) at these low temperatures.

The degree of sulfide oxidation is also affected by the oxygen transfer rate from the gas to the liquid phase which is strongly dependent upon the solubility of oxygen in the liquid which, in turn, is a function of the system temperature and system oxygen partial pressure. The oxygen solubility decreases with increasing temperature to a minimum value near 100°C (212°F), then increases with increasing temperature to an infinite value at 374.1°C (705.4°F), the critical point of water¹. The oxygen solubility is also affected by the oxygen partial pressure, which is a function of the system pressure and the oxygen concentration in the gas phase. Therefore, the oxygen partial pressure can be increased at a given system temperature by increasing system pressure or gas phase oxygen concentration. As discussed above, the wet air oxidation system pressure increases as the temperature increases. This results in higher oxygen partial pressures at a given gas phase oxygen concentration. This increase in oxygen partial pressure will increase the oxygen transfer rate to the liquid phase. To attain the same level of oxygen partial pressure, a wet air oxidation system operating at a lower temperature, 150°C (302°F), will require approximately 200 percent of the stoichiometric oxygen in the gas phase compared to a system operating at 200°C (392°F) which would require a gas phase oxygen concentration of approximately 120 percent of the stoichiometric amount.

Monitoring and maintaining sufficient residual oxygen assures that treatment is taking place. As an instrumentation standard, Zimpro always provides an on-line oxygen analyzer to allow easy monitoring of residual oxygen levels in the off gas from the system. The response of the oxygen analyzer is quite rapid. Typically, a change in residual oxygen will be seen within a few minutes, reflecting a change in feed characteristics. When operating a system on spent caustic, residual oxygen indication will quickly tell if the oil/polymer layer in the feed tank is being pulled into the pump inlet. The change in COD between the spent caustic and the polymer layer is very large and this difference is quickly seen in terms of reduced residual oxygen.

V. Wet Air Oxidation Affects on Spent Caustic

The reactions associated with the oxidation of sulfide species in wet air oxidation are as follows:



The reactions above express sulfides in the form of sodium bisulfide (NaHS). It has generally been assumed that the existence of NaHS and sodium hydroxide (NaOH) are mutually exclusive. It has been erroneously assumed that if any free NaOH was present, there would be no bi-sulfide (HS^-) and that the oxidation of sulfide would produce sodium sulfate (Na_2SO_4), a neutral salt. However, as indicated in Reactions 1, 2 and 3, all of the sulfide can be assumed to exist as NaHS and the end product of oxidation is acid bi-sulfate.

The presence of $[\text{HS}^-]$ in alkaline solutions as the predominant species is borne out by work done by Myers² in 1986 and corroborated by further work done by Schoonen and Barnes³ in 1987. The conclusion of these two research efforts was that the pK_2 value for H_2S was on the order of 17 and that, for all practical purposes, all sulfide in alkaline solutions can be assumed to exist as $[\text{HS}^-]$.

In general, reactions 1 and 2 can be achieved at very low temperatures and is the primary product of low temperature oxidation systems. Reactions 3 and 4 are generally limited to medium temperature systems where all reduced sulfur is converted to sulfate.

With low temperature systems operating at 150°C (302°F) or less, the effluent will contain thiosulfate, sulfite and sulfate as the oxidation products. Increasing temperature, retention time, and oxygen partial pressure will tend to increase the percentage of reduced sulfur converted to sulfate and correspondingly reduce the amount of thiosulfate and sulfite produced.

The extent of oxidation of the organic fraction of the spent caustic will typically be very small in lower temperature systems. At higher temperatures, such as employed in the medium temperature range, 190°C (374°F) and above; an organic COD reduction of approximately 50 percent or greater can be achieved.

VI. Materials of Construction

Selection of correct metallurgy is a very important consideration in the design of a wet air oxidation system. Zimpro has done extensive metallurgical testing on ethylene derived spent caustic and, based on this work, will typically recommend a high nickel alloy for construction of wet air oxidation systems operating at or above 150°C (302°F).

