Modern Chlor-Alkali Technology
Volume 8

EDITED BY

John Moorhouse
Rhodia Ltd
Hollingwood
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UK

Proceedings of the 2000 London
International Chlorine Symposium
Organised by SCI’s Electrochemical Technology Group,
held on 31st May–2nd June, 2000
Modern Chlor-Alkali Technology
Volume 8
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Introduction

The chapters in this volume were presented as papers at the 2000 London International Chlorine Symposium held at the Millennium Conference Centre, Gloucester Hotel from 31st May to 2nd June 2000. This was the ninth in the series organised by the Electrochemical Technology Group of the Society of Chemical Industry.

The symposium, again, attracted strong support. Of the papers submitted, 26 were selected for presentation to address the latest technological, economic, political, environmental and safety developments facing the industry today.

The programme included:

1. A view on the future of the business.
2. The issues of mercury cell phase out and risk assessment of chlorine compounds.
3. Developments in electrodes and electrode coatings.
4. Developments in cell design and operation for all three technologies.
5. Conversion studies and experiences.
6. Developments in chlorine processing technology and effects on economics.

The event was attended by 202 delegates from 29 countries.

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John S Moorhouse
Chairman – Organising Committee
Rhodia Eco Services Ltd
Chapter 1
The Chlor-Alkali Business

D J Hutchison

1.1 Introduction

This chapter examines the business of the chlor-alkali industry. Without a need for chlorine there is no chlor-alkali business. This industry is now in its second century and having passed the millennium bug without any serious interruption, the future can now be examined. In this chapter there is an emphasis on chlorine rather than alkali as the alkali industry is thousands of years old and has been documented extensively since the time of the ancient Egyptians.

The chlorine industry really took off at the end of the 1890s with the installation of the first mercury cell units. Since then the industry has coped with many problems, the main one being the fixed amount of caustic soda per ton of chlorine out of the cells. There have always been imbalances on the demand for chlorine and the demand for caustic soda. The two products quite often go their own way and no reason is seen to change this situation.

What has happened over the years has been an increasing trend in the industry to globalise. This means that the effect on a market at the other end of the world can have an impact on a domestic market. There are several reasons for this: improved communications, multinational purchasing of caustic, more transparency, and, according to one producer, too many consultants.

There have been many pressures on the industry in addition to the need to make a profit. Legislation on the production of chlorine, the technology of choice, the use of chlorine in some applications as well as the destiny of some derivatives have all added to the burden of managing the business. Many great names from the past century have already disappeared or will disappear soon as far as chlorine production is concerned. Several companies have decided to exit the chlorine chain altogether in a move to convert either to specialities or life sciences. This has added to the problems of managing what is in normal times a dynamic business. Constant managerial problems such as downsizing, spinning off and merging can cause the eye to miss the ball or worse miss the big picture altogether. Today there is the possibility of buying and selling caustic soda on the Internet.
The opening chapter of this book looks at current issues in the chlor-alkali business and attempts to look at the issues which lie ahead.

1.2 Chlor-alkali production issues

Chlor-alkali production has been rising steadily over the last few years although the Asian crisis resulted in a global slow-down (see Table 1.1). Demand for chlorine has again been rising; however, this rise in demand was not followed immediately in the market for caustic soda. In early 2000 the market for chlorine appeared to be the stronger of the two though price rises were sought in the USA for both products.

Table 1.1 World chlorine supply/demand (per year $\times 10^3$ tons). Source: Tecnon (UK) Ltd.

