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A SURVEY OF POTENTIAL CHLORINE PRODUCTION PROCESSES

Contract No. 31-109-38-4211

by

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ANL/OEPM-79-1

FINAL REPORT ON

A SURVEY OF POTENTIAL CHLORINE PRODUCTION PROCESSES

PREPARED FOR

THE OFFICE FOR ELECTROCHEMICAL PROJECT MANAGEMENT
ARGONNE NATIONAL LABORATORY
UNDER CONTRACT No. 31-109-38-4211

BY

VERSAR, INC.
6621 Electronic Drive
Springfield, Virginia 22151

APRIL 1979

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ABSTRACT

This report is part of the ongoing study of industrial electrochemical processes for the purpose of identifying methods of improving energy efficiencies. A computerized literature search of past and current chlorine generation methods was performed to identify basic chlorine production processes. Over 200 pertinent references are cited involving 20 separate and distinct chlorine processes. Each basic process is evaluated for its engineering and economic viability and energy efficiency. A flow diagram is provided for each basic process. Four criteria are used to determine the most promising processes: raw material availability, type and amount of energy required, by-product demand/disposal and status of development.

The most promising processes are determined to be the membrane process (with and without catalytic electrodes), Kel-Chlor, Mobay (direct electrolysis of hydrogen chloride), the Shell process (catalytic oxidation of hydrogen chloride) and oxidation of ammonium chloride. Each of these processes is further studied to determine what activities may be pursued.

ACKNOWLEDGMENT

This report was accomplished under Department of Energy Contract No. 31-109-38-4211 by the Staff of Versar, Inc., Springfield, Virginia, under the direction of Dr. Robert G. Shaver, Vice President, and Mr. Robert C. Smith, Jr., Operations Manager. Mr. Jerome B. Strauss, P.E., Chemical Engineer, directed the project. Mr. Edwin F. Rissmann, Chemist, was the Principal Investigator. Dr. Mrinmay Samanta performed the energy calculations. The program was performed over a one-year period from February 1978 to February 1979.

We would like to thank Dr. N. P. Yao, Director, and Dr. Glenn Cook, Contract Manager, Office for Electrochemical Project Management, Argonne National Laboratory and Jeff C. Cole, P.E., Consulting Engineer, for their invaluable contribution to this study.

Versar gratefully acknowledges the cooperation received from the chlorine industry in performing this project.

Acknowledgment and appreciation are also given to the secretarial and design staff of Versar, Inc., for their efforts in producing this document.

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1.0 SUMMARY AND CONCLUSIONS

The chlorine industry is the second largest consumer of electricity among all electrochemical industries. In 1977 alone it consumed almost 35 billion kilowatt-hours of fuel energy, 92 percent of which was used to power diaphragm and mercury cells.[1] These cells have an overall energy efficiency of only 12 percent,[1] and current research indicates that improvements in this situation are not expected in the near future.

Any significant reduction in the chlorine industry's consumption of electricity would require large scale introduction of either electrolytic or non-electrolytic processes with an overall energy efficiency of 15-20 percent. Processes of this nature have been investigated over the years with varying degrees of success. This study was undertaken for the Department of Energy (DOE). Its purpose is to identify chlorine production processes which are economically viable and more energy efficient than the brine electrolysis systems in use today.

The project was initiated by conducting a broad, comprehensive literature and patent search and by soliciting information from personnel in the chlorine industry. As a result of this effort, past and present chlorine production processes were identified and analyzed. Processes were then grouped into 20 basic categories and evaluated numerically according to four pre-selected criteria: raw material availability; type and amount of energy required; by-product salability/disposability; status of development.

Raw material availability was of special importance since DOE is primarily interested in chlorine production processes which are both energy and cost efficient. Supplies of raw material plentiful enough to produce 500,000 metric tons per year (five percent of annual chlorine production) or more were considered acceptable to meet this first criterion.

The type and amount of energy used constitutes a necessary criterion if the principal objective of achieving energy efficient production is to be met. Non-electrolytic, low temperature processes were given highest consideration; electrolytic and high temperature processes (600°C) were judged the least desirable.

The third criterion, salability or disposability of by-products, reflects environmental concern about those processes which produce liquid or solid wastes. Although there are penalties for improper disposal of wastes, this does little to alleviate the environmental problems created by their presence. Therefore, processes which do not produce waste products were given a higher numerical rating than those with major solid or liquid waste streams.

Status of development, the fourth criterion, was chosen because of the need to introduce energy efficient processes as soon as possible. Processes which have been demonstrated only in the laboratory or on bench-scale received a low numerical rating, since they would require considerable time and extensive funding before they could become operational and commercialized.

Based on these four criteria and preliminary economic analyses, the most promising chlorine production processes appear to be:

- The membrane cell (with and without hydrogen and oxygen electrodes);
- Kel-Chlor (homogenous catalytic oxidation of hydrogen chloride);
- Mobay (direct electrolysis of hydrogen chloride);
- The Shell Process (catalytic oxidation of hydrogen chloride); and
- Oxidation of ammonium chloride.

As a result of the in-depth literature search and process review, the authors have identified three areas where recent R&D efforts have led or will lead to development of more energy efficient processes. The first and second are being extensively studied by the chlorine industry, and it may only be necessary for DOE to monitor new findings. The third area, which addresses the most energy efficient of the production methods studied, is unproven from an economic and technological standpoint and will require considerable R&D efforts.

The Membrane Cell

The membrane cell appears to be the most economic and energy efficient chlor-alkali process of the sodium chloride based processes examined. Developmental efforts on this process are underway at several laboratories worldwide and it is considered by many people to be the "chlorine process of the future". This process offers an additional advantage in that it is free of environmental problems plaguing current chlor-alkali production methods.

This report identifies a number of second generation process improvements for the membrane cell area, including generation of co-products other than caustic soda, use of more efficient electrode materials and development of more efficient cell designs. It is recommended that further developments in the three areas be closely monitored and supported, as needed, since significant advances are expected within the next few years.

Conversion of Waste Hydrogen Chloride to Chlorine

Three processes have been identified which convert waste hydrogen chloride to chlorine: Shell, Kel-Chlor and Mobay. The latter two are already operational and have a proven capacity for considerable energy savings. The Shell process, however, is not currently used in the United States and its potential and feasibility should be investigated. Kel-Chlor also requires additional research. Previous economic studies indicate that Kel-Chlor has many economy-of-scale advantages over the other two processes but no R&D work has been accomplished to date on its application to small production plants (100-200 tons per day).

Oxidation of Ammonium Chloride

Conversion of waste ammonium chloride to chlorine was identified as the most energy efficient chlorine production method which is also economically viable. The ability to implement this conceptualized process depends upon four factors which require further investigation:

a. the availability of ammonium chloride itself or means to produce the chemical compounds economically;

b. the conversion efficiency of nitrosyl chloride to chlorine and nitrogen dioxide at low temperatures catalytically. The catalyst is needed to maintain minimal energy requirements;

c. the kinetics of the initial reaction between ammonium chloride and nitrogen dioxide. Neither the reaction rates nor the conversion efficiency were sufficiently characterized by earlier investigators; and

d. the separation of ammonium nitrate from ammonium chloride by fractional crystallization if less than 98 percent conversion efficiency is attained in the initial reaction. The 98 percent conversion efficiency is a requirement of the fertilizer industry.

2.0 INTRODUCTION

This report for the Office of Electrochemical Project Management, Argonne National Laboratory, is one of a series of studies to identify energy efficiency improvements in electrochemical industries. To perform this task, a comprehensive literature and engineering survey, which identified existing and potential chlorine production processes, was undertaken. An energy use study of each process was conducted to determine areas of future energy savings. The baseline technologies from which to determine energy savings are the currently used diaphragm and mercury cells using dimensionally stable anodes.

Section 3 of the report describes the information gathering effort. This effort was subdivided into three activities: computerized literature search, manual literature search and interaction with industry personnel. The section also presents the list of basic processes resulting from the data search.

Section 4 presents a description and analysis of each basic process. Each process is characterized by its development history, scientific basis, engineering design and economic characteristics (if available). The overall feasibility of the process is evaluated.

Section 5 is the energy efficiency analysis. For each process the theoretical energy use per kkg of product is determined. Energy penalties are assigned to those processes which do not produce caustic and/or hydrogen or consume chemicals which are in short supply or which might be used more profitably elsewhere.

Section 6 uses the analyses from the prior sections to rank each process with respect to four criteria: raw material availability, type and amount of energy required, by-product salability/disposability and status of development. From this analysis, recommendations are provided for future activities to enhance energy efficiency in the chlor-alkali industry.

3.0 IDENTIFICATION OF BASIC CHLORINE PRODUCTION PROCESSES

A detailed search was made of the literature to locate information on all proposed chlor-alkali processes. Contacts were established with a number of chlor-alkali manufacturers to gain further input on current research efforts. Each of these efforts is described below.

3.1 Literature Search Using Computer Data Files

Computer searching for alternate chlorine production processes employed 12 data base files, which are briefly described below.

- The National Technical Information Service file (NTIS) contains a listing of reports of government-sponsored research from over 240 Federal agency units and some state and local agencies. Entries date back to 1964.
- The Smithsonian Science Information Exchange file (SSIE) provides a summation of research projects currently in progress or recently completed.
- The Compendex data base is the on-line version of Engineering Index, which abstracts information from approximately 3,500 journals, papers, and government reports. Entries begin with 1970.
- The Chemical Industry Notes file (CIN) contains bibliographic information on current affairs in the chemical marketplace, including new products and processes and corporate actions.
- The Chemcon, CA Condensates/Casia 77 and 72-76, and CA Condensates 70-71 files are on-line bibliographic data bases corresponding to the Chemical Abstracts publications. Coverage in Chemcon is from 1972 to the present and in the CA Condensates files from 1970 to the present.
- The Chemname file is an on-line listing of chemical substances with their corresponding Chemical Abstracts Registry members.
- The Scisearch file includes 90 percent of the world's scientific literature and is indexed by citations referenced in listed articles. Coverage is from 1974 to the present.

- The Energyline file contains multi-disciplinary materials dating back to 1971 and relating to energy. Included are references to journals, conference proceedings, speeches, and statistics.
- The Claims/Chem file contains all patents in the Chemical Section of the U.S. Patent Office's Official Gazette dating back to 1950. Also included are those patents from the Electrical and Mechanical sections which are chemically oriented.

Actual searching in the NTIS, Compendex, Energyline, SSIE, Chemcon, CIN, and CA Condensates files began with combinations of the following key words:

chlorine
chlor-alkali
caustic soda
hydrochloric acid
sodium hydroxide

process
manufacture
production
preparation

In addition, some of these searches were expanded or refined by use of techniques specific to the particular file in question. For example: the CIN file was searched by category code "e" (Products and Processes), by specific manufacturer product name, and by the descriptors "new process" and "energy conservation".

In the NTIS file, the basic strategy was refined to select citations indexed by the following category codes:

71 Q	Solvents, cleaners and abrasives
90 b	Chemistry
90 f	Electrotechnology
94 a	Production planning and process controls
94 g	Manufacturing processes
97 b	Energy use, supply and demand
99 h	Industrial chemistry and chemical process engineering

The CA Condensates files were searched by the Chemical Abstracts Registry Number for Cl_2 (retrieved from the Chemname file) and refined by use of category codes to eliminate unwanted material. For example, the set containing all citations having category code CA070 (Nuclear Phenomena) was subtracted from the general set. An attempt was made to refine the citations by focusing on energy considerations, but nearly all retrievals were of nuclear level and not useful here.

The Scisearch file was searched with names of companies known or potentially active in the field of chlorine manufacture or equipment design.

The Claims/Chem file was searched using sixteen U.S. Patent Office Classification Codes beginning with the numbers 423 (Inorganic Chemistry) and 204 (Chemistry, Electrical and Wave Energy).

3.2 Manual Literature Search

In addition to the computer sources, a list of processes proposed prior to 1962 was obtained from J. S. Sconce, Chlorine, Its Manufacture, Properties and Uses, R. E. Krieger Publishing Company, Huntington, New York, 1972. This text provided valuable references to a number of earlier efforts. A manual search of Chemical Abstracts was performed for the 1962-1978 period in an effort to locate any additional references not found by the computerized searches.

3.3 Industrial Contacts

In addition to literature search efforts, contacts were established with a number of trade organizations and individual producers. Industry respondents are listed in Table 1.

Additional efforts were made to solicit similar information, without success, from a number of other organizations. In all, 21 organizations were contacted concerning new R&D work in the chlor-alkali area.

3.4 Information Search Results

In all, over 200 references were located. All papers and patents were obtained, examined and abstracted to develop information on the processes described in this report.

TABLE 1

CHLORINE INDUSTRY CONTACTS

Organization	Person Contacted	Significant Results
1. Chlorine Institute	Mr. R. L. Mitchell, Executive Director	Reports of plant managers symposium obtained.
2. Diamond Shamrock	Dr. K. J. O'Leary, Director of Research	Literature provided on current electrode and membrane cell efforts.
3. Case Western University	Professor E. Yeager, Department of Chemistry	Limited information on O_2 cathode efforts.
4. Pullman Kellogg	Mr. L. E. Bostwick, Manager, Process Development	Information provided on improvements to Kel-Chlor process.
5. General Electric	Dr. A. B. Conti, Director, Energy Conservation Program	Some discussion of G.E. electrochemical efforts.
6. BASF Wyandotte	Mr. Joe Louver, R&D Director, Inorganic Chemicals	No specific data offered.
7. Allied Chemical	Dr. E. F. Booth, Director, Syracuse Technical Center	Reports provided of current published membrane cell work.
8. PPG Industries	Dr. H. B. Johnson, Sr. Research Supervisor	Reports provided relating to PPG membrane cell efforts.
9. Olin Corporation	Mr. H. A. Mosher, Director of Process Licensing	Reports provided relating to Olin R&D efforts.
10. DuPont	Dr. D. J. Vaughan, Director of Process Development	Meeting with DuPont and data provided on current membrane cell efforts.
11. Asahi Chemical Co.	Dr. T. Miyazaki, Manager, Process Engineer, Asahi Chemical Industry Canada, LTD.	Meeting with Asahi in Toronto and data provided on current membrane cell efforts.
12. Vicksburg Chemical Co.	Mr. F. A. Ahlers, General Manager	Data provided on Vicksburg process.

To include all chlorine production techniques, the systems identified in the literature and patent searches and from contacts with chlor-alkali producers were classified into 20 fundamental processes listed in Table 2.

In the classification system, patents or publications involving successive steps in the development of an overall process have been grouped together as one process. Patents treating minor variations of one basic process have also been grouped together under the one basic process. An example is the heterogeneous catalytic process for oxidation of hydrogen chloride, where a number of similar processes starting with the abandoned Deacon process were developed using iron or copper chloride catalysts. Over the years, several modifications (by Olin, ICI and others) were made in the original process, which included changes in operating parameters and system design, while keeping the basic process chemistry the same. All sub-processes are grouped together for ease of discussion and only the most promising of these are discussed and evaluated in later sections.

Table 2

Basic Chlorine Production Processes

Membrane Cell (E)
β-Alumina Membrane Cell (E)
Downs Cell (E)
Catalytic Oxidation of HCl Using Metal Chloride Catalysts (N-E)
Catalytic Oxidation of HCl Using Rare Earth Catalyst (N-E)
Kel-Chlor (N-E)
Catalytic Electrolysis of HCl (E)
Direct Electrolysis of HCl (E)
Oxidation of $FeCl_3$ - Salt Complex (N-E)
Oxidation of Ammonium Chloride (N-E)
Catalytic Oxidation of Ammonium Chloride (N-E)
Conversion of Salt Using Sulfur Oxides (N-E)
Conversion of HCl Using Sulfur Oxides (N-E)
Conversion of HCl Using Hydrogen Peroxide (N-E)
Nitrification of Potassium Chloride (N-E)
Nitrification of Salt (N-E)
Oxidation of Salt on Clay Media (N-E)
Oxidation of Salt Using Silica Compounds (N-E)
Electrolytic Conversion of Magnesium Chloride (E)
High Temperature Conversion of Salt Plasma (N-E)

(E) - Electrolytic Process
(N-E) - Non-Electrolytic Process

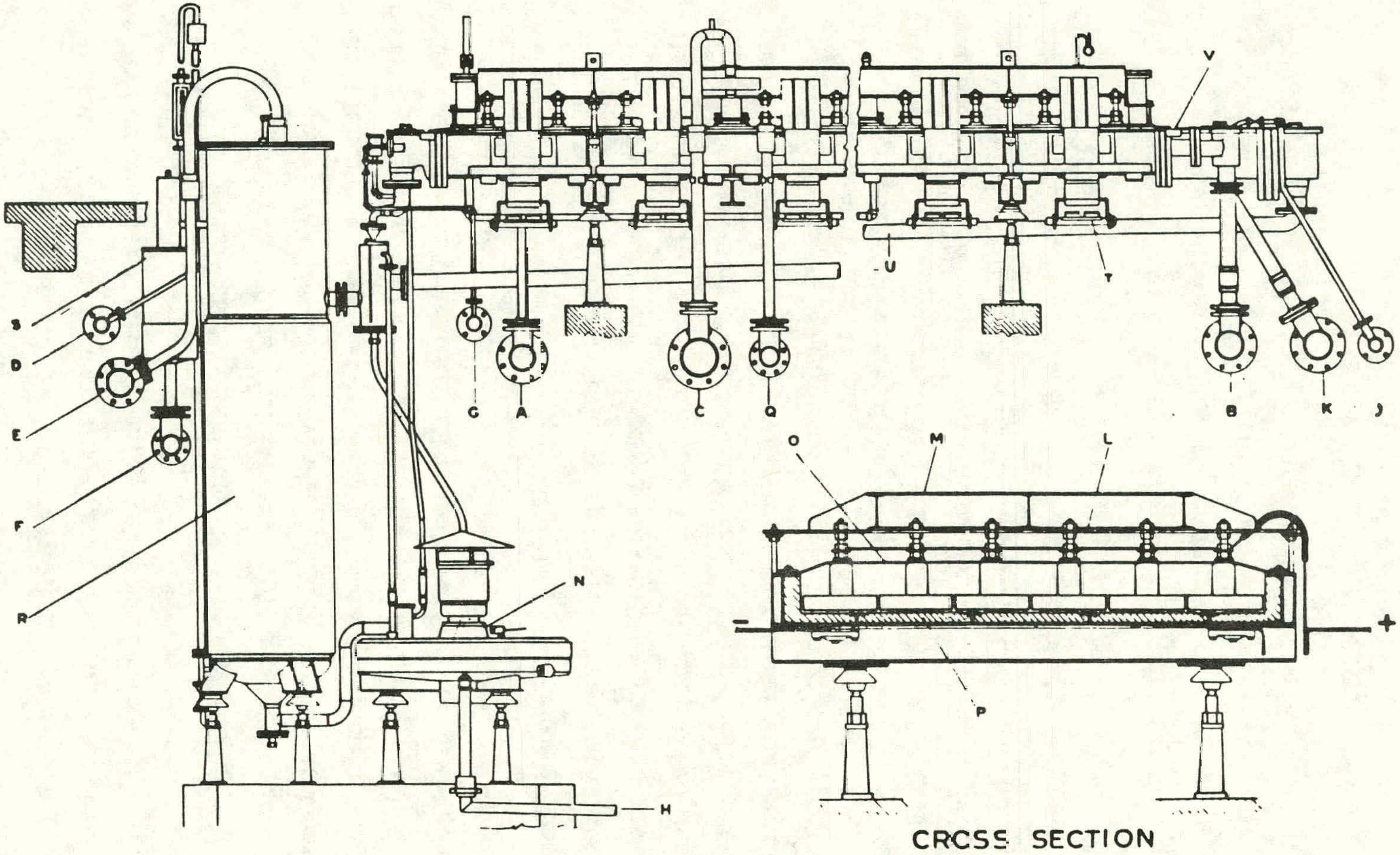
4.0 DESCRIPTION OF BASIC CHLORINE-PRODUCING PROCESSES

As discussed in Section 1.0, current electrolytic chlorine production processes are inefficient relative to energy utilization. As a result, Sections 4 and 5 will attempt to identify chlorine-producing processes that are economically competitive and more energy efficient than present commercial units.

This section describes in detail the process history, scientific basis, engineering aspects, and, where possible, the economics, of the 20 processes identified in Section 3.0 as being potentially competitive with the mercury cell and diaphragm cell processes. For comparative purposes, the following briefly describes existing electrolytic technology.

In the mercury cell process shown in Figure 1, the cells produce chlorine gas and sodium amalgam. The chlorine is pure but must be dried with sulfuric acid and compressed before liquefaction. The sodium amalgam is conveyed to a denuder section where it is washed with water, producing caustic, at a concentration of 50 percent by weight, and hydrogen. The mercury is recycled to the cell. A recent concern with mercury cells is the control of mercury emissions.

In the diaphragm cell shown in Figure 2, a concentrated brine is electrolyzed with the anode and cathode sections separated by a diaphragm which acts to retard the diffusion of hydrogen and caustic from the cathode, where they are produced, to the anode. If such a separator is not present, hydrogen and chlorine could mix, forming explosive mixtures, and hydroxide ions could react with the chlorine to yield undesired chlorates and perchlorates via competing electrochemical mechanisms. In the diaphragm cell process, the chlorine liberated at the anode is recovered, dried by passage through concentrated sulfuric acid, compressed, liquefied and readied for sale. The co-product hydrogen is also compressed and either sold or used on-site for its chemical or fuel value. The caustic formed at the cathode in a diaphragm cell operation is 8 to 11 percent in strength. It normally must be concentrated by evaporation of water, first to 50 percent to effect precipitation of salt values present and, if desired, to higher values to recover solid products.



A. Pure brine feed header
B. Depleted brine collection header
C. Strong chlorine header
D. Pure water feed header to decomposer

E. Hydrogen collection header
F. Caustic collection header
G. Pure water feed header to inlet end
H. To mercury trap and sewer
L. Anode post and plate assembly

M. Anode support structure
N. Mercury pump and sump
O. Rubber cover
P. Concrete grout
Q. Dilute chlorine header

R. Decomposer
S. Current breaker
T. Cell shorting switch
U. Amalgam return
V. Quick flushing device

Figure 1. Mercury cell and amalgam decomposer.
(de Nora 200,000 ampere cell, Ref. 13)

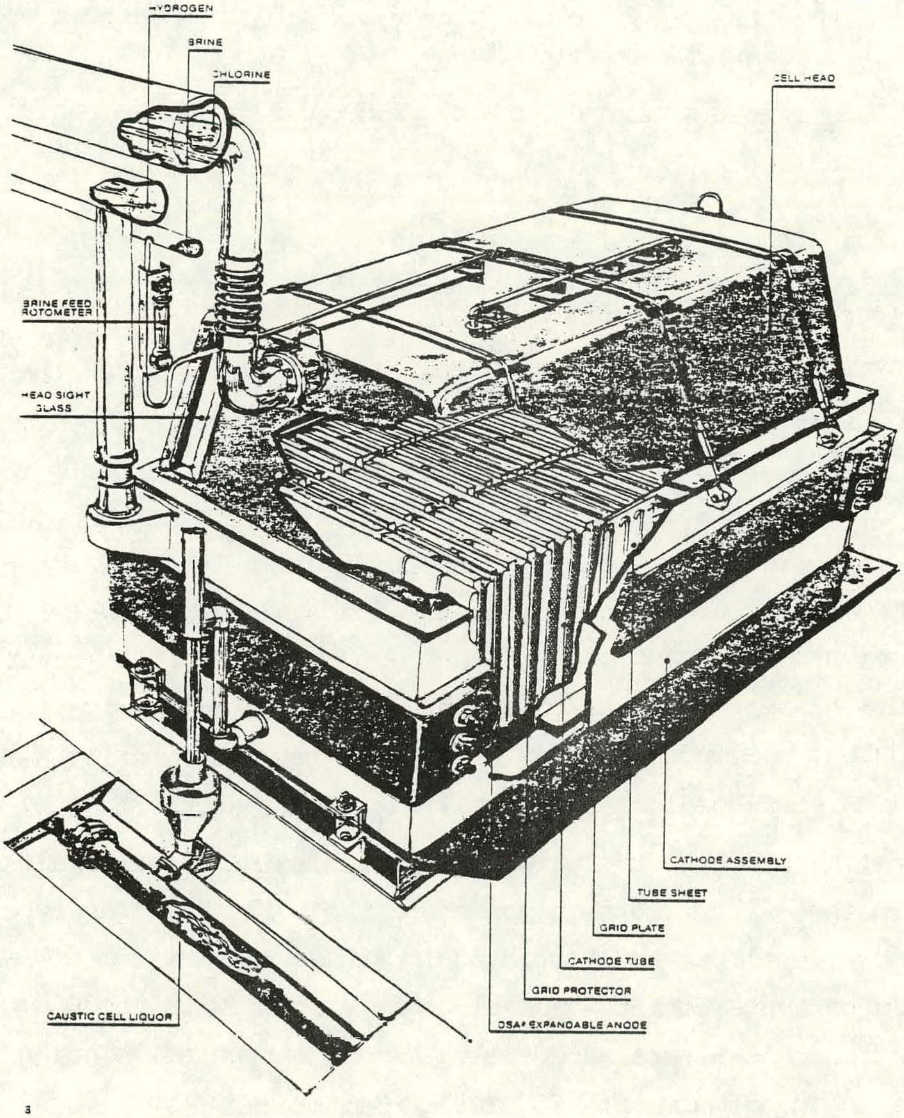


Figure 2. Diaphragm chlor-alkali cell (Hooker Type S4, Ref. 13)

4.1 Membrane Cell

In this subsection, we discuss three emerging areas in chlorine technology:

(a) The membrane cell process itself.