At lower temperatures, carbon steel has been used successfully as a material of construction. At these lower temperatures, carbon steel can be protected from oxidation despite substantial quantities of gaseous oxygen present in the system. This is due to the powerful oxygen scavenging properties of sulfide which keeps dissolved oxygen levels near zero.

Alkalinity is often an overlooked parameter in spent caustic oxidation system design. As shown in Reaction 3 of Section V, the oxidation of bi-sulfide results in the formation of bi-sulfate with an available free hydrogen ion. It is necessary to have the equivalent of one mole of NaOH per mole of NaHS oxidized to prevent the oxidized effluent pH from becoming acidic.

Ethylene derived spent caustic will have varying amounts of alkalinity depending on the operation of the caustic wash tower. However, it is possible to have a spent scrubbing liquor which has sufficient alkalinity to adequately scrub the ethylene gas, but not enough alkalinity to buffer the acid formed during oxidation. As an operational parameter, alkalinity in the spent caustic must be monitored and maintained to assure that the pH of the oxidized spent caustic remains alkaline. In general, the materials of construction that are used for these wet air oxidation systems are not necessarily resistant to corrosion under acid conditions especially in the presence of chloride ion.

As mentioned, carbon steel has been successfully used as a material of construction for low temperature systems. In general, at low temperatures, the primary product of oxidation is thiosulfate (Reaction 1, Section V), which does not consume alkalinity. However, with carbon steel installations, especially those designed for higher conversions of sulfide to sulfite or sulfate, alkalinity should be closely followed to avoid any problems with rapid corrosion due to acid attack.

VII. Low Temperature Oxidation of Spent Caustic

Low temperature wet air oxidation systems for spent caustic are generally designed to operate at temperatures at or below 150°C (302°F). Under these conditions, the oxidation of sulfide to a combination of thiosulfate and sulfate can be achieved. A factor in the degree of sulfide oxidation achieved with low temperature systems is the transfer of oxygen from the gas to liquid. Oxygen transfer can be enhanced by increasing temperature, pressure, and detention time. This change usually results in improved conversion of sulfides to sulfate.

A low temperature design is generally considered when the impact of thiosulfate and/or COD associated with treated spent caustic is less critical. A low temperature design is used to reduce the capital investment. The design conditions associated with low operating temperature allow for savings on piping, pressure vessels, and equipment.

Operational costs for a low temperature system can be higher than the costs associated with systems operating at higher temperatures, i.e. 200°C (392°F). The higher operating cost is due to the substantial increase in air required to meet the oxygen partial pressure needs of the system. At lower operating temperatures, the air requirement can be on the order of 200 percent to 300 percent of the stoichiometric oxygen requirements. Even though pressures are lower, the cost of compressing the additional air increases the power cost.

A flow diagram for the low temperature spent caustic treatment system currently in operation at Phillips Petroleum Company, Sweeny, Texas is shown in FIGURE 2. This system is designed to operate at caustic flow rates between 7.2 m³/hr. and 14.4 m³/hr. (32 and 64 gpm) at a temperature of 150°C (302°F) and a pressure of 690 kPa (100 psig). The system went on-line in July, 1993 and has been processing spent caustic since that time. The effluent has consistently met required sulfide performance since start-up.

As shown in FIGURE 2, the centrifugal feed pump and air compressor supply the spent caustic and air at pressure to the system. This caustic/air mixture enters the cold side of the heat exchanger. The mixture is heated by the reaction products on the hot side of the heat exchanger that have exited from the reactors. After exiting the heat exchanger cold side, the heated caustic air/mixture enters the first of two in a series of reactors. This series design is used to prevent short circuiting of the caustic liquor. Temperature control during start-up and low spent caustic strength instances is accomplished by injecting steam into each of the reactors.