<table>
<thead>
<tr>
<th>Year</th>
<th>1995</th>
<th>1997</th>
<th>1999</th>
<th>2001</th>
<th>2003</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production capacity</td>
<td>46.0</td>
<td>48.7</td>
<td>51.3</td>
<td>52.9</td>
<td>54.5</td>
<td>54.7</td>
</tr>
<tr>
<td>Production</td>
<td>38.0</td>
<td>39.5</td>
<td>40.3</td>
<td>42.0</td>
<td>44.5</td>
<td>46.4</td>
</tr>
<tr>
<td>Capacity utilisation</td>
<td>82.6</td>
<td>81.1</td>
<td>78.5</td>
<td>79.4</td>
<td>81.7</td>
<td>84.8</td>
</tr>
<tr>
<td>Consumption in non-vinyl</td>
<td>26.0</td>
<td>26.0</td>
<td>25.8</td>
<td>26.8</td>
<td>27.9</td>
<td>28.5</td>
</tr>
<tr>
<td>Chlorine contained in PVC</td>
<td>12.4</td>
<td>14.5</td>
<td>15.7</td>
<td>16.5</td>
<td>18.1</td>
<td>19.6</td>
</tr>
<tr>
<td>Chlorine recovered from HCl</td>
<td>(0.4)</td>
<td>(1.0)</td>
<td>(1.2)</td>
<td>(1.3)</td>
<td>(1.5)</td>
<td>(1.7)</td>
</tr>
<tr>
<td>Net chlorine demand</td>
<td>38.0</td>
<td>39.5</td>
<td>40.3</td>
<td>42.0</td>
<td>44.5</td>
<td>46.4</td>
</tr>
<tr>
<td>Annual growth</td>
<td>-1.5%</td>
<td>-2.0%</td>
<td>2.3%</td>
<td>2.0%</td>
<td>2.3%</td>
<td>2.0%</td>
</tr>
</tbody>
</table>

The returns for the industry can be monitored (see Figs 1.1–1.3). The selling price of caustic soda is fairly transparent everywhere and chlorine pricing is transparent in the USA. Chlorine is less transparent outside the USA as most of the consumption is captive rather than merchant. The market for ethylene dichloride (EDC) is, however, transparent and chlorine values can be worked out from the selling price of the EDC and the input price for the ethylene. Knowledge of the chlorine value and the caustic value gives the value of the Electrochemical Unit or ECU. This provides a measure of the profitability of the business at any time. Convenient marker prices can be found in the US Gulf for both EDC and caustic as well as out of north-west Europe.

From several price histories it is possible to establish caustic soda and chlorine values in different markets and hence calculate the ECU value and with it some measure of profitability. The chlorine value in export EDC can be calculated on the formula assuming the ethylene price is known. The chlorine value using hydrogen chloride is complicated by the extra costs of using HCl rather than chlorine and the slightly lower yields with oxychlorination, though that too can be calculated to give a chlorine value.

The industry has to face technology changes. The advent of membrane cells can
allow for an alternative to mercury cell production as well as asbestos diaphragm production. There is pressure on both methods of production and while the solutions are there, in some cases no economic reason can be found for an earlier than expected shutdown of a cell room. The energy savings in Europe would not in themselves justify a conversion of the six million tons of capacity.

If mercury shutdowns were to occur without replacement then Europe would be forced into importing chlorine derivatives such as EDC to compensate. The future of asbestos in diaphragm cells is also an issue, but with a much lower profile in Europe this has attracted less attention apart from in France. In the USA there are pressures on the industry too, which could be more acute depending on who occupies the White

---

**Fig. 1.1** Value of ECU in the United States. Source: Tecnon/Anorganica. Production cost at stated DM/kWh (—).

**Fig. 1.2** Value of ECU in the United States from exported caustic, and from chlorine in exported EDC. Source: Tecnon/Anorganica. Production cost at stated DM/kWh (—).
House after the departure of the Clinton administration. Elsewhere the build-up of capacity in membrane caustic has picked up speed, especially in Asia where there was a slight delay owing to the crisis.

In looking to the future, many chlor-alkali units have either their own in-house power source or a co-generation unit nearby with the avoidance of having to buy from a utility. Many chlor-alkali producers have become power generators in their own right and can control chlorine production by diverting power to the grid instead. An example of this was in 1999 during the very hot summer period in the USA with demand for power in air conditioning offering prices as high as 10 cents per unit compared with power costs of 2.6 cents normally found in the Gulf Coast states.

Energy costs should gradually be lowered for many chlorine producers. Less predictable are the interference of governments and the imposition of taxes in the guise of climate change. The UK government got very near to imposing such a tax, which would have shut down a considerable part of the industry.

