Chlor-Alkali

1. Chlor-Alkali

The chlor-alkali industry consists of the production of three inorganic chemicals: caustic soda (NaOH), chlorine ($Cl2$) and soda ash ($Na2CO3$). Caustic soda and chlorine are produced simultaneously while soda ash is produced during a different process. Hence, this chapter on chlor-alkali is divided in two parts; the first part discusses potential energy savings in the production of caustic soda and chlorine, and the second part focuses on potential energy savings in the production of soda ash.

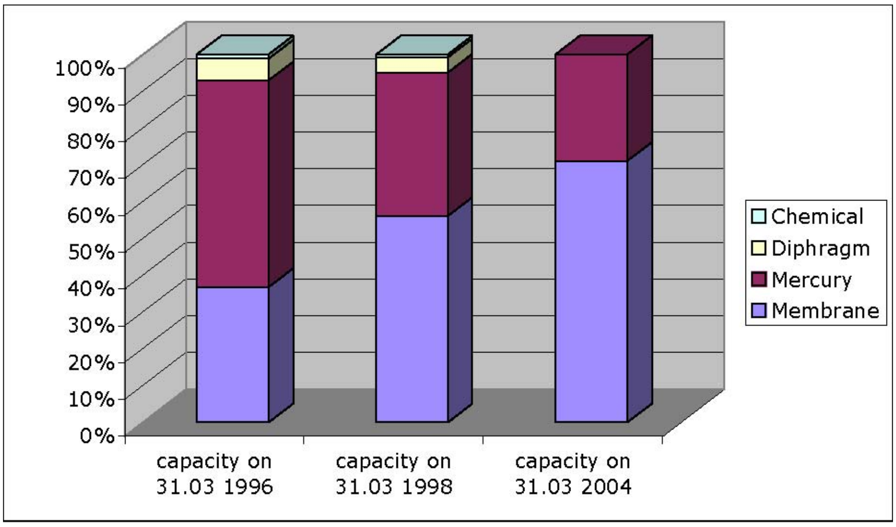
1.1 Caustic Soda and Chlorine Production in India

1.1.1 Caustic Soda and Chlorine Industry Characteristics

The caustic soda industry in India is approximately 65 years old. There are 40 major caustic soda plants with an average plant size of 150 tons per day (TPD), which is relatively small compared to sizes found in developed countries (500 TPD). Five largescale caustic soda units have been commissioned since 1997. During the last 8 years, caustic soda has increased at an average annual growth of 4%. Production of Caustic Soda during the year 2003-2004 was 1,741 thousands of MT.

The production of caustic soda is associated with chlorine. This inevitable co-production has been an issue for the chlor-alkali industry. Both products are used for very different end uses with differing market dynamics and it is only by rare chance that demand for the two coincides. The Indian chlor-alkali industry is driven by the demand for caustic soda, and chlorine is considered a by-product.

Figure 6-1. Process-wise share of installed capacity of caustic soda



Source: AMAI, website 2004.

Over the last 8 years, India has undergone a major change in its process to produce caustic soda and chlorine. In 1996, the majority of the installed capacity used the mercury process (56%). Today India produces 71% of its caustic soda through the membrane process, and 29% through the mercury process. However, unlike most developed countries where mercury cells have been given a specified period to close down, no such timeframe has been stipulated by the Indian government.

1.1.2 Energy Consumption

The raw material necessary in the production of caustic soda consisting of salt and water is abundant and inexpensive. Conversely, the electrical energy required to process salt into caustic soda and chlorine is expensive and occasionally unreliable. Energy costs represent 50 to 65% of the total cost of production.

Table 6-1 shows the final energy consumption in GJ per tonne of caustic soda during different production phases. The electrolysis phase is the most energy intensive. The process necessitates large quantities of direct current (DC) electric power that is usually obtained from a high voltage source of alternative current through a rectifier and involves energy losses. The mercury cell has a higher decomposition voltage and therefore requires more power than the diaphragm and membrane cells. However, the thermal energy requirement is null in the mercury process as the caustic soda solution formed is highly concentrated (50%). The diaphragm process results in a caustic soda solution with a much lower concentration of around 10%, and thermal energy is needed to evaporate and concentrate the solution to 50%. The membrane cells produce a solution of about 3035%, requiring less thermal energy. However, the additional thermal energy requirement is not always necessary as highly concentrated caustic soda need not always be produced.