After the reaction products leave the heat exchanger, they enter a separator/cooler where the gas and liquid phases are separated. The gas phase passes through a packed water column where it is cooled with water and then through the pressure control valve which reduces the pressure. The gas is sent to the plant's central vent gas treatment system for final disposal. The oxidized liquor discharges from the separator/cooler through a level control valve and is mixed with hydrochloric acid for pH adjustment in an in-line static mixer. After the pH adjustment, the oxidized liquor is then sent to the plant's wastewater treatment system for biological treatment.

TABLE 2 shows the measured performance from the Phillips Petroleum installation and illustrates typical results of low temperature treatment of a relatively weak spent caustic. Of the twelve ethylene spent caustic systems designed by Zimpro, this application represents a comparatively low strength spent caustic. Note that the oxidation of sulfide was virtually complete in terms of comparing feed and effluent sulfide levels. However, the percentage of sulfide converted to sulfate was about 73 percent with the remainder being thiosulfate and sulfite. These values have been corrected for the dilution affect of the steam added to the reactors.

**TABLE 2 - Wet Air Oxidation of Spent Caustic at 135°C (275°F)
Phillips Petroleum Company, Sweeny, Texas**

	Feed to System	Effluent from System
NaHS-S (mg/l)	4,031	< 2*
Na ₂ S ₂ O ₃ -S (mg/l)	< 224*	959
Na ₂ SO ₃ -S (mg/l)	< 64*	204
Na ₂ SO ₄ -S (mg/l)	< 55*	2,940

* Detection limit for analysis

VIII. Medium Temperature Oxidation of Spent Caustic

Medium temperature oxidation systems for spent caustic are generally designed to operate at temperatures above 190°C (374°F) and are applicable when the treatment requirements are stringent in terms of reducing COD and/or thiosulfate. At these operating conditions, oxygen partial pressure is no longer a major issue and virtually complete oxidation of sulfide to sulfate is achieved, including the breakdown of mercaptides. This level of treatment can be accomplished with a retention time of one hour and a minimum of excess air being fed to the system.

The medium temperature system has a similar flow scheme to the low temperature system except only one reactor vessel is used. Also, a trim heater utilizing low pressure steam is used for preheat rather than directly injecting steam. Direct injection of steam can be applied, but higher system pressures would require the use of high pressure steam. Considering that high pressure steam is inherently more valuable than the low pressure steam, the use of a heat exchanger rather than direct injection for preheating is usually desirable.

The major advantage that the medium temperature system offers is that virtually all the sulfur-based COD is oxidized. Additionally, a substantial amount of organic oxidation takes place in that 75 percent of the oils and phenol are oxidized. The resultant liquor is then easily treated biologically after pH adjustment. Also, as previously mentioned, lower operating costs can be expected as compared to a low temperature system.

A simplified flow diagram of a medium temperature system (one of three trains) currently in operation at Chinese Petroleum Corporation (CPC), Kaohsiung, Taiwan is shown in FIGURE 3. This is the first wet air oxidation installation for treating spent caustic in Taiwan. The installation consists of three wet air oxidation trains designed to treat spent caustic from CPC's Number 2 and Number 5 Naphtha Crackers. The system operates at a temperature of 200°C (392°F) and pressure of 2760 kPa (400 psig). Each system has the capacity to treat 5.67 m³/hr (25 gpm) of spent caustic.

There are three feed tanks for the wet air oxidation system which were provided by CPC. Each tank can be individually filled with spent caustic from the scrubbing towers while a previously filled tank is being processed by the wet air oxidation system. This arrangement allows for each tank to phase separate before processing. As previously discussed, there is a polymer layer which will rise to the top of the tank forming a layer above the spent caustic. The tanks have decant taps to allow periodic removal of the polymer layer.

The spent caustic from the storage tanks is pumped up to system pressure by the combination of a centrifugal transfer pump and high pressure pump. At the discharge of the high pressure pump, air from the process air compressor is injected into the pressurized spent caustic stream.

