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CAUSTIC SODA (NaOH) PRODUCTION

PREFACE

This information package has been prepared to respond to the considerable interest in the Chlor-alkali industry shown by INTIB users in developing countries.

Chlorine and sodium hydroxide (NaOH) are considered two of the most widely used chemicals in the world, and are the basis of a large sector of chemical products' manufacturing. However, at the same time, it is an area of major concern to manufacturers because of potential pollution hazards caused by the mercury in the effluents.

Another aspect of great concern in this industry, depending on the selected process, is the huge amounts of electrical energy and steam used. This is a very important aspect to be considered, taken into account the increasing energy prices in the world.

This report intends to describe alternative technologies which could solve the mercury pollution problem as well as to ensure a considerable saving in energy.

An information package is intended as a time-saving tool for individuals involved in the development of a specific product since it supplies them with primary information selected from a wide variety of existing sources, which usually are not readily accessible to developing countries.

CONTENT

Introduction

1. Retrospective Information Search 1980-1992
2. UNIDO Reports (abstracts)
3. Available books and Journals for sodium hydroxide and
-- related subjects
4. Worldwide sodium hydroxide producers
5. Some equipment suppliers and consultancy services
6. R & D Institutes
7. Bibliography
8. Relevant technical papers enclosed
 - 8.1 Electrochemicals
 - 8.2 Chlor-alkali membrane cells and optimization of
their design
 - 8.3 Introduction to membrane cell technology in the
production of Chlor-alkali
 - 8.4 Pollution control and energy saving : a case study
in chlor-alkali industry
 - 8.5 Sodium hydroxides derivatives
 - 8.6 Standard specification for liquid caustic soda

INTRODUCTION

The Chlor-alkali manufacturing industry started in 1886, and experienced a slow development during the last century.

Caustic soda (NaOH) was initially made by reaction of calcium Hydroxide and sodium carbonate. The term is broadly used because this compound is corrosive to the skin. In this report the term caustic soda and sodium hydroxide will be used interchangeably.

Although the electrolytic production of caustic soda was known in the eighteenth century, the commercial production only started in 1890. When this electrolytic process for caustic soda and chlorine was developed, the old lime-soda process could hardly compete and its use gradually decreased until 1968, when it was discontinued.

The operation of a chlor-alkali plant depends considerably on direct-current electric power which is often obtained from a higher-voltage source of alternating current.

Nearly all the Chlorine and sodium hydroxide in use today are produced by the electrolysis of aqueous solutions of alkali metals chlorides, especially from sodium chlorides (brines).

Brine electrolysis produces chlorine at the anode and Hydrogen jointly with the alkali hydroxide at the cathode.

Cell design in this process must be according to the end products obtained. If chlorine and sodium hydroxide are to be obtained, cell design must keep them from mixing.

At present, there exist many different cell designs for practical uses. By now, three types of cells are important for industry: the mercury cell, the diaphragm cell and the membrane cell.

In the mercury cell process, the mercury constitutes the cathode whilst the anode is graphite. This is being replaced by more stable types, especially with modified titanium.

The electrolysis produces chlorine at the anode and a sodium amalgam is formed at the mercury cathode. The amalgam is decomposed in another compartment with water to form a caustic solution.

Relating to the diaphragm cell, the mercury cell produces a more concentrated solution (50-70%), and only filtration is needed to remove small impurities such as graphite and mercury to produce a commercial product. However, operating voltages are higher, efficiency is

lower (52-55%) and it is high in capital investment of mercury.

Because of the superior qualities of the products obtained by this process in terms of high quality and the reduced evaporation required, the process was thought to lead the market, but small losses of mercury to the environment have caused enormous problems and serious measures has been taken for different countries to restrict this process.

Countries such as Japan has prohibited its use after Minamata disaster occurred in 1975.

However, mercury cell plants can remain in operation if they meet environmental standards by taking care of the process control along with water treatment and air effluent.

Diaphragm cell is a kind of electrolytic cell containing anode and cathode compartments. They are separated by a porous diaphragm or membrane which allows ions to flow by electrolytic migration and also reduces the diffusion of products. Asbestos fibres are normally used for the diaphragm.

The diaphragm is important because it allows a flow of brine from anode to cathode thus avoiding side reactions. Chlorine is released at the graphite anode and in the cathode, hydrogen is liberated. Caustic soda is collected in the liquid and continuously drained from the cathode.

Anodes are usually made of graphite and cathode of cast iron. The diaphragm must be replaced regularly because it becomes clogged with use. However, cells with metal cathodes such as titanium coated with rare earth oxides, platinum or noble metals hardly develop clogged diaphragms and can work for a long time (12-24months) without need for replacement.

The diaphragm cell can operate on dilute (20%) brine nearly impure brines and produces dilute sodium hydroxide (normally 11% NaOH with 15% NaCl as impurity).

A great deal of energy is consumed to evaporated dilute solutions to concentration of 50% for shipping purposes. Approximately 2600 kg of water must be evaporated to produce a metric ton of 50% NaOH. This fact makes installations of large diaphragm cells difficult and expensive

The basic principle of the membrane cell is similar to that of the diaphragm process but a purer and more concentrated NaOH is obtained. This technology has for many years been a commercial feasible process.

This process uses a semi-permeable membrane to separate the anode and the cathode compartments. Because of its

permselective properties, the membrane allows the migration of sodium ions to the cathode compartment, but rejects the migration of hydroxyl ions. Therefore, caustic soda and hydrogen are formed in the cathode compartment and chlorine gas is released from the anode compartment.

These kinds of ion-exchange membranes are porous chemically active plastic sheets. Naflon (DuPont) is the most commonly used membrane.

By this process, a concentrated NaOH (28%) is obtained. This concentration requires only 715 kg. of water to be evaporated to produce a metric ton of 50% NaOH, which is a considerable saving taking into account energy needed to concentrate dilute NaOH obtained by the diaphragm process.

Many combinations of these processes are being made in order to attain an efficient process in terms of energy saving. Hybrid fuel cells are expected to be developed in this decade.

Caustic soda is mainly used in chemical manufacture, pulp and paper production, textiles, oil and gas treatment, cleaning products, detergents, soaps, vegetable oil refining, and food additives, amongst others.

For some developing countries where conservation of energy and pollution control are a priority, conversion of mercury cell to membrane technology will be advantageous for both, energy saving and pollution control. However, more research is needed to overcome the difficulties that this change involves.

1.- RETROSPECTIVE INFORMATION SEARCH : 1980-1992

- ABSTRACTS :

1.- 101: 194492j Progress and evaluation of ion exchange membranes used in chloralkali technology worldwide. Zhang, Youxoo (Peop. Rep. China). *Xiandai Huogong* 1984, 23, 8-13 (Ch). A review with 6 refs.

2.- 101: 213385v Manufacturing processes in caustic-soda industry. Endo, Masaharu (Tsuetsunashi Kiosangyokyo, Japan). *Sangyo to Kanryo* 1984, 13(8), 18-23 (Japan). A review with no ref.

3.- 013526 INTRODUCTION TO MEMBRANE CELL TECHNOLOGY IN THE PRODUCTION OF CHLOR-ALKALI. A description is given of the basic operation of a membrane cell and the factors which are critical in the design of a cell and membrane system. Bipolar and monopolar electrical circuits and the factors influencing current density are considered. Installation of the cells at either a new site or as a retrofit in an existing cellroom presents challenging engineering and chemical engineering targets and the economics of conversion are reviewed with special reference to the ICI FM21 membrane cell system.

Kelham, S.F. (Imperial Chemical Industries, Mond Div., Engl) *Chem Kew* v 11 n 2 Feb 1984 p 93-97.

4.- 013527 POLLUTION CONTROL AND ENERGY SAVING: A CASE STUDY IN CHLOR-ALKALI INDUSTRY. Since power failure and consequent process interruption in the present Indian working conditions has become a common feature, adaptation of a new technology which eliminates use of mercury, namely "Membrane cell" is explained in the paper. Besides the operational and pollution aspects, the paper explains the economics of both the processes with respect to energy consumption. It is estimated that membrane technology will ensure a saving in energy consumption to the tune of 20 cr. es of rupees a year. (Edited author abstract) 6 refs.

Chatterjee, S.N. (Durgapur Chemicals Ltd, Durgapur, India), Bhattacharjee, B.K. *Chem Age India* v 36 n 1 Jan 1985 p 105-106

5.- 104: 232706d Recent developments of the chlorine industry in Japan. Masuda, F. Y. (Kashima Plant No. 2, Kashima Vinyl Chloride Monomer Co. Ltd., Kamisu, Japan) *J. Appl. Electrochem.* 1986, 16(3), 317-31 (Eng). A review with 18 refs. is given on Cl electroprod. from brines including the conversion of Hg cells to ion-exchanging membrane cells and the conversion of asbestos diaphragm cells to membrane cells.

6.- 104: 26054m Industrial membrane cells. Minz, Franz Rudolf (Bayer A.-G., Leverkusen, Fed. Rep. Ger.). *DECHEMA-Monogr.* 1985, 98(Tech. Elektrolysen), 49-59 (Ger). A review with no refs. is presented. A brief discussion of 4 different cells used in the chlor-alkali industry is given.

Complete documents can be obtained from :

British Library Lending Division,
Boston Spa, Wetherby, West Yorkshire,
United Kingdom, LS23 7BQ

7.- 104-71070z The caustic chlorine industry in Japan. Yoshizawa, Shiro (Fac. Eng., Kyoto Univ., Kyoto, Japan 606). *New Mater. New Processes* 1985, 3, 87-8 (Eng). A review with no refs.

8.- 99878p Manufacturing processes of chlorine and caustic soda. What is the next innovation? II. Suggestion of new chemical processes. Takeuchi, Norio (Natl. Res. Lab. Chem. Technol., Yatabe, Japan 305). *Soda to Enso* 1985, 36(430), 459-76 (Japan). The methods reviewed for manufg. NaOH and Cl₂ are: (1) NaF-NaNO₂ cycle, (2) Na borate-NaNO₂ cycle, and (3) Fe oxide-NaNO₂ cycle. The fundamental thermochem. data are discussed and material and heat transfer of the manufg. processes are illustrated. The process of manufg. Cl₂ and Na₂CO₃ also is suggested. 21 Refs.
Y. Miyahara

9.- 016194 PROCEEDINGS OF THE SYMPOSIUM ON ADVANCES IN THE CHLOR-ALKALI AND CHLORATE INDUSTRY. This conference proceedings contains 24 papers. Various aspects of the chlor-alkali and chlorate industry are covered. The topics cover manufacture of chlorine, caustic soda and hydrogen; electrolysis of brine; electrolytic cells; membrane cells; mercury cathode cells; ion-exchange membranes; mass transfer; electrodes and electrocatalysts. Other topics cover power consumption and control systems. Technical and professional papers from this conference are indexed and abstracted with the conference code no. 06891 in the Ei Engineering Meetings (TM) database produced by Engineering Information, Inc.

Silver, Milton M. (Ed.) (H.K. Ferguson Co., Cleveland, OH, USA). Spore, Everett M. (Ed.). *Proc Electrochem Soc v 84-11*. Proc of the Symp on Adv in the Chlor-alkali and Chlorate Ind., Cincinnati, OH, USA, May 7-9 1984. Publ by Electrochemical Soc., Pennington, NJ, USA, 1984 374p.

10.- 104-135187c Mercury pollution in chlor-alkali industry. Dheer, K. M. (Train. Dep., FCL, New Delhi, India). *Chem. Age India* 1985, 36(8), 755-7 (Eng). Air and water pollution by Hg from the chloralkali industry, Hg loss, and control of Hg loss using various methods are discussed.

11.- 016903 CAUSTIC CHLORINE INDUSTRY IN JAPAN. Recent changes in the caustic chlorine process technology in Japan are described. Mercury pollution problems have necessitated a switchover from a mercury process (M) to a nonmercury process. A plant using the diaphragm cell process (D) was completed in 1975. The ion-exchange membrane cell process (IM) was also developed. Some technological improvements are briefly outlined. Reductions in energy consumptions are indicated. Production figures for each process are given.
Yoshizawa, S. (Kyoto Univ., Kyoto, Jpn). *New Mater New Process v 3* 1985 p 87-88.

12.- 016416 HAZARDS IN CHLOR-ALKALI INDUSTRY. Based on continuous research, improvements in technology have been adopted to make the industry a safe one. Various measures have also been worked out to combat the hazards connected with the products. This paper broadly deals with the hazards in this industry and their prevention. The authors also deal with physical injuries due to contact with liquid chemicals, chemical poisoning due to long exposures, and short term exposure to toxic gases.

Patel, R M (Gujarat Alkalis & Chemicals, Baroda, India), Sharma, J B. *Chem Age India v 36 n 8* Aug 1985 p 751-754

13.-

016417 RECENT DEVELOPMENTS OF THE CHLORINE INDUSTRY IN JAPAN. In response to the June 1986 time limit the conversion of mercury (M-process) cells to ion exchange membrane (IM-process) cells is now well advanced in the Japanese chlor-alkali industry. In parallel with this, many asbestos diaphragm cell (D-process) plants have also been converted to the membrane process (DI-process). These successive conversions are indicative of an acknowledgment of the economies inherent in the IM-process as a result of technical improvements. This article gives an account of the recent developments and progress of the IM-process in Japan. (Author abstract) 18 refs.

Masuda, F.Y. (Kashima Vinyl Chloride Monomer Co. Jpn). *J Appl Electrochem* v 16 n 3 May 1986 p 317-331.

14.-

016414 SIMPLE MODELS FOR DIAPHRAGM-TYPE CHLORINE/CAUSTIC CELLS. I. DYNAMIC BEHAVIOR. A simple model of the dynamic behavior of a diaphragm-type chlorine/caustic cell is presented. The model is based upon measurable diaphragm properties and the mass transfer of hydroxyl ion through the diaphragm. The anolyte is modeled simply as a region in which the OH^- ion concentration is fixed, the diaphragm is modeled as a plug-flow reactor with an electrochemical reaction occurring at the catholyte/diaphragm interface where the cathode is placed, and the catholyte is modeled as a completely stirred flow reactor. Analytical integration of the governing equations for these models yields two mathematical expressions: one for the concentration distribution of hydroxyl ion within the diaphragm and one for the effluent concentration. (Edited author abstract) 34 refs.

Van Zee, John (Univ of South Carolina, Dep of Chemical Engineering, Columbia, SC, USA); White, R.E.; Watson, A.T. *J Electrochem Soc* v 133 n 3 Mar 1986 p 501-507.

15.-

104:135289n Hazards in chlor-alkali industry. Patel, R. M.; Sharma, J. B. (Gujarat Alkalis and Chem., Baroda, India). *Chem Age India* 1985, 36(8), 751-4 (Eng). Reasons for occurrence of hazards (explosions, fire, phys. injuries due to phys. contact with chems., chem. poisoning due to long exposure to chems., and short-term exposure to toxic gases during leakages) and their prevention in the chlor-alkali industry are discussed.

16.-

014539 CHLOR-ALKALI MEMBRANE CELLS AND OPTIMIZATION OF THEIR DESIGN. Chlor-Alkali Industry has already entered the 'Membrane Age'. Developments of this process are described, including the latest 'Hi Process' Japanese Membrane Cell with provision for installation of membrane over the existing mercury cell. Optimization in the design of various cell components and process parameters are described and various areas of cost reduction with special reference to power consumption enumerated. Future possibilities are highlighted. (Edited author abstract) 14 refs.

Chatterjee, S.N. (Durgapur Chemicals Ltd, Calcutta, India). *Chem Age India* v 37 n 3 Mar 1986 p 185-194.

17. -

014540 APPLICATION OF FUEL CELLS TO CHLORINE-CAUSTIC TECHNOLOGY. This paper presents an analysis of a new chlorine-caustic production system involving a coupled membrane electrolysis cell and a membrane alkaline fuel cell reactor. The predicted energy consumption of this system is compared with existing technologies and an analysis of the economics of this system is presented. A coupled electrolytic/alkaline fuel cell system designed to concentrate caustic and generate electricity shows large potential energy saving (30-50 percent reductions) and rapid return on investment. (Ebeded author abstract) 19 refs.

Gelb, A. (Physical Sciences Inc. Andover, MA, USA); Taylor, E.J. *AICHE Symp Ser* n 250 v 82 1986. Recent Adv in Sep Tech - III. Publ by AIChE, New York, NY, USA, 1986 p 99-114

18. -

014542 EFFECT OF BRINE ACIDIFICATION ON THE PERFORMANCE FIGURES OF A DIAPHRAGM CELL IN CHLORINE AND CAUSTIC SODA PRODUCTION. It is shown that by using an acidified sodium chloride solution instead of alkaline solution under the conditions of a diaphragm cell one can raise the current yields of chlorine and alkali at all anolyte pH, improve their quality, increase the limiting sodium hydroxide concentration, lower the concentration of active chlorine, and lower the oxygen content of the chlorine gas while having anolyte pH which are identical with those of the alkali solution. The mechanism suggested for lost current yields of sodium hydroxide which explains the influence of feed brine acidification on the electrolysis figures is confirmed experimentally. (Author abstract) 14 refs.

Kubasov, V.L.; Vorob'eva, V.B.; Ivanter, I.A.; Vorob'ev, G.A. *Sov Electrochem* v 22 n 10 Oct 1986 p 1301-1305

19. -

015309 CORROSION PROBLEMS IN A CHLOR-ALKALI PLANT. An examination is made of elements which contribute to the cost of corrosion, the mechanism of corrosion, the forms of corrosion and factors which promote corrosion. A discussion is presented of the diaphragm cell process, the mercury cell process and, the membrane cell process. The author covers corrosion problems in brine plants, an electrolysis plant, a caustic soda concentration plant, and chlorine manufacturing and hydrochloric acid plants.