(b) Use of the membrane cell with improved cell cathodes employing either the oxygen electrode or a catalytic hydrogen evolution electrode.

(c) Use of the membrane cell to produce co-products other than caustic soda.

4.1.1 Membrane Cell Process

4.1.1.1 Process History

Development of the membrane cell technology began in the mid-1960's with concurrent efforts undertaken at Asahi Chemical Company, in Osaka, Japan, and at the E.I. DuPont de Nemours Corporate Laboratories in the United States. Asahi Chemical Company developed a membrane constructed of a polyperfluorocarboxylic acid, the exact composition of which has not been disclosed. The DuPont efforts centered around development of a polymeric membrane using polyperfluorosulfuric acid and were first reported in W.G. Grot, U.S. Patent 3,718,627, February 1973 (assigned to DuPont).[7] Since then, DuPont has made a number of further improvements in their membrane based upon ethylenediamine modified material.

Testing of these two membrane materials for chlor-alkali applications began in the early 1970's in Japan and the U.S. Membrane type chlor-alkali cells were developed and tested, using these polymeric materials. In the U.S., DuPont entered into a development program with the Diamond Shamrock Corporation to evaluate and develop membrane type cells using the perfluorosulfuric acid polymer (called Nafion) membranes.

The membrane cell is currently in use at several facilities in the U.S. and Canada. Other U.S. organizations including Hooker Chemical, Allied Chemical, and B. F. Goodrich have begun evaluation and developmental efforts based on the use of Nafion-type membranes for this type of cell.

The Asahi Chemical membranes have undergone similar development and evaluation in Japan.[13,16] Two other Japanese firms, the Asahi Glass Company (not affiliated with Asahi Chemical) of Tokyo and Tokoyama Soda Company have entered the membrane field, using fluorocarboxylic acid-type membranes. Thus, there are at least six potential producers of membrane cells, and developmental efforts are underway to utilize this technology fully.

4.1.1.2 Scientific Basis

The membrane cell differs from the diaphragm cell in that the membrane only allows passage of positively charged ions (i.e., Na^+ or H_3O^+). This effectively prevents diffusion of either hydroxide or hydrogen and allows caustic or other solutions to be used as the catholyte. As hydroxide ions are formed at the cathode, overall electrical neutrality of the catholyte is maintained by permitting sodium ions to move from the anolyte compartment through the membrane. This permits direct production of caustic solutions of strengths up to 30 percent, significantly reducing the amount of evaporation required when compared to conventional display cells. Also, since chloride ions do not diffuse through the membrane, a relatively chloride free caustic is generated.

In the operation of a membrane-type cell, concentrated, fresh sodium chloride brine is fed to the anolyte compartment of the cell, while a 20 to 30 percent caustic solution is circulated in the anode compartment. With application of electric power to this system, chlorine is liberated at the anode, and sodium ions diffuse through the membrane to the catholytic compartment, where simultaneously, hydrogen is liberated via the electrochemical reaction:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

In the catholyte chamber, sodium ions enter via the membrane and combine with hydroxyl ions to generate caustic:

$$Na^+ + OH^- \rightarrow NaOH$$

The caustic is drawn off for further concentration of sodium hydroxide as desired.

4.1.1. 3 Engineering

Figure 3 shows an overall membrane cell process diagram. The process consists of the following six operations:

(a) Brine Make-up - Salt is dissolved in water to produce a concentrated brine solution. This solution is filtered to remove any undissolved material and pumped to the brine purification system.

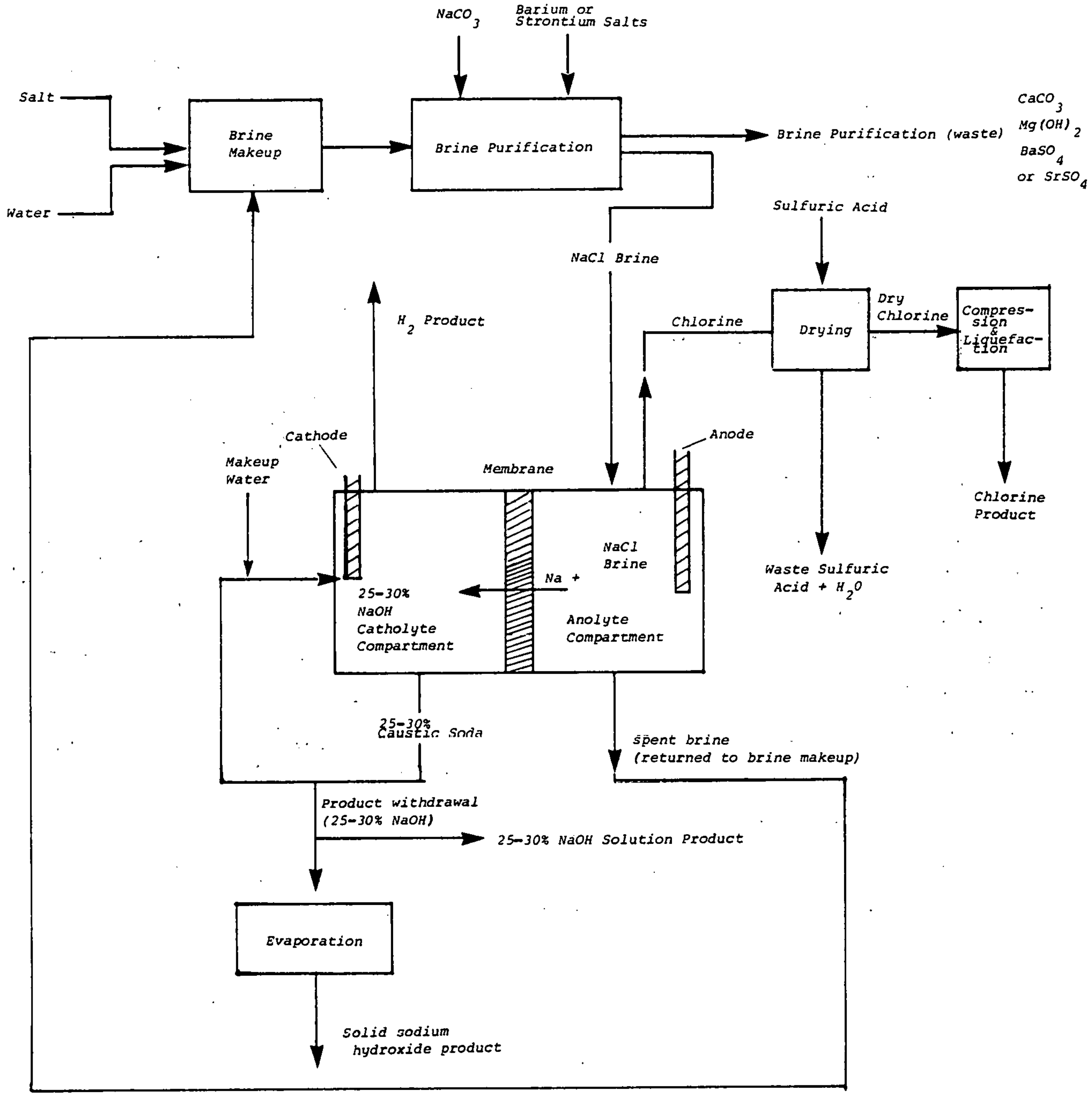
b) Brine Purification - Brine purification is required because the membrane cell is sensitive to impurities, which foul the membrane. An existing commercial chlor-alkali plant that uses membrane cells without brine purification must wash the membrane daily with hydrochloric acid to remove impurities that interfere with process operations. For brine purification, soda ash and strontium or barium salts are added to the makeup to remove calcium, magnesium and sulfate ions via precipitation (i.e., softening process). The precipitates, calcium carbonate and magnesium hydroxide, are removed from the brine by filtration and the purified brine is fed to the anolyte compartment of the membrane cell. Asahi Chemical Industry Company sells an ion exchange unit for brine purification.

(c) Electrolysis - A direct current is passed through the cell between the anode and cathode, and the following chemical activities occur:

- chlorine is liberated at the anode,
- sodium ions enter the membrane and diffuse into the catholyte compartment, and
- at the cathode, hydrogen is liberated.

All three processes operate at comparable rates to maintain overall electrical neutrality of the different cell compartments. In the catholyte chamber, a 20 to 30 percent caustic soda solution circulates. As additional caustic is formed, part of the solution is withdrawn for further processing, and fresh make-up water is added to maintain the caustic concentration in the 20 to 30 percent range. This is required as the membrane cell performance declines if the caustic concentration rises above 30 percent or falls below 15 percent.

Figure 3. Membrane Cell



(d) Chlorine Purification - The chlorine liberated at the anode contains water vapor and 2-4 percent oxygen. This is removed by passing the chlorine through concentrated sulfuric acid (>80 percent). The dried chlorine is then compressed, liquefied, and prepared for shipment or use.

(e) Caustic Purification - The caustic withdrawn from the catholyte section is 20 to 30 percent strength. If this is adequate for the customer, the caustic is directly packaged for sale. For other purposes requiring a higher strength or solid caustic, the desired strength is readily prepared by evaporation of the solution. Evaporation is performed using a standard multiple effect steam evaporator or a heat recovery evaporator patented by Asahi Chemical.

(f) Brine Recycle - The depleted brines from the anolyte section of the membrane cell are recycled to the initial brine make-up step for refortification with salt.

While any concentration of caustic could be directly produced by this method, the overall process has been found to be most efficient when generating caustic solutions in the 20 to 30 percent range.

For a well-operated membrane plant producing caustic soda in the optimum concentration range, current efficiencies of 93 percent have been quoted for the Asahi Chemical polyperfluorinated carboxylic acid membrane.[24,25] For the DuPont Nafion membranes, current efficiencies of over 90 percent have been reported.[2,3,6,12] Operating data for cells in continuous operation over a nine-month period show that, because of impurities present, cell efficiencies are about 88 percent. Efficiency drops produce corresponding increases in cell voltages and power consumption.

One advantage of the membrane cell is high purity caustic production. Analyses of caustic soda product generated by this method are listed below.

Table 3
Caustic Purity Using Membrane Cells

Parameter	Nafian Membrane Cell+ (Diamond Shamrock)	Asahi Chemical Cell*
Caustic Strength	28 wt.%	21.6
NaCl	50 ppm	20 ppm
Ca	1 ppm	0.3 ppm
Mg	0.5 ppm	no data
Fe	1 ppm	1.3 ppm
SO_4	15 ppm	none
ClO_3	<50 ppm	no data
SiO_2	no data	4.4 ppm

+ Diamond Shamrock data (E.J. Peters and D.R. Pulver paper presented at ECS Meeting, Atlanta, Oct. 1977)

* Asahi Chemical data (Maomi Seko, paper presented at 20th Chlorine Plant Managers Meeting, New Orleans, February 9, 1977)

Similar comparisons are available for current efficiency versus concentration between the two types of cells. Asahi Chemical claims that their membrane cell will operate at current efficiencies of over 90 percent while producing caustic in the 10 to 40 percent range.[24] These data were provided by Asahi Chemical Industry Company to show that its membrane was superior to the DuPont membrane.[13] However, an independent comparison of results by E. Hermana et al., showed power usages under identical conditions were 3,054 kwh/ton of chlorine for the Asahi membrane versus only 2,744 kwh/ton of chlorine for Nafion.[9] The results, however, were obtained using a modified mercury cell with a membrane placed between the anode and a modified vertical mercury cathode. For the Asahi membrane cell, a cell voltage of 3.68 V and a DC power consumption of 2,650 kwh (DC)/metric ton of sodium hydroxide has been reported as compared with a Nafion membrane in a Diamond Shamrock cell of 2,765 kwh (DC) metric ton.[24]

Published estimates reveal that these values are expected to drop to about 2,500 kwh/metric ton of product in the near future.

Data have been released on the total energy requirements for the mercury, diaphragm, and membrane cells. Approximate total energy requirements, including cells, evaporation, and other energy needs to produce 50 percent caustic solutions were reported by G. L. Fish of Diamond Shamrock as follows:[20]

Membrane cell ~4,100 equiv. kwh/metric ton of 100% sodium hydroxide
Diaphragm cell ~5,500 equiv. kwh/metric ton of 100% sodium hydroxide
Mercury cell 3,500 equiv. kwh/metric ton of 100% sodium hydroxide

If, however, 20-30 percent caustic soda is acceptable as a finished product, as is the case in some industries, membrane cell energy requirements are reduced to ~3,200 kwh/metric ton of sodium hydroxide. Thus, the membrane cell is competitive with current processes in both product quality and energy needs. On-going development work is expected to reduce power requirements further.

4.1.1.4 Economic Considerations

A comparison of costs involved in the operation for membrane cell plant with the diaphragm cell and mercury cell plants has recently been released by Asahi Chemical[24] and is shown in Table 4.

These costs demonstrate that chlorine can be manufactured economically using the membrane cell. More detailed cost analysis information will be presented in Section 5.

4.1.2 Use of the Membrane Cell with either the Oxygen Cathode or a Catalytic Hydrogen Electrode

To use the membrane cell most effectively, additional approaches have been suggested which, if implemented, would further reduce overall process electrical power requirements.

Table 4

Cost of Raw Materials and Utilities of Membrane Cell, Mercury Cell and Diaphragm Cell (Cost per metric ton NaOH (100%) and 0.89 metric ton Cl_2; Japanese base December 1976; 300 yen = 1 U.S.$)

Technology		Asahi Chemical's Membrane Process		Mercury Process (Metal Anode)		Diaphragm Process (Modified Asbestos Expandable Anode)	
Raw Material	Unit price	Con-sumption	Amount ($/m-ton)	Con-sumption	Amount ($/m-ton)	Con-sumption	Amount ($/m-ton)
Salt	21.34$/m-ton	1.495	31.90	1.495	31.90	1.585	33.82
Electrolysis Power	2.88¢/AC-KWH	2,786	80.24	3,211	92.48	2,371	68.28
Other Chemicals			4.00		7.46		2.72
Power for Motor	2.88¢/KWH	95	2.74	86	2.48	210	6.05
Steam	7.72$/m-ton	0.7	5.40	0.1	0.77	3.6	27.79
Other Utilities			0.10		0.16		0.16
Other Costs (Lease, membrane, etc.)			15.00		5.32		10.63
Total			139.38		140.57		149.45

Power needs for the electrolysis of brines can be reduced by two means:

(a) Reduce the overvoltage required to liberate hydrogen from brine solutions, or

(b) Substitute an oxygen electrode for the hydrogen evolution reaction as the cathodic reaction in electrochemical chlorine production.

4.1.2.1 Catalytically Active Cathodes

The first approach involves reducing the extra amount of electrical energy required to liberate hydrogen from aqueous solutions. The following reactions are involved:

(1) $H_3O^+ + e^- \rightarrow H_2O + H^1$ (adsorbed on electrode)

(2) $2\ H^1$ (adsorbed) $\rightarrow H_2$(gas).

Currently, industry generally uses mild steel as the cathode material, although it is a mediocre catalyst for the above reaction sequence. Its use results in an overvoltage penalty of about 0.2-0.4 volts. Substitution of a better catalytic material than mild steel would greatly reduce the overvoltage values and reduce power consumption.

The problem of hydrogen overvoltage has been previously studied in relation to fuel cell development efforts and a number of promising approaches have been developed. These are:

(1) Use of a catalytic material in the cathode electrode structures. Materials with superior activity include nickel and platinum group metals. Coating of the cathodes with one of these materials should reduce the overvoltage requirements.[37,38]

(2) Development of a hydrogen diffusion electrode.[29,36] As atomic hydrogen is formed (step 1), it diffuses directly into and through a hollow electrode structure. If the electrode material selectively diffuses hydrogen, pure hydrogen gas can then be collected, free of any water vapor. United Technologies Corporation and Leesena Moos

Corporation developed such types of electrodes in their fuel cell study efforts. These hollow, selective electrodes consist of activated palladium and palladium alloys. Such electrodes might conceivably eliminate the overvoltage problem and provide a simple means for direct generation of pure hydrogen. Much of the work in this area has already been performed and patented. What is required is a "technology transfer" from the fuel cell area to the chlor-alkali industry. Energy saved by use of this approach may be as high as 10 percent. However, economics may not favor the use of more expensive cathode materials.

4.1.2.2 Oxygen Cathode

A second approach to reducing power consumption is the use of an oxygen electrode as the cathode. The electrochemical reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

is used to replace the hydrogen evolution which normally occurs at the cathode in membrane cell electrolysis. An oxygen cathode is generated by introducing oxygen into the cell cathode compartment and fabricating the cathode electrode of a material that is active for the electrochemical reduction of oxygen. The concept of applying the oxygen electrode to the chlor-alkali electrolytic process was developed by Gritzner of Dow Chemical[41,42,43] and resulted in the issuance of three patents. Work described in these patents is laboratory scale; however, this type of effort is being continued not only by Dow, but by other chlorine manufacturing organizations as well.

Actually, the oxygen electrode concept itself is not new. A considerable effort was expended in the late 1950's through mid-1960's to develop oxygen electrodes suitable for use in acid and basic media. Electrolyte systems studied included phosphoric acid, molten carbonates and moderately concentrated solutions of potassium hydroxide. Electrode materials recommended include:

(a) Various transition metal oxides and doped oxides including those of nickel and cobalt.

(b) Various transition metals such as nickel, palladium, platinum and rhodium formed into teflon-bonded electrode structures.

(c) Carbon electrodes coated with various noble metals (chiefly platinum and palladium).

(d) Silver and gold black-type electrodes.

(e) Electrodes using dispersed high surface area blacks prepared as alloys of palladium with either silver or gold.

(f) A number of perovskite-type double oxides, chiefly those of cobalt and rare earth metals.

(g) Various redox type systems where a higher valence state salt of transition or rare earth metal is dissolved in the electrolyte, reduced electrochemically to a lower valence state and then chemically oxidized in solution to continue the cycle.

With the exception of (g), the above approaches warrant further study to determine their applicability to the chlor-alkali industry. The last approach is not likely to be useful in chlor-alkali production because of the potential contamination of the caustic products by redox salts.

The oxygen cathode concept is of interest for the following reasons:

(a) The theoretical oxygen electrode potential at 25°C is 1.23 volts higher than the hydrogen electrode.

(b) While overvoltage problems will exist for oxygen electrochemical reduction, at least 0.8 volts of the 1.23 volt difference between the hydrogen and oxygen electrodes could be saved, based on data from past fuel cell efforts. As current chlor-alkali cells operate in the 3-4 volt range, a savings of 0.8 volts translates into a power consumption savings of 20 to 25 percent.

The disadvantage to this approach is that hydrogen is no longer co-produced. For plants where hydrogen is used, this approach may not be desirable; however, at most plants, the hydrogen is burned for fuel values and the oxygen cathode is an appropriate approach.

The oxygen cathode is not expected to require modifications in the overall membrane process other than substitution of electrodes and the use of oxygen in the catholyte cell compartment. This means that capital investment costs for using the oxygen cathode should not be significantly different from more conventional membrane cells.

4.1.3 Use of the Membrane Cell to Produce Co-Products other than Caustic Soda

Since the membrane is permeable only to positive ions, negative ions other than hydroxyl may be used in the catholyte chamber. Based on this principle, at least four modifications of the membrane cell have been developed to produce sodium and potassium carbonates, sodium and potassium phosphates, and organic alcohols as co-products.

Buttre et al., proposed the use of phosphoric acid as the catholyte liquid.[46] As sodium ions pass through the membrane and hydrogen is evolved during cell operation, the phosphoric acid present is converted to sodium phosphate salts. With continuous make-up of phosphoric acid and withdrawal of equal amounts of catholyte liquid, sodium dihydrogen phosphate can be produced as a solid product by subsequent evaporation of the withdrawn catholyte liquor. This modification was developed through the laboratory stage. No pilot plant efforts have been reported.

A similar effort by F.L. Ramp of B. F. Goodrich electrolyzes potassium chloride in place of the normal sodium chloride-based brine.[49] Again phosphoric acid is used in the catholyte section of the membrane cell. Simultaneous migration of potassium ions through the membrane and liberation of hydrogen at the cathode results in generation of potassium dihydrogen phosphate. Because catholyte liquors are continually withdrawn from the system during operation and fresh phosphoric acid is added, the withdrawn liquors need only be evaporated to obtain the phosphate co-product. Efficiencies of 99 percent were reported using a Nafion membrane and a dimensionally stable anode in the test cell. According to patent data, this work was successfully carried through the pilot plant development stage. Current use of this approach has not been determined.

A third proposed modification of the membrane cell process allows simultaneous production of either soda ash or potassium carbonate as a co-product. In both cases, carbon dioxide is continually introduced into the catholyte cell chamber in which a 25 to 30 percent sodium or potassium hydroxide solution is circulating. Reaction of the carbon dioxide with the caustic soda or caustic potash generates the corresponding carbonates. All other operating conditions remain the same. The carbonates can be recovered from the catholyte liquors by evaporation. All tests of the process were performed using Nafion membranes and dimensionally stable anodes. Current efficiencies of over 97 percent were reported for both cases, and chloride impurity levels from the carbonates generated were found to be about 800 ppm for the sodium salt and from 50 to 860 ppm for the potassium carbonate. These carbonate co-product schemes have been successfully carried through the pilot plant evaluation stage. Patents were granted to K. J. O'Leary, C. J. Hora, and D. L. DeRespiris, assigned to Diamond Shamrock Corporation. Comparative cost data for these and other methods of preparing sodium and potassium carbonates have not yet been released. Note that sodium carbonate is currently produced at low cost from natural sources.

A fourth approach to the production of co-products other than caustic soda has recently been reported in a patent issued to H. L. Johnson of PPG Industries.[50] There, the envisioned process involves reduction of tert-butyl hydroperoxide or some other organic peroxide to the corresponding alcohol in the catholyte compartment of the membrane cell. As much as 0.6 volts reduction has been claimed for cases where noble metal-coated electrodes were used with such a scheme. Data were also presented showing that the unreacted peroxide, alcohol and caustic co-products could be separated and recovered in such a system. The overall catholyte process operating for this case is:

$$\text{ROOH} + H_2O + 2e^- \rightarrow 2OH^- + \text{ROH}$$

No scale-up data have been reported for this system and comparative cost information on other current methods of preparation of tert-butyl and other alcohols has not yet been released. Also, projections on the availability and costs of large quantities of tert-butyl hydroperoxide have yet to be published.

4.1.4 Conclusion

The membrane cell appears to be a promising alternative process to current technology. Further discussions are provided in Section 6.2.

4.2 β-Alumina Membrane Process (Japanese Molten Salt Process)

4.2.1 Process History

The Japanese Molten Salt process is being developed under Prof. S. Yoshizawa at Kyoto University.[53] All work reported to date has been from laboratory scale experiments to establish process feasibility.[51,53]

4.2.2 Scientific Considerations

In this process, chlorine and caustic soda are produced by electrolysis of molten salt. The reaction is similar to the present electrolytic processes:

$$H_2O\ (g) + NaCl\ (NaCl - ZnCl_2) \rightarrow 1/2\ H_2(g) + NaOH + 1/2\ Cl_2(g)$$

A cell similar to the membrane cell process (Section 4.1) is used, except the "membrane" material is a β-alumina diaphragm. On the anode side of the diaphragm, a 50 percent sodium chloride/50 percent zinc chloride molten salt mixture is used; on the cathode side, molten caustic soda containing about 5 percent water is employed. During operation, chlorine is liberated at the anode and excess sodium ions migrate through the alumina diaphragm to the cathode compartment where hydrogen is liberated from the water present. The chlorine formed at the anode is already water free and can be compressed and liquefied for use or shipment. The molten caustic from the cathode side is recirculated, with fresh water added and some caustic withdrawn in the molten state, cooled, and recovered as solid product.

