Introduction

Caustic Soda solutions are produced as a co-product with Chlorine electrolytically by three technologies: mercury cells, membrane cells, and diaphragm cells. Each of these processes utilize NaCl salt as the primary raw material. The salt is electrolytically split using direct current (DC) electricity, resulting in Chlorine and an available sodium ion (Na+) that is reacted with water in the cell to make Caustic Soda and by-product Hydrogen. The hydrogen by-product produced is used as a fuel source, sold to hydrogen customers, or to produce high purity (burner grade) Hydrochloric Acid. A fourth technology that produces commercially available quantities of Caustic Soda solutions is a chemical conversion of trona ore. This process produces low quality Caustic Soda, used primarily by west coast consumers.

Following is a brief discussion of the three electrochemical processes that are dominant in Caustic Soda production in North America.

Mercury Cell / Rayon Grade

Approximately 13% of electrolytically produced Caustic Soda in North America is produced by this process.

The mercury cell operation utilizes mercury as the cathode for the electrolytic reaction, as well as for the sodium amalgam that is reacted to deionized water to produce the Caustic Soda solution. There is essentially no net consumption of mercury in process, as all cells are 'closed loop' with regards to mercury flow across the bottom of the cell and through the cell decomposer, where the amalgam is reacted to Caustic Soda solution. The solution produced by this process is 50 - 52% by weight NaOH, produced directly from the cell without any additional evaporation. This process produces the highest purity Caustic Soda commercially available.

The high purity characteristic is descriptive of the very low concentrations of contaminants in the product. Salt, or NaCl, is typically less than 10 ppm, with a maximum of 30 ppm. Sodium Chlorates, or NaClO3, are typically 0.5 ppm, with a maximum limit of 1 ppm. Sodium Carbonates, or Na2CO3, are typically 0.02 weight %, with a maximum limit of 0.06 weight %. Sodium Sulfates, or Na2SO4, are typically 10 ppm, with a maximum of 20 ppm.

The mercury cell produced Caustic Soda is typically referred as Mercury Cell Grade, or more commonly, Rayon Grade. Most production of rayon fiber is dependent on the availability of the high purity Rayon Grade Caustic Soda solution. Another very common use of this high purity caustic solution is for DI water exchangers. The DI unit resin literature often specified Rayon Grade Caustic Soda only for regeneration. One must remember that this literature was published prior to the availability of membrane cell produced solutions.

Total equivalent energy, on a DC basis, needed to produced Caustic Soda via the mercury cell process is approximately 3600 kWh per metric ton.
Diaphragm Cell

Approximately 71% of electrolytically produced Caustic Soda in North America is produced by this process.

This process utilizes asbestos, or alternate substitutes to asbestos, to separate the co-products Caustic Soda and Chlorine. The production of 50% Caustic Soda occurs primarily outside of the electrolytic cell. The diaphragm cell produces a very weak 'cell liquor,' which contains 12-14%, by weight, NaOH and roughly the same concentration NaCl salt. The 'cell liquor' is subsequently evaporated in a three or four 'effect' evaporation process to a final nominal concentration of 50% NaOH by weight (49-52% range). The excess salt is precipitated and filtered through the evaporation process for subsequent reuse/recycle. This process produces the lowest quality electrochemical Caustic Soda solutions.

The quality considerations with respect to the diaphragm cell produced Caustic solutions include relatively high salt, chlorates, carbonates, and sulfates. Salt, as NaCl, concentrations are typically 1.0%, with maximums ranging from 1.1 to 1.3 weight %, depending on producer. Sodium Chlorates are typically 0.15 weight %, with a maximum of 0.3 weight %. Sodium Carbonates are typically 0.1 weight %, with a maximum of 0.2 weight %. Sodium Sulfates are typically 0.01 weight %, with a maximum of 0.02 weight %.

The diaphragm cell produced Caustic Soda is often referred to as Diaphragm Cell Grade. It is also called Commercial Grade, Technical Grade, and occasionally Technical Diaphragm or other similar combinations.

An additional 'grade' of Caustic Soda produced by the diaphragm cell process is the Purified Grade. The production of Purified Grade involves the further evaporation of the 50% Diaphragm Grade Caustic Soda solution to reduce the salt concentration. The higher Caustic Soda concentration forces precipitation of the salts, which are soluble in Caustic Soda solutions in an inverse relationship. The higher concentration solution is then re-diluted to the 50% concentration that is commercially available as Purified Grade Caustic Soda.

Common uses include process and wastewater neutralization, textiles production, soaps and detergents and aluminum production. These uses and applications generally will refer to the Caustic Soda as any of the various grades previously addressed, dependent on supplier's terminology.

Total equivalent energy, on a DC basis, needed to produce Caustic Soda via the diaphragm cell process is approximately 5000 kWh per metric ton.
Approximately 13% of electrolytically produced Caustic Soda in North America is produced by this process.

The membrane cell process utilizes a selective membrane that separates the Chlorine and Sodium ions. The membrane allows the Sodium ion to 'migrate' across the membrane while keeping the Chlorine gas and salt (brine) solution in a compartment on the other side of the membrane. The Sodium ion is reacted with purified water as in the mercury cell to produce the Caustic Soda. The solution produced by the membrane cell process is nominally 33-35 weight %. Evaporation is utilized, as in the diaphragm process, to raise the concentration up to the nominal 50 weight % solution suitable for shipments. The salt concentrations are not concentrated as significantly in this evaporation process due to the selective osmotic nature of the membranes as well as the reduced amount of evaporation required in this process as opposed to the diaphragm evaporation. Minute quantities of salt do migrate across the membrane, concentrating up to the maximum 75 ppm. Note that other producers employing the membrane cell technology may have a higher maximum limit of 100 ppm on the allowable salt concentration in the Caustic Soda solution.

The high purity characteristic is descriptive of the low concentrations of contaminants in the product. Salt, or NaCl, is typically less than 30 ppm, with a maximum of 75 ppm. Sodium Chlorates, or NaClO3, are typically 3 ppm, with a maximum limit of 5 ppm. Sodium Carbonates, or Na2CO3, are typically 0.03 weight %, with a maximum limit of 0.05 weight %. Sodium Sulfates, or Na2SO4, are typically 15 ppm, with a maximum of 20 ppm.

The Caustic Soda produced by the membrane cell process is most commonly referred to as Membrane Grade. Total equivalent energy, on a DC basis, needed to produce Caustic Soda via the membrane cell process is approximately 3360 kWh per metric ton.