Rajagopalan, K.S. (CSIR, Madras, India). *Chem Age India* v 37 n 12 1986 p 861-868

20. -

106:57613p Electrochemicals with special reference to chlor-alkali industry. Ramadurai, V. (India). *CEW, Chem. Eng. World* 1986, 21(10), A1-5 (Eng). A review with 3 refs. A brief discussion is given on the great importance of safety in the electrochem. industry, esp. in the chlor-alkali prodn. Some toxicity effects of Cl₂ are listed.

108:58766u Chlorine industry - achievements and prospects [in the USSR]. Il'in, B. A.; Libman, B. Ya.; Mazanko, A. F.; Treger, Yu. A. (USSR). *Khim. Prom-st. (Moscow)* 1987, (11), 660-4 (Russ). A review with no refs. on the electrochem. prodn. of Cl₂ and caustic soda by the diaphragm and Hg methods, use of Cl₂ in the org. and inorg. syntheses, paper-pulp industry, water treatment, and other fields, and environmental problems of the Cl₂ industry.

22. - 110:181463m Energy conservation and environmental safety in electrochemical membrane technologies for the chlor-alkali process. Nidola, Antonio (Serv. Ric. Elettrochim., S.E.R.E. S.r.l., Milan, Italy). *Acqua Aria* 1988, (10), 1273-88 (Ital). A review with no refs. Scientific, tech. and economical concepts and criteria for studying, developing and realizing a flexible and versatile electrochem. system to be used in the chlor-alkali industries are described and discussed. Typical constructive parameters taken into consider for this anal. are represented by: (1) permselective membranes, (2) selective electrodes (both anodes and cathodes) and (3) cell configurations. Moreover a history concerning all the chlor-alkali cell technologies (Hg and diaphragm), their characteristics (constructive and operative) compared to the new art and, finally, as an example, the industrial performance of DOW-DE NORA monopolar cells installed at ENICHEM plant and operating since August 1986 are given and discussed.

23. - 013349 COMPOSITION OF THE SOLUTION IN A MERCURY CELL DURING PRODUCTION OF SODIUM AMALGAM. Results of previous experiments were based on the view that the pH near the cathode is determined by the electrode reaction of hydrogen evolution and the chemical reaction of spontaneous decomposition of the amalgam, while acidification of the solution in the space between the electrodes is determined by hydrolysis and diffusion of chlorine and its compounds formed at the anode. For confirmation of these views, the authors determined the composition of the solution in the inter-electrode space (IES) and of the anolyte during electrolysis of sodium chloride solution (300-310 kg/m³) in relation to the acidity of the solution and the current density. The experimental results confirm the earlier conclusion that the acidity of the feed solution during production of sodium amalgam and chlorine does not play the decisive part which is often ascribed to it. Therefore in solving the question of optimal acidity it is necessary to take into account numerous factors, including the method of removing impurities from the solution and the corrosion resistance of the equipment. 16 refs.

Ovchinnikova, T.M. (Kirov Polytechnic Inst, USSR); Fuks, S.L. *J Appl Chem USSR* v 60 n 5 pt May 1987 p 944-947.

24. - 013350 RECOVERY OF CAUSTIC SODA FROM CAUSTIC EFFLUENTS. An economically viable treatment sequence has been developed and piloted at two textile factories for the recovery and reuse of water, chemicals and heat energy from sodium hydroxide effluent produced during the scouring of cotton fibre. The treatment sequence involves pretreatment of the scour effluent by neutralisation, using an acidic gas, cross-flow microfiltration and charged membrane ultrafiltration (also called nanofiltration). The sodium hydroxide is then recovered in an electrochemical cell with the simultaneous evolution of acidic gas which is recycled within the treatment process. Two possible configurations of the treatment process, where the acidic gas is either chlorine or carbon dioxide, are discussed. (Edited author abstract) 11 refs.

Simpson, A.E. (Univ of Natal, Durban, S Afr). Buckley, C.A. *Chemsa* v 14 n 3 Mar 1988 p 76-78, 80.

25. - 017991 Chemical products survey. This article attempts to survey the existing state of the caustic soda industry in India and future developmental possibilities. The author discusses the existing supply base and its characteristics. He also attempts to portray the future scenario in terms of likely increases in production capacities and prospects of new technology incorporation. (Edited author abstract)

Satyashayana, P.V. *CFW Chem Eng World* v 24 n 6 Jun 1989 p 63-64.

26. - 111: 122737b Improved performance of membrane chloralkali cells. Anon. (UK). *Res Discl.* 1989, 302, 403 (Eng). Loss of current efficiency in the title cells can often be overcome by 1 of the following methods: (1) a temporary decrease in concn. of the caustic to 20-30% for 0.5 to 5 h during cell operation (2) shutdown of electrolyzer followed by flashing with dil. brine and caustic, or H₂O for 5-60 min followed by recharging and (3) shutdown with removal of the membrane which is washed in H₂O or alc./H₂O with final H₂O rinse.

27. - 111: 177281d Material balance of the chloroalkali industry. Schulze, Joachim. (Inst. Tech. Chem., Tech. Univ. Berlin, Berlin, Fed. Rep. Ger.). *Chem.-Ztg.* 1989, 113(6), 207-14 (Ger). A review, with no refs., on the development of chloroalkali process, product application, and economic factors involving prodn. and trade in the Federal Republic of Germany.

28. - 004611 Reactor analysis of an electrochemical caustic concentrator. Physical Sciences Inc. is developing an electrochemical caustic concentrator (ECC) to reduce the energy requirements of a membrane chloralkali plant. The ECC is a membrane alkaline fuel cell which consumes the by-product hydrogen from the chloralkali cell and oxygen from air to generate dc power and concentrate the caustic soda in the cathode compartment. We are developing a process development unit (PDU) of the ECC in order to verify its operating characteristics. As part of this effort, we developed a detailed reactor model of the PDU. In this model we use data from our gas diffusion electrode and membrane development studies. Our analysis indicates that with state-of-the-art components, the caustic soda from the chloralkali cell can be concentrated to 50 wt% with the generation of dc electricity. (Author abstract) 9 Refs.

Vilambi, N.R.K. (PSI Technology Co, Andover, MA, USA), Taylor, E.J.; Waterhouse, R.; Gelb, A. *Sep Sci Technol* v 25 n 5 Apr 1990 p 627-652.

29. - 003942 Calculation algorithm for combined evaporation and crystallization by a variational method. An entropy variational approach to the modeling of an evaporator is considered for crystallizing solutions. The method was checked for the example of evaporation of a caustic soda solution, which is accompanied by the crystallization of sodium chloride. The method suggested may also be used to model heat and mass transfer in one dimensional moving heterogeneous polydispersed media. (Edited author abstract) 9 Refs

Dorokhov, I.N. (D.I. Mendeleev Moscow Chemical Technology Inst. USSR), Koltsova, E.M., Shipulina, T.A. *Theor Found Chem Eng* v 23 n 5 May 1990 p 390-395

2. UNIDO REPORTS ON SODIUM HYDROXIDE PRODUCTION

DATA BASE : Industrial Development Abstracts (IDA)

RECORD NUMBER: 018728
DOCUMENT DATE: 1990
CALL NUMBER:
PERSONAL AUTHOR: Nowak, Michael
CORP. AUTHOR: UNIDO
TITLE: (R) GHANA. TECHNICAL REPORT COMPRISING OPPORTUNITY STUDIES ON A CAUSTIC SODA/CHLORINE PLANT AND ON CASSAVA STARCH PROCESSING.
PROJ. NUMBER: DP/GHA/87/026
SOURCE: Vienna, 1990. ii, 65 p., tables, diagrams.
DOC. NUMBER: UNIDO-DP/ID/SER.A/1419
ABSTRACT: <UNIDO pub>. <Expert report> on opportunity studies on a <caustic soda> and <chlorine> <factory> and on <cassava> <starch> processing in <Ghana> - covers (1) <summary> of project (2) <market> analysis (3) <raw material>s input: <salt>; requirement; <utilities>; <location of industry> (4) process description (5) <manpower needs> (6) <investment> <costs>; <financing> (7) <profitability>. <Recommendations>. <Statistics>, <diagram>s. Additional references: <capital investment>, <working capital>, <cash flow>. <Restricted>.
LANGUAGES: ENGL
CLASSIFICATION: 35.30

RECORD NUMBER: 016747
DOCUMENT DATE: 1988
CALL NUMBER:
PERSONAL AUTHOR: Walkley, A.J.
CORP. AUTHOR: UNIDO
TITLE: ALGERIA. MERCURY CELL RESTORATION COMPARED WITH REPLACEMENT BY MEMBRANE CELLS. TECHNICAL REPORT.
PROJ. NUMBER: SI/ALG/87/803
SOURCE: Vienna, 1988. 50 p. tables, illus.
DOC. NUMBER: UNIDO-DP/ID/SER.A/982
ABSTRACT: <UNIDO pub>. <Expert report> on assistance to a <salt> <electrolysis> plant in <Algeria>, presently using the <mercury> cell process for the manufacture of <chlorine> and <caustic soda> (reference: <pollution control>) - covers (1) problems posed by mercury losses to the <environment>; proposals for replacing mercury cells by membrane cells (2) operation of the various sections of the chlorine plant (3) mercury loss analysis; mercury <hygiene>; <waste disposal> (4) specifics of membrane cells; sources of <supply> (5) options for renovation of the chlorine plant. <Statistics>, <recommendations>, illustrations. Additional references: <recovery>, <salt water>, <handling>.
LANGUAGES: ENGL
CLASSIFICATION: 35.30

RECORD NUMBER: 014941
DOCUMENT DATE: 1985
CALL NUMBER:
PERSONAL AUTHOR: Herdmann, G.
CORP. AUTHOR: UNIDO
TITLE: ELECTROCHEMICAL INVESTMENT OPPORTUNITIES.
SOURCE: Vienna, 1985. 1 vol. (various pagings). tables, graphs, diagrams, illus.
DOC. NUMBER: ::::
ABSTRACT: <UNIDO pub>. <Expert report> on <investment> opportunities in the electrochemicals sector in <developing countries> - covers: electric arc processes; <hydrogen> and <oxygen> production by means of <water> <electrolysis>; <chlorine> and <caustic soda> production from sodium chloride or natural <salt water> and the production of chlorine from muriatic acid; the production of <hydrochloric acid> from chlorine and hydrogen; the electrolytic production of <sodium> chlorate and <potassium> chlorate and of <bleaching> chemicals; the electrolytic production of <aluminium> and of <magnesium>. <Recommendations>, <diagrams>, <statistics>.
LANGUAGES: ENGL FREN
CLASSIFICATION: 35.30

RECORD NUMBER: 014597
DOCUMENT DATE: 1985
CALL NUMBER:
PERSONAL AUTHOR: Koenigson, Lennart
Schmidt, Egon Boisen
CORP. AUTHOR: UNIDO
TITLE: CHANGES IN THE WORLD'S ALKALI INDUSTRY AND ITS IMPLICATIONS FOR JAMAICA.
PROJ. NUMBER: SI/JAM/84/801
SOURCE: Vienna, 1985. 51 p. tables, diagrams.
DOC. NUMBER: ::::
ABSTRACT: <UNIDO pub>. <Expert report> on <trends> in world <alkali> industry and its implications for <Jamaica> - covers (1) alkali <consumption> in Jamaica (2) alkali processes: <sodium carbonate> and <caustic soda> by respective chemical synthesis; <electrolysis> (3) alkali <marketing> and <handling>; the caustic soda <market> (4) alkali production and use in Jamaica, <Colombia>, <Dominican Republic>, <Guyana>, <Venezuela>, <Suriname>, <Nicaragua> and in other <Caribbean> countries (5) the Jamaican <alumina> industry: future <demand> and options; <financial aspects>. <Statistics>, <flow chart>s, <bibliography>.
LANGUAGES: ENGL
CLASSIFICATION: 35.30

RECORD NUMBER: 014786
DOCUMENT DATE: 1984
CALL NUMBER:
PERSONAL AUTHOR: Messian, Yves F.
CORP. AUTHOR: UNIDO
TITLE: JAMAICA. PRE-INVESTMENT ACTIVITIES. MISSION REPORT.
PROJ. NUMBER: RP/INT/84/011
SOURCE: Vienna, 1984. 18 p.
DOC. NUMBER: :
ABSTRACT: <UNIDO pub>. <Expert report> on assistance in promotion of
<industrial projects in <Jamaica> - covers (1) the
<institutional framework> for <project selection> and
<project evaluation>; visits made (2) assessment of needs
for <training assistance> (3) <preinvestment study>s,
<feasibility study>s. Annexes terms of reference for
projects concerning <caustic soda> and <alumina>.
Conclusions.
LANGUAGES: ENGL
CLASSIFICATION: 14.80

RECORD NUMBER: 013164
DOCUMENT DATE: 1983
CALL NUMBER:
PERSONAL AUTHOR: Adhia, Jayant D.
CORP. AUTHOR: UNIDO
TITLE: SO YOU WANT TO BUILD A CHLOR-ALKALI PLANT?
SOURCE: Vienna, 1983. 19 p. diagrams.
DOC. NUMBER: UNIDO-UNIDO/IO.567
ABSTRACT: <UNIDO pub> on <factory establishment> for production of
<chlorine> and <caustic soda> - (1) covers development
background, uses and <trend>s in manufacture of such
<chemicals>; <demand> in <developing countries>; <choice of
technology> (2) provides guidance in the selection of
<appropriate technology> and <production capacity> for small
scale chlor-<alkali> plants. <Bibliography>, <flow chart>s.
Additional reference: <salt>.
LANGUAGES: ENGL
CLASSIFICATION: 35.30

3. AVAILABLE BOOKS AND JOURNALS FOR SODIUM HYDROXIDE AND RELATED SUBJECTS

- 3.1 Ullmann's Encyclopedia of Industrial Chemistry, 1987
- 3.2 Modern Chlor-Alkali Technology, vol 3, Wall, K. Ed. Ellis Horwood Ltd., 1986.
- 3.3 Modern Chlor-Alkali Technology, vol. 2, Jackson, C.; Ed. Ellis Horwood Ltd., 1983.
- 3.4 Proceedings of the Symposium on advances in the Chlor-alkali and Chlorate Industry. 1984, (see section 1, ref.9).
- 3.5 Small scale electrolytic processing
Symposium 177th meeting, 1990
Electrochemical Society
- 3.6 Modern Chlor-alkali technology
International Chlorine Symposium, London
Society of Chemical Industry
- 3.7 Engineering of industrial electrolytic processes
Symposium, 167th meeting, 1985
Electrochemical Society

4. WORLDWIDE ACTIVATED SODIUM HYDROXIDE PRODUCERS

4.1 European Producers of Caustic Soda

AUSTRIA

Donau Chemie AG,

Am Heumarkt 10, A-1037
Wien
ph.: 0222-732581

Elektron, Bruno Seeliger's
Sohne

Am Kanal 6-7, A-2511
Pfaffstatten
ph.: 02252-80205

Solvay Osterreich
Ges.m.b.H

Parkring 12, A-1010
Wien
ph.0222-5295800

BELGIUM

Solvay & Cie S.A.

Rue du Prince Albert
33, B-1050, Bruxelles
ph.: 02-5166111

CZECHOSLOVAKIA
Chemapol AG.

Kodanska 46, CS-100
10, Praha-10
ph.: 02-715

FINLAND

Veitsiluoto Oy.

P.L.196, SF-90101,
Oulu-10
ph.:981-221411

FRANCE

Societe des Produits
Chimiques d'Harbonnieres

Place de l'Eglise,
F-80131 Harbonnieres,
ph.: 33-22858007

GERMANY

ABR Abfallbeseitigung
und Recycling G.m.b.H.

Postfach 940, D-4250
Bottrop,
ph.: 02041-9903-0

Chemie-Export-Import

Storkowerstr. 133,
Berlin, ph.: 02452220

Hamm Chemie G.m.b.H.

Postfach 100661,
D-4100, Duisburg-1,
ph.: 0203-7971-0

Matthes & Weber G.m.b.H.

Postfach 100954,
D-4100 Duisburg,
ph.: 0203-609-1

Hoechst Aktiengesell-
schaft

Postfach 800320,
D-6000 Frankfurt-80,
Hochst, ph.: 069-305-0

Feddersen & Co.
(G.m.b.H. & Co.)

Postfach 111753,
D-2000 Hamburg-11,
ph.: 040-3618-01

Biesterfeld, Wilhelm,
E.H.

Postfach 1207, D-2210
Itzehoe-Edendorf,
ph.: 04821-74091

Wacker-Chemie G.m.b.H.

Postfach D-8000
Munchen-22,
ph.: 089-2109-0

Deutsche Solvay-Werke,
G.m.b.H.

Postfach 110270,
D-5650 Solingen,
ph.: 0212-704-1

GREAT BRITAIN AND N.I.
Tennant & Co. (London)
Ltd.

Charles, 69, Grosvenor
St. GB-London-WIX OBP,
ph.: 01-4935451

GREECE

Esso-Pappas Chemicals
S.A.

Leoforos Vas. Sofias
& Messoghion str.,
GR-115 26 Athens,
ph.: 01-7705311

ITALY

Sal Sud, S.p.A

Via Comunale delle
Puglie, 64, I-80013
Casalnuovo (NA),
ph.: 081-8423074

Caffaro, S.p.A.

C.P. 1288, I-20121,
Milano, ph.: 02-62011

Montedison, S.p.A.

Foro Bonaparte, 31,
I-20121, Milano,
ph.: 02-63331

Serv. Ric. Elettro-
chim., Sere. S.R.L.

Milan

NETHERLANDS

Akzo B.V.

Postbus 4080, NL-1009
AB, Amsterdam,
ph.: 020-5901911

Chemproha Chemical
Export

Postbus 35, NL-3330
AT, Rotterdam,
ph.: 078-128366

POLAND

CIECH

Postfach 271,
PL-00-950, Warsaw,
ph.: 022-269001

PORTUGAL

Soda Povoá, S.A.R.L.

Apartado 2750, P-1118
Lisboa-Codex,
ph.: 01-535131

Danubiana

Postfach 1-74,
R-70033, Bukarest,
ph.: 90-156051

SPAIN

Energia e iIndustrias
Aragonesas S.A.