4.2.3 Engineering Considerations

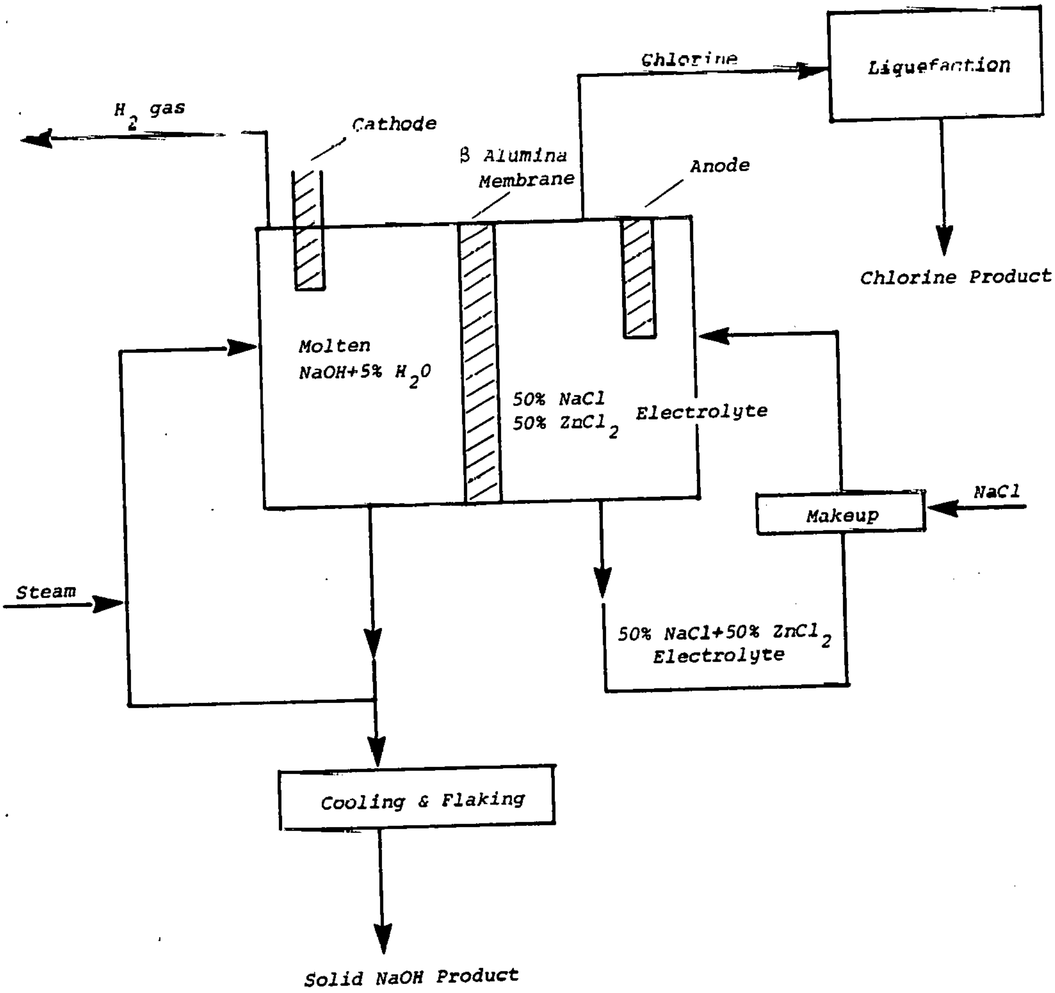
A process flowsheet is shown in Figure 4.

According to laboratory results, the Japanese Molten Salt process operates at 330°C, 50 Amp/dm^2 and 3.18 V. The patent states that current efficiency is about 100 percent. However, no pilot plant or process demonstration unit data have been reported to verify the current efficiency.

This process has several advantages and disadvantages as listed below:

1. The cell operating voltage (3.18 V) is lower than those reported for the membrane cell (3.5-4.0 V), and hence direct electrical energy requirements are lower. There is an additional energy penalty incurred

Figure 4. β—Alumina Membrane Process



in this process, however, because of the need for maintaining the cells and circulating molten salts at the 330°C operating temperatures. Part of this thermal energy requirement includes steam generation, since the water must be injected into the molten caustic as steam. Energy requirements are presented in Table 5.

2. Severe corrosion problems are anticipated with this system caused by both molten caustic and a molten sodium chloride-zinc chloride eutectic at 330°C. Use of these molten salts requires that the electrolytic cells and salt recirculation systems be constructed of special corrosive resistant materials such as tantalum or titanium. These special materials increase the capital cost of the cells compared to conventional membrane or diaphragm cells.

3. There is considerable evidence that the β-alumina diaphragms will not stand up under the proposed operating conditions. β-alumina is a sodium aluminate with the approximate formula of $Na_2O \cdot 11Al_2O_3$. This material, like other aluminates, is expected to exhibit some degree of solubility in molten caustic. Hence, "membrane" lifetimes may be short. Any contamination of the caustic co-product due to β-alumina membrane dissolution or migration of zinc ions through the membrane can result in serious problems involving product caustic salability.

One further disadvantage of this process, as with the membrane cell, is the stringent raw material purity requirements which necessitate that the salt raw materials be pre-purified. The industry standard method of brine purification is removal of impurities by chemical precipitation. If this method is used for the β-alumina membrane process, the purified brine will require evaporation to recover the solid salt used in the process. This entails additional energy requirements. Also, pre-purification of the zinc chloride may be required.

It has been recently reported that the presence of calcium or potassium ions in molten salts in contact with β-alumina accelerates degradation of this proposed diaphragm material.[51,52] The sensitivity to such impurities implies that stringent salt purification methods will be required for this

Table 5

Summary of Process Energy Requirements for β-Alumina Molten Salt Process

1. Electricity (Thermal Equivalent) 54.3 Kcal/mole (Cell run at 3.2 V)
2. Steam Generation 14.4 Kcal/mole
3. Solution Evaporation/Brine Purification 22.3 Kcal/mole

Total Energy Required (30% solution) 91.0 Kcal/mole

Equivalent Energy Membrane Cell (Asahi - 40% product) → 68.0 Kcal/mole

Equivalent Energy Membrane Cell (Asahi - dry product) → 79.2 Kcal/mole proposed process, which will add considerably to process capital and operating costs.

4.2.4 Conclusion

Since this process has not been demonstrated at the pilot plant scale, the overall importance of corrosive problems on process viability is indeterminate and only an estimate of capital or operating costs is possible. Materials of construction and corresponding operating parameters have yet to be specified. Most important, there is considerable doubt that the β-alumina diaphragm can withstand the operating conditions for a reasonable period of time.

This process will not be further evaluated due to the anticipated diaphragm, corrosion, and materials handling problems. However, further laboratory efforts in this area would be beneficial to determine whether a viable process can be developed. To become competitive, energy requirements for steam generation and salt purification would have to be considerably reduced.

4.3 DOWNS CELL

4.3.1 Process History

The Downs cell process for co-production of chlorine and sodium metal was developed and patented by J. C. Downs of the E. I. DuPont de Nemours Company in 1924.[54] The process was commercialized by DuPont at their Niagara Falls, New York plant in the late 1920's. The process rapidly replaced the older Kastner electrolytic process for sodium manufacture, which involved electrolysis of molten caustic soda. By 1940, all Kastner process plants had been replaced. The Downs cell process has been continually operated by DuPont since 1940 and, at present, there are five plants producing sodium via this method. These are:

Company	Plant Location	Capacity (millions of lb per year)
DuPont	Niagara Falls, NY	113
	Memphis, TN	44
Ethyl Corporation	Baton Rouge, LA	90
	Pasadena, TX	60
RMI Corporation	Ashtabula, OH	74
	Total	381

The Downs cell process currently supplies all sodium produced in the United States.[54]

4.3.2 Scientific Basis

In the Downs cell process, pre-purified sodium chloride is mixed in a 42/58 ratio with dry calcium chloride ($CaCl_2$). This mixture is then introduced into a molten salt diaphragm-type cell where the temperature is raised 580°C to liquefy the salt eutectic mixture. The molten salt is then electrolyzed as follows:

$$2NaCl \text{ (melt)} \rightarrow 2Na + Cl_2\uparrow$$

The chlorine is formed at the graphite anodes, collected above the melt, purified, compressed and readied for sale. The sodium co-product forms at a pipe-type electrode of special design. The molten sodium exits the cell through the pipe-type electrode and is then partially cooled to precipitate impurities, especially the sodium-calcium alloy. This material is then removed from the molten sodium by filtration at 110°C. The sodium is then cooled, solidified and readied for sale. The sodium-calcium sludges removed from the product sodium are converted to the corresponding hydroxides for plant use or disposal.

4.3.3 Engineering Considerations

A process flowsheet is shown in Figure 5. In the operating Downs cell a large single cylindrical graphite anode, constructed of several graphite blocks, is inserted through the base of the cell and is surrounded by an iron gauge diaphragm and a cylindrical iron pipe-type cathode.

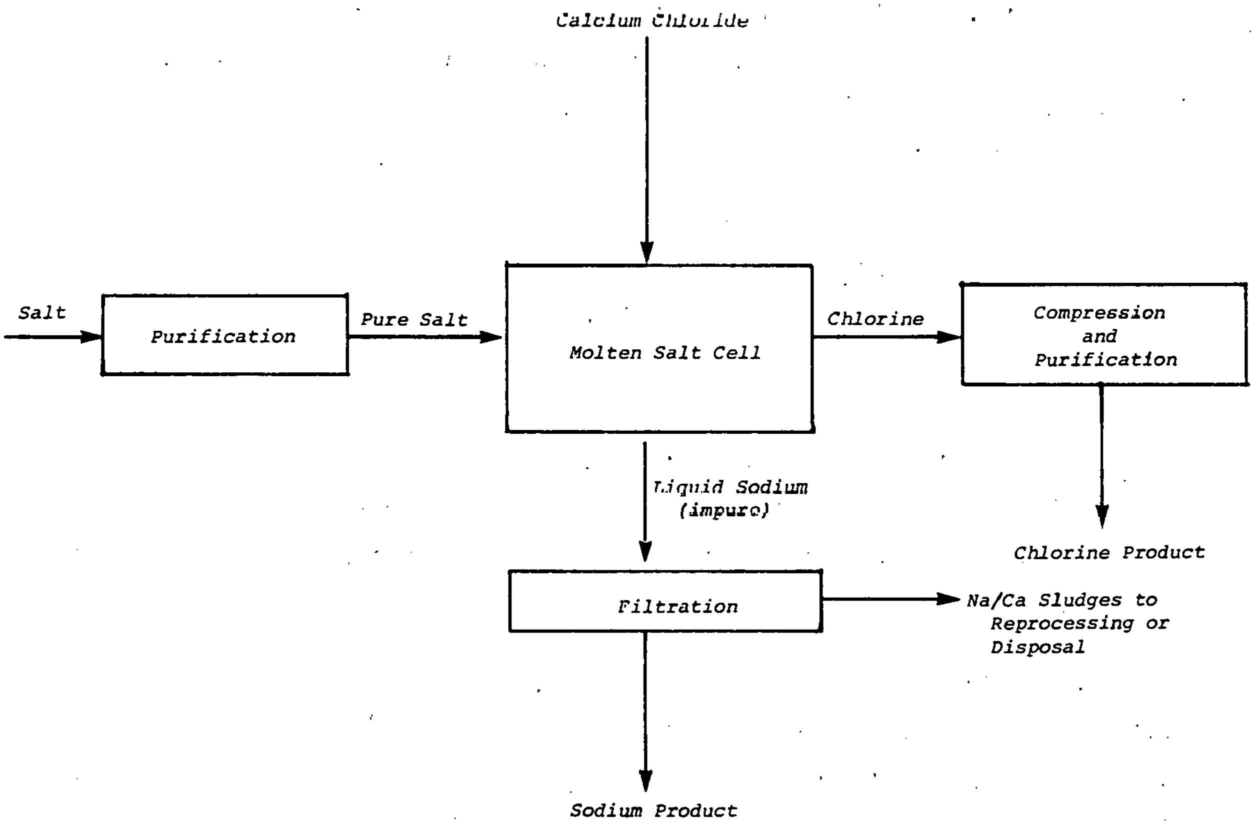
The cell bath is composed of a 58 percent calcium chloride/42 percent sodium chloride molten salt eutectic. This composition is a compromise between melting point and sodium content. Additional calcium chloride would further lower the melting point at the expense of depletion of the sodium in the electrolysis zone with resulting complications. With the 58/42 composition, cells operate at 580°C, a temperature well below the range of high solubility of sodium in the melt. The use of calcium chloride in the bath causes some problems due to the following equilibrium reaction:

$$2Na + CaCl_2 \rightleftarrows 2NaCl + Ca$$

The alloy phase formed during electrolysis contains about 5 percent calcium at cell conditions, an amount intolerable for most industrial uses. The bulk of the calcium is removed by precipitation in the cooled pipe leading from the cell. Any precipitated calcium which adheres to the piping must be removed periodically to prevent plugging. The precipitate drops to the bath-metal interface where it reacts to reform calcium chloride and sodium according to the above equilibrium.

Calcium remaining in the sodium is removed as an alloy of calcium and sodium by filtration at 110°C. The filtered sodium contains less than a 0.04 percent calcium. The filtration also produces a filter cake consisting

Figure 5. Process Flowsheet - Downs Cell Process



of calcium, sodium, chlorides and oxides. The alkali metals are reclaimed by converting the calcium metal to equivalent sodium metal and calcium chloride as shown in the equilibrium reaction. The oxides and chlorides are removed with the salt phase.

Characteristics of Downs cells operated in the United States have not been published. British and German data, however, are listed below:

Property	Value	
	British	German
Bath temperature C	580 ± 15	590 ± 5
Cell current A	25,000 - 35,000	24,000 - 32,000
Cell voltage V	7	5.7 - 6.0
Cathode current density, A/In^2	6.3	6.3
Current efficiency, percent	75 - 80	78
Cell life, days	500 - 700	300 - 350
Diaphragm life, days	20 - 100	20 - 30

In the Downs cell process, salt substantially free of sulfate and other impurities is required as the cell feed. This may require on-site purification. Dried calcium chloride is periodically added to the bath to balance losses. The heat required to maintain the bath in the molten condition is supplied by the electrolysis current.

Cell life is determined by the loss of graphite from the anodes. Oxygen released at the anode by electrolysis of oxides or water in the bath reacts with the graphite to form carbon monoxide and carbon dioxide. In time, erosion of the anode increases the spacing between the electrodes until the cell overvoltages become uneconomical. Cell temperature control also becomes difficult under such conditions. At this point the cells are shut down, dismantled and refurbished.

4.3.4 Conclusion

Although the Downs cell process has been operated on a commercial scale for over 40 years, this process is limited in its ability to generate chlorine by the demand for the co-product sodium. At present, all United States requirements for this metal are met by the five operating plants. In addition, one major use for sodium, production of tetraethyl lead, is expected to decline sharply as lead additives are removed from gasoline. As a result, the United States market for sodium is expected to decrease in the future.

This process will not be considered further in this study because Downs cell capacity in the United States is unlikely to expand in the near future.

There is another commercial molten salt electrolysis process which produces magnesium and chlorine. This process uses a magnesium chloride feed produced on-site from magnesium hydroxide recovered from seawater and waste hydrochloric acid. The process is used by Dow Chemical Company at one site where sufficient quantities of all raw materials are available. No other chlorine plants have sufficient quantities of hydrochloric acid or magnesium hydroxide to operate this process.

4.4 Catalytic Oxidation of Hydrogen Chloride

4.4.1 Shell Hydrogen Chloride Oxidation Process

4.4.1.1 Process History

The first major investigation of chlorine recovery was performed by LeBlanc in the early nineteenth century in connection with a process he developed for alkali production. His process liberated large quantities of hydrogen chloride which could be later used to obtain chlorine. The chemical process was:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$$

No attempt was made to trap the hydrogen chloride gas. In 1836, Gossage took advantage of this excess gas and developed a means to produce chlorine. He used gas wash towers with manganese dioxide sorbent to obtain chlorine. His process was infeasible, however, except on a laboratory scale, because large quantities of costly manganese were required and yields were poor.

In 1866, Weldon improved this process by devising a method to cut down on manganese waste using reconversion and recycling techniques on the manganese products. His yields were 30 percent with a chlorine concentration of up to 90 percent.

Deacon addressed the problem of chlorine production using hydrogen chloride in 1868. His first developments, which are traceable to Oxland, Laurens, and Tregomain, generated chlorine by the oxidation of gaseous hydrogen chloride in the presence of an inert porous catalyst. The reaction is:

$$4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2H_2O$$

Deacon patented his invention in 1868 (British patent 1403). He continued developing his process for the next 10 years, and in this time he registered over 20 patents.

Various two-stage processes of chlorine formation were developed beginning in 1885. These processes were based on forming a metal chloride by reacting a metal oxide with hydrogen chloride, and then oxidizing the metal chloride with air to liberate chlorine. Oxides of iron, magnesium, and nickel were used. Although theoretically these processes looked attractive, operating procedures were inefficient and difficult. One serious drawback was the need for high temperatures (300-600°C) to oxidize the metal chlorides. At such high temperatures some metal chlorides (e.g., nickel chloride and ferric chloride) vaporized before oxidation took place. One process using magnesium oxide was commercially developed by Weldon and Pechiney, but it proved unsatisfactory and was soon discarded. Thus, the primary processes established in the late 19th century were the Weldon and Deacon processes.

In 1937, Grosvenor Labs developed an oxidation process that used a four-component contact mass. The contact mass contained ferric chloride, potassium chloride, cadmium chloride, and diatomaceous earth. Chlorine was formed by treating this mass with oxygen at temperatures around 500°C. In 1947, Dow Chemical patented a similar process in which they used ferric chloride, potassium chloride, cupric chloride, and celite on a moving bed. Based on Dow and Grosvenor patents, Hercules Power Company built a plant to produce 35 tons per day. The plant was shut down, however, because of low yields and high operating and maintenance costs.

An electrolytic hydrogen chloride-based process which appeared promising was developed in 1943 by I. G. Farben. The pilot plant had limited success. A later version of the electrolytic process, using a two-step method, was also investigated by Westvaco. Both of these methods are currently inactive. However, a direct electrolysis method has since been developed by Uhde Corporation and used commercially. (See Section 4.8.)

From a historical perspective the four main hydrogen chloride/chlorine formation processes are:

1. Catalytic oxidation of gaseous hydrogen chloride;
2. Direct oxidation of hydrogen chloride by an inorganic oxidizing agent;
3. Two-stage processes involving intermediate formation of a metal chloride from either its oxide or oxychloride and release of the chlorine by treatment with air or oxygen or by heating; and
4. Electrolysis of hydrogen chloride.

Shell Oil Company researched these four methods and showed that complications existed for each.

Shell found that the catalytic oxidation processes similar to the Weldon type would not be economically or commercially feasible because yields were low. Despite modifications, large losses of chlorine occurred and recovery remained below 50 percent.

Direct oxidation was abandoned due to extreme corrosion problems. Process profitability required favorable market conditions and specific market locations.

Based on technical and economic studies, the two-stage processes were regarded as having no future for commercial development. Shell's conclusion came at a time when considerable work was still being done. On this two-stage process, four patents were granted during this period to: Grosvenor Laboratories (in 1940), Dow Chemical (in 1951), Standard Oil Co. (in 1948), and Socony-Vacuum Oil Co. (in 1947).[56-59]

The electrolysis process, though technically suitable, showed poor economics for all locations, except those with low electricity costs.

Shell Oil Company concluded that the modified Deacon Process was best for future chlorine development.

4.4.1.2 Scientific Basis

The Deacon Process produces chlorine by oxidation (using air or pure oxygen) of hydrogen chloride in the presence of a cupric chloride catalyst as follows:

$$4\ HCl + O_2 \xrightarrow{CuCl_2} 2\ Cl_2 + 2H_2O\ (\Delta H<0\ \text{exothermic})$$

Complete process thermodynamics are available from Arnold and Kobe (1952).[60] They studied the effects of temperature, pressure, dilution with inert gases, and the ratio of reactants on the conversion of hydrogen chloride to chlorine.

They found that greater hydrogen chloride conversions were possible at lower temperatures, higher pressures, and increased air to hydrogen chloride ratios. The use of pure oxygen instead of air slightly increased the conversion percentage (about 2 percent) and produced a higher chlorine content in the product. There are problems associated with using pure oxygen, including difficulties in heat removal, temperature control, and high costs for oxygen. Figures 6, 7, and 8 illustrate the problems associated with temperature control.

The optimum conditions determined by Deacon were within the narrow temperature range of 430° to 475°C. His experiments produced conversion percentages in this temperature range of 60 to 70 percent. Many problems plagued the process, including:

- High reaction temperature requirements;
- Moderate yields;
- Volatilization of cupric chloride, causing a rapid decline in catalyst activity;
- Difficulty in controlling temperature because the highly exothermic oxidation reaction caused hot spots which aggravated the volatilization; and
- Severe corrosion of equipment at reactive temperatures.

4.4.1.3 Engineering

The Shell Process operates by passing a gaseous mixture containing hydrogen chloride and oxygen over the catalyst-containing silica bed. It is presented in Figure 9.

The main aim of the Shell research was to devise a process (similar to the Deacon Process) that had both a satisfactory reaction rate and high conversion. This required development of a catalyst that had sufficient activity, life, and thermal stability. The most effective catalyst developed by Shell was cupric chloride with small quantities of rare earth metal chlorides such as scandium, yttrium, zirconium, thorium and uranium and one or more alkali metal chlorides. The metal chlorides are used in a molten state to increase their activity. All catalyst material is supported by silica gel. This silica carrier has an optimal surface area of 200 m^2/g

Figure 6.

OXIDATION OF HCl TO CHLORINE (WITH AIR OR OXYGEN). THEORETICAL HCl CONVERSION AND % Cl_2 AT EQUILIBRIUM

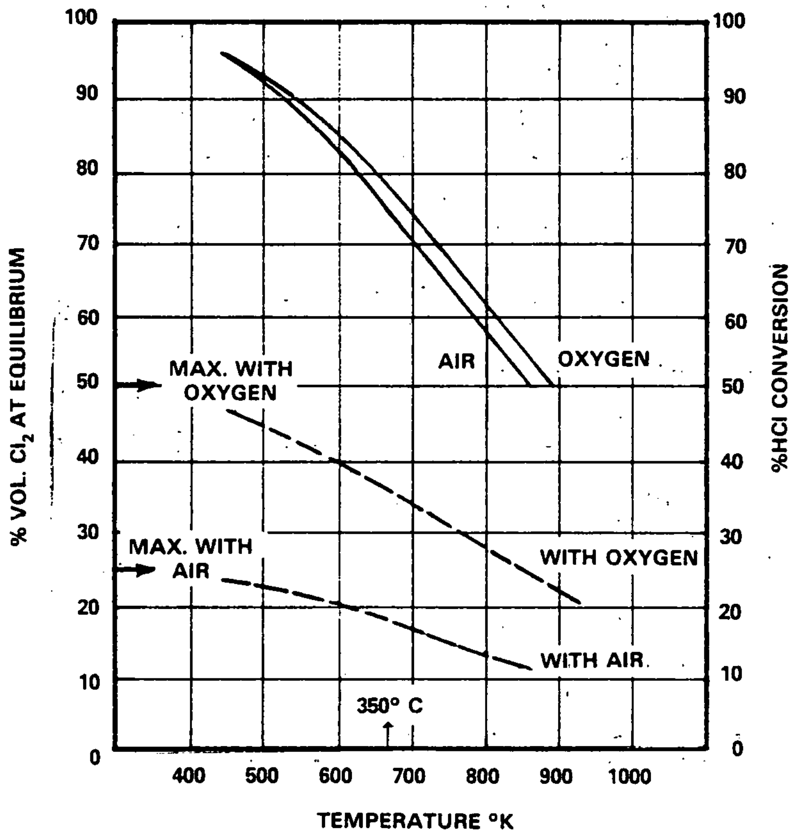
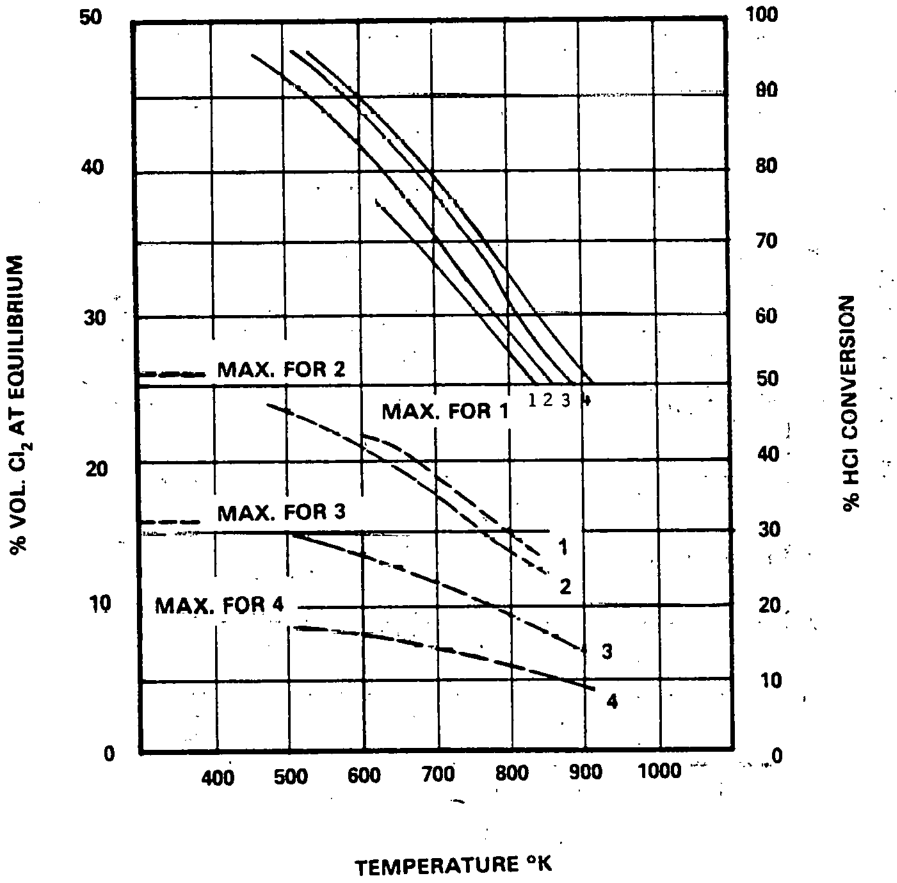


Figure 7.