Table 6-1. Specific Energy Consumption for Manufacturing Caustic Soda Lye*

	Diaphragm (1994)	**Mercury (1999)**	**Membrane (1999)**
Power Consumption (kWh/t of NaOH)			
DC Power	2561	2833	2342
AC/DC losses	107	160	104
Auxiliary	457	307	254
Thermal energy for evaporation	942		148
Total	4067	3300	2848
***total in GJ/t* of NaOH**	***14.64***	***11.88***	***10.25***

*Source: TERI. *sodium hydroxide in aqueous solution with a concentration of 48,5%*

Table 6-2 shows the specific final energy consumption in GJ per ton of caustic soda produced over the last 20 years. As can be observed, major progress in energy consumption per unit of caustic soda product has been achieved over this period. This has been the result of various technological improvements within each type of technology and other factors such as larger sized units.

Table 6-2. Caustic Soda Specific Energy Consumption (in GJ/t of NaOH)

	1982	**1992**	**1994**	**1999**
Diaphragm				
Final energy	21.25	14.04	14.64	-
Primary energy	53.92	35.62	37.14	
Mercury				
Final energy	13.16	15.55	12.36	11.88
Primary energy	39.48	46.66	37.07	35.64
Membrane				
Final energy	-	11.65	10.64	10.25
Primary energy			30.85	29.69

Source: TERI
Note: Primary electricity calculated using an electricity conversion efficiency of 33%.

During the last 10 years, production has shifted to membrane cell technology. This shift, combined with technology improvements in mercury and membrane cell processes and energy conservation programs intended to reduce auxiliary and rectifiers' energy consumption, has resulted in an estimated overall energy savings of more than 10% (Table 6-3).

Table 6-3. Evolution of Indian Average Specific Energy Consumption

Average consumption	1990-91	1994-95	1999-00
kWh/t	3,351	3,130	2,977
GJ/t	12.06	11.27	10.74

Source: GOI, Ministry of Environment and forests and Teri.

This compares favorably with US specific energy consumption of about 16.8 GJ/t (Worrell et al., 2000) Since electricity is the most important form of energy required in the process of caustic soda production, we have also indicated the specific primary energy requirement. The primary energy includes the energy necessary to produce electricity. Almost all of the energy requirement for the mercury process is electricity, which worsens its specific primary energy consumption compared to the other processes.

1.1.3 Future Development of the Caustic Soda and Chlorine Industry

1.1.3.1 Ongoing Changes in the Caustic Soda and Chlorine Industry

As mentioned earlier, the Indian domestic market is driven by the demand for caustic soda rather than the demand for chlorine. Because of the inevitable co-production of both products, European and North American markets are characterized by caustic soda surpluses. As India needs and imports this product, it is argued that excess production from abroad is dumped in India. In contrast, chlorine is a very hazardous product which is very dangerous to transport, meaning that export of chlorine from India to the rest of the world is difficult.

This report focuses on analysis of energy consumption in the chlor-alkali industry. However, it is worth noting that this sector is plagued with serious environmental issues. The mercury cell technology, besides consuming excessive power also causes mercury pollution. Some mercury is lost from the process to air and water and shows up in products and wastes.

1.1.3.2 Potential for Energy Efficiency Improvement

The type of process used in the production of caustic soda has a significant impact on the quantity of energy used. In that regard, India performs favorably compared to most of the industrialized countries. The geographic distribution of caustic soda processes differs noticeably worldwide. In Western Europe, the mercury cell process is still largely used, representing 55% of installed capacity, diaphragm cell process represents 22% and membrane cell process only 20%. In the US, diaphragm cell process predominates with 75%, and in Japan, it is the membrane cell process that covers 90% of installed capacity. India went from 37% of membrane cell capacity installed in 1996 to 71% in 2004 and as a consequence has significantly lower specific energy consumption. As seen earlier, the average specific energy consumption per tonne of caustic soda in India using mercury cells is about 11.88 GJ/t and about 10.25 GJ/t when using the membrane cells (**Table** 6-4).

Table 6-4. Comparison of Specific Energy Consumption across Technology (GJ/t NaOH)

	India (1999)	Best Practice New Plant India (2002-03)	Best Practice New Plant EU (2000)
Mercury cell	11.88		11.21
Membrane cell	10.25	8.91*	8.1

Source: TERI; IPPC, 2001, Indian Rayon Ltd.Note: Including energy used for the evaporation process to concentrate caustic soda solutionto 50%.
** We estimated the evaporation energy requirement for a 50% solution according to TERI's average data for membrane cell technology, conf Table 6-1.*

1.1.3.3 Categories of Energy Efficiency Improvement

Energy is used both as electricity and as heat. About half of the energy expended is converted into the enthalpy of the products. The rest is converted into heat transferred to the air in the building and the products, which have to be cooled. Energy savings are possible by redistributing the excess heat where it is necessary. Insulation of the cells and salt dissolvers reduce the need for ventilation of the cell room and increase the amount of heat transferable.