Paseo de Recoletos,
27, E-28004, Madrid,
ph.: 91-4194600

SWEDEN

Exa Nobel AB

S-445 01 Surte,
ph.: 0303-98000

TURKEY

Rati Pazarlama Ithalat
ve Ihracat A.S.

Buyukdere Cad.Polat Is
Hani 87/3-4,
Gayrettepe
TR-Istanbul,
ph.: 1-1721980

USSR
Sojuzchimexport V/O

Smolenskaja-Sennaja
32/34, SU-121200
Moskau,
ph.: 0095-2442284

YUGOSLAVIA
Kempro

Terazije 8,
Yu-11000Belgrad,
ph.: 011-324751

Sodaso-Oour

P.O.Box 35, YU-75300,
Lukavac,
ph.: 075-34111

Centrohemiija

P.O.Box 91, YU-91001
Skopje,
ph.: 091-225033

Feroelektro-Ro
Rudhem

P.O.Box 254, YU-75001
Tuzla,
ph.: 075-215211

Sodaso

Bratstva i jedinstva
17, Yu-75000 Tuzla,
ph.: 075-211111

KemiKalija

P.O.Box 1022,
YU-41001, Zagreb,
ph.: 041-514000

4.2 IMPORTANT U.S.A. PRODUCERS

Alfa Products, Morton
Thiokol, Inc.

152-T Andover St.
Danvers, MA 01923
ph : 617-777-1970

Ashland Chemical Co.

Columbus, OH.

Baker, J.T., Chem. Co.

Phillisburg, N.J.

Diamond Shamrock Chem.
Co.

Irving, Tx.

Dow Chemicals

2020 Dow Center
Midland
MI 48640

FMC Corp. Industrial
Chemical Group

Philadelphia, PA

Georgia Pacific Corp.

Atlanta GA

Harshaw-Filtrol
Partnership

30100-T Chagrin Blvd.
Cleveland, OH 44124,
ph : 216-292-9200

Jones Chemicals, Inc.

Caledonia N.Y. 14423
ph : 716-538-2311

Kaiser Chemicals, Inc.

Cleveland, OH.

LCP Chemicals &
Plastics, Inc.

Edison, N.J.

Mallinckrodt Inc.

P.O.Box 5439, St.
Louis, MO 63147.
ph : 314-895-2000

NL Baroid, NL Ind. Inc.

Houston, Tx.

Occ. Chemical Co.,
Industrial & specialty
Chemicals Group

Niagara falls, N.Y.

Olin Co., Chemical
Group

120 Long Ridge Rd.
Stamford, CT 06904
ph. : 203-356-2000

PPG Industries, Inc.
Chemicals Group

One Gateway Center,
Pittsburgh, PA 15222
ph. : 412-434-3131

Pennwalt Co., Inorganic
Chemicals Div.

Philadelphia, PA.

Stauffer Chemical Co.
Basic Chemicals Div.

Westport, CT.

Texaco Chemical Co.

P.O.Box 430, Bellaire
ph.: 713-656-8000

Thompson-Hayward
Chemicals Co.

Kansas City, KS 66106

Vulcan Chemicals, Div. of
Vulcan Materials, Co.

Birmingham, AL.

4.3 SOME ASIAN PRODUCERS

INDIA

Durgapur Chemicals Ltd.

Durgapur, West Bengal

Gujarat Alkalis &
Chemicals

Baroda

Industan Heavy
Chemicals Ltd.

Sopan, WB

JAPAN

Kashima Vinyl Chloride
Monomer. Co. Ltd.

5. SOME EQUIPMENT SUPPLIERS AND CONSULTANCY SERVICES

BRAZIL

Natron Consultoria e
Projetos S.A.

Rua Teofilo Ottoni
61/63, 11 Andar,
Centro, 20090 Rio de
Janeiro, R.J. Brazil,
ph.: 021-2966171

CANADA

Chemetics International
Co.

1818 Cornwall Avenue,
Vancouver, British
Columbia, Canada VGJ
1C7,
ph.: 604-734-1200

FRANCE

Krebs & Cie S.A.

8 Rue Jean Pierre
Timbaud-BP 68, F-7839,
Bois D'arcy Cedex,
ph.: 3-056-92-56

GERMANY

Krebskosmo Gesellschaft
fur Chemie-Ingenieur-
Technic mbH.

Zeltinger Platz 16,
D-1000 Berlin 28,
ph.: 030-4011051/53

VEB ChemieAnlagen Bauk
kombinat Leipzig-Grimma

Bahnhofstr. 3/5, 7240
Grimma/SA

ITALY

Oronzio de Nora-Impiante
Electrochimici SpA.

Via Bistolfi 35,
1-20134 Milan,
ph.: 23941

JAPAN

Hitachi Zosen Corp.

6-14 Edobori 1-chome,
Nishi-ku, Osaka 550,
ph.: 06-443 8051

Toyo Engineering Corp.
(TEC)

Kasmigaseki Building,
2-5, 3-chome
Kasmigaseki,
ph.: 03-5816311

Nisso Engineering Co.

6-1 chome, Kanda
Jinbocho, Chiyoda-ku,
Tokyo 101,
ph.: 03-296 9204

NETHERLANDS

Comprimo BV

P.O.Box 4129, 1009 AC
Amsterdam,
ph.: 020-598911

SOUTH AFRICA
Simon Carves (Africa)

Private Bag X3033,
Randburg 2125,
ph.: 789-1935

SPAIN
Tecnicas Reunidas S.A.

Arapiles 14,
Madrid-15,
ph.: 445-7000

SWITZERLAND
Bertrams AG

Eptingerstr.41,
CH-4132, MuttENZ,
ph.: 01-262-8080

Krebs & Co. Ltd.

20 Claridenstr,
CH-8022 Zurich,
ph.: 1-2026905

Sulzer Escher Wyss Ltd.

Escher Wyss-Platz,
CH-8023, Zurich,
ph.: 01-2462211

UNITED KINGDOM
Cremer & Warner Ltd.

140 Buckingham Palace
Road, London SW 1W
9SQ, ph.: 01-7300777

John Brown Engineers &

20 Eastbourne Terrace,
London W2 GLE,
ph.: 01-262 8080

Kerr J.G. & Co. Ltd.

76, Norfolk St.,
Liverpool.L1 OBG

U.S.A.
Airco Carbon

St. Maris, PA

Andco Division
of Marsco Co.

Ashland Chemical Co.,
Specialty Metals &
Alloys Group

Cleveland, OH

Astro Div. of Marsco Co.

Wooster, OH

Barnard & Burk Group Inc.

10252 Mayfair Drive,
Baton Rouge, LA 70809,
ph.: 504-293 400

Brown & Root Inc.

4100 Clinton Drive,
Houston,
ph.: 713-6763011

Cortech Plastics Inc.	
Crawford & Russell Inc.	17 Amelia Place, P.O.Box 1432, Stamford, CT 06904, ph.: 203-327 1450
CPAC Inc.	
Diamonds Shamrock	Irving, TX
Dow Chemicals	2020 Dow Center Midland MI 48640
Dupont Inc. Electric materials Co. Engelhard Co.	Edison, N.J.
Habing Plastics Inc. Handy & Harman	New York, N.Y.
Harshaw/Filtrol Partnership	30100-T Chagrin Blvd. Cleveland, OH 44124, ph : 216-292-9200
Heil Process Equipment Xerxes Co.	Avon, OH
Ionics Inc.	
Kaiser Chemicals	Cleveland, OH
Lancy International Inc.	
Leeds & Northrup Instruments	
Ney Products Inc.	
Nu-Tech Precision Metals Inc.	Waterbury, CT
Pacific Engineering & Production Co. of Nevada (Pepcon)	
Sigri Co.	Somerville, NJ
Southern Tank & Mfg. Inc.	Owensboro, KY
Stearns Catalytic World Co.	P.O.Box 538, Allentown, PA 18105, ph.: 215-481 4911
Technic Inc.	Cranston, RI

Teledyne Energy Systems

Titanium Industries Inc. Fairfield, NJ

6. R & D INSTITUTES

<u>COUNTRY</u>	<u>INSTITUTE</u>	<u>ADDRESS</u>
GERMANY	Instit. Tech. Chem. Univ. Berlin	
INDIA	Train. Dep., FCL	New Delhi
	Central Electrochem. Research Institute	Karaikua
JAPAN	Fac. Eng., Kyoto Univ.	Kyoto, Japan 606
	Natl. Res. Lab. Chem. Technol.	Yatabe, Japan 305
S.AFRICA	Univ. of Natal	Durban
URSS	D.I. Mendeleev Moscow Chem. Tech. Institute	
U.S.A.	Electrochem. Society	10 S. Main St., Pennington, NJ 08534
	Internat. Society of Electrochemistry	Berkeley, CA

7. BIBLIOGRAPHY

7.1 Books, reports and journal articles :

- Ullmann's Encyclopedia of Industrial Chemistry
1987
- Shreve's Chemical Process Industries
5th. Ed., 1985
- Industrial Chemicals
Faith, Keyes & Clark's, 4th. Ed., 1975
- Chemical and Process Technology Encyclopedia
Considine, D. M. (ed.), 1974
- Electrochemicals (with special reference to Chlor
Alkali Industry.
Ramadurai, V., in : CEW, vol. XXI. No 10, Oct. 1986,
pp.81-85

- Chlor-alkali membrane cells and optimization of their design.

Chatterjee, S.N., in : Chemical Age of India, vol.39, No 3, March 1986, pp.189-194

- Mercury pollution in Chlor-alkali industry

Dheer, K.M., Chemical Age of India, vol.36, No 8, Aug. 1985, pp.755-757

- Pollution control and energy saving : a case study in chlor-alkali industry

Chatterjee, S.N., Bhattacharjee, B.K., in ; Chemical Age, vol:36, No 1, Jan.1985, pp.105-108

- Introduction to membrane cell technology in the production of chlor-alkali

Kelham, S.F., In : Kemia-Kemi n : 02, 1984, pp.93-97

7.2 On line searches : 1980-1992

7.2.1 Data Base CA search (chemical abstracts)

7.2.2 Data Base IDA (Industrial Development Abstracts)

7.3 Directories

- ABC Europe Production 1988

- Chemical Engineering Catalog 88 (CEC)

- Index of conferences Proceedings 1985-1991, (British Library)

- Seiss Catalog 88

8. RELEVANT TECHNICAL PAPERS ENCLOSED :

- 8.1 Electrochemicals
- 8.2 Chlor-alkali membrane cells and optimization of their design
- 8.3 Introduction to membrane cell technology in the production of Chlor-alkali
- 8.4 Pollution control and energy saving : a case study in Chlor-alkali industry
- 8.5 Sodium hydroxide derivatives
- 8.6 Standard specification for liquid caustic soda

Electrochemicals †

(With Special Reference to Chlor Alkali Industry)

- V. Ramadurai

In the recent past there has been a great awakening in the awareness of safety aspects in the operation of chemical industries. The Bhopal tragedy has given a dimension to the consideration of safety in operating maintaining chemical plants. However many industries had not paid sufficient attention to the safety aspects in the earlier years and the safety slogan was only used as a code for inaction. The value of human resources as contributory forces for a productive management has been emphasised by the Government and the formation of "councils" in a number of industries has been a step towards this thinking. Since shop floor personnel are regularly faced with problems of safety, their suggestions and the various deficiencies in safe practices could be treated as an important tool in the 'safety management' of various companies. However it is difficult to gauge how the workers would react to unsafe conditions if their own relatives had been involved in or exposed to such unsafe conditions.

Safety as an aspect of life is not confined to industries but is all pervading. Human instincts always tend to avoid unsafe acts or conditions. The main constraint in reducing unsafe acts lies in the identification of such unsafe conditions/acts. Many times the problems encountered in life or industries arise out of the ignorance of safety aspects. The basic requirements of creating a better working atmosphere pertain to the creation of awareness of the hazardous properties of chemicals or acts connected with the handling of such chemicals. This also brings into light a great lacuna that generally exists due to the lack of dissemination of information to shop floor personnel on the hazardous properties of chemicals handled by them and the risks involved therein. A great deal of effort has to be achieved on the 'education' on a long term basis by the industry.

Safety in industry can have two connotations. Considerations of safety have to reckon with the factors within production facilities as well as those connected with the external environment. Whilst there have been regulations in existence in the statute books for dealing with unsafe acts within the manufacturing units, the conditions that could come into the fore on the external environment as a result of the handling or storage of manufactured goods outside its premises have not been fully codified particularly for the safe handling of hazardous chemicals which are transported from the production unit to the consumers. Many times consumers are not fully aware of the steps to be taken in handling hazardous products within their premises and in reacting to emergencies. The interaction between the producer and the consumer on the salient safety aspects will

reduce the hazards. Consumer education is a vital link in any safety programme. If safety has to be dealt with on a "totality" basis, besides safety in production, safety in distribution and storage have also to be attended on a priority basis.

Pollutants from manufacturing facilities have assumed significance in recent years as one of the major factors affecting the safety in the operation of the units as well as in the environment. Whilst in some cases the gas or liquid pollutants may result in the impairment of the organs of a human being immediately or in a very short time, many other pollutants if allowed to exist in the environment will show their effect only after a considerably long time. To avoid any bad effects on the health of the workers and the citizens at large the maximum allowable concentration of the different pollutants for specific periods of exposure have been worked out by scientists. These values known as 'TLV' serve as guiding figures in the handling of hazardous chemicals.

CHEMICAL INDUSTRY

The growth of chemical industry in the country in the last few five year plans has been phenomenal. Large scale and small scale units with new technologies processes and products have been established. Some of the new technologies are based on the indigenous know how, however many of the large scale plants still continue to be built on foreign or modified foreign technologies. Due to the variety of chemicals handled and the process conditions employed, the horizon of the chemical industry has widened vastly. The industry had therefore to build expertise on the toxicity of the chemicals with reference to their manufacture as well as end use in the consuming industries. Chemical industry involving handling of hazardous gases, liquids, etc. has therefore to keep pace with the introduction of new manufacturing facilities for new products in the country.

THE AUTHOR

Mr. V. Ramadurai, a well known Technologist in chlor-alkali field is basically a chemical engineering graduate. He has served in various capacities in industries connected with man made fibre, sodium hydrosulphite and caustic-chlorine. He has been instrumental in introducing zinc/amalgam process for sodium hydrosulphite in the country.

Joining the Standard Mills Co. Limited in the year 1966 as a Production Manager he rose to the position of Director by 1974. He is also a Director on the board of a number of companies and President of Standard Mills Co. Ltd., (Chemicals Division).

He has extensively travelled and has been actively associated with many professional bodies. Presently he is Chairman of the Basic Chemicals, Pharmaceuticals and Cosmetics Export Promotion Council and Inorganic Chemicals Sub-Committee of the ICMA.

† This paper was presented at the Seminar on Safety in Chemical Industries organised by the Indian Chemical Manufacturers Association in 1985, at Bombay.

Whilst the introduction of new technologies and manufacture of new chemicals should be encouraged, great care has to be taken in looking into safety aspects of the processes and the handling of chemicals before deciding to build up such facilities. Selected technologies should pay specific attention to the toxicology of the new products and build in safe operating conditions in the design of the plants.

ELECTROCHEMICAL INDUSTRY

Electrochemical industry is a part and parcel of the chemical industry, which has gained ground in view of the superior quality of the products that are obtained from electrochemical reactions. Electrochemistry has a lot to do with electricity. Any precaution to be taken in the electrochemical manufacturing facilities should include safety aspects in the operation and maintenance of electrical systems besides the safety aspects connected with the chemicals being handled.

In India the largest electrochemical industry is the caustic-chlorine industry manufacturing caustic soda and chlorine by one or the other of the processes i.e. diaphragm, mercury or membrane. In all these processes the final products are the same although one has to reckon the hazards of asbestos in case of diaphragm cells and mercury in case of mercury cells. Electrolysis of water for the manufacture of hydrogen and oxygen, electrolysis of brine for the manufacture of chlorate and perchlorate, manufacture of manganese dioxide are some of the well known electrochemical manufacturing facilities established within the country. Sodium hydrosulphite has also been manufactured by the electrolysis process in some of the units in the country. The production of potassium and ammonium persulphate, cuprous oxide, recovery of zinc from zinc hydroxide via zinc sulphate are some of the other electrochemical processes in vogue in the country. Whilst it may be desirable to deal with each and every electrochemical technology to gauge the extent of safety to be employed in the manufacturing process or in handling of the chemicals of each industry, it is virtually impossible to consider each and every industry. Therefore discussed here under is the largest electrochemical process in the country, i.e., the process for the manufacture of caustic soda and chlorine for this presentation.

CHLOR ALKALI INDUSTRY

In considering safety in chlor alkali industry, The following aspects have to be taken care of:-

Safety aspects connected with handling and storage of raw materials

Alternate routes for the manufacture of caustic/chlorine and safety aspects connected with each of the process

Properties of the end products, their storage, handling etc.

Electrolysis with salt or potassium chloride gives rise to chlorine, caustic and hydrogen as the end products. Raw materials that are mainly used in the manufacture of alkalies are common salt, potassium chloride and electrical power for electrolysis. Details of the subject enunciated above are given herewith.

Common Salt/Potassium Chloride

Common salt available from the salt pans in the country is mainly used as the basic raw material for the manufacture of caustic soda. The salt contains large amount

of impurities such as magnesium, calcium, sulphate, etc. and these are precipitated and purified by settling the sludges. If the alkaline electrolysis utilises the amalgam process some quantities of mercury will inevitably adhere to the sludges and in spite of best devices used for removal of mercury from the sludges, the mercury level will range from 50 to 100ppm. If the quantity of sludge formed is large, mercury loss is also considerable and this will pose a problem for the environment as well as to the society. If the sludge is allowed to be accumulated and not disposed of in a proper fashion leaching of the sludge could create imbalances in the ecology. Therefore alkali producers will have to look for the use of purified salt and/or find out a solution for disposing of the brine sludge. Efforts are already on way in both the directions and may be in the near future this problem will be solved by minimizing hazards associated with the sludge. Also the use of purified salt will increase the cost of production. Hence to encourage the use of purified salt the Government should look into some means of compensation.