The rise in capacity of EDC and caustic exporting units has implications for some high-cost integrated units especially in Europe where a decision will have to be taken on the future of the mercury cell units. Does it make sense to import EDC and use that in the vinyl chain or to continue to compete against a market fed by ‘cheap’ EDC out of the Middle East? The same would apply to Japan, though Japan has been importing considerable amounts of EDC for years (see Figs 1.4 and 1.5).

Looking further ahead, the commercialisation of the EVC process for the direct chlorination of ethane with its expected cost savings would challenge the cost structures of conventional plants leading to VCM capacity being built in very low-cost regions for both ethane and power. Obviously where the chlorine is made will
dictate where the caustic is produced. EVC commissioned a pilot plant in Wilhelmshaven in Germany in May 1998 and trials have proceeded to prove the process under full industrial conditions. More research will be done to confirm a commercial process. EVC has said that the technology could reduce the cash costs of PVC by one-third as well as decoupling the vinyl chain from ethylene crackers.

Fig. 1.4 Build-up of chlorine capacity in Asia and world total. Source: Tecnon/Anorganica.

Fig. 1.5 Chlorine capacities: process profiles for 1999. Source: Tecnon/Anorganica.
1.3 Cost structure issues

Consolidation in the next century will result in cost savings from the economies of scale alone. The trend to focus chlor-alkali in low-energy-cost regions will continue. Energy savings will also likely be made in the cell technology.

The development of the membrane cell cut the energy consumption in chlor-alkali production. A good cell will produce a ton of caustic for around 2400 kWh. Membrane caustic can only be produced up to around 35%. Several cell designers have tried to develop a cell and membrane combination that would allow 50% caustic to be made, but this has proved to be commercially elusive so far. Membrane cells have probably reached the theoretical limit on energy consumption for a commercial plant. In Japan, power consumption has been cut by 30% over the last 20 years as the conversion from mercury cell progressed.

There will be a trend to large green-field sites using the bipolar membranes designed to work at high current densities, i.e. in excess of 6 kA m$^{-2}$. Looking even further ahead there are new methods of electrolysis being developed to cut down the energy consumption in producing the ECU. For example, MITI in Japan has been developing a gas diffusion electrode, which may cut the power consumption further by 30 or even 40%. This electrode would be used as the cathode in a cell system and there would be no production of hydrogen. The energy savings come from the lower theoretical electrolysis energy as well as the cancellation of the hydrogen overvoltage. The cell development has been taking place at various companies and cell life of two years is now expected with further research being done to extend the electrode life to five years. The Japan Soda Association has estimated the power consumption to be 1500 kWh per ton of caustic produced.

The progressive savings on the development of cell technology can be seen in the chart shown in Fig. 1.6. These savings are significant and may encourage rapid change from mercury cell in countries where the benefits of membrane have not yet been proved in terms of energy cost savings. If this technology is proved there will be great pressure on some countries to force this method through with the imposition of a carbon tax.

1.4 The balance

There are no grounds for believing that the chlorine and caustic soda balances will eventually become manageable. Consolidation in the company portfolio may result in the number of producers becoming much smaller and with that a degree of control will be gained, especially in the operating rates. With fewer producers chasing a ‘market’ share there may be some stability in controlling the downside in the cycle. Chlor-alkali producers lose heavily when operating rates are low and demand for caustic is sluggish. The ECU then generates very low returns as was seen last year in the USA.
Increased consumption of HCl in the vinyl chain has allowed for better chlorine management. For example, it is now quite common to tie in a VCM complex to an isocyanate unit. This has two effects. Firstly, the hydrochloric acid production is usefully consumed and obtains real chlorine values rather than the acid market values. Secondly, increased use of HCl cuts the need to build some chlorine capacity and hence cuts the amount of caustic soda produced and which has to be sold. The balance can therefore be ‘adjusted’ by the recycling of HCl in the system.

Nevertheless the age-old problem of balancing will not go away. Chlorine cannot be stored so if demand falls there has to be a rate cut eventually or wholesale conversion of EDC back to the 3 cent per pound level. At the other extreme, caustic soda cannot be put into inventory for ever. Caustic soda at the $30 level implies high chlorine values, which implies better use of the chlorine, especially where HCl is a co-product. Again, looking into the future, more isocyanate and epichlorohydrin units will be tagged on to the vinyl chain as is projected for China and Qatar in the twenty-first century. This ought to minimise the amount of co-product caustic produced (see Fig. 1.7).