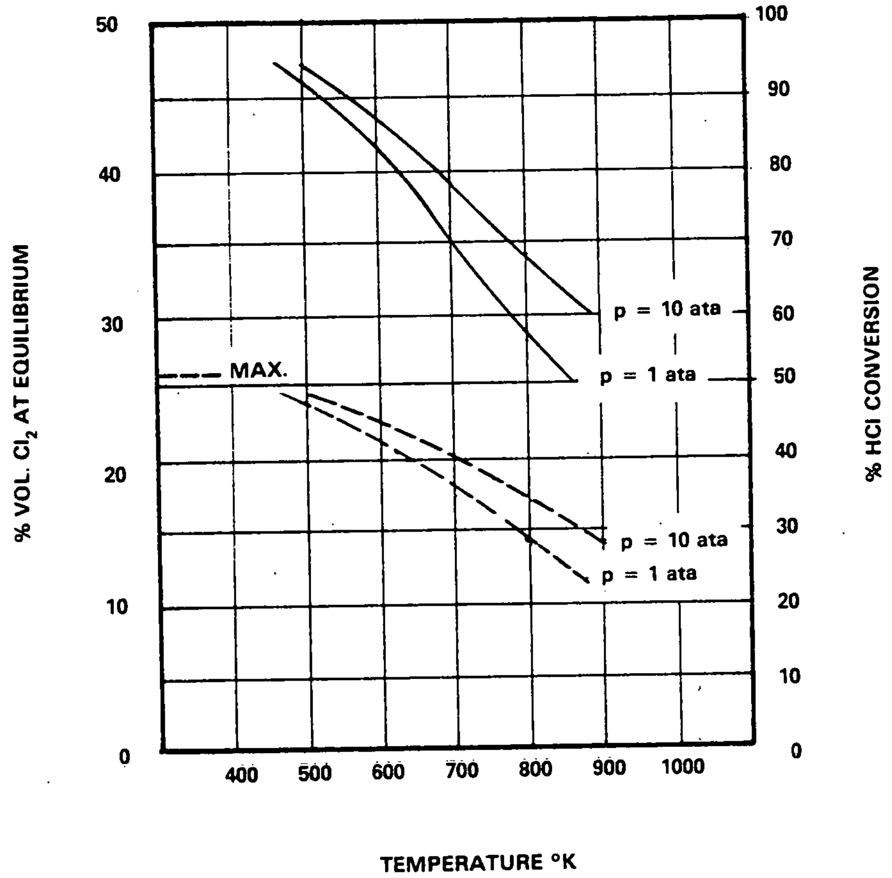
OXIDATION OF HCl TO CHLORINE. INFLUENCE OF HCl/AIR RATIO ON HCl CONVERSION AND ON % Cl_2 AT EQUILIBRIUM



1. HCl/AIR = 1.05 MOLE RATIO
2. HCl/AIR = 0.84 (STOICHIOMETRIC)
3. HCl/AIR = 0.42
4. HCl/AIR = 0.21

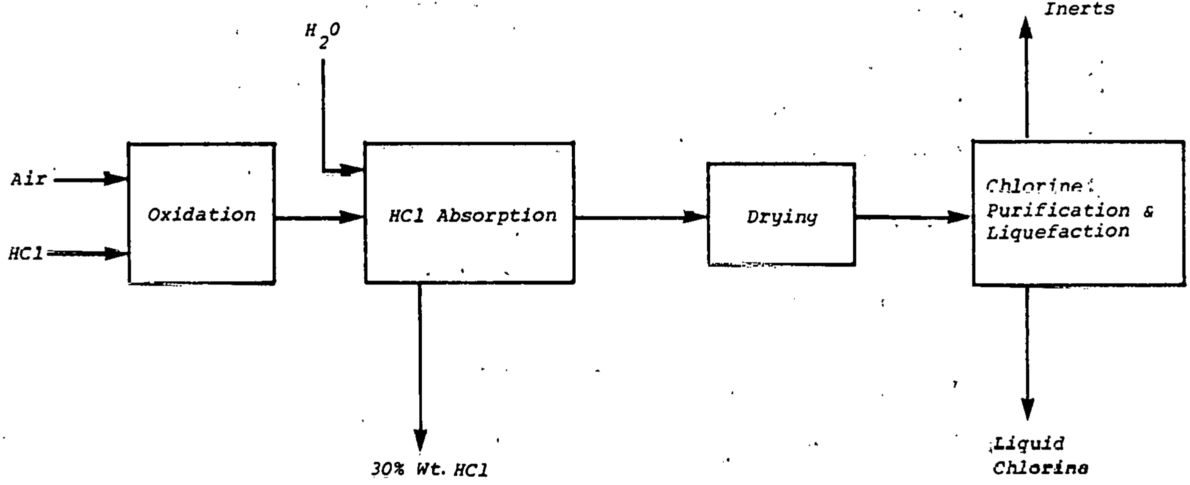
Figure 8.

OXIDATION OF HCl TO CHLORINE. EFFECT OF PRESSURE ON HCl CONVERSION AND ON % Cl_2 AT EQUILIBRIUM



% HCl CONVERSION
% Cl_2 AT EQUILIBRIUM
HCl/AIR = 0.84 (STOICHIOMETRIC)

Figure 9. Flow Diagram for the Shell Hydrogen Chloride Oxidation Process.



with an average pore diameter of 60A°. Proportional ratios are also important here in determining the optimal conversion. For best results, the rare earth metals to copper ratio should be about 0.15, and the ratio of alkali metals to copper can range from 0.8 to 1.2.

In experiments with actual industrial waste hydrogen chloride, this catalyst material performed satisfactorily. Catalyst activity remained unaffected by acid contaminants. High conversions were attained at both low temperatures and high space velocities.

Preferable process temperatures are 330°C to 400°C. In this temperature range, increased pressure does not significantly increase conversion. Because of the low temperatures, copper volatilization is eliminated and corrosion due to heated reactants is greatly reduced.

Sample yields are as follows:

1. Fixed bed, 350°C: 76.5 percent conversion.
2. Fluidized bed, 365°C: 77.5 percent conversion.

The use of pure oxygen slightly increases conversion and subsequent purification, but problems of temperature control preclude its use.

4.4.1.4 Economics

Shell claims that its process is commercially competitive and has a rate of return significant enough to warrant a large capital investment. Table 6, prepared by Shell, shows the process has the highest return and lowest capital cost of any of the processes used by major hydrogen chloride/chlorine producers.

4.4.1.5 Conclusion

The Shell process, while apparently attractive from an energy and economic standpoint, has never enjoyed large scale commercialization. Currently, the only operating unit using this method is a 19,000 TPY pilot unit at Pernis in the Netherlands. This process will be further studied in Section 6.

Table 6

HCl/Chlorine Process Economics

(1962 Dollars*, Plant Size: 100t/d)

Producer	**SHELL**	**DEACON**	**DeNORA**	**IFP**
Process	Catalytic	Catalytic	Electrolysis	Acid Oxidation
Raw Material $/t Cl_2	-	-	-	-
Chemicals "	3.92	3.92	1.12	4.76
Utilities "	7.56	15.12	26.88	8.40
By-products "	-	-	(0.7)	-
Fixed Costs "	7.56	10.08	8.40	12.04
Total Manufacturing Cost $/$Cl_2$	19.04	29.12	34.44	25.20
Net back $/t Cl_2	56.0	56.0	56.0	56.0
Gross Profit $/t	36.96	26.88	21.56	30.80
Capital Cost	1.31×10^6	1.99×10^6	2.24×10^6	2.06×10^6
Profitability (% return on capital)	76%	31%	19%	35%

(* Using conversion 1 British pound = $2.80)

4.4.2 Kellogg Modified Deacon Process

4.4.2.1 History

This process for chlorine production using clay materials was developed and expanded by the M. W. Kellogg Company. The company applied for an English patent on August 23, 1960 and the patent was granted on January 15, 1964.[61] Overall, this process involves the continuous oxidation of hydrogen chloride or other halogen acids to produce chlorine, bromine or iodine in a higher yield and in a higher degree of purity than was normally obtained in the late 1950's. Work was only performed on the laboratory scale. Once the patent was obtained further development ceased. The project is currently inactive.

4.4.2.2 Scientific Basis

The M. W. Kellogg Company process produces chlorine by oxidizing an inorganic halide such as hydrogen chloride in the presence of a metal- or silica-containing oxidation catalyst and a dissimilar material containing a clay desiccant. The clay desiccant must have a reversible water content of at least 0.5 percent by weight and a crystalline structure stable to at least 1,400°F.

The possible sources of inorganic halides include the following: hydrogen chloride, hydrogen bromide, hydrogen iodide, nitrosyl chloride, nitrosyl bromide, nitrosyl iodide, ammonium chloride and ammonium bromide. The chlorides and bromides are preferred.

The primary oxidizing agents used for these halides includes molecular oxygen, air, ozone, nitric acid and nitrogen oxides. Catalysts that can be used for this reaction include: chromium sesquioxide (Cr_2O_3), elemental chromium, potassium chromate (K_2CrO_4), cerium oxide (CeO_2), manganese dioxide (MnO_2), uranium trioxide (UO_3), cupric chloride ($CuCl_2$), a ferric oxide/ferric chloride mixture ($Fe_2O_3/FeCl_3$), a chromium sesquioxide/alumina mixture (Cr_2O_3/Al_2O_3), calcium chloride ($CaCl_2$), and silica gel. For the oxidation of hydrogen chloride with molecular oxygen, chromium sesquioxide is preferred.

The basic conversion reaction for the process is the same as that for other oxidation processes using hydrogen chloride:

$$4HCl + O_2 \rightarrow 2Cl_2(g) + 2H_2O$$

The clay desiccant used in the process absorbs water as it is formed in the reaction zone. This shifts the equilibrium toward the right, increasing yield and purity of the halogen product. The clays are preferably bentonitic in nature. Montmorillonite is the most desirable of these types. They are regenerated after absorbing about 1 percent by weight of water.

4.4.2.3 Engineering

The basic reaction is carried out on a fluidized or moving bed. The solids run countercurrent to the gaseous and/or liquid materials comprising the oxidizing agent and the halide. The fluidized bed avoids development of "hot spots" during operation and facilitates continuous removal of spent clay and water from the reaction zone for immediate regeneration and recycle.

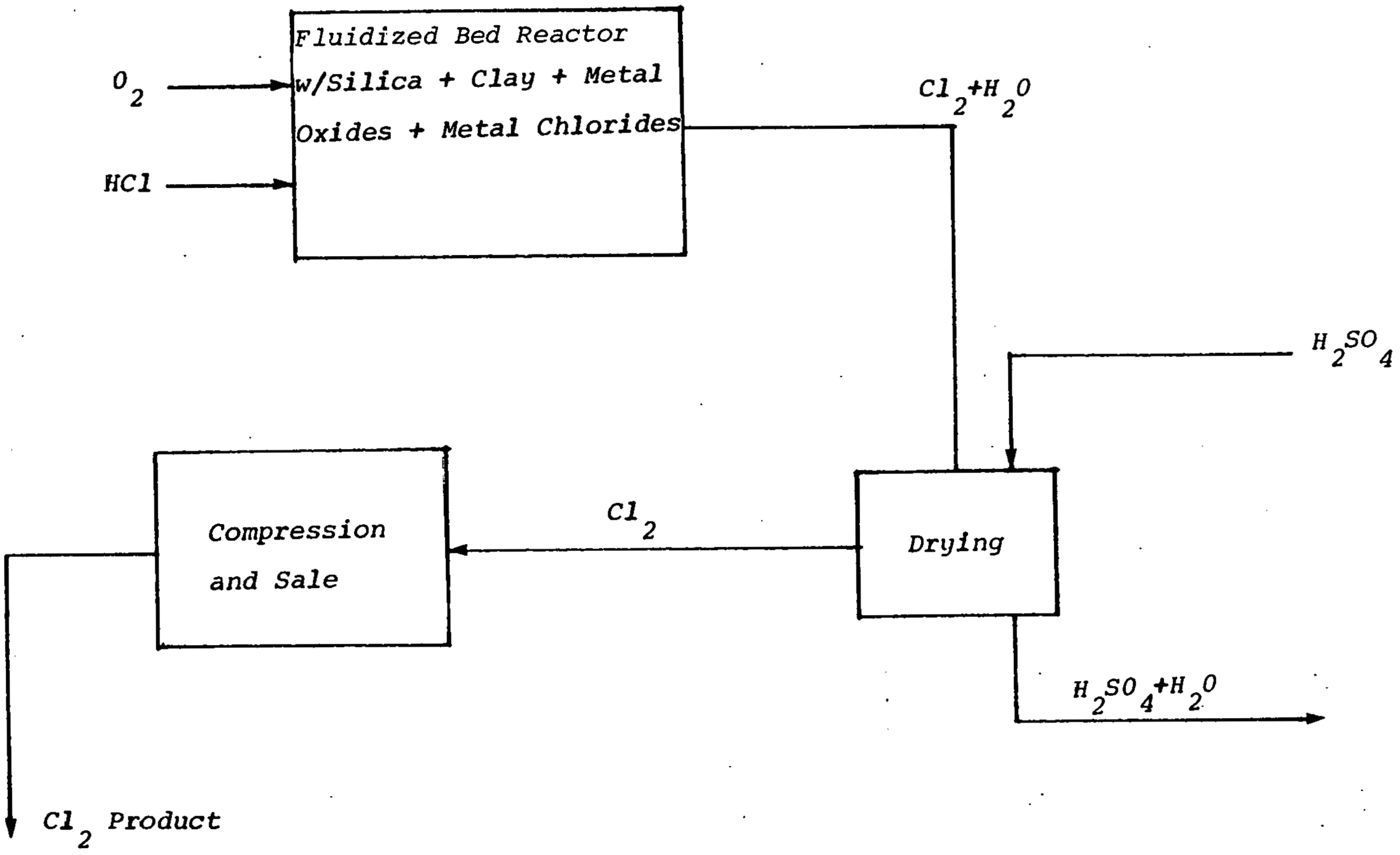
Figure 10 is a flow diagram of this process.

The catalysts involved in the reaction are supported on carriers such as silica, alumina, or pumice, although the bentonitic clay desiccant may also be used for support. The carrier must be of sufficient hardness to resist attrition when the mass is subjected to the fluidized bed condition.

The operating temperature range is between 300°C and 550°C. Maximum benefit is derived from a temperature range of 400°C to 500°C. Preferred pressures are between 3 and 12 atmospheres. The optimal space velocity for oxidation is between 100 cc and 400 cc of halide per hour per gram of catalyst. Based on the metal or silicon in the catalyst, the clay desiccant optimally should be present between 80 and 98 percent by weight. Optimal mole ratio range of oxidizing agent to halide is 1:1 to 1:5.

The process may be carried out by a continuous or batch method. Continuous operation requires continual withdrawal of both product and desiccant.

Figure 10. Flow Diagram for Kellogg Modified Deacon Process



4.4.2.4 Economics

No cost data or economic assessment were given on the process in the documents available.

4.4.2.5 Conclusion

This process can be dismissed from consideration for large scale chlorine production. Although production conversions were high (average 93 percent), three major disadvantages exist:

1. Low availability of large quantities of hydrogen chloride.
2. High process temperatures required, i.e., high energy and power costs.
3. More energy efficient processes exist using the same basic raw materials for making chlorine, namely Kel-Chlor, Mobay, and the Shell process. In fact, Kel-Chlor was developed by the same company which invented this process and M. W. Kellogg chose Kel-Chlor for commercial development.

These factors indicate that the Kellogg halide oxidation process for making chlorine is not a viable alternative to existing production methods.

4.5 Catalytic Oxidation of Hydrogen Chloride using Metal Oxide Catalysts

4.5.1 Preparation of Chlorine using Hydrogen Chloride with a Vanadium Catalyst

4.5.1.1 Process History

This process of chlorine formation results from the oxidation of hydrogen chloride in the presence of a catalyst similar to the Shell process (Section 4.4.1). The original process was developed by Imperial Chemical Industries (ICI) in 1967.[62] Their patent made claims of 63 percent conversion. It used vanadium pentoxide (V_2O_3) as a catalyst. Also in 1967, BASF patented an improvement to this process.[63] Their improvement dealt with the addition of several other catalytic materials (CeO_2, MnO_2, CoO, NiO, etc.) to the vanadium. Once patented on a bench scale, BASF abandoned the project. The current status of the process, including improvements, is inactive.

4.5.1.2 Scientific Basis

This process operates by thermal, catalytic decomposition of hydrogen chloride. The reaction mechanisms for the ICI process is:

$$4HCl(g) + O_2 \xrightarrow[\text{heat}]{V_2O_5} 2H_2O + 2Cl_2$$

The final chlorine product is obtained by drying the liberated water/chlorine mixture with sulfuric acid. The dilute sulfuric acid is reconcentrated and recycled.

In the BASF method, the catalyst material is specially prepared. Vanadium is added to a melt of potassium pyro-sulfate ($K_2S_2O_7$) and sodium bisulfate ($NaHSO_4 \cdot H_4O$) and heated to 375°C for one hour. The product catalyst and catalyst activators then are pulverized and an inert support (silica gel) added. The catalytic bed is formed from this heated (350°C) mixture. Once the bed is formed, the hydrogen chloride/oxygen mixture is in a ratio of 4 to 1 and at a temperature of 380°C. The hourly output of product gas contains the following percentages of materials.

Chlorine	22.2 percent
Hydrogen chloride	44.5 percent
Oxygen	22.2 percent
Water	11.1 percent

Yields can be increased by using temperatures greater than 380°C.

For the overall reaction of this process, the free energy change was equal to 12.67 Kcal/mole Cl_2 at 25°C. This makes the reaction endothermic.

4.5.1.3 Engineering

A flow diagram for the process is provided in Figure 11. The overall operation is similar to the Shell process (Section 4.4.1) except that a different catalyst and slightly different operating temperatures are used.

4.5.1.4 Conclusion

This process is infeasible for commercial chlorine preparation for several reasons:

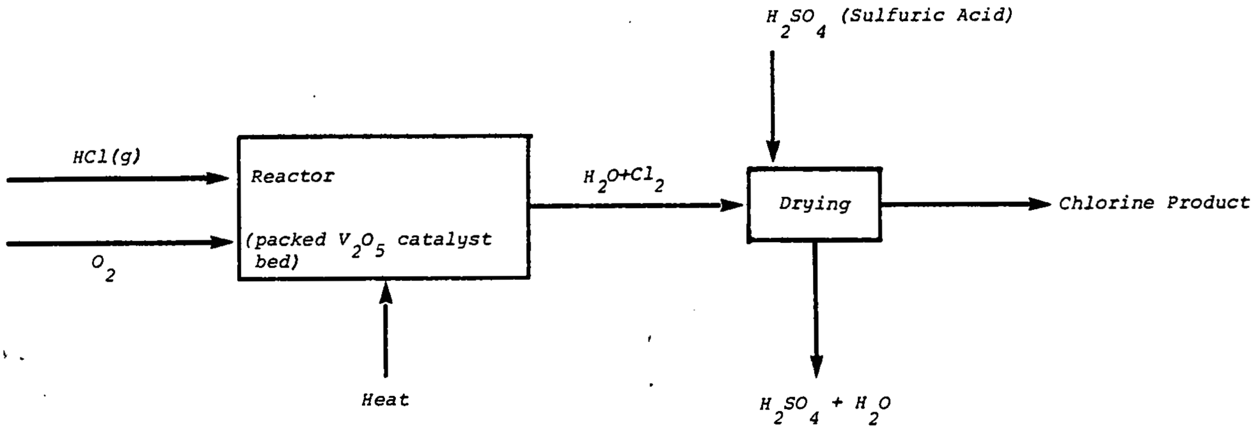
(1) Other catalytic processes (e.g., Kel-Chlor) already exist for more efficient conversion of hydrogen chloride to chlorine.

(2) Current cost of vanadia ($1.00 per lb) means even small catalyst losses would impose a severe operating cost penalty on the process.

(3) Yields obtained are relatively low, and the product exits the reaction as a dilute constituent of a gas stream. In general, this dilute gas stream will require pressurization to recover the chlorine by liquefaction followed by fractional distillation and drying.

A process yielding a more concentrated product gas stream would be preferred. The process thermodynamics are the same as that discussed for other gas phase hydrogen chloride oxidation processes.

Figure 11. Flow Diagram for Rare Earth Catalytic Process



4.5.2 Hydrogen Chloride Oxidation over Chloride/Cerium Oxide Catalysts

4.5.2.1 Process History

This process was investigated on a laboratory scale by personnel of the Farbwerke Hoechst Aktiengesellschaft and patented by that organization in several West European countries. The data presented here are abstracted from Belgian Patent No. 658,435 assigned to that organization.[64] The patent was granted in 1965, and no other work concerning this process has been reported.

4.5.2.2 Scientific Basis

This process involves the oxidation of gaseous hydrogen chloride with oxygen over catalysts of special composition. The catalysts are supported mixtures of cerium dioxide (CeO_2) with either iridium trichloride ($IrCl_3$) or iridium tetrachloride ($IrCl_4$). The ratio of cerium dioxide to iridium salts is specified as being between 10 and 1,000 to 1. The support material was not specified in the patent. The oxidation reaction is:

$$4HCl + O_2 \xrightarrow[\text{Catalyst}]{IrCl_3 - CeO_2} 2Cl_2 + 2H_2O$$

and is conducted in the low (30-250°C) temperature range. Yields vary with catalyst composition, temperature, and retention time. At temperatures below 50°C, yields of 21 to 38 percent were reported for a 20-minute retention time with low iridium content catalysts. For higher iridium content, yields of up to 83 percent were found with the same retention times and temperature.

At 70°C, the same low iridium content catalysts gave 71 to 96 percent yields with 200-minute retention times. Above 150°C yields greater than 80 percent were reported for low iridium content catalysts at 15-minute retention time. No data relating either to the catalytic reaction or to recovering chlorine from the product gas stream were reported. It can be assumed, however, that recovery processes would be similar to other hydrogen chloride catalytic oxidation processes.

4.5.2.3 Engineering

The data presented in the patent were obtained from a bench-scale evaluation of potential catalysts. A full process was never studied. However, the overall process should be similar to others which use catalytic oxidation of hydrogen chloride. A complete description of catalytic oxidation of hydrogen chloride processes is given for the Shell process (Section 4.4.1). What is of particular interest in this process is that the oxidation reaction in the presence of cerium dioxide and iridium trichloride apparently proceeds at a significant rate at temperatures below 250°C. Other gas phase catalytic processes all require temperatures well above 300°C to obtain yields greater than 70 percent.

4.5.2.4 Conclusion

Although only laboratory work has been done with this process, the data available indicate that the use of cerium-iridium catalysts might be developed into a viable process for hydrogen chloride oxidation. There already exist two other processes (an electrochemical process developed by Uhde, and the Kel-Chlor process) which are in commercial operation and accomplish the same end of converting waste hydrogen chloride gas to chlorine. The amount of by-product hydrogen chloride available for conversion to chlorine is 600,000 tons per year, and more than half of this material is currently converted using the other two processes. Insufficient raw material is available to develop another process in competition with the Uhde and Kel-Chlor processes. For this reason, this process will not be included in the detailed evaluation (Task 5) even though it does demonstrate that improvements in gas phase hydrogen chloride oxidation methods are indeed possible. However, the energy requirements for Kel-Chlor will be studied to determine if a 200 to 250°C process would make a significant difference in process economics and energy efficiency.