Further great care has to be taken in getting bulk supply of salt and lorries carrying loose salt have to be thoroughly washed prior to the salt service. In case lorries had been earlier used for carrying fertilizers containing nitrogen such as ammonium sulphate, ammonium chloride, etc. there is a possibility of contamination of salt by nitrogen containing material. This results in the ingress of ammonium radical in the brine culminating in the formation of nitrogen trichloride in the cells. Nitrogen trichloride is extremely explosive and its collection in the liquifier/storage vessels/containers may lead to serious explosions.

The problem is not so severe in the case of potassium chloride, since purified salt is being made use of which gives very small quantities of sludge.

Electrical Power

Electrical power constitutes one of the major raw materials for the manufacture of alkalies and the handling of power requires careful planning, i.e. care similar to that taken in the engineering industry such as preventing short circuits, earthing, etc. In addition, sufficient precautions should be taken in the cell house to prevent any shorting in electrical switchgear to avoid possibilities of fire hazards. Suitable precautions have also to be taken to make sure that electrical units being attended to are switched off from the main supplies to prevent any injuries to the maintenance personnel.

Continuity of power supply is of vital importance to the chlor alkali industry. Repeated voltage drops, or power trips will result in considerable losses of mercury in the brine and consequent undesirable over-loading of brine sludge with mercury. Suitable polarisation rectifiers will have to be provided to take care of this contingency so that mercury losses are reduced to a minimum. In addition, it would be necessary to have an auxiliary source of emergency supply of power preferably a diesel generating set to operate mercury pumps, hypochlorite circulating pumps/blowers in the hypochlorite plant and lighting in the cell house and few other critical areas. This will make sure that in case of any failure of power supply, the emergency diesel set will automatically start and the connected equipments in the emergency circuit can be restarted and chlorine remaining in the system can be

vacuated to the hypochlorite tower and chlorine nuisance can be avoided. This provision has to be considered as one of the important requirements of a chlor-alkali plant to ensure the safety of workers in the plant.

PRODUCTS
Caustic Soda

Caustic soda is mainly produced as 50% solution in case of mercury cells and 11% solution in case of diaphragm cells. It is driven out of the decomposer at a higher temperature and care has to be taken to make sure that operators use proper hand gloves, gum boots and goggles. Any time the use of goggles is dispensed with and such safe acts will one day or other result in loss of eye sight. This is true in a cell plant as well as in the caustic evaporation plant.

Chlorine

Chlorine is one of the most toxic reactive halogens. It causes anywhere from mere respiratory irritation to death depending upon the concentration to which one is exposed to. Table I indicates the effects of chlorine at various concentrations. In view of the dangers associated with the chemical, one has to take precautions in each step of manufacture including storage and filling.

TABLE I EFFECTS OF CHLORINE AT VARIOUS CONCENTRATIONS

No.	Effects	Parts of chlorine gas per million parts of air by volume
	Least amount required to produce slight symptoms after several hours of exposure	1.0
	Least detectable odour	3.5
	Maximum amount that may be inhaled for 1 hour without serious disturbances	4.0
	Noxiousness, impossible to breathe for several minutes	5.0
	Least amount required to cause irritation of throat	15.1
	Least amount required to cause coughing	30.2
	Amount dangerous in 30-minutes to 1 hour	40 to 60
	Kills most animals in very short time	1000

operation of a chlorine plant is intimately related to the awareness of its properties by the operatives, whilst chlorine is corrosive to steel, dry gas can be handled in steel equipments and pipe lines. Special materials of construction such as PVC, PVC/FRB are better for handling chlorine. Moist chlorine is generally dried by concentrated sulphuric acid.

Chlorine by itself is not an explosive gas but in the presence of hydrogen, forms explosive mixture within certain concentrations. The knowledge of the explosive limits is a must for the safe operation of the plant. It is the knowledge that due to side reactions during elec-

trolysis always some hydrogen is formed along with chlorine in the anode gas. The percentage of hydrogen in the chlorine gas sometimes increases due to presence of heavy metals, and impurities in the cell freed brine. If the volumetric percentage increases beyond the limit, explosions are likely to happen in the cells. Variation of pH of feed brine and disruption in the flow of mercury are other factors which necessitate extra care, since these lead to the formation of explosive gas mixtures.

The presence of nitrogen containing compounds in salt lead to the formation of nitrogen trichloride which liquifies along with chlorine and collects as liquid NCl₃ in storage. When the liquid chlorine is withdrawn from the storage or the container, NCl₃ concentration inside increases resulting in the formation of the explosive mixture and the possibility of serious explosions.

Continuous monitoring of hydrogen concentration is resorted to in modern plants both in the cell gas as well as the sniff gas from the liquifiers. Magnetic rotameters are installed in the chlorine line to HCL synthesis units where sniff gas is burnt. This is to avoid any reaction in glass tube due to the actinic rays.

The storage and handling of liquid chlorine require special attention. Tanks and containers are constructed with thickness not only to take care of the pressures likely to develop within when exposed to direct sunlight but also for the likely corrosion. Strict control on the quality of plates used as well as on the production process, e.g. radiography of welded joints are insisted upon by the authorities. These units are also to be tested periodically and the test records have to be maintained to ensure the safety of the equipments. If the loss of weight of any container is above 5% of the original tare weight, the containers have to be taken out of circulation, cut into pieces and destroyed to avoid its reuse.

The storage tanks may be insulated or bare depending upon the way in which liquid chlorine is condensed and transferred. However, the storage tanks and the containers should never be exposed to direct sunlight. Excessive pressures should develop as a result of such exposures. Containers should not be stored in places where there are high ambient temperatures and/or the likelihood of naked flames.

Handling of liquid chlorine in cylinders/containers is beset with hazards if proper precautions are overlooked. The containers should be loaded/unloaded with pulley blocks for safety of the units. The protective domes for the valves should be fixed up in all the containers to protect the valves and avoid any damage in transportation. Suitable kits available for handling chlorine leakages from the valves and the body of the cylinders should be used extensively both at the producers' and consumers' end.

Before attending to any maintenance work in the storage tanks, the contents of the tank should be purged with dry air. Work should be started only after tests are carried out on the chlorine content in the air inside and the safety officials are satisfied with the tests. The personnel trained in attending to the maintenance should be provided with compressed air breathing apparatus. For this purpose all the respiratory and protective appliances should be stored in an easily accessible place.

These precautions enunciated above are by no means exhaustive and the complete ones; they are only indicated

to bring out the serious safety measures needed to handle chlorine. Institution like American Chlorine Institute have specialised data on chlorine handling and they could be of great assistance to the Indian Chlorine Industry in assessing potential hazards and taking corrective measures in advance.

Hydrochloric Acid

Hydrochloric acid is often prepared by the direct synthesis of hydrogen and chlorine in a chlor alkali plant. In many cases where chlorine cannot be disposed of, the manufacturers synthesise hydrochloric acid from chlorine and hydrogen. This can be sold as commercial hydrochloric acid or destroyed by treating it with lime.

In the past when the demand for chlorine was not sufficiently developed and where caustic had to be produced to cater to the various consuming industries, chlorine that could not be utilised adequately had to be converted into hydrochloric acid and/or destroyed by treating it with lime. The neutralisation operation has to be done with great care to make sure that no unreacted hydrochloric acid emanates out.

Hydrochloric acid by itself as a commercial acid has to be handled with all the safety appliances such as goggles, gum boots, etc. and filled in plastic or rubberlined vessels. Further in the synthesis unit for the manufacture of hydrochloric acid, attention has to be paid that absorption of the gases is complete and hydrochloric acid content of the exit gases is not more than 450 mg per cubic meter at the tail gas vent. Also, in the HCl plant area the limit of HCl content is governed by the TLV which is 8.35 mg/cu. meter and away from the HCl plant the limits are 1/10th of the TLV i.e. 0.84 mg per cu. meter. In order to enable the operators to work without any hazards these values have to be maintained. In case the values are higher the absorbers have to be checked up for chokes or additional capacities of the absorbers have to be built in. It is also possible to bring down this concentration well below the limits specified by using chilled water.

Hydrogen

Hydrogen emanating from the secondary cell is at a very high temperature and carries mercury by way of entrainment as well as by the vapour pressure consideration. As hydrogen forms explosive mixture with air, care has to be taken that the entire hydrogen system is under slight positive pressure. Hydrogen leakages should also be controlled carefully and gas should not leakout from joints as any spark or any naked flame is likely to ignite hydrogen resulting in fire hazards. Suitable arrestors have to be provided in the hydrogen line to prevent any fire.

To separate mercury from hydrogen care has to be taken to cool the gas to temperatures of 15 to 20°C so that the amount of mercury carried forward with hydrogen can be minimized if hydrogen is not fully utilised for the synthesis of hydrochloric acid or for other uses such as bottling, hydrogen will have to be let out into the atmosphere through the gas holder. Thus venting of hydrogen will result in polluting the atmosphere with their mercury content in the hydrogen. It would therefore be necessary that hydrogen gas is treated suitably by scrubbing with hypochlorite solution or treating with molecular sieve/activated charcoal to remove mercury so that the final treated gas will not endanger the atmosphere or pollute the environment.

Since the operators of alkali/chlorine plants are subject to contacts with mercury, frequent medical check ups have to be conducted to make sure that mercury content in the urine or in blood does not rise up. It is also necessary to make sure that mercury is not handled by bare hand since mercury has got tendency to accumulate below the finger nails.

TECHNOLOGIES FOR CHLOR ALKALIES

Technologies for the manufacture of caustic/chlorine have taken a tremendous stride from the days of diaphragm cells. Whilst these developments have been done mainly to conserve the energy, yet the effects of new technologies have been useful in preventing pollution hazards. Diaphragm cells have almost gone out of vogue in view of the high cost involved in converting weak cell liquor into 50% solution. The amalgam technology is still in vogue but beset with hazards arising out of presence of mercury in the various effluents such as liquid, gas and solid. Modern technologies have been able to contain the mercury within approved parameters in the effluents.

The latest membrane cell technology besides affording a reliably low energy consuming process has to its advantage the complete absence of any mercury pollution. It is therefore highly desirable that wherever it is feasible new installations should be put up based on the membrane technology and whenever the economics permit, some of the existing installations should be converted to membrane cell technology. This will completely eliminate one of the greatest hazards from chlor-alkali industry.

DEVELOPMENT OF SAFETY IDEAS

The inhouse development of safety ideas has to originate from the design stage itself in a new installation. The latest technologies of mercury type cells utilise a close circuit so far as mercury is concerned. All the possible areas where mercury may get into the atmosphere are kept hermetically closed to prevent any leakage of mercury into the atmosphere. All the condensates from the gas streams where mercury is present are collected and put back into system. Further by a careful judicious control of precipitation process the mercury content in the sludge has also been reduced to a very low level. These have been achieved by a careful consideration of the design of the plant to avoid mercury emission. Once such plants are visualised with an eye on the pollution problem, the hazards connected with emission are practically reduced to the barest minimum. In addition suitable treatment system for the liquid and gaseous effluents also are incorporated in the original design itself to enable the installations to operate well below the maximum limits of mercury allowed to be thrown out into the atmosphere. Along with the choice of proper design it is also necessary to practise good house keeping especially in the cell house. Leaking pipes and equipments handling liquid or gases containing mercury are to be replaced well in advance of their life cycles. All the spillages if any are collected in suitable drains and put back into the systems. A careful manipulation of the operational and maintenance aspects in running chlor-alkali industry will be an asset in reducing the pollution and its hazards.

Apart from the development of internal safety it is also necessary to lay down emergency procedures and emergency kits, to handle hazardous chemicals during transport and storage at the consumers end. Particularly for chlorine where it would be necessary to create an awareness amongst the transporters and consumers about the properties of chlorine, hazards connected with its handling in containers or cylinders and immediate preventive steps to be taken in case of any emergency. Lack of such an emergency drill results in the consumers or the governmental authorities taking altogether unsatisfactory steps to control emergencies. It has been recommended that producers should visit the consumers plants periodically and correct unsafe handling of their products. Alternatively consumers should be supplied with tools to tackle the emergencies. It has also been visualised that some emergency squads located in the key factories in the country could volunteer their services to attend any problems of emergencies in a zone within their reach. This would enable the manufacturers to discharge the social objective of handling the emergencies where the knowledge of such handling has not yet percolated to the consumer, transporter and governmental agencies.

Safety, should be given a position equivalent to production and maintenance as safe operating conditions improve the morale of the workers and create a climate and consequently better productivity. Compromises in unsafe working conditions have to be done away with. Electrochemical industry is no exception for the safety code. The chlor-alkali industry as a premier electrochemical industry only illustrates the hazards connected with such an industry and the need to be watchful at all times.

(Contd. from page 80)

dh/dt — Slope of the curve in Fig.(3)

dP/dt — Slope of the curve in Fig.(4)

Subscript:

A — Active slurry element

A_0 — Initial state of 'A'

B — Bio-gas

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Chlor-Alkali Membrane Cells and Optimization of their Design*

by

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ABSTRACT

Chlor-Alkali Industry has already entered the "Membrane Age". Developments of this process are described, including the latest "Hi Process" Japanese Membrane Cell with provision for installation of membrane over the existing mercury cell. Optimization in the design of various cell components and process parameters are described and various areas of cost reduction with special reference to power consumption enumerated. Future possibilities have been highlighted.

INTRODUCTION

The manufacture of Chlor-Alkali, first started in 1886, underwent a slow development over the last century or so. Due to the escalation in oil prices between 1973 and 1980 and stringent effluent regulations the need for a new chlor-alkali technology was felt and as a result of research and development in pilot plant studies throughout the world, the first commercial Chlor-Alkali Membrane Cell was commissioned in 1975. There is now a continuous effort from every corner to further bring down energy consumption, capital cost and operating cost in commercial membrane cells. DC energy consumption of 4000 KWh/ton in the mid-fifties, for instance, was brought down to 2200 KWh/ton in 1984. With the world-wide increase in the cost of energy and the simultaneous fall in product price, the only way of survival for chlor-alkali industry is conversion to membrane technology. At present 5% of world production is based on membrane process and it is estimated by the industrial experts that within 5 years this figure will be 25%. Conversion from mercury cell to membrane cell is most economical when there is a project taken up for conversion-cum-expansion. This is due to the fact that lateral conversion to the same capacity needs only 25% of brine volume and 25% of space of mercury cells. So conversion is becoming difficult, due to the high capital cost, for those plants which have no expansion program. The future for this type of plant is in "HORIZONTAL ION EXCHANGE MEMBRANE CELLS" where the existing mercury cells can be directly converted to membrane cells.

MEMBRANE CELLS :

The membrane chlor-alkali cell is constructed with anode and cathode compartments separated by a cation-conducting membrane. Sodium ions are transported selectively by electrolytic migration through a membrane composed of a sulfonated and/or carboxylated fluorocarbon. The development of membrane

cell technology took place in a phased manner from 1975 to 1982, as a result of which caustic concentration could be increased from 8% to 40% and DC power consumption could be brought down from 3400 KWh in 1974 to 2200 KWh in 1984. Electrode designs were changed and the anode/cathode gap was reduced from 5 mm to practically zero. Development of the membrane cell can be traced in three phases as follows :

First phase—1975-79 :

Nafion 324 and 390 membranes were used to produce 8 to 15% caustic soda. Anodes were mesh type titanium with activation and cathodes mesh type steel with an electrode gap of 3 to 6 mm. Cell element frames were made of plastic with internal busbars. Energy consumption was around 3400 KWh (50% caustic basis).

Second Phase—1979-81 :

Both Nafion 901 and Flemion 230 membranes were used to produce 35% caustic. Cathode design was changed to mesh type steel with activation and a 3 mm electrode gap. Cells were both monopolar and bipolar type. Cell elements were changed to metal with internal busbars. Energy consumption was around 2800 KWh (50% caustic basis).

Third Phase—1981 onwards :

Nafion NX 902, NX 960, NX 961, Flemion 723, 753 and Flemion DX membranes are in use for 35% to 40% caustic production. Cathodes have been changed to steel/nickel activation with zero electrode gap. During this phase, the cells have been mainly monopolar type. Cell elements are of the plate type. Energy consumption around 2200 KWh has been claimed (50% caustic basis) in 1984.

In the last 9 years, chlor-alkali membrane cell technology has been established as a proven commercial one. Energy cost, capital cost and production cost in this technology are at least 20%, 20% and 10% less respectively compared to mercury cell. (Table-1) Capital investment for a 100 TPD Plant is 37 million US Dollars (Table-2). Production capacity of mem-

* Paper presented at the 35th Session of the International Society of Electrochemistry at Berkeley, California, U.S.A.

TABLE — 1

	Amalgam	Diaphragm	Membrane
Material	13	13	20
Energy	28	30	22
Labour	14	14	13
Maintenance	15	20	11
Capital Cost	30	30	24
TOTAL	100	107	90

Basis 100 TPD Production Cost Comparison (%)

TABLE — 2

Capital Investment and Operating Costs vs. Plant Capacity

Plant Capacity MT/D NaOH	Capital Investment \$/MT/D NaOH	Operating Costs \$/ECU
25	\$ 700,000	605
50	550,000	550
100	370,000	470
1,000	185,000	320

brane cell plants worldwide was nearly 1 million MT³ in 1983 out of 28 plants. Production capacities of I.C.I.⁴, Asahi Chemical⁴, Asahi Glass⁵ will be 192,000, 672,000 and 470,000 MT respectively within 1986 including 13 new plants. Diamond Shamrock of U.S.A. will be having 13 membrane cell plants having a total yearly capacity of 160,000 MT. Taking into consideration similar proposed projects of other reputed companies, membrane cell production is expected to be at least 2 million MT by 1986 which will be approximately 5% of world production⁶. Major types of membrane cells available (projected upto 1986) are shown in Table-3.