In the twenty-first century the mixture of politicians, bankers and, dare I say it, some consultants will have seen to it that we still have periods of ‘boom and bust’, in other words periods of strong growth and periods of recession. The demand for chlorine and caustic will not be the same and hence the imbalances are likely to be a fact of life though how they are controlled will be a function of the producers if there is some serious consolidation.

While the industry has to balance out globally there are none the less regional imbalances. Asia still has a deficit of chlorine derivative production and a large demand for PVC. Much of this is met with imported EDC as the feedstock. The EDC in normal times comes mainly from low-energy-cost regions such as the Middle East.

![Electric power consumption rate by each method.](image-url)
and the US Gulf. Europe still has a caustic soda surplus which has declined over the last ten years. The USA exports both chlorine derivatives and caustic soda. Australia is a large importer of caustic soda, primarily for the alumina industry with a demand exceeding one million tons.

The changing balances which do occur have to be ‘resolved’. This can be by trade changes such as increasing exports of either EDC or caustic to balance the plant. Some markets are not easy to enter. For example, while Australia imports over one million tons of caustic soda it does so in 25 000 DMT shipments. This is 50 000 liquid tons of material. Relatively few plants have access to such facilities or can indeed store such a quantity. With some Asian countries becoming more self-sufficient in caustic production Japan had to increase its port handling facilities, raising the load size as well as increasing the number of ports to three.

1.5 The caustic return

Caustic soda prices vary with time. They usually cycle between $30 and $300 in the USA and from around DM300 to DM550 per Dry Metric Ton (DMT) in Europe. A
good return in caustic is vital to the industry. High-valued caustic implies low-cost chlorine. Caustic therefore has a ‘price’ whereas chlorine has a cost. Several companies have complex ways of transferring chlorine within the system, especially a company with many uses for chlorine. A useful way of looking at costs is to take the overall cost structure of the ECU, power, salt, labour, etc. and take out the return of 1.1 tons of caustic soda.

We show the ‘cost’ of chlorine in the case of caustic credits from export and domestic business (Figs 1.8 and 1.9). It is one of the many paradoxes in the business that although the plant is built for the chlorine, for most of the time the profit comes from the caustic soda. (Figure 1.10 shows the origin of the chlorine in the derivative trade.) The management of the caustic return is vital to the industry. The cyclicality in the demand for caustic with the supply will continue though the number of players in the business will probably reduce.

The influence of distributors will probably increase as more companies are preferring to outsource the selling of the caustic. This then reduces the level of control that producers may have in the market. One area of control is of course the supply of caustic in the first place. Although at first glance the stoichiometry of the business suggests a rather rigid 1 ton of chlorine, 1.1 tons of caustic, there is nevertheless the hydrogen chloride or HCl calculation.

With more consideration being given to hydrogen chloride recycling it has been estimated that between one million and two million tons of HCl will be increasingly recycled. There are costs in using hydrogen chloride rather than chlorine but there are also benefits. If this hydrogen chloride is used rather than chlorine then the chlorine
will not need to be made and this in turn means that caustic soda supplies would be tighter than otherwise would be the case.

Several chlor-alkali producers have some control over surplus caustic inasmuch as they use large quantities in-house. In some cases, if caustic is tight then the weak cell liquor can be upgraded and placed on the market. Dow’s propylene oxide (PO)
system is a good example of this as the company could in theory use lime instead of caustic, though in practice it is only the Aratu plant in Brazil which can switch alkali. The caustic effectiveness of derivative production varies with the products and there is some scope for varying the alkali used internally, again with a view to controlling the supply.

Caustic pricing is becoming more global. In the past the domestic markets would have been immune from events elsewhere. Domestic surpluses could enter the deep-sea market with low prices without any impact on the domestic price. This is no longer the case. Some producers have been reluctant to dispose of caustic soda in the deep-sea market and have sought to sell in the home market by increasing market share. In the USA this has led to the two markets tracking each other and occasionally the domestic market is weaker than the contract market for Australia (see Figs 1.11–1.13).