4.6 Kel-Chlor Process

4.6.1 Process History

The Kel-Chlor process was developed by the M. W. Kellogg Company (now Pullman-Kellogg). Its principal inventor, C. P. van Dijk, filed for a patent in 1975 and was granted the patent on May 31, 1977.[65] This patent was a continuation of a similar patent which was never issued. The Kel-Chlor process is referred to by its developers as an up-to-date Deacon process.

Pullman-Kellogg, in conjunction with DuPont Corporation, operates a 600 ton per day facility at Corpus Christi, Texas. Pullman-Kellogg has made improvements on this facility to increase production to 1,000-1,100 TPD using the existing train.

A process that operates by oxidation of hydrogen chloride using nitrosyl chloride (NOCl) catalyst did not have its start with Kellogg. As early as 1919, Datta described such a process.[66] Another process using nitrogen dioxide as a catalyst for the oxidation of hydrogen chloride was studied by Stow in 1962. A third process also designed to use nitrosyl chloride was patented by Jonas Hamlet of New York in 1964 while working for DuPont.[67] Development for all three processes was only on a bench scale and they were dropped due to poor results.

4.6.2 Scientific Basis

The Kel-Chlor method is based on the oxidation of hydrogen chloride. The Kel-Chlor process combines an active homogeneous catalyst with a strong dehydrating agent. An overall representation of the process is:

$$4HCl + O_2 \xrightarrow[NOCl]{N_2O_3} 2Cl_2 + 2H_2O$$

This overall reaction equation can be reduced into the four steps of the total reactive process, including recycle-acid stripping, oxidation, absorption-oxidation, and recycle-acid flashing. After conversion by the above process, chlorine gas can be dried and liquefied.

In the recycle-acid stripping step, gaseous hydrogen chloride contacts hot aqueous sulfuric acid. The countercurrent sulfuric acid stream has a concentration of 80 percent and contains the water of reaction and a catalyst which were taken up in the absorber. In this step the following reaction occurs:

$$HNSO_5 + HCl \rightarrow NOCl + H_2SO_4 \qquad (1)$$

This represents a stripping of the catalyst from the acid. The catalyst is primarily nitrosylsulfuric acid ($HNSO_5$). In the second section of the stripper, the unreacted hydrogen chloride is stripped out by introducing oxygen. The original acid mixture exits the stripper carrying only small amounts of $HNSO_5$ and reaction water. Equation (1) proceeds practically to completion because of the countercurrent flow.

The oxidation occurs in a series of reactions as follows:

$$2NOCl \rightarrow 2NO + Cl_2 \qquad (2)$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad (3)$$

$$NO_2 + 2HCl \rightarrow NO + Cl_2 + H_2O \qquad (4)$$

The hydrogen chloride gas mixture contains nitrosyl chloride, excess hydrogen chloride, oxygen and water. In the oxidizer, this mixture is heated to increase the rate of nitrosyl chloride decomposition, which is an exothermic reaction. The generated heat must be removed for the desired conversion to take place. This removed heat is then used to generate steam to run the sulfuric acid vacuum flash system and to provide all necessary process heat.

During the absorption-oxidation phase the three reactions (2,3,4) continue until complete hydrogen chloride conversion is achieved. Besides the oxidation reactions, the sulfuric acid absorbs all nitrogen oxides. This additional step is represented by:

$$NO + NO_2 + 2H_2SO_4 \rightarrow 2HNSO_5 + H_2O \qquad (5)$$

$$NOCl + H_2SO_4 \rightarrow HNSO_5 + HCl \qquad (6)$$

$$NO_2 + 2HCl \rightleftarrows NO + Cl_2 + H_2O \qquad (7)$$

The chlorine gas produced is virtually free of hydrogen chloride, oxygen, and nitrogen compounds. The product chlorine gas is cooled and dried with a small stream of cold sulfuric acid.

The final phase of the Kel-Chlor system is known as recycle-acid flashing. In this step the reaction water is removed from the sulfuric acid by means of an adiabatic flash. The flashing mechanism occurs in a reduced pressure environment. The flashed acid stream is recycled to the absorber-oxidizer.

The majority of the recycled acid is hot, but a small percentage is cooled and used to provide a cooling medium for the product gas at the top of the tower.

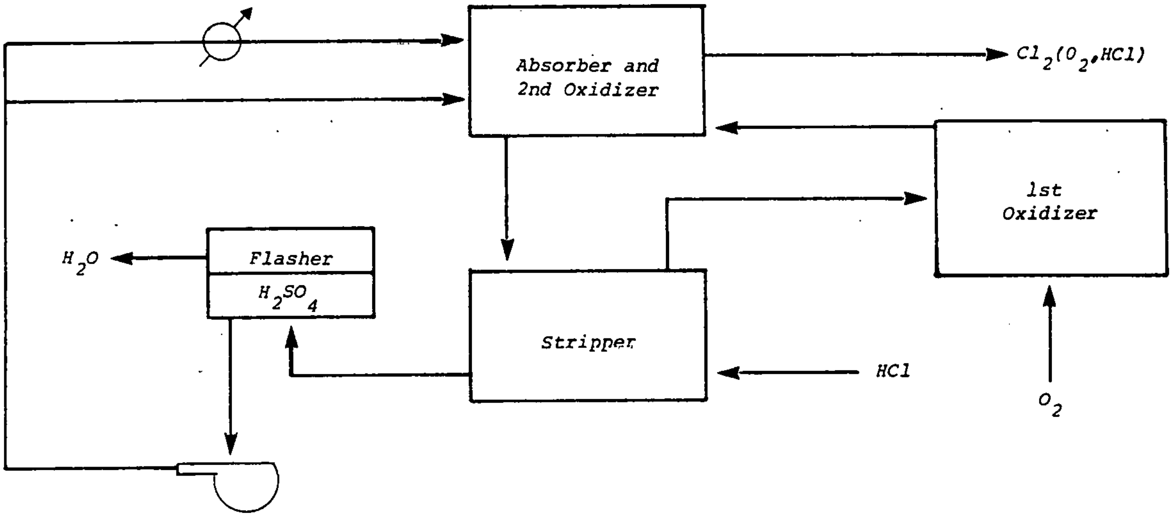
4.6.3 Engineering

A flow diagram of this four-stage process is shown in Figure 12. Hydrogen chloride enters the system under pressure at the bottom of the stripper. The hydrogen chloride reacts with hot nitrosylsulfuric acid coming from the absorption-oxidation vessel, then contacts with oxygen in the oxidizer. The effluent gas mixture from this phase contains chlorine, steam, oxygen, catalyst components and unconverted hydrogen chloride and is sent to the absorber-oxidizer where it contacts first hot, then cool, sulfuric acid. The catalyst components react with the sulfuric acid, water is absorbed, and hydrogen chloride conversion is completed. Stripped hot sulfuric acid is dried by sending it to the flasher. Cooled sulfuric acid is recycled to the absorption-oxidation stage.

Equipment design and construction are important considerations for this process because of the highly corrosive mixture of chemicals which flow through the system. The two factors that control the extent of this corrosive atmosphere are temperature and pressure. The range of these factors governs the types of materials used, with some ranges allowing glass or teflon-lined equipment to be used, while others rely on acid resistant brick or expensive alloys (tantalum), and metals.

The operation of this unit in terms of start-up time, shutdown time, and response to perturbations has been studied in depth by process developers using the following variable conditions:

Figure 12. Flow Diagram for the Kel-Chlor Process



Pressure	1-15 atm absolute
Acid Strength	70-85 wt%
Acid Circulation Temp.	127-182°C
Excess Oxygen	-15 to +40%
HCL to Oxidizer	0.2-1.0
HCl Conversion	80-100%

Upon completion of testing at these conditions only minor catalyst losses occurred, nitrogen impurities in the product were below detectable levels, and yields above 99 percent were consistently obtained.

It was found that the required quality product could be obtained in a few hours once acid circulation rate, temperature, and unit pressure were stabilized. Key control parameters include oxidizer conversion, catalyst inventory, and acid strength. Expensive combinations of alloys and metals are presently used to combat corrosion in an effort to reduce down time.

4.6.4 Economics

The basic economic principle behind the Kel-Chlor process is economy of scale. Capital requirements follow the six-tenths power rule. Table 7 gives an estimate of production cost for two levels of Kel-Chlor operation.

The incremental cost incurred by raising output by 400 tons per day is $12.14 per ton. The rates of return, as a function of chlorine market value, assuming negligible hydrogen chloride costs, are provided below:

Plant Capacity	Cl_2 price, $/ton		
	45	50	55
500 tons/day	39%	45%	50%
900 tons/day	52%	60%	67%

Present studies are concentrating on reducing temperature and pressure levels so that cheaper construction materials can be used.

Table 7

Cost of Chlorine Production Via the Kel-Chlor Process [69]

(Based on 90 percent steam factor)

				Plant Size	
				900 ton/day	500 ton/day
Fixed Capital Investment*				$20 million	$14.1 million
Materials	Units/ton Cl_2	Unit Cost	$/ton Cl_2		
Oxygen	0.2576 ton	$10/ton	2.576		
Lime	39 lb.	0.01/lb.	0.390		
98% H_2SO_4	11 lb.	0.01/lb.	0.110		
HCl	1.0547 ton	-	-		
		Total		3.076	3.076
Power	40 kwhr.	$ 0.007/kwhr.	0.280		
Steam	40 lb.	0.50/thousand lb.	0.020		
Cooling Water	9,100 gal.	0.02/thousand gal.	0.182		
Refrigeration	10 ton-hr.	0.05/ton-hr.	0.500		
		Total		0.982	0.982
Labor: 2 men/shift @ $4.00/man-hour				0.237	0.427
General Overhead @ 100% of Labor				0.237	0.427
Maintenance @ 5% of Investment/yr.				3.382	4.292
Taxes & Insurance @ 3% of Investment/yr.				2.030	2.576
Depreciation @ 10% of Investment/yr				6.764	8.584
Total Manufacturing Cost ($/ton)				16.708	20.364

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* This is based on U.S. Gulf Coast plant location and price. Excluded are utilities such as cooling tower, boiler and associated equipment, feed and product storage, acid storage and disposal.

4.6.5 Conclusion

Tables 7 and 4 show that the Kel-Chlor process is cost competitive with current chlorine manufacturing techniques and the power and steam requirements are less for Kel-Chlor. The process is also proven commercially. The major drawback is a limited supply of hydrogen chloride raw material. Because of its competitive position, however, Kel-Chlor will be studied further in Section 5.

4.7 Electrolysis of Hydrochloric Acid with Metal Chloride Catalysts

Three processes have been developed that electrolytically convert hydrochloric acid to chlorine using metal chloride catalysts. The three processes are the Schroeder process (using $NiCl_2$), the Westvaco process (using $CuCl_2$), and the South African process (using $MnCl_2$).[70-74] In each case complications prevented development of the process past the pilot plant stage. Since all three processes have similar scientific bases and engineering methods and problems, the Schroeder process is presented in detail as representative of the three.

4.7.1 History

The Schroeder process was developed by David W. Schroeder of Seattle University. His first patent was filed on August 11, 1958, but he abandoned his efforts before any patent was granted. The existing patent, which was filed on June 13, 1960, was granted on January 28, 1964, and is a continuation of the original process.[70] The process (as well as the Westvaco and South African processes) is presently inactive.

4.7.2 Scientific Basis

The Schroeder process is cyclic and involves two main steps. The first step is the decomposition by electrolysis of a metal chloride (preferably nickel chloride) into the metal component and chlorine. The second step combines the metal element with hydrochloric acid to reform the metal chloride for recylcing. The equations are:

$$NiCl_2 \xrightarrow{\text{electricity}} Ni + Cl_2 \quad (1)$$

$$Ni + 2HCl \longrightarrow NiCl_2 + H_2 \quad (2)$$

$$\text{(Overall)} \quad 2\ HCl \longrightarrow H_2 + Cl_2$$

The reactions are carried out by using two sets of cells. In the first cell, electrolytic deposition occurs, with nickel metal plating out at the cathode and chlorine gas evolving at the anode. In the second cell, the nickel is dissolved in hydrochloric acid with the resultant metal chloride fed back into cell number 1. The use of current in the second cell is optional. A reaction without the use of current proceeds slowly unless nickel chloride or other metal chloride salts are present in the hydrochloric acid solution. By increasing the chloride concentrations, the rate of reaction becomes commercially practical.

4.7.3 Engineering

The process flow chart is given in Figure 13.

The operation of this system continues until the nickel deposit on the cathode of the first cell gets too thick for efficient decomposition. This build-up rate is about 0.035 in./day. Once this point is reached, the roles of the cells are reversed. The standard cycle time for the operation is 48 hours. Utility and chemical requirements for chlorine production are presented below:

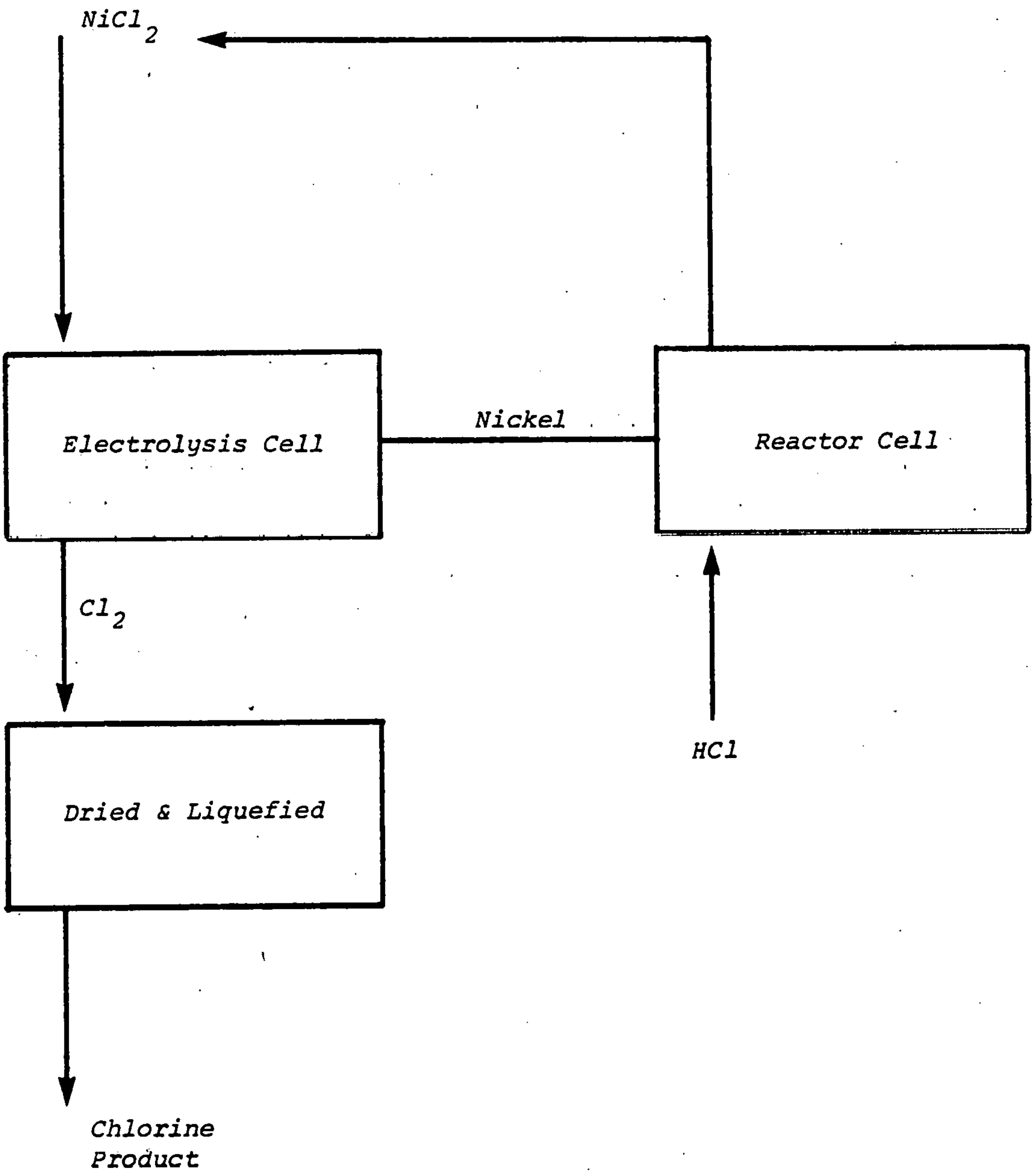
Table 8

Utility and Chemical Requirements

Utilities		Chemicals	
Electricity	1350 Kw-hr/ton Cl_2	HCl (100%)	2060 lb/ton Cl_2
Steam	None	H_2SO_4 (60° Be)	39 lb/ton Cl_2
Cooling Water	4900 gal/ton Cl_2	$CaCO_3$	39 lb/ton Cl_2

The decomposition step is best carried out by using carbon anodes and cathodes separated by 0.25 inches. Solution temperature should be about 105°F and the pH should range between 1.3 and 3.5. With these conditions the required voltage can be completed, since voltage is related to the current density (CD). For a 22 percent nickel chloride solution, the voltage (E) = 1.65 + 0.0038 CD. For a similar 41 percent nickel chloride solution, the required voltage E = 1.54 + 0.0048 CD. When using all the specified conditions, no diaphragm is required and no hydrogen will be produced.

Figure 13. Flow Diagram For The Schroeder Process



In the current patent, three methods are listed for reforming the metal chloride.[70] They include the electrolytic process with hydrochloric acid, the non-electrolytic process with hydrochloric acid, and the intermediate nickel hydroxide formation process. For the electrolytic process, a voltage above 0.1 volts is required. The exact amount of voltage depends on the electrolyte concentration, the temperatures, current density requirements, and cell arrangement. This voltage is passed through either the hydrochloric acid-electrolyte solution or a hydrochloric acid/nickel chloride-electrolyte solution. This resultant reaction dissolves the deposited nickel and forms hydrogen. At present this method is the least preferred because of the low current efficiencies and high voltage requirements.

The second method involves the following two equations,

$$Ni + 2H_2O \xrightarrow{elec.} Ni(OH)_2 + H_2 \quad (3)$$

$$Ni(OH)_2 + 2HCl \rightarrow NiCl_2 + 2H_2O \quad (4)$$

Reaction (3) takes place using a direct current in a sodium chloride electrolyte. The nickel hydroxide formed is easily dissolved in hydrochloric acid in reaction (4). This process has good commercial possibilities because of high regeneration yields and high current efficiencies.

The last reformation technique deals with a non-electrolytic method. In this process the nickel is dissolved by means of a hydrochloric acid solution to which is added nickel chloride to increase the corrosion rate sufficiently that the process becomes commercially applicable. The increase in the rate can readily be seen by examination of the following data with and without the nickel chloride addition.

Table 9

Corrosion Rate Data Showing Effect of $NiCl_2$ Addition

HCl (gm)	H_2O (gm)	$NiCl_2$ (gm)	Temp.F°	Corrosion Rate in/day
0.5	99.5	0.0	Boiling	0.00083
1.0	99.0	0.0	Boiling	0.00186
5.0	95.0	0.0	Boiling	0.0157
10.0	90.0	0.0	218	0.0163
10.0	90.0	67.0	220	0.034
1.0	99.0	83	238	0.0173

4.7.4 Conclusion

The indirect electrolysis methods could be implemented but are difficult to automate. Since these processes were patented, however, a more operable, direct electrolysis method has been developed and commercialized. For this reason, the Schroeder and related indirect electrolysis processes are excluded from further consideration.

4.8 Direct Hydrogen Chloride Electrolysis

4.8.1 Process History

The history of direct hydrogen chloride electrolysis is presented in Section 4.4.1. This particular electrolysis process was invented by Stefon Payer of Germany and developed by the Hoechst-Uhde Corporation.[75,76] The first hydrogen chloride electrolysis plant was built at Farbwerke Hoechst in Leverkusen, West Germany, in 1964 with an output of 43,000 tons per year of chlorine. Since 1970, seven other plants have been built in various countries with combined output of more than 400,000 tons per year. The major U.S. plant of this type is in Baytown, Texas, and is operated by Mobay Chemical Company, a subsidiary of Mobil Oil. The facility, built in 1972, was expanded in 1976. The driving force for using this technology was the desire to recover and reuse waste hydrogen chloride rather than sell dilute hydrochloric acid in an uncertain market.

4.8.2 Scientific Basis

This electrolytic-type process uses direct current to decompose hydrogen chloride. The chemical equation for this mechanism is as follows:

$$2\ HCl \xrightarrow{\text{electricity}} H_2 + Cl_2$$

The waste hydrogen chloride raw material has inert gas components which are removed by absorption in a dilute hydrochloric acid solution prior to electrolysis. The acid product is fed to the electrolytic cells for chlorine production. The unreacted dilute acid is recycled to the absorption system. Similar to the membrane cell, the inlet acid product concentration should be maintained at 20-26 percent for best electrical efficiency. The dilute acid recycle stream should be maintained above 16 percent to avoid oxygen evolution in the cell.

The above reaction can be divided into two separate electrode processes,

$$H^+ + e \rightarrow 1/2\ H_2 \quad \text{(cathode)}$$

$$Cl^- - e \rightarrow 1/2\ Cl_2 \quad \text{(anode)}$$

The electrolytic cell uses a polyvinyl chloride diaphragm to separate the electrodes and prevent gas bubble migration. As a result, the chlorine product stream contains only about 0.2 percent hydrogen by volume and the hydrogen stream contains 1.0 percent chlorine by volume.

The product gases are saturated with water vapor and hydrogen chloride. Each gas is cleaned separately to remove these impurities. The chlorine is cooled with water to condense the water vapor and dried with sulfuric acid before liquefaction and storage. The hydrogen gas is also cooled, but with dilute hydrogen chloride. The cooled hydrogen gas stream is then scrubbed of chlorine with caustic to form sodium hypochlorite as follows:

$$H_2 + Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O + H_2$$

Product recovery for direct electrolysis of hydrogen chloride is about 98-99 percent for both chlorine and hydrogen.

4.8.3 Engineering

Figure 14 is a flow diagram for the hydrogen chloride electrolytic process.[75] Depleted aqueous hydrogen chloride is withdrawn from the catholyte cycle and sent to the absorption unit where it is saturated with fresh gaseous hydrogen chloride produced in a separate chlorination plant.

A 30 percent acid mixture is sent to the electrolytic cell from the adsorption stage. This procedure ensures a continuous supply of fresh acid to replace the decomposed material.

The electrodes used are vertical graphite plates. To prevent product mixing (i.e., hydrogen and chlorine), these plates are separated by polyvinyl chloride fabric diaphragms which are permeable to liquids but impermeable to gases. The anode, cathode, and diaphragm form a cell and 30 to 36 cells together form the electrolyzer. The end plates of the electrolyzer act as the monopolar electrodes connected to the DC power supply. All other electrode plates are bipolar. The monopolar end-plates are steel lined with rubber.

A typical electrolyzer is shown in Figure 15.[75] Inlet channels for fresh hydrogen chloride and individual cell inlet openings are located along the bottom half of the frame. The top of the frame is for product discharge and depleted acid removal.