TABLE — 3

Major Suppliers of Membrane Cell Plants*

	Type of Cell	Capacity MT/Year	Upto Year	No. of ref. Plants
Asahi Chemical	Bipolar	672,000	1986	11
Asahi Glass	Monopolar	470,000	1985	8
ICI (FM21)	Monopolar	192,000	1986	7
Diamond Shamrock	Monopolar	160,000	1984	13

* Reference Plants of M/s. HOOKER, IONICS, TOKUYAMA SODA, UHDE and DENORA were 3, 2, 1, 3, 2 respectively in 1983. Updated information is not available with the Author. All data are on the basis of information gathered upto June '84.

Conversion of a 100 TPD mercury cell to membrane cell will cost 40% less compared to a new plant, though optimum capacity utilization of this conversion is possible only if it is a conversion-cum-expansion project. On the basis of budgetary data available a mercury cell can easily be converted to a membrane

cell of 30%-40% expanded capacity by spending 40% of the plant cost⁶.

Kanegafuchi Chemical Industry Co. Ltd., Japan, have developed a new "Horizontal Ion Exchange Membrane Cells" Technology for conversion of existing mercury cell plants directly to membrane cell. A 20M² area cell has been operating at 100 KA for one year. Power consumption at 5 KA/M² current density is 2470 KWh DC. They have 52 such cells and all were to be converted within January, 1985. Rough estimated investment for a 100 TPD plant would be 4 million US Dollars. Long term success of this technology will definitely enhance the rate of conversion for mercury cells upto 5 KA/M² current density⁷.

Another company from Japan, Chlorine Engineers Corporation (Tokyo), are also converting mercury/diaphragm cells to membrane cells by retrofitting¹⁰. By October '86 close to 500,000 MT/year of Japanese capacity will be retrofitted by this technique. Olin Corp. (Stamford, Conn.) will convert their 100 TPD diaphragm cell plant to membrane cell retrofitted by Kanegafuchi. In retrofit technology the membrane encloses the anodes, sealing them to form a bag. Power for the electrode is supplied through a hole in the bottom of the membrane bag.¹⁰

Chlorine Engineers' Corporation have retrofitted 8 diaphragm cell plants to membrane cells by using their MBC or Membrane Bag Cell Technology. For a 50,000 MT/year chlorine diaphragm cell plant, cost of conversion is 3-4 million US Dollars. Cost of production is 10% less taking into account depreciation period as 7 years. Cost comparison and performance of retrofitted diaphragm cells of Chlorine Engineers' Corp. are shown in Table-4 and Table-5 respectively.

DESIGN, DEVELOPMENT AND OPTIMIZATION:

Optimum design of a plant mainly depends on capacity, location and local conditions. For overall improvement in design and economic operation of a membrane cell plant, the following areas are to be taken care of:

(a) Membrane — The following factors are to be taken into consideration while selecting a membrane for membrane cells:

- (1) high current efficiency
- (2) low back migration of OH⁻ ions
- (3) low electrical resistance
- (4) heat resistance
- (5) perfect chemical resistance to service conditions
- (6) dimensional stability
- (7) low diffusion of salt and low permeability of water
- (8) long life and low cost.

Three basic types of membranes are in use (i) perfluoro sulfonic acid; (ii) perfluoro sulfonamide; (iii) perfluoro carboxylic acid. The first and third types are more often used in industry. Both of these have their advantages and disadvantages. It became difficult initially to centre all the advantageous properties in one single membrane. However, the following firms have developed the technology to fabricate ion-exchange membranes:

- DuPont-Nafion
- Asahi Glass — Flemion

TABLE — 4
Retrofitted Diaphragm Cell
Typical Cost Comparison in Japan

Process	Diaphragm	Diaphragm MBC	Diaphragm Filter Press
Facility Cost (Million \$)		3-4	8-10
Utilities :			
Electrical *2 (AC KWh/ton Cl ₂)	3,000-3,200	2,900-3,100	2,700-2,900
Steam (tons/ton Cl ₂)	2.9-3.1	0.5-0.7	0.5-0.7
Variable costs :			
Electrical & Steam	256	200	188
Lease Fee & Others.	93	104	97
Sub Total :	349	304	285
Fixed Costs			
Depreciation & Maintenance	19	25	41
Labour Cost	12	10	10
Others	23	20	21
Sub Total :	54	55	72
Total	403	359	357
Interest*3	—	3	8
Grand Total	403	362	365

Plant Capacity : About 50,000 tons Cl₂/year
 Unit : US\$/ton Cl₂

Notes : *1) Electrical power: 0.0625\$/AC KWH
 Steam: \$20.83/ton
 *2) Including motor power

*3) Depreciation period: 7 years
 Interest: 10%
 *4) Exchange rate: Y 240 = US \$ 1

TABLE — 5
Typical Performance Data of
Retrofitted Diaphragm Cell
by Chlorine Engineers Corpn. Ltd.

Cell Voltage	— 3.35
Current efficiency	— 97%
Power consumption	— 2350 DC KWH/MT Caustic
Current Density	— 2.07 KA/M ²
Cell Temperature	— 90°C
NaOH Concentration	— 32%

- Asahi Chemicals
- Tokuyama Soda — Neosepta F

Better electrical conductivity of the membrane resulted in swelling of the membrane, high water content, and lower current efficiency. This problem may be overcome by using a multilayer membrane. The anolyte side has a thick layer of high conductivity perfluorosulfonic acid group which has a high equivalent weight. In contrast, the catholyte side has a thin layer of perfluorocarboxylic acid group membrane which has a lower equivalent weight. To increase mechanical resistance of this type of combination membrane a teflon cloth lamination is applied between the two layers of membrane.

(b) Energy saving across the cell -- Initial design of membrane cell had an electrode gap of 3-6 mm. This has been brought down gradually to the zero gap electrode where anode and cathode are as close as possible. Due to hydrophobic properties of membranes resulting in enhancement of gas adhesion, it became difficult to reduce the electrode gap to the minimum.

This problem has been eased considerably by designing an improved variety of membrane, the surface of which is covered with porous non-conductive inorganic material. This results in an improved hydrophilic property of the membrane. In some other designs the membrane surface is roughened to avoid hydrogen gas adhesion and bubble effect. Zero gap cells provide an energy saving of 0.6 volts at 2 KA/M² current density.

Activation of the cathode reduces hydrogen over-voltage by 0.2 volts. Instead of steel cathodes being used initially, activated cathode coatings are being used at present. Cathode overvoltage of various types of cathodes are shown in Table-6¹².

TABLE — 6
Cathode overvoltage of various types of cathodes
Cathode overvoltage (mV) at 3KA/M²

MS	— 400
Stainless Steel	— 400
Grit blasted SS	— 350
Etched SS	— 100-200
Polished nickel	— 500
Nickel sheet	— 400-450
Grit blasted nickel	— 350
Raney nickel	— 200
Proprietary coatings	— 50-100

Current density has an important role to play in the design of a membrane cell. The factors in this respect are membrane, electrode, electrolyte, internal busbars and cell inter-connections. Various process parameters can improve current density which we shall discuss afterwards in detail.

There are two types of membrane cells: monopolar and bipolar. Whether a cell will be monopolar or bipolar is decided very much on local conditions.

In a monopolar system, each cell unit in an electrolyzer is electrically connected in parallel, and each electrolyzer is connected in series. These are high amperage/low voltage cells having a comparatively higher voltage drop. In a bipolar system, however, each cell unit in an electrolyzer is electrically connected in series, and each electrolyzer is connected in parallel. In this system one potential problem is leakage of current and resultant corrosion. Table-7 shows a comparison between monopolar and bipolar cell structure with special reference to ohmic voltage drop (mV)*.

TABLE—7
Comparison of Monopolar and Bipolar Membrane Cell Structure

	Monopolar Cell	Bipolar Cell
Cell Volume & Weight		
Volume (m ³)	0.060	0.035
Total weight (Kg)	85	50
Titanium weight* (Kg)	12.5	7.5
Copper weight§ (Kg)	65	11
Ohmic Voltage drop (mV)		
Anode structure	15	15
Anode current conductor	30	15
Cell to Busbar**	45	20
Cathode current conductor	20	—
Cathode structure	5	10
Contacts	15	10
Total Voltage drop	130	70

* Cell structure and anode.

§ Incl. cell to cell busbars.

All data referred to 1 sq. m. of active membrane surface.

** In case of Bipolar Cell referred to one cell element.

Improved design of monopolar cell intercell copers with simplified easily removable connection has resulted in a total voltage drop of 5 mV in each joint. Similarly, improved design of bipolar cells has achieved a voltage drop of 3 mV through partition wall at 5 KA/M² and vertical ohmic drop in electrode is negligible.

(c) Electrode configuration — Anodes used for membrane cells are coated with titanium. They must be resistant to alkaline solution arising out of back-migrating hydroxide ions and should have low chloride overvoltage as well as high oxygen overvoltage. Improved coating technology of anodes has resulted in longer service life. Conventional coating with RuO₂-TiO₂ has been replaced by (Ru + PGM)O₂-TiO₂ coating resulting in service life of 4-7.2 years¹³ (PGM = Platinum Group Metal). Shape of the anode is an important factor in cell design; perforated plate anode is in a slightly more favourable position than the conventional expanded metal anode. Optimum design of a perforated plate anode can save 80 KWh/MT caustic. Improved design of cathode provides the largest

cathode surface area, resulting in uniform current density and low cathode overpotential. Modern activated cathode coating contains at least two components — (i) Electrochemical catalyst, (ii) Stabilizer, which will prevent electrolytic reduction of catalyst.

(d) Cell frame design — An important factor in the design of a membrane cell element is the frame. Plastic frames being used initially were not dimensionally stable or leakproof on use. They have been replaced by an electrode plate fabricated from a single metal. The width of the electrode in the direction of current flow was significantly reduced to hold ohmic loss across the electrode to the minimum. The following advantages were obtained.

(i) better tolerance in mechanical fabrication, resulting in exact spacing of electrodes and less cell leakage,

(ii) longer life than plastic frame,

and (iii) higher operating temperature of cells, resulting in reduced energy requirements.

(e) Caustic concentration — Prime requirement in determining concentration of caustic soda in cell design for a plant is local condition. Electrolytic power consumption in a membrane cell is optimum at 20% caustic concentration, so that, considering the cost of power for electrolysis and steam for evaporation, the desired caustic concentration should be selected. In case bulk supply is to be sold outside the factory, cost of transportation also is to be taken into account. However, with gradual development of membranes, a present day membrane cell can operate at a current efficiency of around 90% producing caustic in the range of 20%-40%.

COST REDUCTION AND POWER CONSUMPTION

Commercial success of a new technology depends on optimum balance between cost of plant, longer life of plant/machinery and efficient process parameters. With gradual improvements of Membrane Cell Design, substantial cost reduction and energy conservation has become possible in the following areas:

(a) Cell, Cell Hardware & Membrane — Design of larger capacity cell with large electrodes can reduce investment cost substantially. Construction cost index of electrolysis plant with 1.2 M × 1.2 M cell is 10% more than with a standard cell of 1.2 M × 2.4 M. Same cost index for a super-size cell of 1.5 M × 3.6 M is 10% less than for the standard size cell. Higher size cell will reduce capital cost and also will result in (i) ease of maintenance, (ii) reduction of space requirement.

Limiting current density in a membrane cell is the current density at which the concentration of the salt at surface of the membrane is zero. Considering the high cost of ion exchange membrane, it is economically advantageous to operate at a high limiting current density.

Hydrochloric acid is added to the anolyte for neutralization of the back-migrated hydroxide ion. If this is not taken care of, the oxygen content in chlorine and chlorate content in the anolyte will increase. Higher oxygen level will have a tendency to reduce anode life.

Calcium and magnesium level of 50 ppb total in earlier design cells has recently been reduced to 20 ppb.

This is easily possible with secondary brine purification with improved chelating resin. Higher concentration of calcium in feed brine has a tendency to accumulate over the ion exchange membrane. This tendency is further accelerated at higher caustic concentration. By maintaining feed brine Ca⁺⁺ concentration at 20 ppb level life of the membrane can be improved.

New multilayer membranes can operate commercially at 4 KA/M² resulting in lower capital cost for a particular plant capacity. Membranes are normally fitted in the electrolyzer in wet condition. Latest developments permit the use of dry, pretensioned membrane, resulting in better gas releasing property and higher current efficiency.

Improved design provides internal porting system in the electrodes for incoming and outgoing fluids. This will save space and will require less maintenance.

Maintenance of zero gap depends on the dimensional accuracy and life of cell gasket for a long duration. Compression moulded EDPM rubber gaskets are used for this purpose. This type of gasket has a longer service life.

(b) Pressurized cell operation — Some of the plants which are to be erected now will have pressurized cell operation. Cell voltage will accordingly reduce due to reduction of gas volume and uniform distribution of current density. This will also save gas transportation/handling cost. Capacity of chlorine drying unit will be less in this case. Operation of pressurized cell at higher temperature will result in reduction of cell voltage. Operating temperature in this case can go as high as 100°C. This rise in temperature is expected to reduce cell voltage by 8% at 4 KA/M². At present pressure is being kept at a range of one bar. Developmental work is going on to maintain pressure at both sides of the membrane equal at higher pressure upto 5 bars. High operating temperature will also facilitate better diffusion of NaCl in the depleted layer.

(c) Modular design of cell — Another breakthrough in cell design will be the modular cell. This consists of a number of cell blocks tied together by a single frame while the electric current flows from cell block to cell block through directly connected anode plate and cathode plate. Space requirement in this case is about two-thirds compared to separate cell blocks. This will provide the following advantages for cost reduction:

- (1) Capital cost reduction in cell and cell room, due to:
 - (i) simple electrode design
 - (ii) simplification of end plates and clamping device
 - (iii) pipings and valves are in simpler form
- and (iv) each cell module will have around 400 elements in several rows.
- (2) Requires less space
- and (3) Easier handling during cell renewal, resulting in a cut in labour cost.

(d) Power consumption — DC power consumption of 4000 KWh/MT for production of caustic soda during the mid fifties has been claimed to be around 2200 KWh/MT in 1984. But worldwide the percen-

tage of membrane cell plants as of today is within 5%. Further developments in this technology, specially the method of retrofitting existing cells to membrane cells, may bring down power consumption further in the existing mercury cell caustic-chlorine plants. Gradual reduction of Asahi Glass Flemion Process power consumption is shown in Table-8. Feed brine specifications and product specifications of membrane cells of Diamond Shamrock are shown in Tables-9 and 10 respectively.

TABLE — 8
ASAHI — AZEC
Progress of Flemion Process

Year	Description	DC KWh/MT NaOH
1976	Prototype Ion Exchange	3200
1977	Improved Ion Exchange Membrane	2700
1978	Improved Cell Structure	2600
1979	Improved Cell Structure	2500
1980	DX Membrane	2350
1981	AZEC	2070

* 2070 DC-KWh at 2 KA/M² and 2210 DE-KWh at 3 KA/M².

TABLE — 9
Diamond Shamrock Membrane Cell
Brine Specifications

NaCl	305-320 gpl
HCl	1-2 gpl
Ca ⁺⁺ + Mg ⁺⁺	0.05 ppm
Fe ⁺⁺	0.02 ppm
Hg ⁺	0.04 ppm
Al ⁺⁺⁺	0.2 ppm
Mn ⁺⁺	0.01 ppm
SO ₄	10 gpl
ClO ₂	30 gpl
TOC	1 ppm
Anolyte	
NaCl	180-200 gpl

TABLE — 10
Diamond Shamrock Membrane Cell
Product Specifications

Caustic	
Concentration	33 ± 1 weight %
NaCl	30-50 ppm
NaClO ₂	5-15 ppm
SO ₄	10-50 ppm
Chlorine (Air Free)	
Chlorine	97-99.5 Vol. %
Oxygen	0.5-0.3 Vol. %
Hydrogen	Nil
Hydrogen	
Hydrogen	99.9 Vol. %

FUTURE OF MEMBRANE CELLS :

Membrane cells being offered at present can operate at a power consumption of around 2200KWh/MT caustic. Future of the membrane cell depends on the following : (Table-11)

TABLE — 11
Future of Membrane Cells

- (1) Membrane Retrofit Technology
- (2) SPE Cells
- (3) Oxygen Cathode Cell.

(a) Membrane Retrofit Technology — At present these technologies are being offered by two Japanese companies, as mentioned earlier. Further developmental work in this respect along with commercial experience from the plants being set up may open up a new avenue for faster conversion from mercury/diaphragm cells to membrane cells.

(b) SPE Cells — This technology is yet to be accepted on commercial basis. At present two plants are under operation, a 5000 TPY Plant in Indonesia and a 12000 TPY Plant in Saudi Arabia. Voltage and D.C. energy consumption at cell electrodes have been reported as 3.15 V and 2200 KWh/MT caustic respectively¹¹. Table-12 shows present and future performance of SPE Cells⁶.

TABLE — 12
Voltages and Power Consumption in SPE Cells

	SPE	
	As of today	Future
Theoretical Dissociation Voltage, Volts	2.25	2.25
Anode Over-potential, Volts	0.03	0.03
Cathode Over-potential Volts	0.10	0.05
Membrane IR Drop, Volts	0.54	0.40
Brine IR Drop, Volts	0.13	0.13
Structure IR Drop, Volts	0.15	0.10
Total Voltage Drop, Volts	3.20	2.96
Power Consumption (DC KWh/Tonne 100% NaOH) at 95% current efficiency.	2260	2090

(c) Oxygen cathode cell — In this process cathodic reaction takes place due to the reduction of oxygen. Cathodic reaction is :



Cathode chamber of this cell is divided into parts by a porous cathode. Electrolyte is passed through the portion next to the membrane, the other portion has air flowing. Oxygen reduction takes place inside the porous cathode. Eltech Systems Corpn., U.S.A. have commissioned a test cell at Muscle Shoals, Ala. This 1 M² commercial is reported to consume 1600 KWh/MT caustic. In this type of cell there will be no by-product hydrogen, unlike conventional membrane cells. Hence, while selecting this process, fuel value or value for sale as a chemical is to be taken into account⁶.