Adoption of membrane technology: energy savings by adopting membrane cell plants compared to mercury are about 1.3 GJ per ton of NaOH produced. Plus, the additional thermal energy requirement for the membrane process is not constantly necessary, as concentration of caustic soda is not always needed.

Installation of Advanced Cell Controls: Advanced instrumentation systems such as short circuit elimination, anode control and protection devices help to operate the cells at minimum gap, thereby reducing power requirements. The range of power savings obtained by these means is above 75 kWh/t. The cost of installating such control systems depends upon the intended version (i.e.

automatic, semi-automatic) and age of the plant. Realizing its importance as a potential energy saver, a few plants in the country have installed such advanced instrumentation systems and many others are intending to adopt them.

Conversion From Rubber Lined To Bare Bottom Configuration: Even today, many of the plants are still equipped with rubber lined cells, and hence there is scope for energy savings through their conversion to bare bottom orientation which will reduce millivolt drops and bus losses. This will reduce the cathodic mV drop to the tune of 40%.

Revamping Of Electrical Systems: Rectifier equipment is an important element on which power consumption depends. An old generation mercury-arc rectifier, if it exists, could be replaced with a newer generation silicon rectifier, which offers much better ACDC conversion efficiency. Installation of correct capacity rectifiers is essential, as under-utilization of its capacity reduces transformer losses.

Effective Utilization Of Hydrogen As Fuel: Hydrogen gas is produced as a by-product of caustic soda; it can be captured and used as a fuel in on-site power co-generation. The heat can be used for the evaporation of caustic soda and for the preparation of the brine. Moreover hydrogen is clean fuel. The use of by-product hydrogen gas can substitute up to 35% of the total fuel requirement in a caustic fusion plant.

Adoption Of Energy Efficient Chlorine Handling Systems: Considerable energy savings can be achieved by revamping chlorine compressors, refrigeration systems and avoiding inefficient capacity control practices such as hot gas bypass.

Other Alternatives: Alternatives other than those discussed above for energy savings in the chlor-alkali industry are wide ranging, and other methods that can be used effectively are listed below:

- Brine recycling up to 40% for retention of thermal energy.
- Direct hot lye pumping to concentrator plant for heat saving.
- Minimization of exposed surface area of clarifiers and lagging of the same for surface loss reduction.
- Modifications in brine pumping system to reduce the pumping power.
- Application of modern flat belts in place of conventional V-belts to reduce transmission losses.
- Application of energy savers in drives with varying duty and machine side capacity controls.
- Application of variables speed drives for energy efficient capacity control in varying duty fans and pumps.
- Effective insulation of pipelines carrying hot cell liquor at 85^{0}C from the cells to the evaporators to save about 0.3 tonne of steam per tonne of caustic soda.
- Controlling the water addition in the filters to save steam.

1.1.4 Scenarios of Future Energy Use

1.1.5 Future Trends In Energy Efficiency

New developments in the production of caustic soda are expected to emerge on the market in the near future. The current technology based on cell membrane process is a mature technology, from which no significant energy savings can result from further development without a change in the fundamental approach to chlor-alkali electrolysis. A new technology called Oxygen Depolarized Cathodes (ODC) is currently developed with substantial potential energy savings of around 440-530 kWh per ton of caustic soda (1.5 to 2 GJ final energy/t NaOH) (IPPC, 2000). The new approach consists in diffusing oxygen gas through the cathode and avoids the production of hydrogen. When the hydrogen-evolving cathode is replaced by an oxygen-consuming cathode, the voltage of the cell could be reduced, in principle, by about 0.9 V. The standard chemical reaction and the new ODC reaction are represented under the following equation:

Standard chemical reaction: $2H20 + 2NaCl \rightarrow 2NaOH + H2 + Cl2$
ODC chemical reaction: $O2 + 2H2O + 4NaCl \rightarrow 4NaOH + 2Cl2$

In the second equation, as no hydrogen is formed, the cell voltage is lower and so is the power consumption. Energy savings of nearly 30% are expected.

In Europe, a new plant using the ODC technology has been built in Germany. This plant is using hydrochloric acid (HCl) as input instead of salt (NaCl) which results in the production of chlorine only.

