The Wet Oxidation Process:

Wet oxidation is the oxidation of soluble or suspended components in water using oxygen as the oxidizing agent. When air is used as the source of oxygen the process is referred to as wet air oxidation (WAO).

The oxidation reactions occur at temperatures of 150º C to 320º C (275º F to 608º F) and pressures from 10 to 220 barg (150 to 3200 psig).

Typical Wet Oxidation Reactions

The process can convert organic contaminants to carbon dioxide, water and biodegradable short chain organic acids. Inorganic constituents such as sulfides and cyanides can also be oxidized. Wet oxidation can involve any or all of the following reactions:

Organics + O₂ → CO₂ + H₂O + RCOOH*
Sulfur Species + O₂ → SO₄²⁻
Organic Cl + O₂ → Cl⁻ + CO₂ + RCOOH*
Organic N + O₂ → NH₃ + CO₂ + RCOOH*
Phosphorus + O₂ → PO₄³⁻

*short chain organic acids such as acetic acid make up the major fraction of residual organic compounds
The wet oxidation process can pretreat difficult wastewater streams, making them amenable for discharge to a conventional biological treatment plant for polishing.

The process is also used for oxidation of contaminants in production liquors for recycle/reuse.
Common wet air oxidation applications include:

- treatment of high strength wastewater,
- including spent caustic streams generated by ethylene crackers and refineries in-process,
  - for treatment and recycle/recovery of process liquor streams
  - biological sludge conditioning and destruction.

Wet oxidation has historically been used for municipal wastewater sludge applications.

- At lower temperatures and pressures, sludge is conditioned to improve dewatering. This is referred to as Low Pressure Oxidation (LPO). At higher temperatures and pressures, biological sludge can be destroyed, as an alternative to incineration.

Features and Benefits

- Pretreatment of high strength wastewater to produce biodegradable residual organics
- Destruction of specific compounds
- Elimination of toxicity or reactivity
- Process liquor treatment for recycle/recovery
- Gross reduction of Chemical Oxygen Demand (COD)
Spent caustic liquors typically come from:
ethylene production - from the scrubbing of cracked gas with aqueous sodium hydroxide
oil refining - from the extraction or treatment of acidic impurities, such as hydrogen sulfide, mercaptans and organic acids in hydrocarbon streams.

These spent caustic streams are a significant odor source as well as disruptive to the operation of a biotreatment facility. In addition, the Chemical Oxygen Demand (COD) load in spent caustic is usually very high (10,000 - 100,000 mg/l), and the contaminants in spent caustic typically include sodium carbonate, sodium sulfides, mercaptans, phenols, and emulsified hydrocarbons.

**Wet air oxidation is commonly used for treating spent caustics.**

Depending upon specific contaminants and treatment objectives, spent caustic wet air oxidation systems can be divided into three ranges of operation:

**Low temperature (<150°C):** Achieves partial oxidation of sulfides to both sulfate and thiosulfate. Applicable for dilute sulfidic caustics when thiosulfate is not a concern for downstream treatment.

**Medium temperature (approx. 200°C):** Achieves complete oxidation of sulfides to sulfate. Also destroys mercaptans. Commonly used for sulfidic ethylene spent caustic treatment.

**High temperature (approx. 260°C):** Achieves complete oxidation of sulfides and mercaptans, plus destruction of organic contaminants such as cresylic acids. Applied to refinery spent caustics.
Wet oxidation treatment can be used to treat high strength waste streams in order to make them more suitable to conventional treatments such as biological polishing, or as pretreatment for product recovery.

Wet oxidation destroys the large molecules in waste (e.g., phenol), converting them predominantly to carbon dioxide with some formation of low weight carboxylic acids such as acetic acid, which is highly biodegradable.

The effect of this treatment is to condition a waste that is: toxic / reactive / refractory to biotreatment / or hazardous into a waste readily suitable to biological treatment. Wet oxidation also achieves a gross reduction of the waste Chemical Oxygen Demand (COD), and reduces loading to any downstream treatment process. In addition to waste destruction, wet oxidation can be used for chemical recovery by oxidation of organic contaminants.
Wet air oxidation for the treatment of sludge, from conditioning for dewatering, to complete volatile solids destruction. Sludge applications of wet air oxidation technology include:

- **Sludge Conditioning**: Low pressure/temperature oxidation is used for sludge conditioning to allow for dewatering.

- **Sludge Destruction**: At higher temperatures, volatiles in sludge can be destroyed.

  - **Wet Air Regeneration**: Wet air oxidation is used in conjunction with the PACT® system for both regeneration of carbon and destruction of biological sludge.