ACKNOWLEDGEMENTS :

The author is thankful to M/s. UHDE India Limited, Asahi Chemical Industry Co., Limited, Japan, Asahi Glass Co., Ltd., Japan, Diamond Shamrock, India, Eltech Systems Corporation, U.S.A. and Chlorine Engineers' Corporation, Japan for their kind assistance.

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Introduction to Membrane Cell Technology in the Production of Chlor-alkali



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The paper describes the basic operation of a membrane cell and the factors which are critical in the design of a cell and membrane system. Bipolar and monopolar electrical circuits and the factors influencing current density are considered. Installation of the cells at either a new site or as a retrofit in an existing cellroom presents challenging engineering and chemical engineering targets and the economics of conversion are reviewed with special reference to the ICI FM21 membrane cell system.

Membrane cells for chlor-alkali manufacture were first developed in the late 50's but the non-availability of suitable membranes prevented significant advances at that time. It was not until the introduction of fluoropolymer ionexchange membranes, coupled with the advances in metal anodes and electrode coatings, developed originally for diaphragm and mercury cells, that significant advances could be made, and development since the mid-70's has been very rapid. Fully commercial plants are now operating and membrane manufacturers and licensors of membrane cell technology are all trying to establish dominant positions in an area of considerable market potential, with over 40 million tonnes per year of production capacity.

History of production

Chlorine and caustic soda are two of the most widely used chemicals in the world and the basis of a large sector of the inorganic and organic chemical industries. Historically, caustic soda was the first on the scene with processes geared up to make this material on the large scale, while chlorine was only a chemical curiosity. However, by the beginning of the 20th century, there were a number of users creating a demand for chlorine, and the diaphragm and mercury cell processes had been invented, with the diaphragm cell

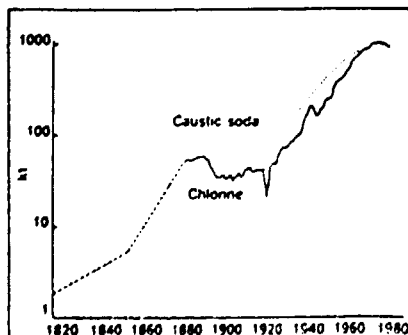
process dominating in the United States and the mercury cell process in the UK and in Europe and until recently Japan. Since the late 1920's when solvents and plastics started to come on the scene, demand has taken off and chlorine production has increased to something of the order of 40 million tons per year. An even larger amount of caustic soda is produced at the same time by virtue of the chemistry of the process itself. However, the balance has been maintained between the caustic and chlorine demands with older processes for manufacture of caustic soda being phased out as the chlorine demand increased. For a time it looked as though the chlorine demand might outstrip the caustic soda demand so that there would be a world glut of caustic soda but this does not now appear to be happening and it is expected that the balance will be maintained for some time to come. Prior to the late 1970's the rate growth of chlorine demand was of the order of 7% per year. Since then, with the economic recessions and the increase in power prices, this growth rate has slowed dramatically and a rate of no more than 2% per annum is predicted for the next decade.

The electrochemical method of manufacture of chlorine and caustic soda uses vast amounts of both electrical energy and steam depending on the process adopted, and in a world of ever increasing energy prices this is inevitably an area of great concern to manufacturers. Major cost reductions have been made over the years by the development of both mercury and diaphragm cell technologies, with the introduction of metal anodes in the late 60's and by continuing to increase the current density of the cells to reduce capital costs. Modern diaphragm cell units now run at a current density of about 2.8 kA/m² and are coupled to energy efficient 4 effect evaporator plants to evaporate caustic soda from the production strength of about 12% up to the market specification of 50%. Var-

ious developments in diaphragms have led to longer life being achieved for the cell as a whole with power consumptions of typically 2.800 kWh/te of chlorine. Similarly, mercury cells have seen developments which have pushed the current densities up to 12 kA/m² with automatic computer control systems maintaining the gaps between the anode and the mercury at very close tolerances. It is interesting to note that, despite the increasing of current densities, power consumptions per tonne of product have remained reasonably constant over the last 50 years with the technological changes giving reduced capital, rather than operating costs. Environmentally, the mercury cell has also been cleaned up with losses from these units now being well within the acceptable world standards.

Membrane cell development

Despite these continuing developments, there is always a search for new technology and the membrane cell, using a cation exchange membrane had long been a theoretical possibility. It was not until the early 1950's that real progress was made and a number of patents were obtained, some of which foresaw many of the current



UK chlorine production 1820-1980 and chlorine equivalent of caustic soda production

developments. The non-availability of a suitable membrane and the consumable graphite electrodes prevented significant advances in the work. However, the introduction of titanium anodes with their electro-catalytically active coatings led to the possibility of a much simpler design of cell and the development of the perfluorinated ion-exchange membranes created the break-through which made membrane cell technology a reality. The first membranes which showed real potential for chlor-alkali manufacture were manufactured by Du Pont under the 'Nafion' trademark. These were relatively low efficiency membranes and contained a back-bone of carbon and fluorine atoms to which were appended side chains terminating in sulphonic acid groups to provide the active ion-exchange sites. These end groups gave membranes a high conductivity and therefore a low voltage drop but not a very good current efficiency. Developments took place to give membranes which were more chemically effective and the break-through came with the manufacture of a membrane containing both sulphonic acid and carboxylic acid end groups which gave the high efficiency with the minimum loss of conductivity. Progress in these areas was then very rapid, with competition to reduce voltage drops in the membrane, to increase current efficiencies, to extend the lifetime of the membrane, to give it structural strength, to improve its operation in a full scale electrochemical cell and in so doing, to obtain a dominant patents position. Typical membrane performance would now be to give a current efficiency of between 96 % and 97 % and a voltage drop of about 250 mV. The membranes look like a typical thin plastic film, and often contain a mesh reinforcing and inorganic coatings to reduce bubble resistances and cell voltages.

Despite the development in the membranes themselves, their effective use depends on the design of the electrochemical cell and the quality of the reagents fed into the system. The membrane is permeable to sodium ions and impermeable to chloride and hydroxyl ions. However, if other ions are present in the system, such as calcium and magnesium these will also be drawn into the membrane and will precipitate out as their solubility product is exceeded in contact with the strong caustic solutions. The brine quality has therefore to be such that the effects of the calcium and magnesium ions does not lead to significant deterioration of the performance of the membrane. Other ions, for instance sulphate and chlorate have limits but these are significantly higher than the ppb level for the calcium and magnesium. The operability of the membrane depends very much on its tolerance to impurities, and membrane manufacturers need to be aware that resistance to trace materials

Membrane operation

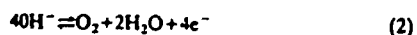
The membrane acts as an ion-exchange resin providing resistance to the movement of anions. The electrical field set up in the cell tends to attract sodium ions towards the cathode and chloride and hydroxide ions towards the anode. As the membrane is essentially impervious to the anions it is the movement of sodium ions through the membrane which carries the electrical current. Electro-osmotic and chemical diffusion effects also apply in carrying water molecules across the membrane from the anolyte to the catholyte. In an operating cell, the main transfer of material is of sodium ions and water from the anolyte to the catholyte compartments. Very small quantities of chloride ions will leak from the anolyte to the catholyte compartment and a larger quantity of hydroxide ions from the catholyte to the anolyte side. When released from the membranes, the hydroxide ions react in the anolyte compartment giving the main contribution to the loss of current efficiency in the cell. Transfer of materials create stable ionic and water concentration gradients within the membrane. However, if operating conditions change, these concentration gradients can also change and lead to loss of membrane performance, so it is important that the operation of the membrane cell is such as not to create major changes within the concentration profiles in the membrane.

The basic chemical reactions within the membrane cell can be summarised by the following equations:

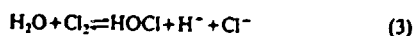
Reactions in the anolyte:



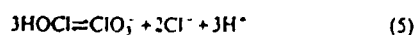
Not all the caustic soda made in the cells goes out with the product stream. Hydroxyl ions equivalent to a small proportion of total product transfer across the membrane in the reverse directions and react in the anolyte as follows:



In addition,



Reaction 2 produces oxygen electrolytically and this leaves the cell in the chlorine gas stream. In a membrane cell operating under positive pressure, this is the principal source of impurities in the chlorine gas. The hypochlorous acid produced by Reaction 3 can leave the cell in the anolyte or further react as follows;



The exact split between the quantities of hydroxyl ion utilised by these reactions depends on a number of factors, including

Reactions in the catholyte



The characteristics of the membrane in the cell are geared to minimise the loss of current efficiency due to the various reactions that have been described.

It should be noted that most production and performance figures for membrane cells are based on the production of the equivalent of 1 te of 100 % caustic soda. This avoids interpretation difficulties which stem from the use of acidified or alkaline brine feed to the cells, and can lead to differences in the quality and the quantity of chlorine produced in the system. Current efficiency measurements on the cell are determined by the quality and the quantities of the various liquors and gas streams which are produced.

Membrane cell design

I will now describe the basic components of a membrane cell. The membrane is of course the fundamental item and while the design of the cell itself may differ, all cells must have this common feature. The protection of the membrane is service is a primary consideration in the design of cells as the membrane is inevitably a relatively fragile item and can suffer from perforations, cracking or fatiguing which will lead to its failure and very high costs of replacement.

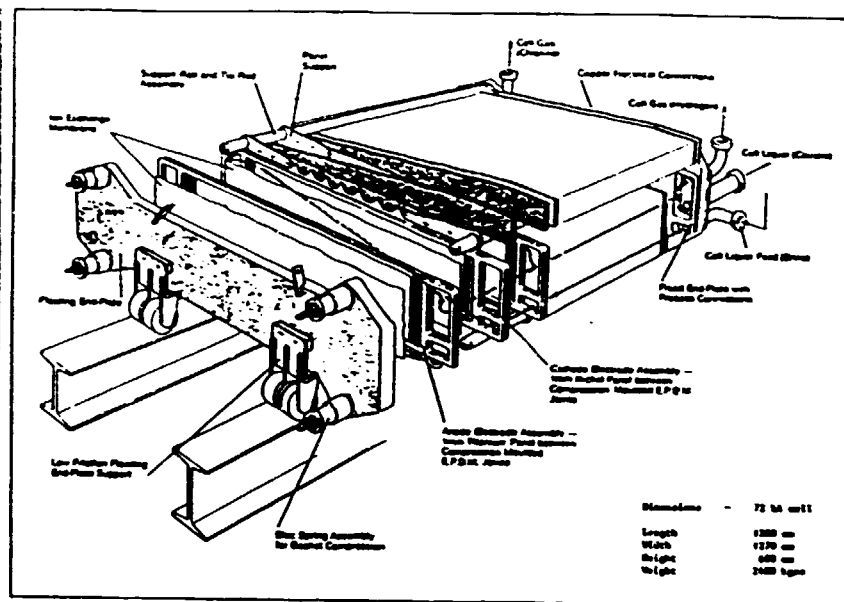
Bipolar cells

A membrane cell can be of either of the bipolar or the monopolar variety. The early designs were mainly of the bipolar variety. In a bipolar cell, the voltage is applied across a stack of membranes and electrodes such that all the individual electrolyser compartments or cells are running in series. The current passes through each cell in turn going in sequence; anode, membrane, cathode, anode, membrane, cathode etc. The design of this type of cell means that the anode and cathode are fabricated as a single unit. The electrodes for the anode side are made from titanium and usually coated with Ruthenium and Titanium oxides. The titanium is essential to withstand the conditions within the anode compartment of highly acidic brine at 90 °C saturated with chlorine. The cathode should be made from nickel to withstand the equally hot 32-35 % caustic soda. An electroactive coating may be used on the cathode to improve the power performance of the cell. To get an efficient electrode design the power has to be transferred from the anode to the cathode with the minimum resistance loss. This is usually achieved by

successfully in other applications but there are doubts as to the effectiveness in the long term of this method of approach for membrane cells. This is because of the hydrogen diffusion through the cathode material to form a titanium hydride compound at the explosion bond junction. This will ultimately destroy the bond itself unless a hydrogen barrier is included in a composite bonded system. The active electrode surfaces are secured to the base structure using current distribution systems and welding operations which are, of necessity, relatively complicated. Once the electrode structures have been built then they can be sandwiched together with the membrane, using gaskets for sealing, to form a stack of compartments of whatever length is appropriate. Normally this could be up to 100 units giving a cell voltage drop of the order of 300-350 volts. The liquids that feed the cells are fed to the individual anode and cathode compartments through headers which are normally external to the cell using long non-conducting distribution pipes to each compartment. This has to be done because of the difficulties with current leakage from the bipolar type of cell. There is a significant current passage through the conducting fluids from one end of the cell to the other due to the high voltage drops within the short distances involved and this can be a major problem if not effectively suppressed with very rapid rates of corrosion taking place and disastrous effects on the electrode units. Normally a bipolar cell would be about 8 ft x 4 ft with a compartment membrane area of typically 2.5 m² allowing a total current of 10,000 amps to be applied to the cell at a current density of up to 4 kA/m². The cell is closed by means of rams, often hydraulically operated which can be used to maintain a constant pressure on the cell and allow for expansion. With the use of such large individual areas of membrane, there are difficulties encountered with the support of the membrane material and the design of suitable gasket systems which give an effective long term life, together with the sheer size and weight of the components that have to be handled. However, it must be said that a bipolar cell will often give a lower voltage drop than the alternative, the monopolar cell, and for small units it also has an advantage in that the rectifiers used are of the high voltage, low current type and may be relatively cheap.

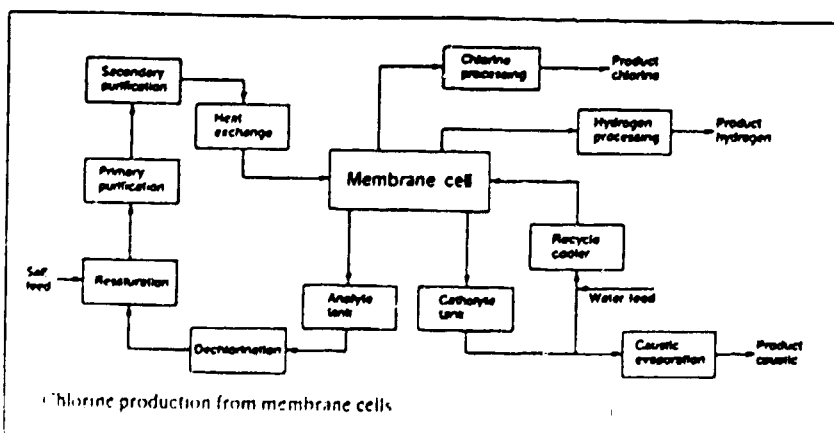
Monopolar cells

The more recent cell developments have concentrated on the monopolar cell design. In a monopolar cell, the electrodes and the membrane are arranged so the cells are in parallel rather than in series. Each cell has the same voltage applied across it and the current is spread between the various cells in the unit. The arrangement would therefore be anode, mem-



brane, cathode, membrane, anode, membrane, cathode etc. with the electrode structure being either wholly anode or wholly cathode based. This construction leads to a much simpler arrangement for the electrodes than for the bipolar cell but there is a need to be able to optimise the design to overcome the problem of bringing the current into the electrode on a uniform basis and taking it away again afterwards. For this reason, monopolar cells have relatively low electrode heights to cut down the voltage drop across the height of the electrode and give good current distribution. The electrodes are either fabricated from sheets of titanium or nickel with mesh structures attached to them in a similar way to the bipolar cell or, as in the case of the ICI FM21 cell, the electrode structures are pressed from sheets of the appropriate materials and coated directly. This has advantages for any recoating operations that may be necessary as unlike the fabricated bipolar unit, there is not the need to disassemble a major component and the small lightweight electrodes of a monopolar cell make the operation very much more straightforward. As with the bipolar cell, the liquors are fed to the compartments of the cell with brine feeding the anolyte

compartments and caustic circulating around the catholyte compartments. However, unlike the bipolar cell the monopolar cell is not so susceptible to current leakage problems as the voltage difference across the cell itself is only about 3-3.5 volts and all the compartments are at a constant potential difference. Complex inlet and outlet pipework is therefore not required and while some monopolar cells still use external pipe headers and individual feed pipe connections, the system has been simplified significantly by incorporating these pipework systems within the cell itself, a fundamental feature of the FM21 cell. The membranes and electrodes are sandwiched between gaskets and the whole unit is then compressed between end-plates. Because of the small size of the cell, complex hydraulic rams or other closure methods are unnecessary and a simple disc spring assembly is used to provide the correct compression and compensation for thermal and other stresses set up in the cell under operating conditions. Not surprisingly, in view of the simplicity of construction the filter press monopolar type cell is significantly cheaper and easier to construct and maintain than the bipolar cell on an installed capacity basis.



Chlorine production from membrane cells

The cellroom itself consists of a number of monopolar cells linked together in series to give the required capacity. The current rating and the size of the cellroom can be altered by varying either the number of cells in series or the number of compartments in an individual cell with an almost infinite number of combinations for plants of say 3000 t/year up to 200 000 t/year using essentially the same basic design of cell unit.