2. Soda Ash

2.1 *Soda Ash Production Processes*

Sodium carbonate or soda ash can either be obtained through a process by reacting trona (the principal ore from which soda ash is made) with water, or it can be produced by the Solvay process referred to as the synthetic process. Soda ash is then produced by reacting an ammoniacal brine with carbon dioxide to produce bicarbonate, which is then calcinated to produce sodium carbonate. About 25% of the world's production is produced from natural sodium and 75 % through the synthetic process. Soda ash is mostly used in the production of glass, chemical, soaps and detergents, paper and paper pulp production, and water treatment.

2.2 Soda Ash Production in India

2.2.1 *Soda Ash Industry Characteristics*

The Indian soda ash industry is highly concentrated with three players accounting for nearly 80% of the total installed capacity. Plants are mostly located in Gujarat to take advantage of the availability of inputs like salt, limestone, coke, water, chemical compounds and power. Soda ash in India is not obtained as a naturally occurring product. Soda ash is produced by a total of 6 units with an average size of 1000 TPD. Out of the six plants, three are based on the standard Solvay process, one unit uses the *modified Solvay process* or *dual process* and the two other units use the *Akzo dry lime* process. The dual process produces soda ash in co-production with ammonium chloride, which is used as a fertilizer. The dry lime process uses dry lime instead of lime milk for ammonia recovery. This last process is considered as the state of the art technology. In India, around 40%of the soda ash produced is consumed by the detergents industry, 20% by glass, 16% by sodium silicate, and the remainder is consumed by the chemical industry.

2.2.2 *Energy Consumption*

The energy needs for the production of soda ash take on different forms: electrical, thermal and mechanical energy and feedstocks. Coke is used as a source of carbon dioxide in the soda ash production during the limestone calcination.

Two types of soda ash are produced: "light soda ash" with a specific weight of about 500 kg/m and "dense soda ash" of about 1000 kg/m. Light soda is directly used in the detergent sector and certain chemical intermediates. The remainder is transformed by crystallization after drying to produce dense soda mainly used in the glass industry. This extra step requires further energy. Table 6-4 shows the energy requirements at different stages in the production of soda ash for the standard Solvay process and the dual process. Unfortunately, this level of detail is not available for the dry lime process. However, the basic advantage of the use of dry lime instead of milk lime is a better steam balance and the reduction in the raw material inputs, resulting in energy savings. The consumption of steam and lime is much lower as compared to other processes.

Table 6-4. Specific Final Energy Consumption in Different Sections in a Soda Ash Plant (1994)

(GJ/t)	**Solvay Process**			**Dual Process**		
Manufacturing	Thermal	Electrical	**Total**	Thermal	Electrical	**Total**
Limestone Calcination	4.2	0.1	**4.3**	-	-	**-**
Salt purification	0.4	0	**0.5**	0.4	0	**0.5**
Calcination of sodium bicarbonate	4.2	0.1	**4.3**	4.2	0.1	**4.3**
Crystallization, drying and purification	4.2	0.1	**4.3**	4.2	0.1	**4.3**
Ammonia recovery	2.5	0	**2.5**	-	-	**-**
Manufacture of ammonia chloride	-	-	**-**	-	0.7	**-**
Utilities and general requirements	0.4	0.7	**1.1**	0.4	1.2	**1.6**
Total	**15.9**	**1.1**	**17.0**	**9.2**	**2.2**	**11.4**

Source: TERI, 1999.

2.3 Future Development of the Soda Ash Industry

2.3.1 Ongoing Changes in the Soda Ash Industry

Demand for soda ash is mainly affected by the demand from glass industry. Demand has decreased due to the fall in demand for container glass. Bottles made of container glass are being replaced with PET (Polyethylene Terephthalate) bottles; this has affected the demand for soda ash and driven up the demand for chlorine.

One of the main specific problems of the soda ash industry in India is that most of the units are located in the western region, which has the advantage of being in close proximity to the raw material source but far from consumers. Since soda ash is a high volume low cost commodity, costs of transportation are very high. This leaves other markets like the eastern and the northern regions vulnerable to imports. Further, being a high-power consuming product, Indian producers are always at a disadvantage compared to their foreign counterparts.

2.3.2 Potential for Energy Efficiency Improvement

Table 6-5 shows the detail of the soda ash industry plants in India. 34% of the total production capacity consists of the state of the art dry lime process, 4% the dual process and 62% the standard Solvay process.