![Fig. 1.11](image-url) United States export and domestic caustic soda prices. Source: Tecnon/Anorganica.

Europe too is now facing increasing pressure to offer international prices for caustic soda. There are indeed few markets currently where the domestic caustic market has immunity from caustic turbulence elsewhere though there are areas with freight advantages.

One of the most important contracts in caustic soda is the contract for the alumina industry in Australia. This is just over one million tons out of world production of about 44 million. Some have questioned why this contract should have an influence on the markets elsewhere. Although the Australian demand is a fraction of world demand the alumina price there is ‘adopted’ elsewhere, notably in the USA in the pulp sector and detergent sector. Thus a considerable part of the user industry is indirectly following events in Australia. In the past Australia has bought caustic soda from...
North America, Europe, Saudi Arabia and Japan. Europe has gradually dropped out of the contract. While Australia has bought from Korea and Indonesia from time to time the contract supplies are restricted to those countries mentioned above. That will change as the Qatar plant comes on stream in 2001. Should the Pilbara project in

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**Fig. 1.12** West European caustic soda prices: liquid market (Germany only). Source: Tecnon/Anorganica.

**Fig. 1.13** Australian contract price excluding US Gulf. Source: Tecnon (UK) Ltd.
Australia eventually be built then the whole trade issue will change once again with ‘local’ caustic being used in the alumina industry.

### 1.6 Diaphragm versus membrane

In Asia the membrane grade is standard. Japan is now totally membrane cell as far as caustic soda production is concerned (see Fig. 1.14). In Europe mercury cell predominates while in the USA it is diaphragm grade that predominates. Given that at some point membrane will grow to be the standard it is likely that some form of diaphragm discount will have to be offered in the future to maintain business. If caustic is long then diaphragm caustic will become increasingly difficult to sell. If caustic is tight and customers are desperate then a salt content would be overlooked.

![Fig. 1.14 Japanese caustic soda processes: 1995 versus 2000.](image)

In Australia one alumina producer has started to specify membrane-only caustic soda for consumption in the process. Yields of alumina production can be increased if membrane caustic soda is used.

### 1.7 Anhydrous caustic soda

The business has gradually declined with fewer producers in Europe making the product. At the same time capacity for prills has increased in the Middle East and in Thailand thus changing the delivered pricing in some markets. India has continued to expand capacity of flaked caustic soda and this production is now regularly quoted as far afield as South Africa. There are some expanding markets still in Africa and Asia but as these have been more geared to the new supply sources out of the Middle East and Asia it has become increasingly difficult for European suppliers to get a decent margin on the product. We expect this decline to continue
with more capacity in Europe being closed down. This can put pressure on inventory control for the liquid.

1.8 Ownership issues

Many chlor-alkali companies are changing hands and the degree of focus on chlorine is changing. As large mergers are being proposed in the cracker and refinery sectors, the chlorine unit does not come high on the list of priorities. Consequently several names are starting to disappear from the history books. ICI, Rhône Poulenc and Hoechst are three such examples. There will be more mergers in the USA, Europe and even Japan where major restructuring of the vinyl chain is now underway.

The aim of the restructuring will be to ensure competitive state-of-the-art vinyl units fed by either EDC or a state-of-the-art chlorine unit. Average plant sizes will increase, the number of producers will be reduced. However, this is still a long way off. Mergers in the vinyl chain have not always been easy. Both the OxyChem and Geon merger and the Solvay–BASF merger of interests were finalised after much discussion. EVC and Norsk Hydro fell fairly quickly and the Shell–Shin Etsu deal at Rovin took a long time.

On the customer side there are also changes as groups get larger. In the alumina sector there has been recent activity involving the consolidation in the industry with moves by Alcoa and Alcan in forming huge enterprises. These are subject to regulatory approval. In pulp and paper there has been gradual consolidation within the Nordic countries and in North America. In February two large transatlantic mergers in this sector were proposed. Gradually the number of large customers will decrease as will the number of suppliers.