Figure 14. Cross Section of an Electrolyzer

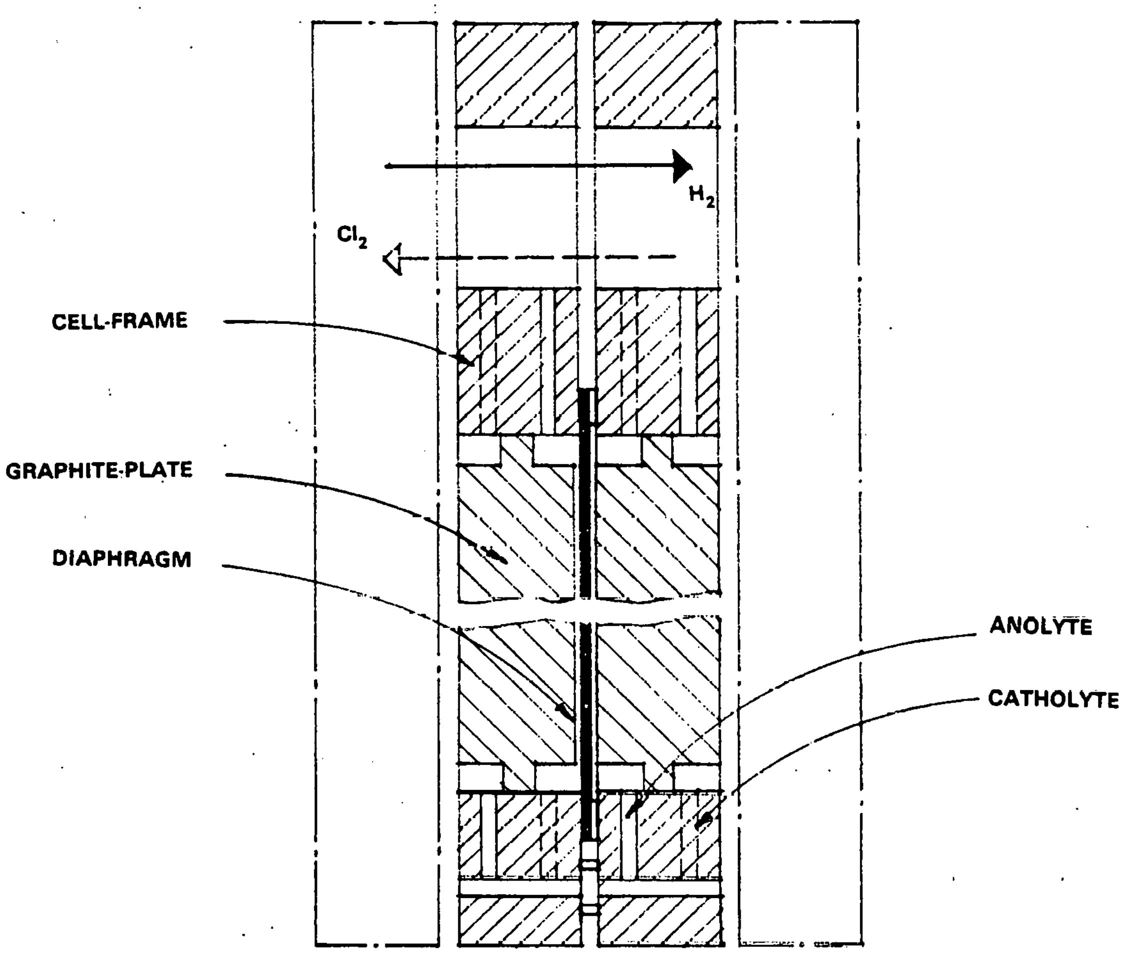
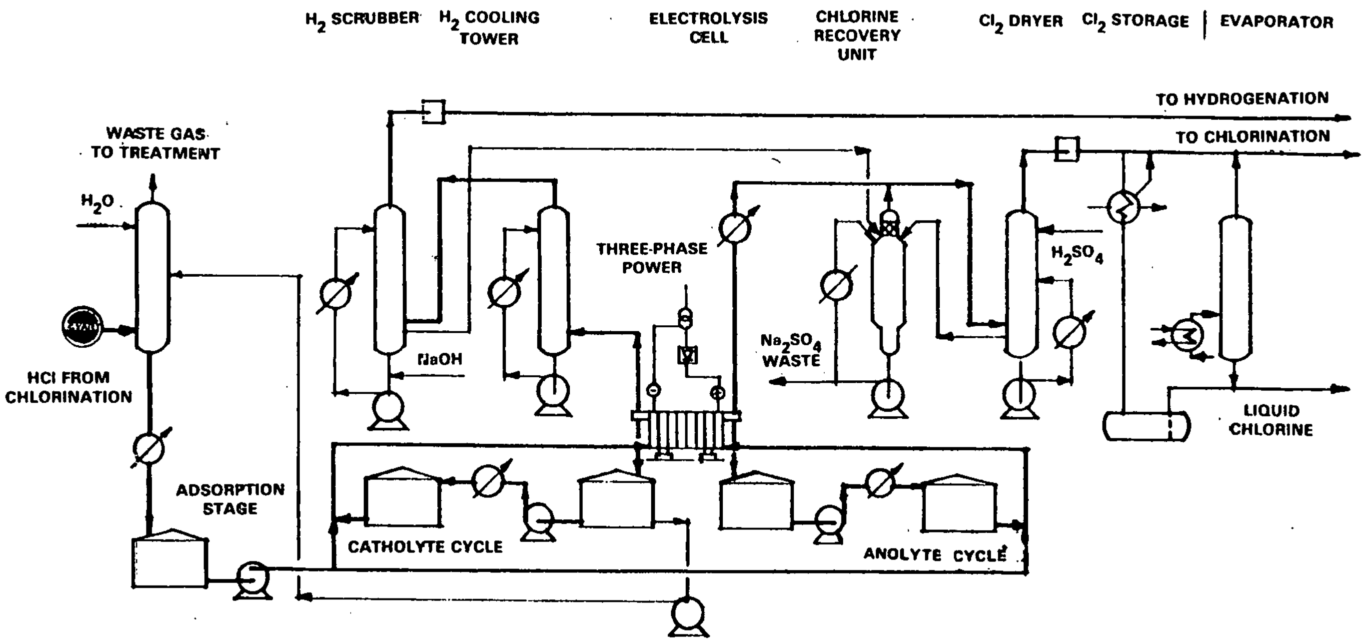


Figure 15. Flow Diagram of the Electrolytic Process for Recovery of Chlorine from Hydrogen Chloride Solution



Electrolysis produces chlorine and hydrogen gases at 75° to 80°C. Each is saturated with water vapor and hydrogen chloride gas at concentrations corresponding to their respective partial pressures. Both gases are cooled and scrubbed. The gaseous chlorine is then dried with sulfuric acid. As appropriate to requirements of the chlorination plant, the chlorine may be compressed and further purified.

The chlorine and hydrogen need no further treatment. Using new diaphragms, chlorine yields of 99.8 percent have been obtained. Due to deterioration of the diaphragms over time, average yields of 99.5 percent are expected with diaphragm replacement every 2-3 years.

Power consumption in any electrolytic process is of major importance. The maximum electrolyzer load is 12 KA. This is equivalent to a specific current density of 4.8 KA/m^2. With proper operating practices, the current efficiencies of cells today can reach 98 percent. In 1965, commercial electrolyzers of hydrogen chloride used cell voltages at 2.5 V at a cell load of 10 KA. This corresponded to a DC power consumption of 1,720 kwh per kkg of chlorine. Under the same cell load, present facilities operate at cell voltages of 2 V with power consumptions of 1,405 kwh per kkg of chlorine. These power reductions are a result of improvements in diaphragms, narrower electrode gaps, and the addition of noble metal salts to the catholyte. The salts were added to reduce hydrogen overvoltage.

Besides using the metal salts to increase efficiency, other material criteria must also be met. The hydrogen chloride used should be dry gaseous material to minimize addition of water to the process. Waste hydrochloric acid may be converted to the gaseous form and reintroduced into the electrolyzer by absorption distillation with sulfuric acid.

Other impurities, particularly organics, will severely affect the process. These impurities can cause deposits to form on the electrodes and diaphragms, reducing product quality. Chlorine derivatives of cyclic compounds (benzene or phenols) containing hydrogen chloride have two effects on the electrolysis cycle.

1. Diaphragm clogging and
2. Electrode deterioration due to crystal growth.

Both these effects increase cell voltage. This situation can be ameliorated through adiabatic absorption of the hydrogen chloride followed by adsorption of the chlorine derivatives by activated charcoal. Inorganic impurities, specifically multivalent ions, can reduce current efficiency. Also, metal ions that have a deposition potential more positive than that of hydrogen will plate on the electrodes and thus increase the hydrogen overvoltage.

4.8.4 Economics

Operational costs (1974) are given below for a hydrogen chloride electrolysis plant.[75]

Raw Materials	\$/ton of Cl_2
HCl	0 (waste product)
NaOH	.85
Auxiliary materials (diaphragms, etc.)	.26
Power and Utilities	
Electricity	12.24
Cooling Water	.41
Capital Expenditure	10.81
Maintenance	1.63
Personnel	1.53
Subtotal	27.72
Credits	
Hydrogenation hydrogen	7.41
Total Production Costs	20.30

The production costs of \$20.30 per ton of chlorine is contrasted with the \$26-27 per ton figure for chlorine by the Kel-Chlor process. Even if the hydrogen could only be used as fuel, the costs are comparable. Kel-Chlor is cost-effective for large facilities because of increased economies of scale.

4.8.5 Conclusion

Direct electrolysis of hydrogen chloride has proven to be a commercially successful process for chlorine production. If no costs are charged for using waste hydrogen chloride, the process becomes extremely attractive compared to other current production methods. The Bayer-Hoechst-Uhde process also uses about 40 percent less electricity per ton of chlorine than other commercial electrolytic processes. As a result, this process will be studied in more detail in Section 5.0.

4.9 Chlorine from Oxidation of Ferric Chloride Salt Complex

4.9.1 DuPont Process

4.9.1.1 Process History

Of the chlorine production processes that use ferric chloride ($FeCl_3$) for the raw material, the DuPont Process is considered the most efficient and economic.

The principal inventors of this method were Wendell Dunn, Jr. and John Maurer, both assignors to DuPont Co. of Delaware. The patent for their process was filed on August 3, 1965 and was granted on April 2, 1968.

Prior to this invention the primary process considered for iron chloride oxidation was:

$$3O_2 + 6FeCl_3 \longrightarrow 6Cl_2 + 2Fe_2O_3$$

This process, however, did not perform satisfactorily in pilot plant operation.[78] Alternatives using high temperatures for adequate reaction rates, low temperatures with a salt melt, and high pressures to cause ferric chloride liquefaction all proved inadequate. Each alternative required the operation of complicated equipment and careful control over operating conditions during the process. The DuPont patent sought to remedy these problems. One of the main objectives of this patent was to provide improved operation during the rate-limiting step of the ferric chloride oxidation. This invention described continuous operation of a commercial plant under a wide latitude of controlled uniform conditions, which would ensure high recovery/increased yields of chlorine and a high degree of purity. However, DuPont was not able to meet these goals. Development of this process went no farther than pilot plant stage. Current status of the operation is inactive.

4.9.1.2 Scientific Basis

The basic step in this method is to flow a molten salt complex of the formula, $XFeCl_4$, where X is an alkali metal, as a thin film over a moving bed of inert particulate material. This molten salt flows concurrently with an oxygen-containing gas.

The salt complex and the oxygen react under the process conditions as follows:

$$3O_2 + 4NaFeCl_4 \rightarrow 2Fe_2O_3 + 4NaCl + 6Cl_2$$

Product gas evolves while the ferric oxide and sodium chloride-coated particulate beds are withdrawn, treated, and recycled.

The major reactant to the process, $NaFeCl_4$, is normally in a liquid state as it enters the reactor. However, a system exists for sodium chloride feed as a solid and ferric chloride as a solid, liquid, or gas. The introduction of chemicals is usually accomplished through the flow stream of the oxygen-containing gas.

Although sodium is the preferred alkali metal to complex with ferric chloride, other alkali metals (potassium, lithium, etc.) may be used as substitutes. These alternates would react in a general equation as follows:

$$3O_2 + 4XFeCl_4 \rightarrow 2Fe_2O_3 + 4XCl + 6Cl_2$$

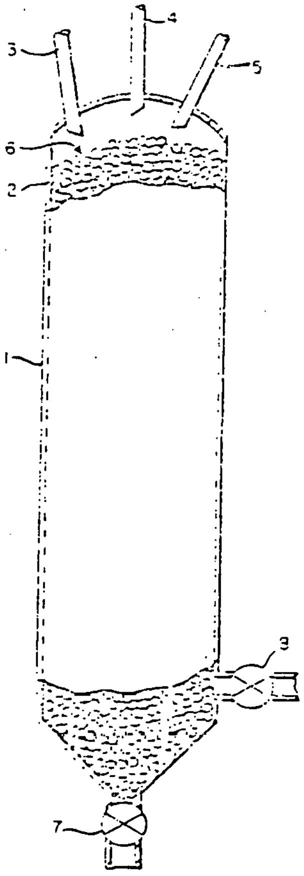
Where X is the substitute alkali metal. The particular state and concentration of the ferric chloride used is not a critical factor in the preparation of the salt complex. The ferric chloride can be in either a liquid (preferred) or solid state. If solid material is used, the reactor must provide sufficient heat to vaporize the ferric chloride. A liquid final complex reactant is preferred because of its relatively low vapor pressure.

4.9.1.3 Engineering

The reactor is shown on Figure 16. The process is carried out at a temperature range of 500-650°C. The main reaction should occur in controlled anhydrous conditions. Within the reactor, pressure levels should be slightly above atmospheric to prevent gas leakage into the bed. Exit pressures may range anywhere from 0.5 to 7 atmospheres. The reactor moving bed rate is dependent on the recycle ratio. Rates from 1.0 to 100 feet per hour are used. This moving bed can operate either concurrently or countercurrently to the reactant flow. However, the oxidizing gas flow must remain concurrent with the reactants. In this particular patent, the optimum gas

April 2, 1968 W. E. DUNN, JR., ET AL 3,376,112

PRODUCTION OF CHLORINE THROUGH OXIDATION OF FILM
OF FERRIC CHLORIDE SALT COMPLEX
Filed Aug. 2, 1965



The numbers represent the following:

(1) Closed reaction vessel made of or lined with a corrosion-resistant metal, alloy, or refractory material. Vessel should be inert toward both reactants and reaction products at the temperature of reaction.

(2) Moving bed made up of inert material (iron oxide, galss beads, flint pebbles, silica chips, etc.), which should average about 1/8" in diameter. The acceptable range would be 1/16" to 1/2". Particle size should be selected to provide maximum surface area and minimum pressure drop. Too small a particle must be avoided though as both excessive pressure drops and reactor agglomeration may occur.

(3,4,5) Feed inlets for the bed material, oxidizing gas, and reactant components.

(6) Oxidation deposits of ferric oxide and sodium chloride on bed material.

(7) Removal duct for used bed particles.

(8) Removal value for product chlorine gases.

INVENTOR
WENDELL E. DUNN, JR.
JOHN F. MAURER

BY

ATTORNEY

Figure 16. Reactor used for Oxidation of Ferric Chloride Salt Complex Film

flow rates defined as the number of pounds of gas fed to the reactor per hour per square foot of reactor cross-sectional area, are from 75 to 325 $lb/hr/ft^2$.

The yields from the experimental runs of this patent were excellent with about 92.5 percent chlorine recovery. Reaction rates ranged from 0.94 lb/min to 3 lb/min, depending on the relative proportions of the reactant materials involved.

4.9.1.4 Conclusion

Factors to be considered when deciding on the feasibility of the procedure for commercial chlorine production include the availability of ferric chloride and the high energy cost to sustain the necessary process temperatures. As mentioned previously, ferric chloride is only produced at a small number of plants in the United States. Total ferric chloride production in 1976, if applied to chlorine formation, would amount to about two percent of U.S. chlorine production. Also, high fuel costs pose economic disadvantages for this method of chlorine preparation. On a small scale basis, this process could be feasible for the recovery of chlorine from certain waste ferric chloride. Such an operation would be performed on a localized scale with the probable user of the produced chlorine or source of ferric chloride nearby. Because of its raw material limitations, however, this process will not be considered further.

4.9.2 Cyanamid Chlorine Process ($FeCl_3$ 2-step oxidation)

4.9.2.1 History

This chlorine preparation process was developed by American Cyanamid Company engineers, John Wikswo and Earl Nelson. They applied for a patent on February 26, 1964, and were granted one on June 13, 1967. This particular patent is a continuation of their earlier patent work. Cyanamid has since dropped work on all the patents.

4.9.2.2 Scientific Basis

This patent invention involves the production of iron oxide and chlorine by combusting ferric chloride with oxygen. It describes a method to increase the efficiency of the ferric chloride oxidation process in using two combustion zones to generate chlorine. The overall chemical reaction in the two zones is:

$$4FeCl_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6Cl_2$$

At 25°C, this reaction is endothermic with a change in free energy of 5.3 Kcal/mole Cl_2. The yield of chlorine is about one ton of chlorine for every three tons of ferric chloride, or a 50 percent yield from theoretical.

4.9.2.3 Engineering

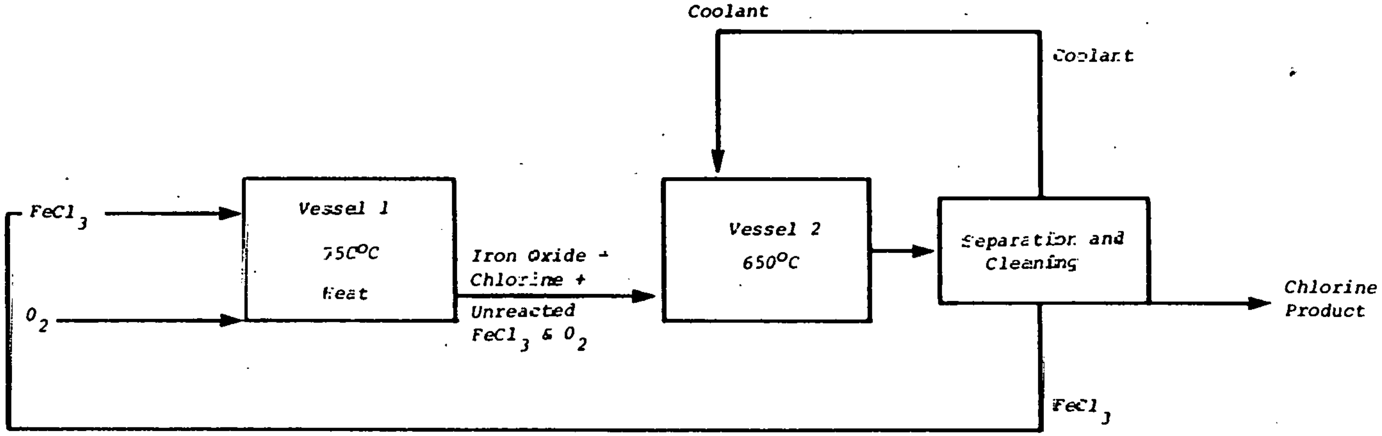
Figure 17 is a flow chart for this two-step process.

In the first reaction vessel, the oxygen and ferric chloride react at a temperature between 650° and 1,000°C. The product in this first vessel is an equilibrium mixture consisting of iron oxide, chlorine, unreacted ferric chloride and oxygen. The time spent in the first vessel must be sufficient to attain equilibrium. The preferred operating temperature in the first vessel is 700° to 900°C. In the second operating vessel, the temperature is reduced. The reduction must be at least 25°C, but preferably between 50° and 100°C. The temperature drop must be controlled, however, so that conditions in the second vessel do not go below 450°C. This is done so that at least 75 percent equilibrium is attained. Once the mixture is transferred to the second vessel, it undergoes another equilibrium change at the reduced temperature. The new equilibrium is richer in both iron oxides and chlorine. Less unreacted ferric chloride and oxygen appear in the product of this second combustion zone.

4.9.2.4 Conclusion

This process was never commercialized due to its high energy requirements and operational problems and will not be further considered.

Figure 17. Flowchart for Cyanamid Iron Chloride Process



4.10 Oxidation of Ammonium Chloride with Nitrogen Dioxide

Because of the complexity of nitrogen oxide chemistry and its temperature dependence, two processes, both developed by Imperial Chemical Industries, Ltd. (ICI), to convert ammonium chloride to chlorine are presented in this section.

The first process operates at ambient temperature and generates ammonium nitrate and chlorine as co-products. From the overall process chemistry, it consumes oxygen and nitrogen dioxide in addition to ammonium chloride.

The second process operates at higher temperatures and uses more nitrogen dioxide in the initial oxidation. Nitric acid and chlorine are the final products.

4.10.1 ICI Ammonium Nitrate Process

4.10.1.1 History

This process was patented in the United Kingdom by Gordon Diprose in 1960 and assigned to Imperial Chemical Industries, Ltd.[80,81] All work quoted in the patent was performed on the laboratory scale, and no development work or other commercialization has since been reported.

The process is similar to the Vicksburg and the U.S. Department of Agriculture processes (Sections 4.15 and 4.16) which produce chlorine by reaction of nitric acid and/or nitrogen dioxide with potassium chloride. For the ICI process, ammonium chloride is used as the raw material in place of potassium chloride.

4.10.1.2 Scientific Basis

Solid ammonium chloride containing 1 to 5 percent water is reacted with nitrogen dioxide on a slowly moving bed under ambient conditions. With agitation, a 97.7 percent conversion of the ammonium chloride is claimed via the reaction:

$$NH_4Cl + 2NO_2 \rightarrow NH_4NO_3 + NOCl$$

The nitrosyl chloride (NOCl) is then oxidized to nitrogen dioxide and chlorine by already established means. Although the separation of nitrogen dioxide from chlorine is not discussed in detail in the patent, it is known from other processes (i.e., the Vicksburg process) that these materials may be successfully separated by a fractional distillation operation. The separated nitrogen dioxide may then be returned to the initial process step.

Process kinetics have not been developed; however, thermodynamic calculations show that, at room temperature, the process is strongly exothermic, liberating 47.5 Kcal/mole of nitrosyl chloride generated in the initial process step. The secondary reaction step (i.e., $2NOCl + O_2 \rightarrow 2NO_2 + Cl_2$) is also exothermic, liberating 7.0 Kcal/mole. Process energy needs would be minimal, if use can be made of the considerable volumes of heat released by the initial reaction.

4.10.1.3 Engineering

The process of producing chlorine from ammonium chloride and nitrogen dioxide consists of the following operations and is shown in Figure 18.

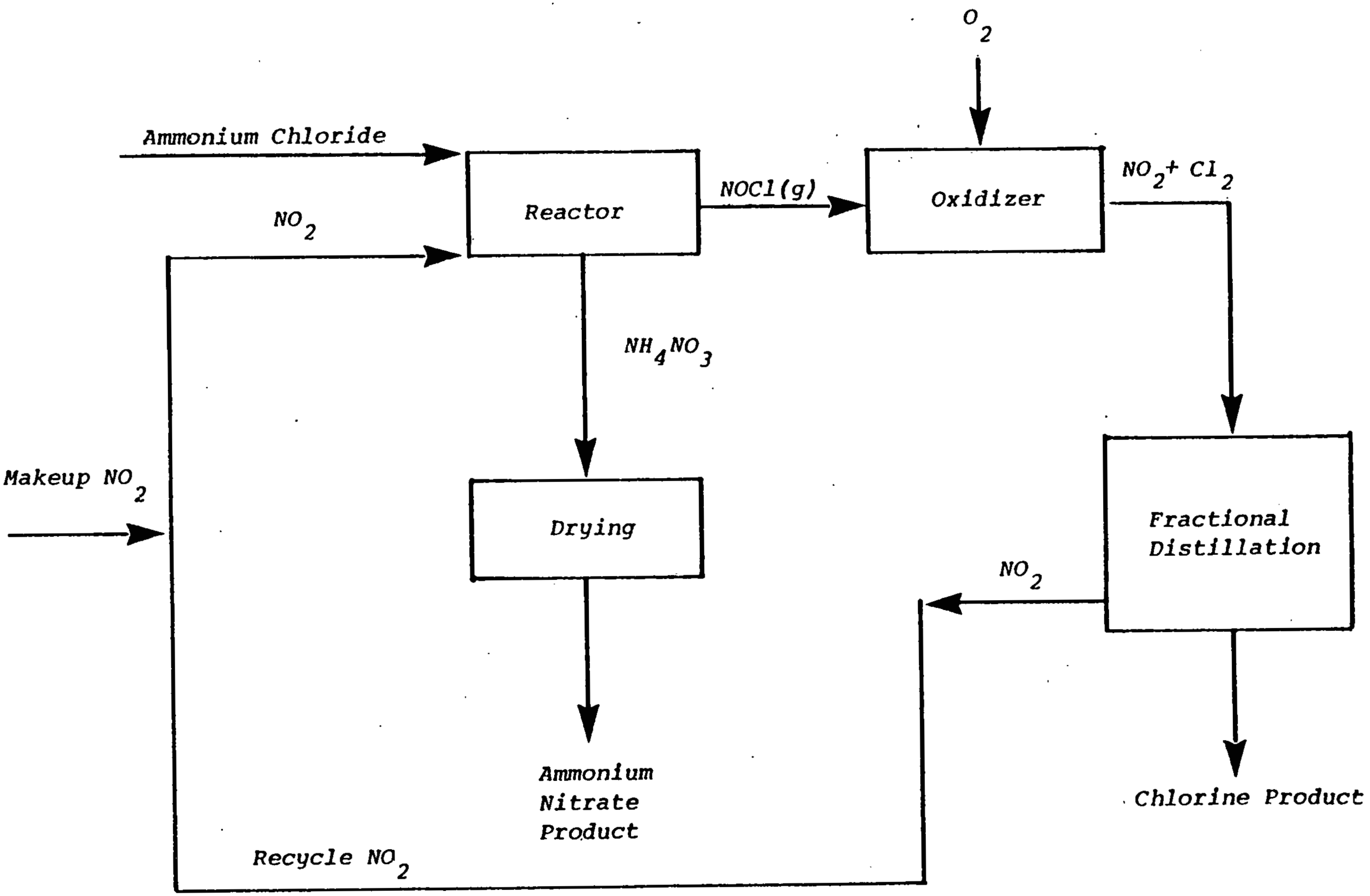
1. Reaction at room temperature of nitrogen dioxide with moist ammonium chloride in an agitated system to produce ammonium nitrate and nitrosyl chloride (NOCl).
2. Recovery of the ammonium nitrate co-product (NH_4NO_3) from the reactor and drying it to remove moisture.
3. Oxidation of the nitrosyl chloride product with oxygen at temperatures below 200°C to yield nitrogen dioxide and chlorine.
4. Separation of nitrogen dioxide and chlorine in liquid phase by fractional distillation at -20°C.
5. Compression of the chlorine product and recycle of the nitrogen dioxide to the initial process step.