Optimisation of design

The emphasis on improving power performance on membrane cells has led to a continual drive to reduce voltages and resistance losses in the system. The irreversible cell voltages are fixed although there are areas where some changes can be made, for instance by the use of air or oxygen depolarised cathodes which produce water instead of hydrogen gas at the cathode. However, most of the other improvements are based on the fine tuning of the design itself. If we look at a monopolar cell, the voltage breakdown across the components would be typically as follows:

FM21 Cell Voltages at 3 kA/m²

Anode assembly and over voltages	210 mV
Cathode assembly and over voltages	140 mV
Anolyte	130 mV
Catholyte	100 mV
Membrane	250 mV
Reversible anode voltage	1220 mV
Reversible cathode voltage	1000 mV
Total	3050 mV

Areas where improvements can be made are in reducing the resistance loss within the liquid film by bringing the electrodes closer to the membrane and most modern membrane cells are essentially zero gap in that the interelectrode distance is nil. This is achieved by bringing the electrodes so close together that they virtually touch. In the ICI FM21 cell, the electrodes interlock so the membrane can fit between the electrode structure while not being tightly compressed by it and therefore still allowing adequate room for gas evolution. For mesh structure electrodes this is less satisfactory and there is a real danger of losses of tolerance, particularly with the large area of electrodes, leading to excessive pressure in specific areas of membrane and subsequent damage. Bubble resistance is also an important feature. The higher the cell on a vertical basis, the greater the bubble density will be and therefore the higher the resistance of the bubble liquor at the top of the electrode. This can lead to poor voltage distributions, although a certain amount of bubble flow is advantageous to give increased circulation within the cell and improve mixing. A tall thin cell may acquire a better circulation

through gas lift effects but have high resistance losses. A low horizontal cell will avoid this difficulty but may have marginally lower internal circulation rates. Similarly, the resistance losses within the electrode structures depend on the thickness of the metal and there is an economic balance between the voltage gained by increasing the panel thickness *versus* the cost of so doing.

Membrane lives are predicted to be of the order of 2-3 years in service. It is vital therefore that there should be no requirement to take the cell off-line to recoat electrodes or change gaskets while the membrane is still usable. The drive in membrane cell design is to extend the component lives to ensure that a membrane cell rebuild is governed only by the membrane life and not for other reasons. To this end, cell designers are having to look very hard at their gasketing systems and if cathode coatings are used, these have to still retain an effective performance for the lifetime of the unit as a whole. The time when a membrane is changed will depend very much on local power costs and the type of membrane and cell system used. In the economic assessments for membrane installations, a high priority must be placed on obtaining the right system overall including the costs of electrode recoating, membrane replacement and other maintenance activities for the system together with the correct choice of current density. As current densities increase, so do power consumptions, while capital costs reduce. However, higher current densities will tend to lead to shorter operating lives which must be assessed correctly. Too often a customer tends to go solely for the minimum power usage initially and pay little attention to the ongoing costs which for complex cell systems may be very much higher than initially anticipated. We in ICI confidently believe that the FM21 membrane cell meets all the important design criteria and this is borne out by the advent of systems developed by other manufacturers which follow its main features.

Membrane cell plant design

A cell should be simply constructed, easily maintained and have a long operational life at a high sustained performance. Above all, it must be cheap, both to produce initially and to install in the chlor-alkali plant. However, the cell itself comprises only of a small part of total chlorine complex, typically 15-20 % of the capital cost of a new installation. The system of handling the product chlorine, the hydrogen and the primary brine purification is essentially the same as for a diaphragm or mercury unit. A simple caustic evaporation stage is required to bring the caustic strength up from the 32-35 % manufacturing concentration, to the 50 % level as required by the commercial market. The main difference between

a membrane cell unit and other technologies is the need to obtain a high purity feed brine stream. The primary purification will typically reduce the calcium and magnesium levels to a total of about 10 ppm. The brine is then filtered to remove any solid materials from the stream which could be harmful and then super-purified using chelating ion-exchange resins. Normally two columns are used although some proposals use three columns which are cycled to ensure that at least one bed is always on line. The system gives a brine purity of the order of 25-50 ppb total hardness. If sulphates are present these have to be removed either by purging the brine stream at an appropriate point or by reaction to precipitate the sulphate as calcium or barium sulphate. Excess chlorate removed either by purging with the sulphate or by reaction at high temperature and low pH using hydrochloric acid. Before entry to the cells, the brine may be acidified to a greater or lesser extent depending on the product chlorine quality required. If a very low oxygen content gas stream is needed the acidity level is high. If this is not required the brine is fed to the cells at essentially neutral pH. Brine depletion would be typically 50 % within a cell circuit. The depleted brine is dechlorinated initially by either vacuum or air stripping techniques followed by a final dechlorination using reducing agents or decomposition on activated charcoal. The brine is then returned for resaturation. The caustic circuit is straightforward with liquor entering the cell at typically 31-32 % and leaving the cell at 33-35 % caustic strength. The cellroom design is critical to the effective cell operation and it is essential that the detailed requirements of any cell are fully understood in this area. Most of the cell inefficiencies appear as heat either in the anode compartment or the cathode compartment. The aim is to try to minimise heat transfer across the membrane to cut down thermal stresses and remove the heat from the circulating liquors. The heat conservation within the system is critical but by careful design, there can be full heat recovery and no steam requirement for operation of the cell itself apart from a very low loads.

Conversion of plants to membrane cell technology

Finally, I would like to discuss the conversion of plants from existing technology to membrane cell technology. For a Greenfield site with new capacity, the case for installing membrane cells compared to either diaphragm or mercury cell technologies is extremely good. There have been a number of papers written and studies carried out on the conversion of existing technology to membrane cell systems. The views expressed differ and the economic case very much depends on the status of the plant to be converted. The power

savings generated by use of membrane technology are partially offset by the additional cost of the membrane and the small extra costs for brine treatment and steam compared to mercury cell technology. In the case of diaphragm cell technology, the main savings are in the reduction of steam usage and operation of the complex evaporator plant. Membrane cells are much easier to maintain and operate than either diaphragm or mercury cell systems and the ancillary plant such as those required to remove mercury from product and effluent streams are eliminated. The capital cost of a conversion depends on how much equipment may be re-used, in particular the rectifiers and the cellroom building itself. The monopolar type of membrane cell is much more amenable for a conversion project as either diaphragm or mercury cells can be replaced directly. Schemes have been proposed to mount cells on the base plates of the mercury cells, so retaining the switching facilities associated with the base plates. However, the preferred alternative for a mercury cell conversion is to build a new cellroom alongside an existing unit, with space requirement being of the order of only one third that for the mercury cell equivalent capacity. Brine systems can usually be modified to accommodate the requirements of the membrane cell with the

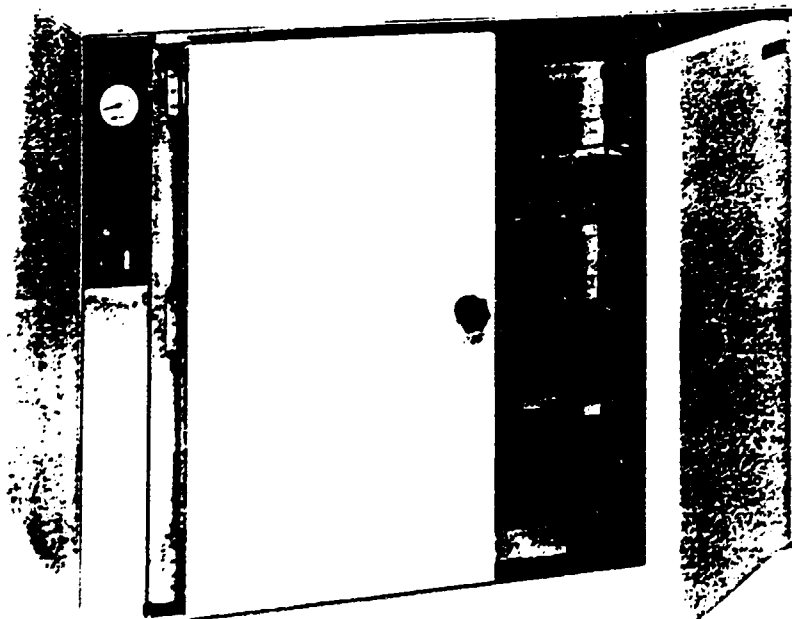
addition of ion-exchange and dechlorination facilities for a diaphragm cell plant and the filtration and ion-exchange for the mercury cell plant. Only if the diaphragm cell plant operates with borehole sourced brine is there a problem in the conversion and this can be overcome by evaporation, borehole resaturation or waste brine operation depending on circumstances. Most of the rest of the systems associated with chlorine production are identical and the cost of converting an existing plant to membrane cell technology is only a fraction of that of installing a new plant - possibly 25-30 % of the new capital. Overall therefore the potential for converting old diaphragm or mercury cell plants to the new technology is very considerable. The long term view for both the European scene and the American scene is that there will be an increasing move to either shut-down of the old inefficient mercury and diaphragm cell plants or convert production to membrane cell technology. Any new capacity will be in membrane cells. The more modern diaphragm and mercury cell units will remain in operation for some time to come but these manufacturers will inevitably be looking at the new technology and the continued developments in it with increasing interest. It is a certainty that energy prices will continue to rise and with the energy contribution to the costs of

the chlorine being of the order of 60 % this is the area where membrane cells can show a significant advantage.

The competition from the licensors of the various membrane cells system is intense, with an urgent requirement by all to have demonstration plants around the world and increase operating experience. The developments that have taken place in the membrane cell over the last five years are significantly greater than in the mercury or diaphragm cell scene over the last 50 years and the amounts of money, that have been spent on research and development have been considerable. However, the proof of the technology will be in the long term performance of the various plants which are either operating or under construction and not just the promises and paper predictions of the sales forces. As these plants come on line throughout the world, their performance and operational acceptability will become widely known and as a result of this there will inevitably be rationalisation with some technology suppliers dropping out and the emergence of perhaps three or four market leaders with a vast potential of business for this new technology in the chlor-alkali industry.

Ref: *Modern Chlor-Alkali Technology* Vol 2, 1983. Editor C Jackson. Δ

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- tarkkuus 30-70°C $\pm 0,5^\circ\text{C}$
(parempi kuin DIN 58945)
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- lämpötila-alue 30-230°C
(erikoistilauksesta aina 300°C:een)
- tarkkuus $\pm 1,5^\circ\text{C}$
- tilavuudet 15-720 l

Faktoja, joita on vaikea sivuuttaa

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Pollution Control and Energy Saving : A Case Study in Chlor-Alkali Industry

by

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Abstract

Mercury pollution, caused by the chlor-alkali industry, has become a problem of national dimensions. The national average for the consumption of mercury per ton of caustic soda produced is 350 gm. Concentration of mercury in the trade effluent as stipulated by the Central Board is 0.01 ppm. So the situation demands very stringent control of pollution due to mercury. Higher consumption of mercury is effected by the higher conversion of metallic mercury to ionic mercury as Hg^{++} . Accelerated rate of conversion is caused by the entrapped chlorine in the cell during power failures and frequent shut-downs. Treatment plants for the control of mercury in the trade effluent involve ion exchange process. The ion exchange resin is an expensive imported item and incurs very high operational cost.

Since power failure and consequent process interruption in the present Indian working conditions has become a common feature, adaptation of a new technology which eliminates use of mercury, namely 'Membrane cell' is explained in the paper. Besides the operational and pollution aspects, the paper explains the economics of both the processes with respect to energy consumption. It is estimated that membrane technology will ensure a saving in energy consumption to the tune of 20 crores of rupees a year.

INTRODUCTION

Indian chlor-alkali plants are primarily based on mercury cells using mercury as cathode in the process of electrolysis of brine. The 39 such plants in the country include 13 based on the diaphragm cell process, producing 6 lakh tons of caustic soda per year.

For many years the chlor-alkali industry all over the world has become a matter of grave concern, because of potential pollution hazards due to mercury in the effluents. After the Minamata (Japan) tragedy the whole scientific world looked at mercury with agonised eyes.

Mercury is not a product, but a component used in the process. Proper attention and housekeeping can reduce mercury to a great extent in the effluent. But during the operation some mercury is converted to soluble Hg^{++} ion and more so when there is a sudden interruption of power, because the entrapped chlorine in the primary cell reacts with mercury to form soluble Hg^{++} . Such an interruption in all the caustic chlorine plants all over the country has become a common feature, resulting in the increased concentration of mercury in the effluent. Accelerated rate of formation of Hg^{++} ion in the primary cell in turn enriches the mercury concentration in the brine mud, which also finds its way into the environment through water-courses.

The environmental status of the Indian caustic

chlorine industry needs some highlighting. It is estimated that the Indian quality of industrial salt produces sludge to an extent of 0.03 tonne per tonne of caustic soda produced. This sludge has a bearing on the loss of mercury because the soluble mercury present in the depleted brine gets absorbed in the sludge during the process of purification of brine. Mercury content in the sludge has been estimated to be 2.4 gm per gm of sludge on dry basis and thus stands to be 72 gm per tonne of caustic soda produced. Taking into account the country's annual production of 6 lakh tonnes, 43 tonnes of mercury is consumed every year through this route^{1,2}.

A recent survey conducted by the Central Board for the Prevention and Control of Water Pollution, New Delhi has revealed that 64.5% of the loss of mercury takes place through brine sludge. The loss through the liquid effluent is only 0.3%. The survey reveals the seriousness of the situation in the Indian caustic chlorine industry.

Mercury is not a part of the product and theoretically no mercury is necessary for replenishment. So any replenishment means loss, and subsequent discharge into the environment. Thus prevention of loss is a primary factory rather than that of the treatment of the effluent. Many methods of treatment have been suggested from time to time but the success behind the prevention and control is entirely dependent on

the in-plant control measures. Some of the mandatory suggestions on this aspect are worth mentioning :

- 1) Steady supply of electricity.
- 2) Total prevention of all sorts of leakages.
- 3) Segregation of mercury-bearing waste effluent.
- 4) Collection pits for mercury in the cell room and painting by epoxy resin.
- 5) Use of metal anodes instead of graphite anodes.
- 6) Pollution consciousness amongst working people.

It is estimated that for a plant of 100 tonne per day capacity, the cost involvement is to the tune of Rs. 40.00 lakhs (0.40 million US Dollars). But for all practical purposes total prevention and control is rather difficult in old design plants. Minimisation to the recommended level could be possible provided the aforesaid line of action is met meticulously, but (1) and (2) can hardly be ensured in the present Indian working conditions.

In view of the above the Indian caustic chlorine industry now looks toward new technologies which aim at the elimination of mercury and ensure an appreciable saving in energy. This forms the subject matter of the present paper.

ANTIPOLLUTION TECHNOLOGY AND ITS ADAPTATION IN THE INDIAN CAUSTIC CHLORINE INDUSTRY

Due to economical and ecological reasons rapid developments have taken place in the caustic chlorine industry in recent years with the twin objectives of (a) energy saving and (b) elimination of mercury pollution problems.

Development of cation exchange membranes of perfluorosulphonic acid and perfluorocarboxylic acid and development of metal anodes have paved the path towards achieving this objective¹. Membrane cell and SPE cell have drawn the attention of the Indian caustic chlorine industry because of their inherent merits.

In the ion exchange membrane cell, a cation exchange membrane is used as a separator between the anode compartment and cathode compartment. The membrane prevents OH ion migrating to the anode compartment but selectively permits Na⁺ ions to migrate from the anode compartment to the cathode compartment. Caustic soda and H₂ gas are formed in the cathode compartment and Cl₂ gas is liberated from the anode compartment. The basic principle is similar to the diaphragm process, but high purity, high concentration caustic soda is produced because of the permselective properties of the membrane. SPE cell is typical in its mode of performance^{2,3}. It is based on the utilisation of activated permselective membrane. Activation is done by the application of electrocatalysts bounded on both sides of the membrane suitable for the desired reaction. In the case of a brine electrolyser Na⁺ ions are the charge carriers which travel across the electro-active solid polymer as electrolyte to form sodium hydroxide. Chloride ions produced from the brine at the anode are immediately oxidised to chlorine gas. In both the cells the brine quality needs to be of very high purity having less than 1 ppm of Ca⁺⁺ and Mg⁺⁺ hardness.

Some operating data of the membrane cell, under

operation elsewhere, is reproduced in Tables 1 & 2 so that its suitability in the Indian working conditions can be assessed.

TABLE 1

Diamond Shamrock Membrane Cell Performance and Operating Conditions

Cell voltage, volts	3.6
Current density, KA/m ²	3.1
Current efficiency, % average:	
— over one year	94.0
— over two years	92.0
Economic membrane life Yrs. min.	2
Anode coating life, Yrs. Min.	5
Power consumption, DC KWh/MT NaOH	2570
Production per cell:	
— MT/D NaOH	0.1742
— MT/D Cl ₂	0.1543
Caustic concentration, wt. present	33±1

TABLE 2

Diamond Shamrock Membrane Cell Brine Specifications

NaCl	305-320 gpl
HCl	1-2 gpl
Ca ⁺⁺ ++Mg	0.05 ppm
Fe ⁺⁺	0.02 ppm
Hg ⁺	0.04 ppm
Al ⁺⁺⁺	0.2 ppm
Mn ⁺⁺	0.01 ppm
SO ₄ ⁻	10 gpl
ClO ₃ ⁻	30 gpl
TOC	1 ppm
NaCl	180-200 gpl

A comparative study of the operating conditions and voltage characteristics of the conventional membrane cell and solid polymer electrolytic cell is reproduced in Table 3. As per information available, SPE cell has not yet been commercialized but it is definitely one of the future commercial membrane cells.

The voltage characteristics are recorded at a current density of 3.0 KA/m² and a temperature of 80-90°C. Diamond Shamrock, a reputed caustic chlorine plant supplier, installed a prototype Air/O₂ cathode⁴ cell at their Muscle Shoal works. After studying the various merits and demerits of this process they expect to market this technology commercially during '84-'85. This is expected to reduce power consumption by 500 KWH/tonne of caustic soda. In the perspective of the foregoing studies it is worthwhile having a comprehensive picture of the energy consumption in the various types of cells so that there is a practical approach to the new technology, conclusive to Indian working conditions.