Another trend in sales and marketing has been for the large multinational or transnational groups to favour single sourcing for a large part of the tonnage or at least to seek a supplier who can bid for all the business. This has been the case within the continental USA for some time and with the advent of the euro there is increased pressure for the large users to consolidate purchases in Europe if not on both sides of the Atlantic.

1.9 Chlorine demand changes

Many companies have said that if an alternative route to a derivative was economically justifiable that would be used in preference to a chlorine route. This has already had an impact on the technology of choice in some production routes to isocyanates, polycarbonate, propylene oxide and epichlorohydrin.

Some of the low-tonnage isocyanates are made without chlorine but this has yet to be proved for MDI and TDI. GE and Bayer have been adding polycarbonate capacity
without the use of chlorine. Dow has invested in Russian technology to make PO without chlorine and chlorine consumption can be cut in the epichlorohydrin process. Bayer and Lyondell are to co-operate in PO production.

These processes all vary in terms of the caustic effectiveness of the system as well as the implications on HCl generation and scope for recycling. It is really only PO and the isocyanates which would have an impact on the balance.

Environmental issues are discussed below. It is worth pointing out now that the industry has had to adapt to chlorine demand changes in this sector such as CFCs, pulp and paper and solvents. In Europe no chlorine is used in the pulp industry and it is being run-down elsewhere. Many of the plants which supplied chlorine into the pulp sector are situated a long way from other chlorine end-users and there have been closures of chlorine units, mainly in Scandinavia, Canada and the West Coast of the USA.

With PVC being the main driver for chlorine demand there is increasing pressure on the need to obtain cheap power, salt and ethylene feedstocks. Export-driven EDC and caustic plants have some place in meeting world demand though with the need to export both chlorine, in the form of EDC, and caustic soda there can be occasions when these plants are vulnerable to low returns if demand is much lower than supply. Traditional locations for these plants have been in the US Gulf and the Middle East, but there are plans to site such plants in Venezuela and Australia with both these countries having a large caustic soda demand in alumina.

1.10 Environmental restrictions

Many of the changes in chlorine consumption in the past ten years have arisen out of the environmental concern about the use of chlorine in some processes such as pulp and paper as well as the concern of the loss of the ozone layer with the use of CFCs.

These pressures have worked their way through the chain and now we have no chlorine consumption in pulp production in Europe and a much diminished consumption of chlorine in the HFC precursors. In addition the solvents sector saw a reduction in the demand for chlorine as many solvent applications changed.

There are restrictions in some countries on the surface movement of chlorine and this has forced some focusing of chlorine plant locations and shut down those with no or little captive consumption.

PVC still faces environmental pressure from two directions: there is hostility in the use of PVC in children’s toys using the phthalate argument and building a new PVC complex faces severe regulatory pressure—witness the experience of ShinTech in the USA.

PVC and chlorine are still targets for environmental action. While there may be other targets for the environmental activists, such as GM foods in Europe, chlorine and PVC are still in the limelight for attacks on all fronts. No reason is predicted in the
industry for that to change and companies remaining in the chlorine chain will find that there will be a continued need to be seen to be using the best available techniques.

1.11 Chlorine: a utility or a product group

If the ideas described above are extended one can develop the ‘Chlorine Park’ concept. A chlorine park is a chemical complex with the supply of chlorine made by pipeline, HCl returns are made, other utilities are provided and the chlorine costed on a reasonable share of the revenues.

Several chlorine parks already exist. Geismar in Louisiana and Botlek in The Netherlands are good examples of these in operation today (see Figs 1.15 and 1.16). These sites are multi-customer based. The internal movements of chlorine and hydrogen chloride in a Dow site are also examples of a single-company chlorine park. Other, once single-owned complexes are splitting apart. The ICI complex at Runcorn could develop that way depending on who buys the chlorine chemicals business, the fluorochemicals business and how EVC develops. Several companies are seeking to attract users of chlorine to their site as there are moves to restrict chlorine transportation and this is one way of avoiding the movement of chlorine.

These are therefore some mechanisms for the development of chlorine complexes and the continued supply chain of chlorine through the derivatives. These also allow the increased use of HCl in the system and some control of the caustic supply.

Fig. 1.15 Schematic of the ‘chlorine park’ in Geismar, Louisiana: 1996 appearance.