For this process, corrosion resistant materials such as titanium or stainless steel will be required for all system units in contact with either chlorine or nitrogen dioxide.

4.10.1.4 Economic Considerations

This process consumes ammonium chloride, nitrogen dioxide and oxygen and produces ammonium nitrate and chlorine. According to 1977 figures,

Figure 18. Ammonium Nitrate Process Flowsheet



U.S. consumption of ammonium nitrate is 8.3 x 10^6 tons per year; this co-product should be marketable in significant quantities.

4.10.1.5 Conclusion

This process, although only developed to the laboratory stage, may be of some promise because of its extremely low energy requirements. It will be further considered in Section 6.

4.10.2 Nitrogen Dioxide/Ammonium Chloride High Temperature Process

4.10.2.1 Process History

This process was developed as a parallel process to the Vicksburg (Section 4.14) and Allied (Section 4.16) processes using ammonium chloride instead of potassium chloride as a raw material. Work in this area was performed by ICI on a laboratory scale in the late 1950's and culminated in the issuance of a number of British, Belgian, and German patents to ICI in the early 1960's.[81,82] No further work was performed on this process after the issuance of the patents.

4.10.2.2 Scientific Basis

Laboratory scale efforts demonstrate that ammonium chloride would react with gaseous nitrogen dioxide to yield nitrosyl chloride and nitrogen oxide (and water), and that the nitrogen dioxide-chlorine mixtures produced by oxidation of these products could be separated by fractionation. No other laboratory efforts were performed to establish a complete process.

The gaseous nitrogen dioxide reacts in a mobile bed of solid ammonium chloride to yield nitrosyl chloride, according to the reaction:

$$3NO_2 + NH_4Cl \rightarrow NOCl + 2H_2O + 3NO$$

The resulting gaseous products are further oxidized after removal of water, as follows:

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NOCl + O_2 \rightarrow 2NO_2 + Cl_2$$

The chlorine and nitrogen dioxide are then separated and the nitrogen dioxide is recycled to the process. Kinetics of the initial reaction have not been reported. Thermodynamic calculations show the reaction is exothermic at room temperature by 20.2 Kcal/mole.

4.10.2.3 Engineering

The Nitrogen Dioxide/Ammonium Chloride High Temperature Process flowsheet is shown on Figure 19. The process is carried out in three steps as follows:

(a) Solid moist ammonium chloride is introduced into a mobile bed reactor where it is contacted with gaseous nitrogen dioxide at about 100°C. The chemical reactions produce nitrogen oxide, nitrosyl chlorine, and water vapor, which exit the reactor.

(b) The gaseous mixture is then stripped with either concentrated sulfuric acid or other solvent to remove water vapor, and the dried gas stream is fed to an oxidizing chamber. The spent solvent, which contains the removed water, is reconcentrated by heating and is recycled.

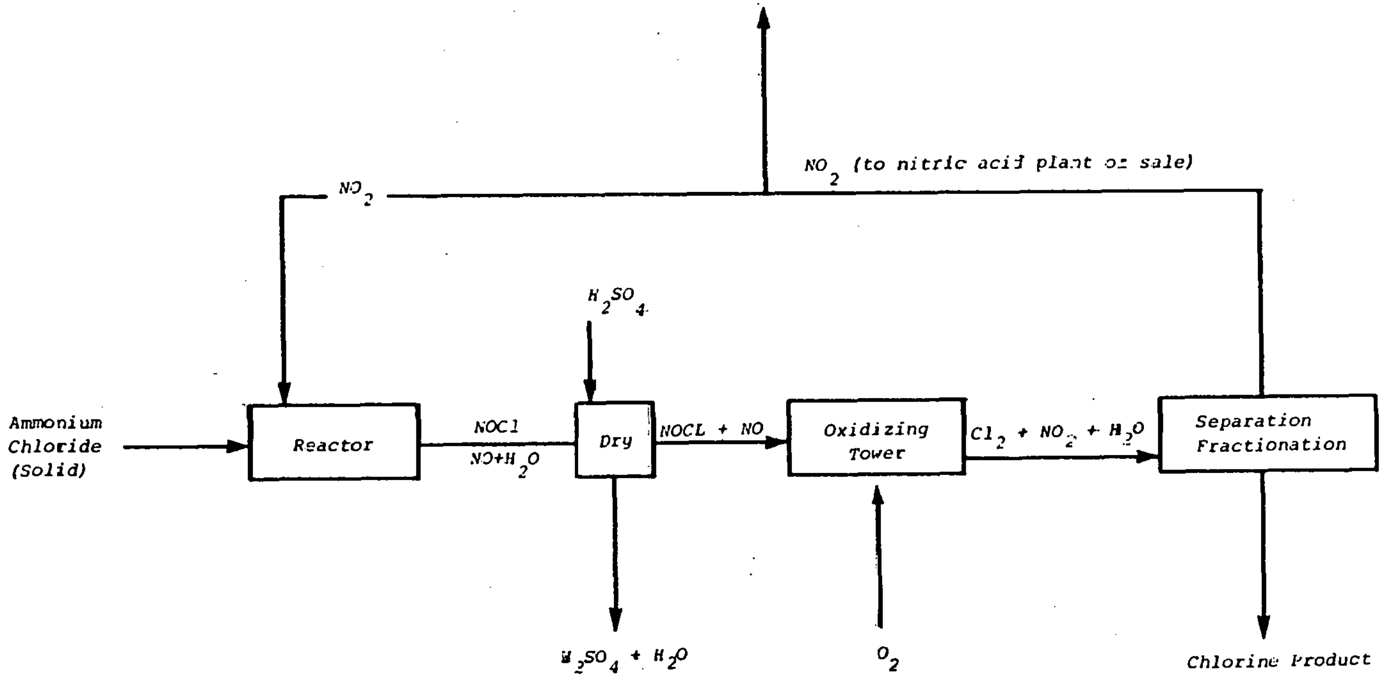
(c) The dry gaseous products ($NO + NOCl$) are reacted with oxygen at about 200°C to convert these materials into a mixture of nitrogen dioxide and chlorine. This mixture is fractionated, most of the nitrogen dioxide is recycled, and the chlorine is compressed and sold. The additional nitrogen dioxide created by the process could be converted on-site to nitric acid for sale. For this process, special corrosion resistant equipment will be required.

Work on this process was continued only on a laboratory scale, and only certain process steps were studied.[82] No pilot plant efforts were ever conducted. One unresolved question concerns the potential losses of nitrogen oxide or nitrosyl chloride to the sulfuric acid or other solvent used to remove water from the reaction product mixtures. Another question concerns loss of nitrogen dioxide values of conversion to nitrogen or nitrous oxide during ammonium chlorine oxidation because of unwanted side reactions; the degree to which such reactions may occur is not known.

4.10.2.4 Conclusion

This process depends on the use of ammonium chloride as a raw material. However, only 30,000 tons per year of ammonium chloride are generated

Figure 19. Process Flowsheet for the Nitrogen Dioxide/Ammonium Chloride Process



directly in the United States. As a result, this process cannot have widespread application and is limited to sites close to ammonium chloride production facilities.

This process would be ideal, however, for incorporation into a Solvay-process soda ash plant. The Solvay plant produces ammonium chloride during the initial reaction step, which generates sodium bicarbonate and ammonium chloride. Instead of recovering ammonia, as in the normal Solvay process, the ammonium chloride could be converted to chlorine and nitrogen dioxide. The nitrogen dioxide would then be further processed to nitric acid. While this process increases ammonia usage, sales of additional chlorine and nitric acid products would more than offset the lost ammonia sales revenue. However, a number of questions involving nitrogen oxide losses and ammonium chloride purity requirements need to be resolved before this process can be fully assessed. The process is also less energy efficient than the low temperature process described in the previous section.

The Solvay soda ash process is in declining use in the United States. Currently, only one plant remains which uses this technology, thus limiting supplies of cheap ammonium chloride as a raw material for this process. However, the capacity of this facility could provide 0.7 x 10^6 tons per year of ammonium chloride raw material which would generate about 400,000 tons per year of chlorine using this process. Therefore, about five percent of the nation's chlorine supply could be theoretically generated via this route with no reopening of closed Solvay plants or construction of new plants. Based on the above discussion, this process will not be studied further.

4.10.3 Comparison of the Two Nitrogen Dioxide-Based Processes and Conclusions

4.10.3.1 Energy Use

Intuitively, the process generating ammonium nitrate (4.10.1) will have lower energy requirements because (a) the initial reaction involves no heat input and, in fact, is a considerable generator of heat; (b) there is no need for removal of water from the product gas mixtures, and therefore, reconcentrating spent, dilute sulfuric acid is not necessary.

4.10.3.2 Raw Material Requirements

For raw material needs, the ammonium nitrate producing process is a net consumer of both oxygen and nitrogen dioxide. The higher temperature process, without side reactions, requires only oxygen. However, at higher temperatures, ammonium nitrate is known to decompose to nitrous oxide and water. Therefore, formation of nitrous oxide via side reactions is possible, which could produce corrosion problems.

Input ammonium chloride quality is less important for the ammonium nitrate process. Most ammonium chloride used will be generated via the Solvay process and will contain small amounts of sodium bicarbonate and sodium chloride. In the ammonium nitrate process, these are converted to sodium nitrate, which do not pose a problem for prospective fertilizer producers who would use the ammonium nitrate co-product. For the higher temperature process, the presence of sodium salts results in a buildup of sodium nitrate solids in the initial reactor where only gaseous products are desired. This could lead to operational problems. Capital costs are expected to be lower for the ammonium nitrate process since a nitric acid plant is not needed.

4.10.3.3 Conclusions

Because of the lower energy needs, less stringent raw material purity requirements, lower probability of side reactions with attendant corrosion problems, and lower capital costs, only the ammonium nitrate producing process will be studied in Section 6.0. Much of that analysis, however, will be applicable to the high temperature process as well. Also, the reaction kinetics and side products associated with the reaction of nitrogen dioxide with ammonium salts are common to both processes.

4.11 Metaizeau Process

4.11.1 History

This process was developed by Paul Metaizeau of Belgium in the mid-1960's as a method for recovering chlorine from waste ammonium chloride produced by the Solvay process. Patents were issued for the process and after a few modifications, all were assigned to Solvay et Cie. of Belgium.[83-86] Following the issuance of the patents, no further work was reported on the process by the Solvay Company although efforts in this area have since been reported by others.[87,88]

4.11.2 Process Chemistry

The reaction for this process may be written as:

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \qquad (1)$$

$$2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl \qquad (2)$$

$$4FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 4Cl_2 \qquad (3)$$

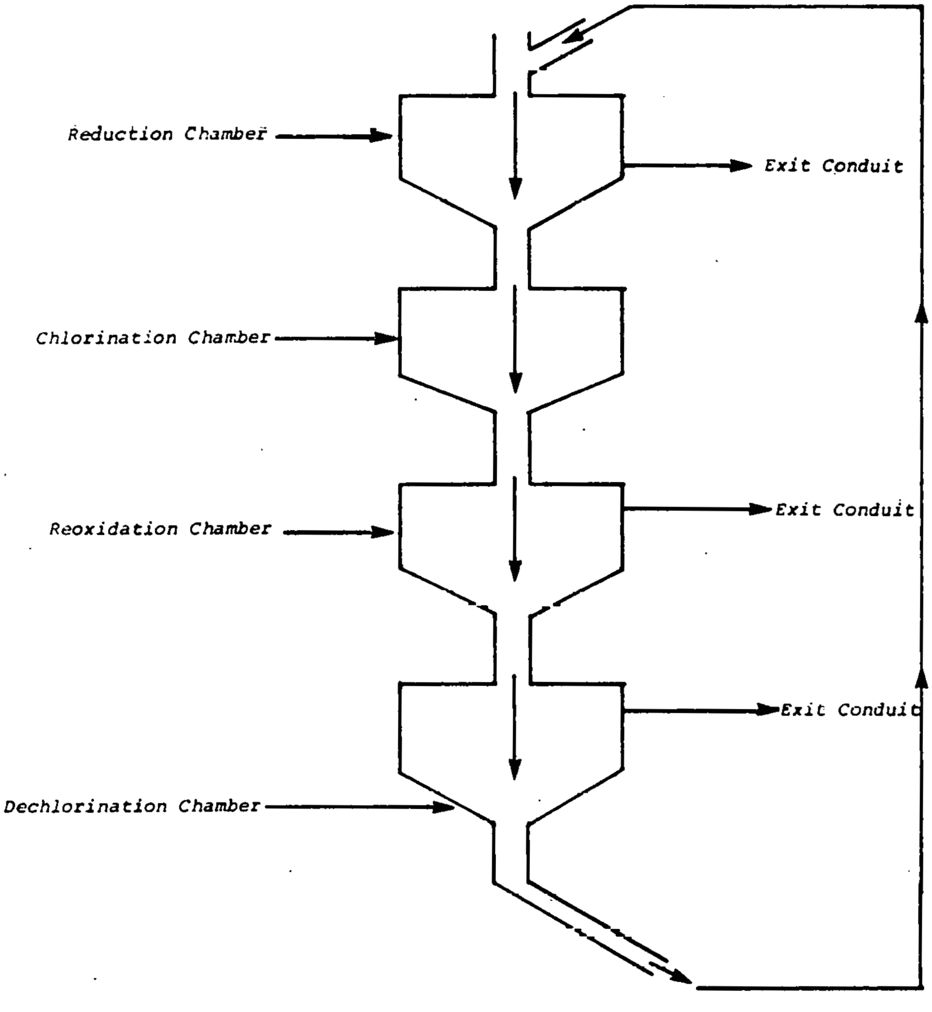
$$2HCl + O_2 \rightarrow H_2O + Cl_2 \qquad (4)$$

In this process, ammonium chloride is first sublimed and dissociated to yield a gaseous mixture of ammonia and hydrogen chloride. This mixture is then passed over a bed of supported iron oxide catalyst. The hydrogen chloride reacts with the iron oxide to yield iron chlorides and the separated ammonia can then be recovered for reuse in the Solvay process. After recovery of the ammonia, the iron chlorides formed are reduced with hydrogen to the ferrous state and the hydrogen chloride and ferrous chloride are reacted with oxygen to yield ferric oxide, chlorine and water. The ferric oxide is recycled to the initial process step and the water-chlorine mixture is dried with sulfuric acid to prepare the chlorine product.

4.11.3 Engineering Considerations

The original process is as described above. However, there were several drawbacks which led to a process modification as shown in Figure 20. In the improved version, the reactant mixture circulates through four vessels by means of a moving bed. The first reaction step in the modified process involves reduction of the supported catalyst to ferrous oxide (FeO) by means of hydrogen. This initial reduction is accomplished with

Figure 20. Flow Chart for Improved Metaizeau Process



the gases and solids moving countercurrently in the first vessel. In the second vessel, into which the reduced catalyst then flows, ammonium chloride vapors are introduced and these react with the reduced catalyst to yield ferrous chloride and free ammonia. The ammonia is received from the second chamber and the solids are then fed to the third and fourth chambers, where the ferrous chloride is oxidized in two steps to chlorine and ferric oxide. The ferric oxide is then recirculated to the initial process step.

Other patents granted for this process involved regeneration of the ferric oxide catalyst, process equipment design modifications and the choice of catalyst support materials.[87,88]

Operating temperatures for the process steps are:

(1) 400° - 500°C for the initial ferric oxide reduction step.
(2) 350° - 480°C for the ammonium chloride reaction step.
(3) 550°C for the conversion of ferrous chloride to chlorine and ferric oxide.

All reactions are conducted at near atmospheric pressure.

4.11.4 Process Economics

The overall economics of this scheme are unfavorable because:

(1) The process, with its high operating temperatures, requires a considerable energy input. Hydrogen is also required.

(2) The conversion efficiencies for ferrous chloride to ferric oxide are only about 95 percent and there may be a build-up of unconverted ferrous chloride in the catalytic bed with time.

(3) The process may suffer from operational problems because it is operated at temperatures above the melting point of ferrous chloride (306°C). At higher temperatures small amounts of liquid ferrous chloride and ferric chloride may become entrained with process gas streams.

For the above reasons, the process was apparently abandoned.

4.11.5 Overall Outlook

Due to the high energy requirements and operational problems, this process can be dropped from further consideration.

4.12 Chlorine from Salt and Sulfur Trioxide

4.12.1 History

This chlorine generation process developed from the commercial production of chlorosulfuric acid ($HOSO_2Cl$), chlorosulfonate salts (e.g., $NaSO_3Cl$), thionyl chloride ($SOCl_2$) and sulfuryl chloride (SO_2Cl_2).

Research efforts can be traced back to 1940, when a patent was issued to Tauch and Iler for a new method of producing sodium chlorosulfonate.[89] Other patents issued to Iler of DuPont dealt with further developments in productionof other chlorosulfonate compounds.[90] Other patents in this area were issued for other organizations, including American Cyanamid Corporation.[91,92]

In 1942 a patent was issued to A. H. Maude of Hooker Chemical for separation of sulfur dioxide from chlorine.[93] Similar patents were received by Hexon and Miller; McAdam, Farrell and Eichelburger; and Bouchard and Iler. During World War II a process evolved to produce chlorine using chlorosulfonate salts as follows:

(1) Preparation of sodium chlorosulfonate from sulfur trioxide and sodium chloride.
(2) Thermal decomposition of this material to sodium sulfate (Na_2SO_4), sulfur dioxide and chlorine.
(3) Separation of the sulfur dioxide and chlorine with removal of the chlorine as product and oxidation of the separated sulfur dioxide to sulfur trioxide for recycle in the process.

Work continued on this process until 1950 when other processes for chlorine generation became more attractive. The process never developed past the laboratory stage. However, a number of current commercial operations evolved from these efforts including:

(1) The manufacture of chlorosulfonic acid and chlorosulfonates.
(2) The use of carbon tetrachloride and sulfur monochloride (S_2Cl_2) for separation of chlorine from sulfur-bearing gases.
(3) The manufacture of sulfuryl chloride.

4.12.2 Scientific Basis

The first stage of this chlorine production process is the absorption of sulfur trioxide by salt at relatively low temperatures to form sodium chlorosulfate as shown in equation (1).

$$NaCl + SO_3 \rightarrow NaSO_3Cl \qquad (1)$$

Above 225°C sodium chlorosulfonate begins to decompose into pyrosulfate, sodium chloride, sulfur dioxide and chlorine [Equation (2)]:

$$3NaSO_3Cl \xrightarrow{(225^\circ C)} Na_2S_2O_7 + SO_2 + Cl_2 + NaCl \qquad (2)$$

Reaction kinetics results show that this process is first order with respect to temperature. Laury suggests that thionyl chloride will be produced by the decomposition in a competing reaction as follows:[92]

$$4NaSO_3Cl \rightarrow Na_2SO_4 + Na_2S_2O_7 + SOCl_2 + Cl_2 \qquad (3)$$

Furthermore, in the presence of oxygen the thionyl chloride may be oxidized to sulfur dioxide and chlorine:

$$2SOCl_2 + O_2 \rightarrow 2SO_2 + Cl_2 \qquad (4)$$

Other side reactions are also possible. One product formed could be pyrosulfuryl chloride. This will occur when the sodium chlorosulfonate is heated in the presence of excess SO_3 [Equation (5)]:

$$2NaSO_3Cl + SO_3 \rightarrow Na_2SO_4 + S_2O_5Cl_2 \qquad (5)$$

Above 250°C the pyrosulfuryl chloride will decompose into sulfur trioxide, sulfur dioxide and chlorine. Complications in production can arise from these side products.

The main reactions following from the sodium chlorosulfonate decomposition step are:

$$2Na_2S_2O_7 + 2NaCl \rightarrow 3Na_2SO_4 + SO_2(g) + Cl_2(g) \qquad (6)$$

$$2NaCl + 2SO_3(g) \rightarrow Na_2SO_4 + SO_2(g) + Cl_2(g) \qquad (7)$$

$$2NaSO_3Cl \rightarrow Na_2SO_4 + SO_2(g) + Cl_2(g) \qquad (8)$$

The adsorption reaction of salt and sulfur trioxide [Equation (7)] and the overall yield reaction that produces sulfate and the chlorine/sulfur dioxide gaseous mixture are both exothermic. The intermediate decomposition reactions are endothermic, however. These two facts could be important since they indicate the possibility of technical problems with energy requirements and heat removal during the production process. The high temperature environment (>300°C) is responsible for the exothermic reaction and the energy balance becomes more favorable as the temperature increases. Conversely, at ambient temperatures the overall process is endothermic.

4.12.3 Engineering

There are two routes - a single-stage and a two-stage process - for obtaining chlorine. Figure 21 represents the process flow chart for the single-stage system. The single-stage process is carried out at high temperature and requires that pure sulfur trioxide be used unless the gas product of the reaction will be diluted by oxygen and nitrogen.

The two-stage process, shown in Figure 22, isolates the intermediate product sodium chlorosulfonate and uses sulfur trioxide in a contact gas form.

For both processes, there are four main steps as follows:

(1) Manufacture of sulfur trioxide from sulfur or from recovered sulfur dioxide.

(2) Manufacture of sodium chlorosulfonate from salt and sulfur trioxide.

(3) Decomposition of the sodium chlorosulfonate into salt-cake and the gaseous products, chlorine and sulfur dioxide.

(4) Separation of the gaseous chlorine-sulfur dioxide mixture and production of liquid chlorine.