The spent caustic/air mixture is passed through the feed/effluent heat exchanger and trim heater where it is preheated prior to entering the reactor. Under normal conditions, the total preheat required is added in the feed/effluent heat exchanger while cooling the hot reaction products exiting from the reactor. Low pressure steam is applied to the shell of the trim heater for preheat during start-up and during periods of low feed COD.

The heated spent caustic/air mixture enters the reactor vessel. The bulk of the oxidation takes place in the reactor which raises the temperature of its contents to the operating temperature of 200°C (392°F). The hot reaction products are passed back through the feed/effluent heat exchanger where they are partially cooled while preheating the incoming spent caustic/air mixture.

Final cooling of the reactor effluent is accomplished in the reactor effluent cooler prior to the pressure control valve. After being depressurized, the oxidized liquor enters the separator where the gas is disengaged from the liquid. The vapors are passed through a direct contact cooler and finally through a caustic scrubber. The caustic scrubber was required by CPC to ensure that there would be absolutely no sulfide emissions even under upset conditions. Based on operational experience, CPC has now determined that caustic scrubbers were not necessary.

The oxidized liquor is neutralized in the separator by adding concentrated sulfuric acid with a metering pump on pH control. The separator contains an agitator to ensure good mixing. The liquor from the separator is passed through a plate heat exchanger prior to final discharge to remove any added heat of neutralization.

The system went on line in late November of 1990 and has been in continuous operation since then. The oxidized liquor has been monitored closely because the refinery had been facing strong public protests stemming from odors. The elimination of sulfide odors associated with the ethylene spent caustic is critical to the refinery's continuing operation. Since start-up, the sulfide content of the oxidized liquor has always been below 1 mg/l. In addition to the elimination of the sulfides, greater than 90 percent of the spent caustic's soluble oil content has been oxidized producing an effluent that is water clear. The influent and effluent analysis are shown in TABLE 3.

**TABLE 3 - Wet Air Oxidation of Spent Caustic at 202°C (396°F)
Chinese Petroleum Corporation, Kaohsiung, Taiwan**

Na ₂ S*	3.48%	< 1.0 mg/l**
NaSR	0.64%	< 0.5 mg/l**
Na ₂ S ₂ O ₃	---	92.0 mg/l
Oil	168.0 mg/l	7.0 mg/l

* Sulfide was expressed as Na₂S per CPC convention.

** Below detection limit

After three years in operation, CPC has never experienced heat exchanger fouling or coking due to organic deposits. However, after about 28 months of operation, the feed/effluent heat exchanger required cleaning to remove a calcium carbonate scale which built up over time on the cold side. This scale results from the plant water used during start-up. The high pH of the spent caustic should sufficiently soften and eliminate any inorganic fouling tendencies.

IX. Conclusion

The two full scale wet air oxidation systems described in this paper effectively treat olefin derived spent caustic. Yet, the design of each system is quite different in terms of operating temperature, operating pressure and reactor configuration, among others.