Table 6-5. India Soda Ash Plants Characteristics

Company	**Location**	**Year**	**Process**	**Capacity**	
				'000 t/y	%
Tata Chemicals	Gujarat	1948	Standard Solvay	875	33%
Saurashtra Chemicals Ltd.	Gujarat	1960	Standard Solvay	650	25%
GHCL	Gujarat	1988	Dry lime	525	20%
Nirma Ltd	Gujarat	1998	Dry lime	365	14%
Tuticorin Alkalis	Tamil Nadu	1982	Dual/ Modified	115	4%
Dcw Limited	Gujarat	1939	Standard Solvay	96	4%

India's average specific energy consumption is about 13.6 GJ/t (Table 6-6). The EU best available technology has a specific energy consumption of about 10.8 GJ/t according to the recent study from EU IPPC. The US specific energy consumption is very low since most of its industry uses the natural process, which is much less energy intensive.

Table 6-6. Specific energy Consumption of Soda Ash, GJ/ton

	US*	**EU best practice**	**India**	**India Best Practice Nirma Ltd**
Energy use	8.5	10.8	13.6	11.3

Source: Energetics , EU IPPC, Teri and Nirma Ltd.
** Energy use in Manaufacture of Soda Ash from Trona Ore (1997)*

Potentials for energy savings in the soda ash industry in India are about 17%. Even though India possesses some of the best technology available, potential savings remain large and would require revamping the oldest plants. Nirma Ltd represents the best technology available in India, its specific energy consumption comes close to the EU best practice.

2.3.3 Categories of Energy Efficiency Improvement

Cogeneration: The Solvay process requires a large amount of steam, a big part of which is used as low pressure steam, injected directly into the process for the recovery of ammonia (steam stripping). Energy savings can be realized by reducing steam pressure in a set of turbo-generators while generating electricity. This electricity is produced with a "cogeneration" of steam, with an excellent efficiency (about 90%) because all the steam leaving the turbines is used in the process. In comparison, the same quantity of energy will be generated, in a classical power station, with a much lower efficiency (about 30%) because of the lost released steam. Comparison of the primary energy needs of a co-generation unit (based on gas) - for a soda ash plant - with that required for the separate production of steam and electricity (by a classical power station for electricity and boilers for steam), shows that it is possible to achieve 30% savings with co-generation.

Heat Recovery: The recovery of heat has been gradually improved throughout the history of the process by optimizing energy fluxes of different thermal levels contained in gas and liquids flowing through the process. Low-grade heat is used to preheat different streams such as:

- raw brine entering the brine purification step to improve purification efficiency
- raw water used for milk of lime production
- boiler feed water
- mother liquor from the filtration to the recovery of ammonia by the distillation off gas.

Vacuum flashing of distillation liquor may be used for producing low pressure steam available for distillation and any evaporation units like salt production.

Energy minimization: The following techniques may be considered:

- careful control of the burning of limestone and a good choice of the raw materials allow a reduction of the primary energy necessary for the operation
- improvement of process control by the installation of distributed control systems (DCS) - reduction of water content of the crude bicarbonate by centrifugation before calcination to minimize energy need for its decomposition
- back-pressure evaporation (e.g. calcium chloride liquors)
- energy management of stand-by machinery
- equipment lagging, steam trap control and elimination of energy losses

2.4 Scenarios of Future Energy Use

2.4.1 Future trends in Soda Ash production

No additional capacity of soda ash is expected in the near future. In 2001-02, customs duty on soda ash was drastically reduced from 35% to 20%. This steep reduction in customs duty has adversely affected indigenous manufacturers. Recently, the GOI increased the customs duty back to 25% in order to protect domestic industry.

2.4.2 Future trends in energy efficiency

Potential energy savings in the soda ash industry are large, estimated at about 17%. The sector is very concentrated; only six companies produce soda ash in India, which makes the scope of the possible plants retrofit more focalized. However, the soda ash industry is rarely perceived to be an energy intensive one, and hence inadequate attention is given to its potential energy savings.

3. Summary and Conclusions

The chlor-alkali sector is a very energy intensive sector where energy represents approximately 60% of total production cost. In a country like India, where the cost of industrial electricity is high, industries using large quantities of electricity such as the caustic soda industry have been focusing more attention on reducing energy consumption. Hence some caustic soda companies are closely monitoring their energy consumption, resulting in overall moderate specific energy consumption. Internationally, India compares positively with a substantial share of membrane cell technology. Both caustic soda and soda ash production have energy saving potentials of around 17%. The main weakness in this sector seems to be its lack of indigenous technology equipment production. For example, membrane cell equipment which needs to be changed every three years must be imported. There is no indigenous producer. The potential development of caustic soda production through new ODC technology is gradually emerging in market. India needs to take part in this future advancement.

Reference:

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