1. Mercury cell 3500 KWH/tonne of NaOH*
2. Diaphragm 3400 KWH/tonne of NaOH*
3. Membrane cell 2500 KWH/tonne of NaOH

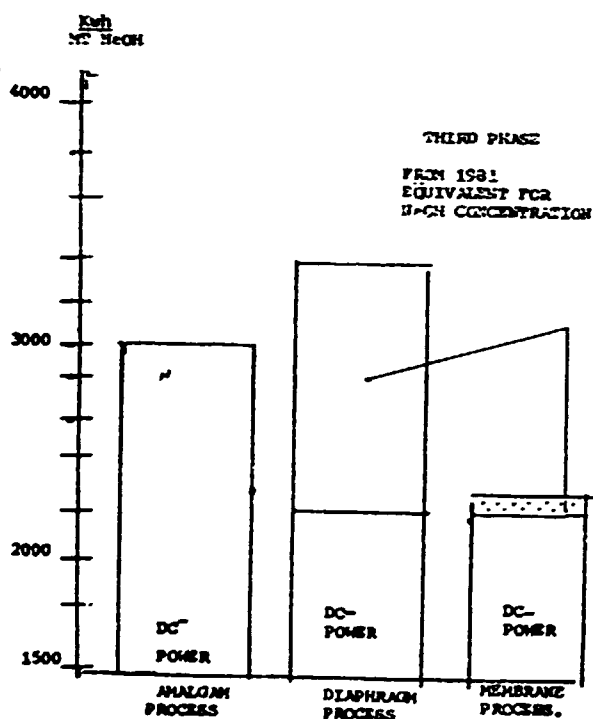
* Mercury cells commissioned in India after 1975 have achieved a power consumption of 3100 KWH but most of the plants commissioned prior

TABLE 3

Comparison of Voltages and Power Consumption in Membrane and SPE Cells

	Membrane		SPE	
	As today	Future	As today	Future
Theoretical Dissociation Voltage, Volts.	2.25	2.25	2.25	2.25
Anode over-potential, Volts.	0.05	0.03	0.03	0.03
Cathode Over-potential, Volts.	0.40	0.20	0.10	0.05
Membrane IR Drop, Volts.	0.54	0.40	0.54	0.40
Brine IR Drop, Volts.	0.47	0.37	0.13	0.13
Structure IR Drop, Volts.	0.04	0.04	0.15	0.10
Total Voltage Drop, Volts.	3.75	3.29	3.20	2.96
Power Consumption (DC KWh/Tonne 100% NaOH) at 95% current efficiency.	2040	2520	2260	2090

to this have an average total power consumption of 3500 KWH A.C.



Energy Requirement Basic NaOH (50%)

ENERGY SAVING AND ECONOMICS :

The country's total capacity of production of caustic soda at the end of 1983 will be 10.9 lakh tonnes. Considering capacity utilisation of a plant at a level of 70%, annual production of caustic soda will be 7.63 lakh tonnes. Assuming conversion from mercury cell to membrane technology, saving of power per MT Caustic is Rs. 400 (considering power saving of 1 MWH per tonne of caustic and power rate of Rs. 400/- per MWH). Total yearly saving on this basis is Rs. 30 crores. Saving of foreign currency for importing mercury is at best Rs. 4 crores.

CONCLUSION

The foregoing discussion reveals that conventional

membrane cells for the caustic chlorine industry in India will be desirable at this hour of environmental consciousness and power crisis. The membrane cell ensures a saving of Rs. 30 crores of the national exchequer, but the fact remains that the entire success behind these new technologies in India pivots on the development of the salt industry to meet the exact quality requirement. First and foremost this must be done at the national level before any attempt is made at installation; otherwise, solely because of the non-availability of the appropriate quality of salt, the entire venture will be an abortive bid. This is equally applicable to all developing countries including Pakistan and Indonesia, who have recently gone in for 40 T.P.D. and 10 T.P.D. membrane cell plants.

As per information available from the Data Calendar (published in June '83) and MINAS (Minimum National Standard) published by the Central Board for Prevention and Control of Pollution, average quantity of mercury charged to cells per tonne of caustic during 1977 was 394 gm. In countries having the latest mercury cell technology, technological mercury loss has been brought down to 0.08 gm per tonne of chlorine. There has been sufficient improvement in the working of the mercury cell caustic-chlorine plants in India in the last 10 years through the modernization and updating of technology. But in spite of this improvement, there is reason to believe that mercury charging in mercury cells as in 1983 in India cannot be as low as those modern plants abroad.

As per Data Calendar mentioned above 6 plants out of 24 in India have installed treatment plants for removal of mercury. But except for one (as in June

TABLE 4
World Electrolysis Plants with Membrane Cells

Year	No. of plants	NaOH capacity t/a
1975	2	50,000
1976	3	120,000
1977	5	180,000
1978	8	230,000
1979	9	240,000
1980	13	290,000
1981	19	390,000
1982	24	700,000
1983	28	1,000,000

TABLE 5
Position of Membrane Cell Plants in the World

Name of the Company	Caustic Capacity in operation MT	Caustic Capacity under erection MT	Location and country
1. Asahi Chemicals Ltd., Japan	220,000	280,000	Saskatoon (Canada) Nobeoka, Osaka, Ohmi (Japan). Rotterdam (Holland) NackAWIC, Canada
2. Asahi Glass Co., Japan	60,000	—	Osaka (Japan).
3. Hooker International	20,000	41,600	Muskogea (U.S.A.) Dryden, Canada.
4. Uhde/Hooker	14,000	24,500	Tofte (Norway) Glasgow (Scotland).
5. Diamond Shamrock U.S.A.	60,000	102,750	Sakala (Japan). Iwopin (Nigeria). Skoghall (Sweden). Victoria (Brazil). Bremangar (Norway).
6. Ionics, U.S.A.	10,000	—	
7. Olin, DeNora	—	35,000	
8. Tokuyama Soda, Japan	—	—	Tokuyama (Japan).
Total :	394,000	483,850	
GRAND TOTAL :	377,850		

'83) none are able to maintain the prescribed Indian norm of 0.01 ppm. mercury in the final effluent. This corresponds to 0.1 gm/MT caustic as per the Indian norm.

Taking mercury loss through liquid effluent as 0.3% of total loss/fresh charge, this figure becomes 33.3 gm/MT caustic. It has been observed that in a tropical country like India monitoring of effluent is comparatively difficult in older design plants commissioned before 1970. Moreover there is enough scope for developing pollution consciousness amongst the working people in our country.

Along with continuous effort by all caustic-chlorine manufacturers to achieve further improvement in pollution control, we shall also have to consider alternative technology like other developed countries. By conversion of existing cells to membrane cell plant, we can get rid of mercury pollution. As of 1983/84, membrane cell technology is definitely an established commercially viable process. Total production capacity of membrane cells was 1 million tonnes in 1983 from 28 plants. Tables 4 and 5 present the data relating to membrane cell plants throughout the world. As we have shown earlier, there is substantial saving of power and cost of imported mercury in this process. On the basis of design condition, capital cost is much lower for a conversion-cum-expansion project than a new grass roots project. For example, cost of a grass roots membrane cell plant would be approx. Rs. 37 crores (37 million U.S. Dollars) in India, whereas cost of conversion of a 50 tpd plant to 100 tpd is much lower. This saving is mainly due to the fact that membrane cells need 1/4th the cell room space and 1/5th the brine volume as compared to mercury cells.

Further developmental work on membrane technology is being undertaken throughout the world, which is expected to bring down power consumption by 400-600 KWH per tonne in the next 2-3 years. So to

utilize the benefit of this improvement, we must enter the membrane-age at a faster speed. A time bound programme for conversion along with softer import duty terms by the Government will help companies in this respect. For a country like India where conservation of energy is of utmost importance, conversion of mercury cell plants to membrane technology will have the dual advantage of energy saving and pollution control.

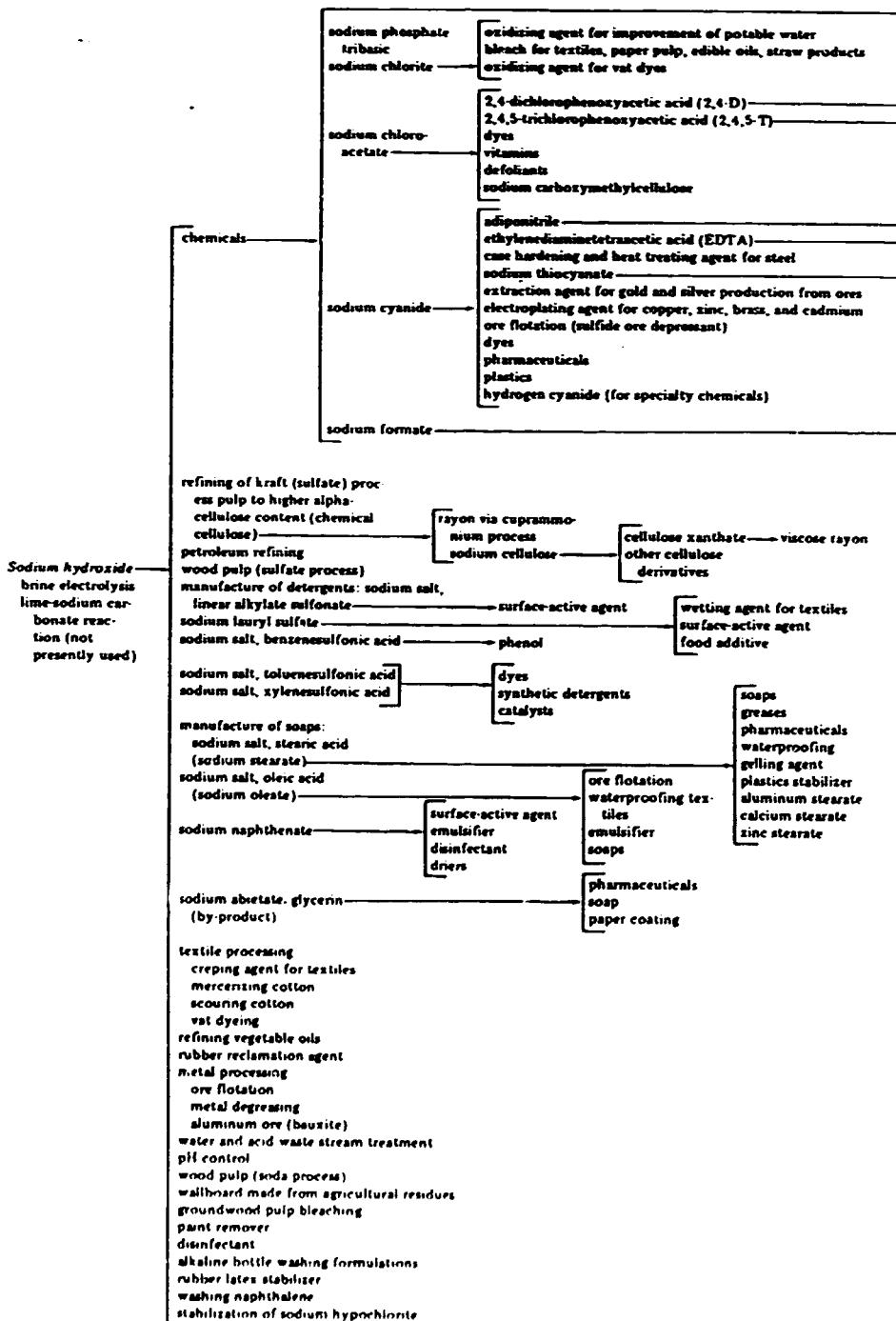
Acknowledgements

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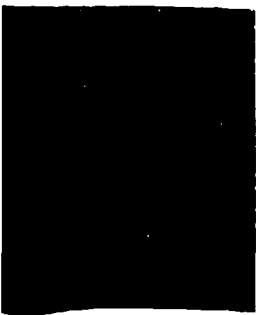
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Table 20. Sodium Hydroxide Derivatives^a



^aRef. 37

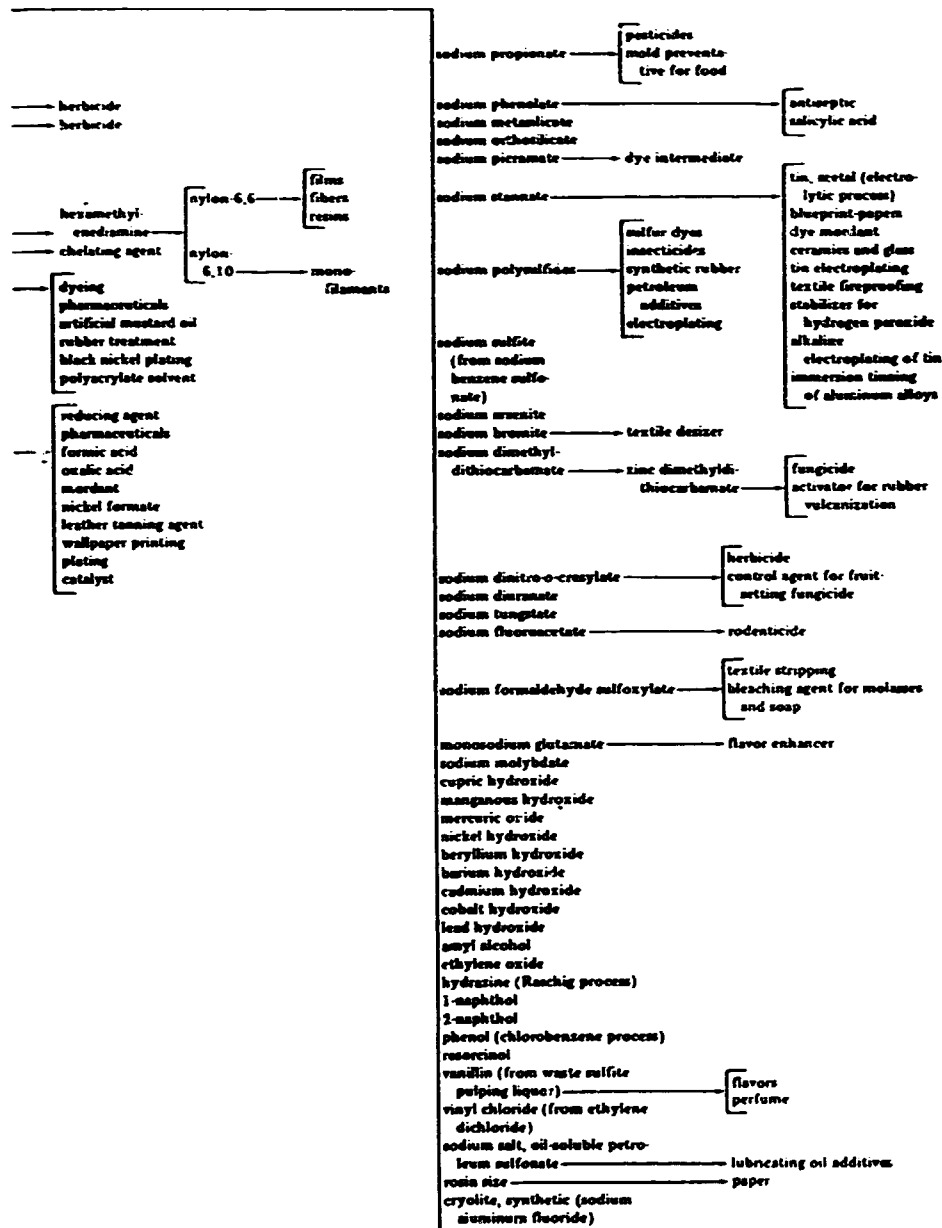


→ herbicide
→ herbicide

hexamethyl-
→ enediamine-
→ chelating agent

→ [dyeing
pharmaceuticals
artificial must
rubber treatment
black nickel plating
polyacrylate]

→ [reducing agent
pharmaceuticals
formic acid
oxalic acid
mordant
nickel formate
leather tanning
wallpaper printing
plating
catalyst]





Standard Specification for Liquid Caustic Soda (Sodium Hydroxide Solution)¹

This standard is issued under the fixed designation E 1098; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This specification covers regular-grade and rayon-grade liquid caustic soda (sodium hydroxide solution).

2. Referenced Documents

2.1 ASTM Standards:

E 291 Test Methods for Chemical Analysis of Caustic Soda and Caustic Potash (Sodium Hydroxide and Potassium Hydroxide)²

E 300 Practice for Sampling Industrial Chemicals²

2.2 Other Documents:

49 CFR 100 to 199 Department of Transportation Hazardous Materials Regulations³

PPP-C-2020 Federal Specification, Chemicals, Liquid, Dry, and Paste: Packaging of⁴

3. Classification

3.1 *Type A*—Regular-grade liquid caustic soda.

3.2 *Type B*—Rayon-grade liquid caustic soda.

4. Chemical Requirements

4.1 Liquid caustic soda shall conform to the following chemical requirements:

	Type A	Type B
Total alkalinity, as Na ₂ O, percent by weight	37.6 to 40.4	37.6 to 40.3
Total alkalinity as NaOH, percent by weight	48.5 to 52.1	48.5 to 52.0
Na ₂ CO ₃ , percent by weight	0.2 max	0.2 max
NaCl, percent by weight	1.3 max	0.1 max
Fe, ppm	13 max	6 max

5. Sampling

5.1 Liquid caustic soda shall be sampled in accordance with the procedure for simple liquids of Practice E 300.

6. Test Methods

6.1 Analyze liquid caustic soda in accordance with the applicable sections of Test Methods E 291.

7. Packaging and Labeling

7.1 Industrial and commercial quantities shall be packaged and labeled in accordance with DOT regulations as found in 49 CFR 100 to 199 and state and local regulations.

7.2 When specified, Department of Defense procurements shall be packaged and labeled in accordance with the applicable paragraphs of Federal Specification PPP-C-2020.

¹ This specification is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.41 on Specifications for Industrial Chemicals.

Current edition approved Jan. 31, 1986. Published March 1986.

² Annual Book of ASTM Standards, Vol 15.05.

³ The Code of Federal Regulations may be obtained from the Superintendent of Documents, US Government Printing Office, Washington, DC 20402.

⁴ Single copies of Federal Specifications required for bidding purposes are available from General Services Administration, Specification Unit, WFSIS, 7th and D St., SW, Washington, DC 20406, or from General Services Administration Business Service Centers in Boston, MA, New York, NY, Philadelphia, PA, Atlanta, GA, Chicago, IL, Kansas City, MO, Fort Worth, TX, Houston, TX, Denver, CO, San Francisco, CA, Los Angeles, CA, and Seattle, WA.

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