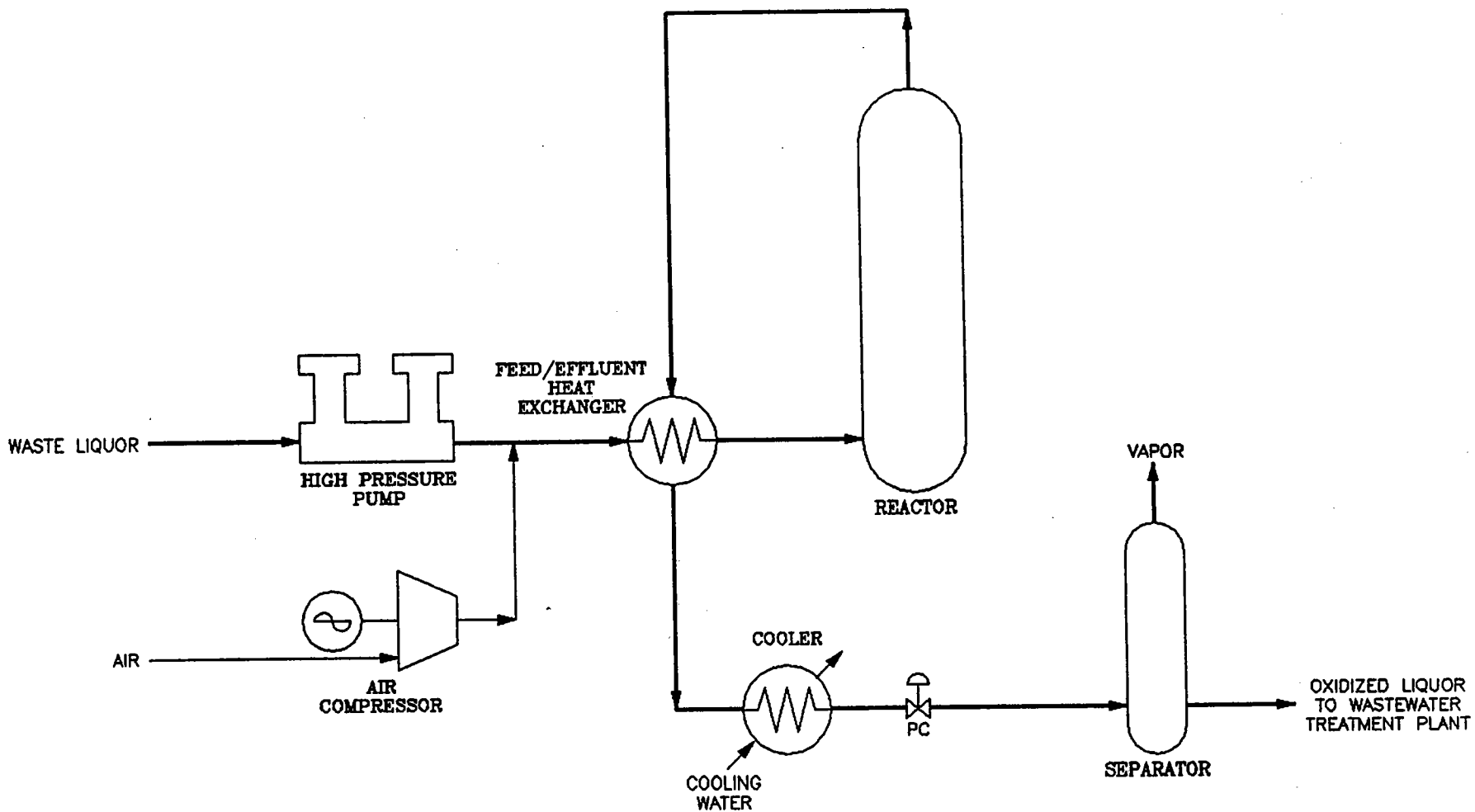
With full scale implementation of wet air oxidation for treatment of spent caustic, various design options can be considered. Optimal system design should account for a number of factors including variation in spent caustic characteristics and the level of treatment required prior to discharge. These variables have significant impact on design and affect critical design parameters such as materials of construction. A well designed system ensures that spent caustic is thoroughly treated regardless of plant feed stock and operational variations.

The focus of an olefin plant should be manufacturing a product, not dealing with waste treatment difficulties. As proven by full scale application, a properly designed wet air oxidation system provides effective, reliable, long term treatment of spent caustic.

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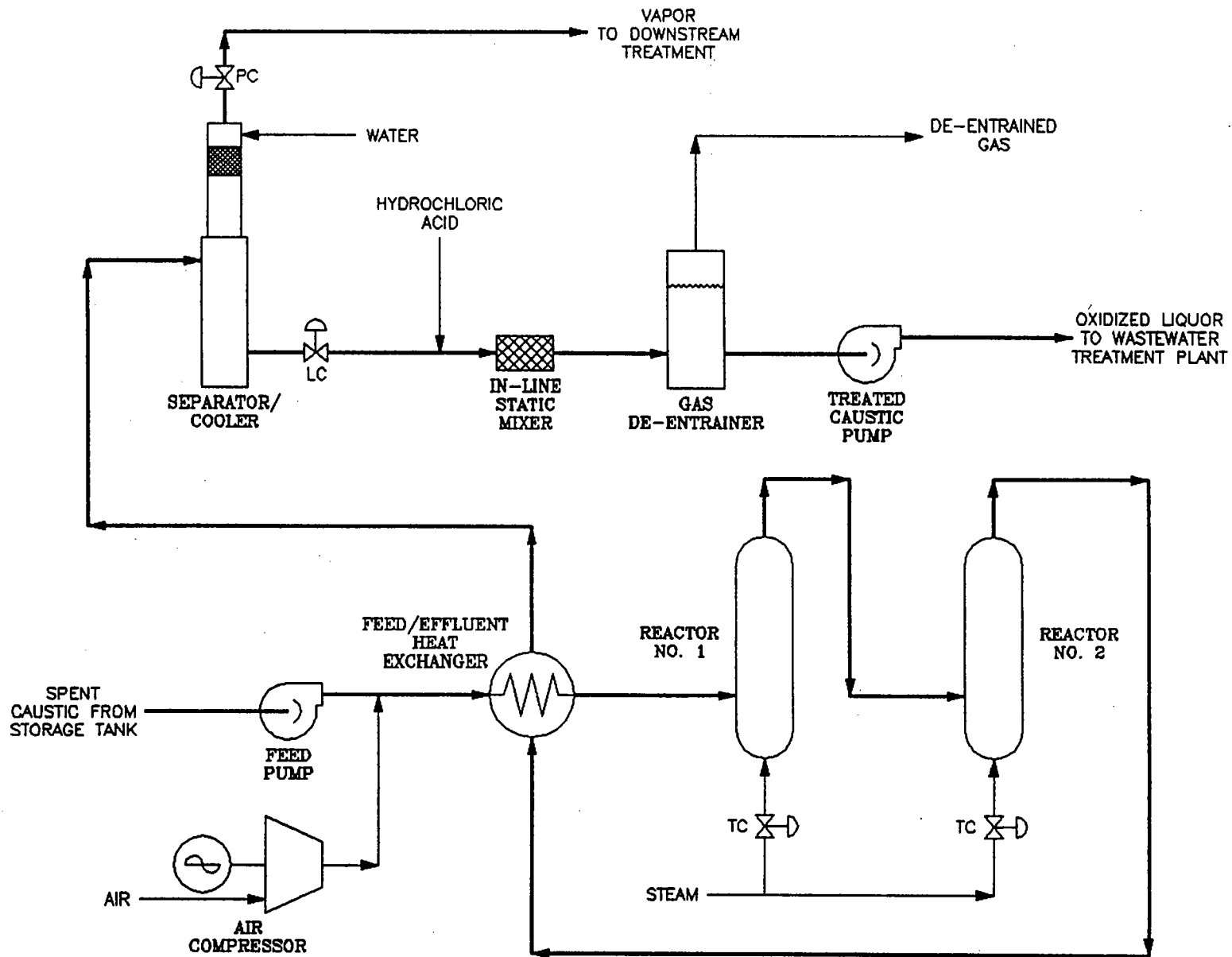
PROCESS FLOW DIAGRAM TYPICAL WET AIR OXIDATION SYSTEM



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FIGURE 1

PROCESS FLOW DIAGRAM PHILLIPS 66 PETROLEUM – SWEENY, TEXAS



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FIGURE 2

PROCESS FLOW DIAGRAM CHINA PETROLEUM CORPORATION (CPC), KAOHSIUNG, TAIWAN

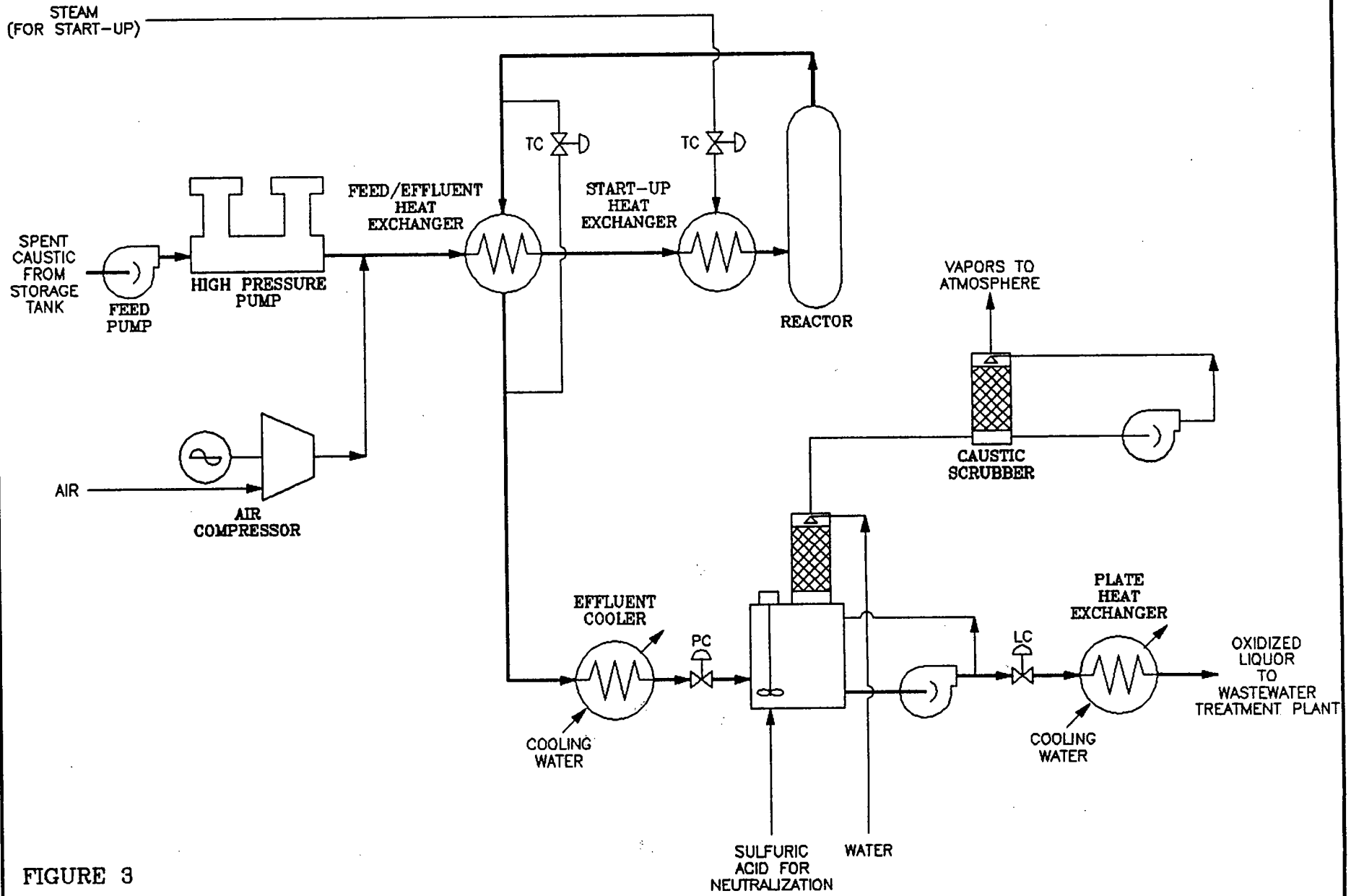


FIGURE 3