The two-stage process has several drawbacks compared to the single-stage process. First, technical difficulties are reduced with the single-stage because there is no intermediate product separation. Secondly, since these intermediate decomposition reactions are endothermic, heat must be contained within the walls of the reaction chamber. Construction

Figure 21. Flow Diagram for the Single-Stage Salt + Sulfur Trioxide (DuPont) Process

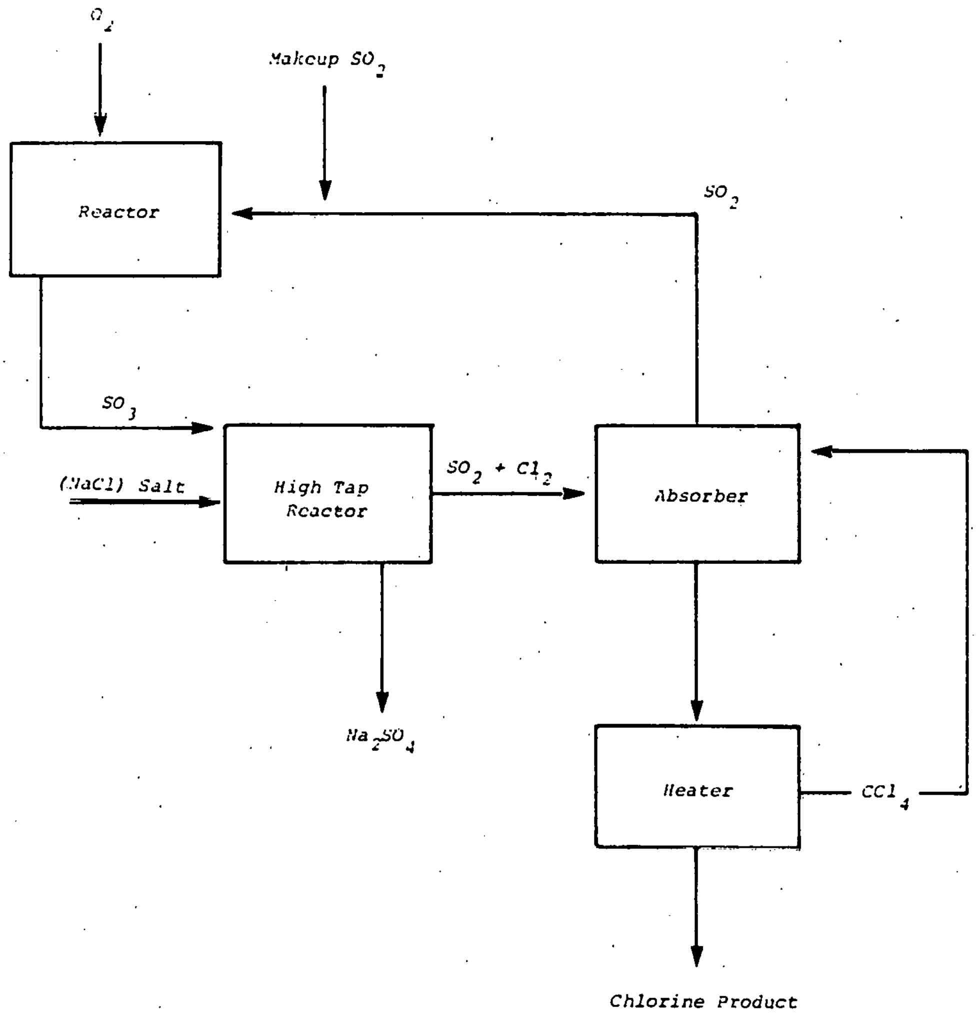
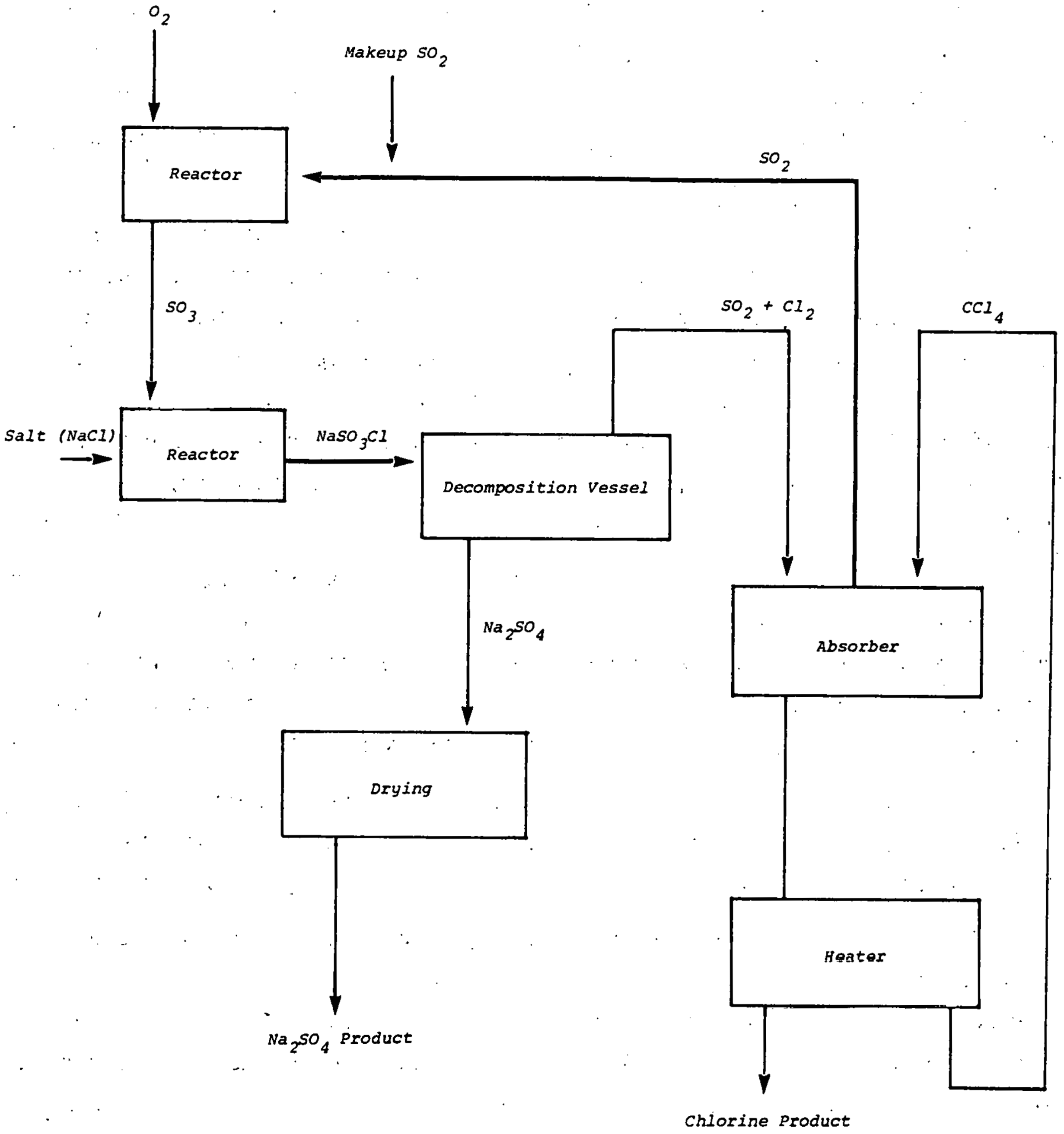


Figure 22. Flow Diagram for the Two-Stage Salt + Sulfur Trioxide Process



material limitations hamper this process. For these reasons, the single-stage process is more attractive and is discussed further.

The primary equipment used in the single-stage system is:

1. A unit for the production of oleum which uses either sulfur or pyrites as raw materials.
2. An oleum desorber made up of Reymersholms sulfur trioxide stills.
3. Grinders and preheaters for salt preparation.
4. A series of reactors, such as fluidized bed or rotating drums.
5. A means of separating chlorine and sulfur dioxide and producing liquid chlorine.

Maximum conversion efficiency for this process is reached when the salt particles are suspended in the gas. Caking of the reactive materials occurs, however, which decreases the effective contact between gas and salt. High temperatures in excess of 500°C are necessary to prevent caking which is caused by the 300°C adiabatic temperature rise of pure sulfur trioxide. Since the chlorine/sulfur dioxide mixture is extremely active at these high temperatures, reactor walls should be constructed of a highly corrosion-resistant material.

A main study area for this process was the separation of chlorine from the chlorine/sulfur dioxide mixture. Two separation techniques were considered -- selective absorption in a suitable solvent and formation of sulfuryl chloride (SO_2Cl_2) from the azeotrope. Selective oxidation was suggested by one researcher but was not actively pursued.[94]

Selective absorption uses a suitable chlorinated solvent, such as sulfur monochloride or carbon tetrachloride, to separate the mixture. Study results showed that carbon tetrachloride is the preferred solvent.[95]

For the second separation procedure, the chlorine/sulfur dioxide mixture is fractionated to give sulfur dioxide and the azeotrope which is further converted to sulfuryl chloride. Some chlorine is separated in the fractionation process itself. The sulfuryl chloride is then converted to sulfur dioxide and chlorine and the separation cycle repeated. This process encountered corrosion problems in the fluidized bed reactors during laboratory tests. Discussions with the original researchers revealed that this problem was solved satisfactorily. An economic and environmental problem is the disposal of two tons of salt cake (sodium sulfate contaminated with about 10 percent salt) and one ton of sulfur dioxide for every ton of chlorine made.

Another process for separating the chlorine/gas mixture was developed after World War II in Oppau, Germany, by I. G. Farben.[94] Chlorine was obtained by the oxidation of hydrogen chloride. An important aspect of this process was the mechanism for chlorine gas separation. The dry gas mixture produced in the plant was scrubbed at 8 atmospheres of pressure with sulfur monochloride. Chlorine was absorbed and the oxygen was recycled for use in oxidation. The chlorine product was desorbed under pressure and liquefied.

4.12.4 Economics

When determining the economic feasibility of this process, one must consider the production costs versus revenue generated by the sale of co-products. In the salt-sulfur trioxide process, chlorine, sulfur dioxide and sodium sulfate are potentially marketable. Sulfur dioxide is used in the sulfite pulp industry and sodium sulfate is a raw material for Kraft paper and glass production. Income received from the sale of these products is obtained by multiplying the total quantities consumed by the unit price of the item. The total consumption of sodium sulfate is 1,486,000 tons per year (see Table 10) and the price is $55 per ton. It is probable, however, that the sodium sulfate will not be salable because it will contain salt up to 10 percent by weight.

If chlorine production by this process were more than 700,000 tons per year, the amount of sodium sulfate produced would exceed total U.S. demand. Disposal of excess sodium sulfate would be necessary and might cause environmental as well as economic problems.

4.12.5 Conclusion

Discussions with DuPont and the original research personnel revealed that this process was abandoned in the late 1940's because of the inability to separate sulfur dioxide and chlorine gases completely and the disposal problems associated with impure sodium sulfate.[96] Difficulty in carrying

Table 10

Sodium Sulfate Production in the U.S.

Total U.S. Production (1977)	1,486,000 tons
Amount from natural sources	720,000 tons
Other By-Product Recovery (rayon, cellophane, Li_2CO_3, dichromate)	581,000 tons
Mannhein Process	50,000 tons
Hargreaves Process	135,000 tons
TOTAL	1,486,000 tons

Source: Directory of Chemical Producers, U.S.A., Stanford Research Institute, 1977.

out certain process steps on a large scale, uncertainties about equipment function, corrosion, and operational methodology are further reasons for questioning the efficacy of this process. The relative magnitude of these problems is unknown because no full-scale operations of this type have ever been undertaken by which data could be obtained and studied.

In conclusion, this process has insufficient advantages to outweigh its uncertainties and costs, so it will not be studied further.

4.13 Chlorine from Hydrogen Chloride and Sulfur Trioxide

4.13.1 Holme and Hooker et al., Process

4.13.1.1 Process History

Sulfur trioxide, when used in an oxidation reaction with hydrogen chloride, produces chlorosulfonic acid (HSO_3Cl) from which a final chlorine product can be retrieved.

Work on this decomposition reaction using mercuric salts as catalysts was done by Rutt in the early 1900's.[98] He conceptually designed some commercial applications for the manufacture of sulfuryl chloride (SO_2Cl_2). Decomposition of the acid without using a catalyst was performed by Mellor, but his work was not carried through extensively. Sanger and Reige also worked on the non-catalytic decomposition reaction to obtain a sulfuryl chloride product. The kinetics of this particular reaction have been studied in depth by Payne, Pearce, and Fernelius.[99] A process for using higher temperatures to prevent pyrosulfuryl chloride formation was also set forth by Farbenind.[100] An expansion of these pyrosulfuryl control methods was later set forth by Edwards in the early 1940's.[101] In the 1940's Kallal concentrated once again on the use of mercuric salts as catalysts.[102] Kallal worked extensively on decomposition rates of chlorosulfonic acid using varying catalyst concentrations.

Once the basic processes have been established, the major effort was to improve process efficiency, especially chlorine separation procedures. Johnstone in 1942 did important studies in this area along with Bouchard who focused on absorption processes for separation.[103,104] Carbon tetrachloride was the preferred absorber. These absorption processes and ongoing improvements were continually patented until the late 1950's. Two of the more prominent patents were by Holme in 1956 and Hooker, Geeroog, and Maude.[105]

All the research work was laboratory scale. No extensive test facilities were developed. Further work on all the patents received has been abandoned.

4.13.1.2 Scientific Basis

The initial step of this process is the formation of chlorosulfonic acid. This is accomplished as follows:

$$HCl(g) + SO_3(g) \xrightarrow[70\text{-}100°C]{} HSO_3Cl(l)$$

Commercially chlorosulfonic acid is produced from contact plant gas and dry hydrogen chloride. The chlorosulfonic acid product is then decomposed by using mercuric chloride with the whole system under pressure. This decomposition reaction is:

$$2HSO_3Cl \xrightarrow[HgCl_2]{160°C} H_2SO_4(l) + SO_2Cl_2(g)$$

The effects of pressure on the conversion rate can be seen in Figure 23. With pressure maintained between 3 and 11 atmospheres the reaction proceeds at a continuous and faster rate. The change in free energy at the temperature of reaction is $\Delta F = 6190-16.27(T)$. At 110°C the reaction is spontaneous Note that the sulfuric acid produced is sufficiently pure for sale as a by-product.

The next step involves the decomposition of the sulfuryl chloride to sulfur dioxide and chlorine. This is accomplished using activated charcoal as a catalyst and high temperature as follows:

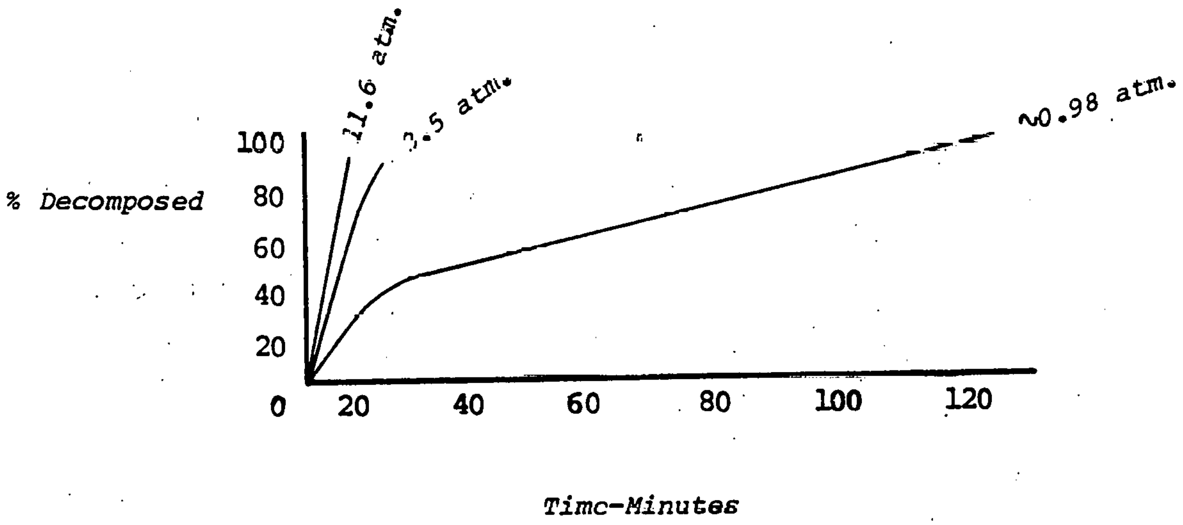
$$SO_2Cl_2 \xrightarrow[\text{catalyst}]{\text{heat}} SO_2 + Cl_2(g)$$

At the temperature of reaction the free energy change $\Delta F = 7760-22.67T$. At room temperature, decomposition does not occur, but at temperatures above 70°C, the reaction theoretically becomes spontaneous.

The mixture of sulfur dioxide and chlorine is then passed through a solvent absorber using carbon tetrachloride or sulfur monochloride. In this solvent, sulfur dioxide is relatively insoluble, while chlorine is soluble.

The free energy change is, $\Delta F = 10{,}500-4.61(T) \log T - 16.08(T)$, at the temperature of reaction. At high temperatures (above 350°C), the reaction theoretically becomes spontaneous.

Figure 23. Decomposition of Chlorosulfonic Acid As A Function of Pressure Using A Mercuric Chloride Catalyst



The next two steps in this process are recycling procedures. The first deals with the recycling of sulfur trioxide to the initial process step. The sulfur dioxide produced in step 3 is combined with oxygen to make the sulfur trioxide.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

In the second operation the absorbing solvent is recycled and the chlorine product is recovered:

$$Cl_2 \text{ in } CCl_4{}^* \xrightarrow{\text{heat}} \underset{\text{(product)}}{Cl_2\uparrow} + CCl_4{}^*$$

$^*S_2Cl_2$ may be used as the absorbing solvent.

The overall free energy change of the total reaction is about 115 Kcal/mole at 25°C. The overall process reaction is:

$$SO_3 + 2HCl \rightarrow H_2SO_4 + Cl_2 + SO_2$$

The overall free energy change is exothermic. Process electricity necessary for the production of one kkg of chlorine is 305 kwh.

4.13.1.3 Engineering

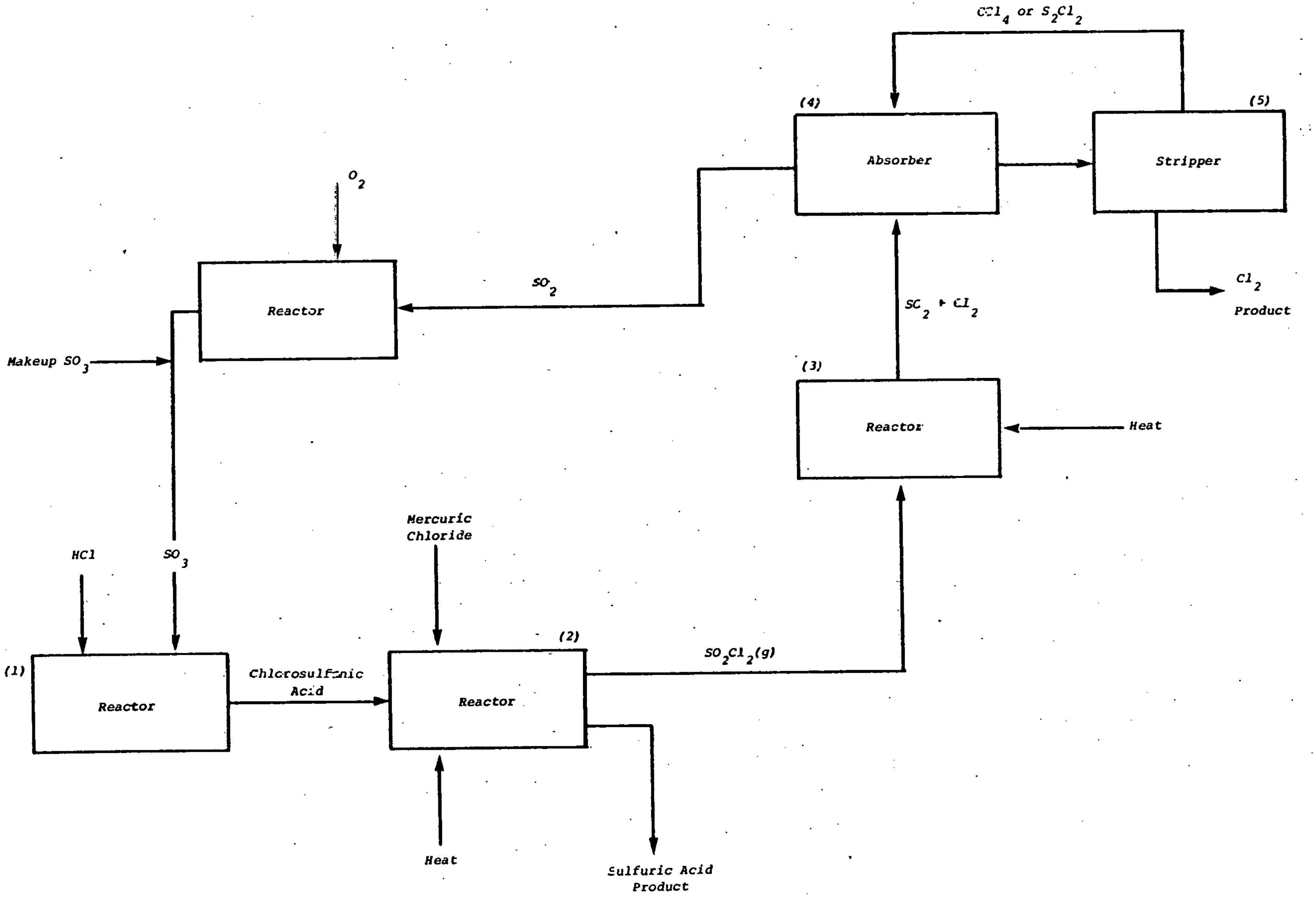
An overall flow chart for this process is shown in Figure 24. The selective absorption mechanism is used to separate the chlorine and the sulfur dioxide.

The operation can be described as follows:

(1) Manufacture of the chlorosulfonic acid using sulfur trioxide contact gas and hydrogen chloride. This is carried out by passing both gases to the base of a packed tower. Cool chlorosulfonic acid is circulated to the tower such that it dissolves the sulfur trioxide and exposes it to the hydrogen chloride for reaction. Circulation must be maintained so that the excess heat of reaction can be removed. A temperature of around 100°C is required.

(2) The catalytic (mercuric chloride) decomposition of the chlorosulfonic acid then occurs. Sulfuryl chloride and sulfuric acid are generated at temperatures from 150°C to 300°C. This reaction

Figure 24. Flow Diagram for Hydrogen Chloride + Sodium Trioxide Process (Holme and Hooker et al)



is slow and is the controlling process in continuous operation. With pressure maintained between 3 and 11 atmospheres the reaction proceeds at a continuous and faster rate (see Figure 23, page 104). The only difficulty is separation of the process catalyst (mercuric chloride). The use of these higher pressures requires high capital expenditures for purchasing both the pressure generating equipment and pressure resistant systems.

(3) The catalytic (activated charcoal) decomposition of sulfuryl chloride into sulfur dioxide and chlorine occurs at a temperature above 200°C.

(4) Separation of the sulfur dioxide/chlorine mixture by selective adsorption onto carbon tetrachloride or sulfur monochloride.

(5) Recycling of the carbon tetrachloride to step (4) and the removal of the chlorine from the carbon tetrachloride.

Some process problems did arise with the bench testing of this method. Unsatisfactory yields were obtained due to clogging in the tower. Combined with this problem was that of balancing the feed rate and heat input rate. Further testing is needed to improve process efficiency.

Corrosion problems must also be addressed. In the absence of leaks and moist air, steel and iron casings are protected; however, surfaces of copper, nickel, and silver alloys are eroded slowly. The acids present are strong enough to damage cement and brick, so all substances of this type used should be acid-proof. Leakages from these towers could have serious environmental effects, especially from mercury salt catalysts and sulfur dioxide.

4.13.1.4 Economics

This hydrogen chloride/sulfur trioxide process has some advantages which makes it attractive. The raw materials needed are easily obtained, although hydrogen chloride supply may be limited, and the process reactions are easily controlled. It has the disadvantages of having to separate sulfur dioxide and chlorine, and remove mercuric chloride from the sulfuric acid product, but if these problems can be solved, then large-scale quantities may be generated.

The economic feasibility must still be proven. A post-World War II (1948) estimate on the capital cost of starting a 100 ton-per-day facility was $3,000,000. Combining all the operating costs with this capital cost figure puts the total cost of producing chlorine at $45 per ton (still in 1948 dollars). This figure neglects the revenue earned from by-product sales.

4.13.1.5 Conclusion

This process has a number of technical problems. The most important one is removal of mercuric catalysts from the sulfuric acid by-product. Unless better removal of these mercuric salts can be achieved, the co-product will be unsalable. Add to this the corrosion of sulfur dioxide-chlorine separation problems, and we conclude that no further efforts will be devoted to this process.

4.13.2 Kuhlmann Chlorine Production Method

4.13.2.1 History

This chlorine production process uses hydrogen chloride, oxygen, sulfur dioxide and a catalyst and is considered an improvement over the Holmes and Hooker et al., process. The principal developer was the Kuhlmann Corporation of Paris, France, which received a patent on June 6, 1968.[113] Development work on this method was carried out only on a laboratory scale and further process refinement has ceased.

4.13.2.2 Scientific Basis

The chemistry of the Kuhlmann Method is an improvement on a similar process developed by the Holme and Hooker et al., which utilized sulfur trioxide as an oxidizing agent for converting hydrogen chloride into chlorine. The following equations summarize this mechanism:

$$\mathrm{HCl(g)} + \mathrm{SO_3(g)} \xrightarrow{70°\text{-}100°\mathrm{C}} \mathrm{HSO_3Cl(l)} \tag{1}$$

$$2\mathrm{HSO_3Cl} \xrightarrow[\mathrm{HgCl_2}]{160°\mathrm{C}} \mathrm{SO_2Cl_2(g)} + \mathrm{H_2SO_4(l)} \tag{2}$$

$$\mathrm{SO_2Cl_2(l)} \xrightarrow[\text{activated charcoal}]{} \mathrm{SO_2(g)} + \mathrm{Cl_2(g)} \tag{3}$$

Pragmatically, these reactions must be carried out separately because reactions (1) and (3) are rapid, while reaction (2) is slow. As such, chlorosulfonic acid must react under pressure in the liquid phase to attain sufficient speed. This condition is detrimental since continuous operation of the process is difficult and separation of the catalyst, sulfuric acid and sulfuryl chloride is a problem.

Kuhlmann's improvement, shown in Figure 25, involves oxidizing the hydrogen chloride in a single step to produce liquid sulfuric acid and gaseous chlorine. This reaction is represented by the following equation:

$$SO_2(g) + O_2(g) + 2HCl(g) \xrightarrow[\text{catalyst}]{} H_2SO_4(l) + Cl_2(g)$$

The catalyst in this case is an inert support material combined with 3 to 15 percent vanadium compounds and 5 to 20 percent alkali metal/alkaline earth metal oxides. The resultant products are gaseous chlorine, liquid sulfuric acid, sulfur trioxide, chlorosulfonic acid and a small quantity of unreacted sulfur dioxide. Further treatment of this mixture involves condensing the chlorosulfonic and sulfuric acids, absorbing the sulfur trioxide in sulfuric acid and separating out the desired chlorine.

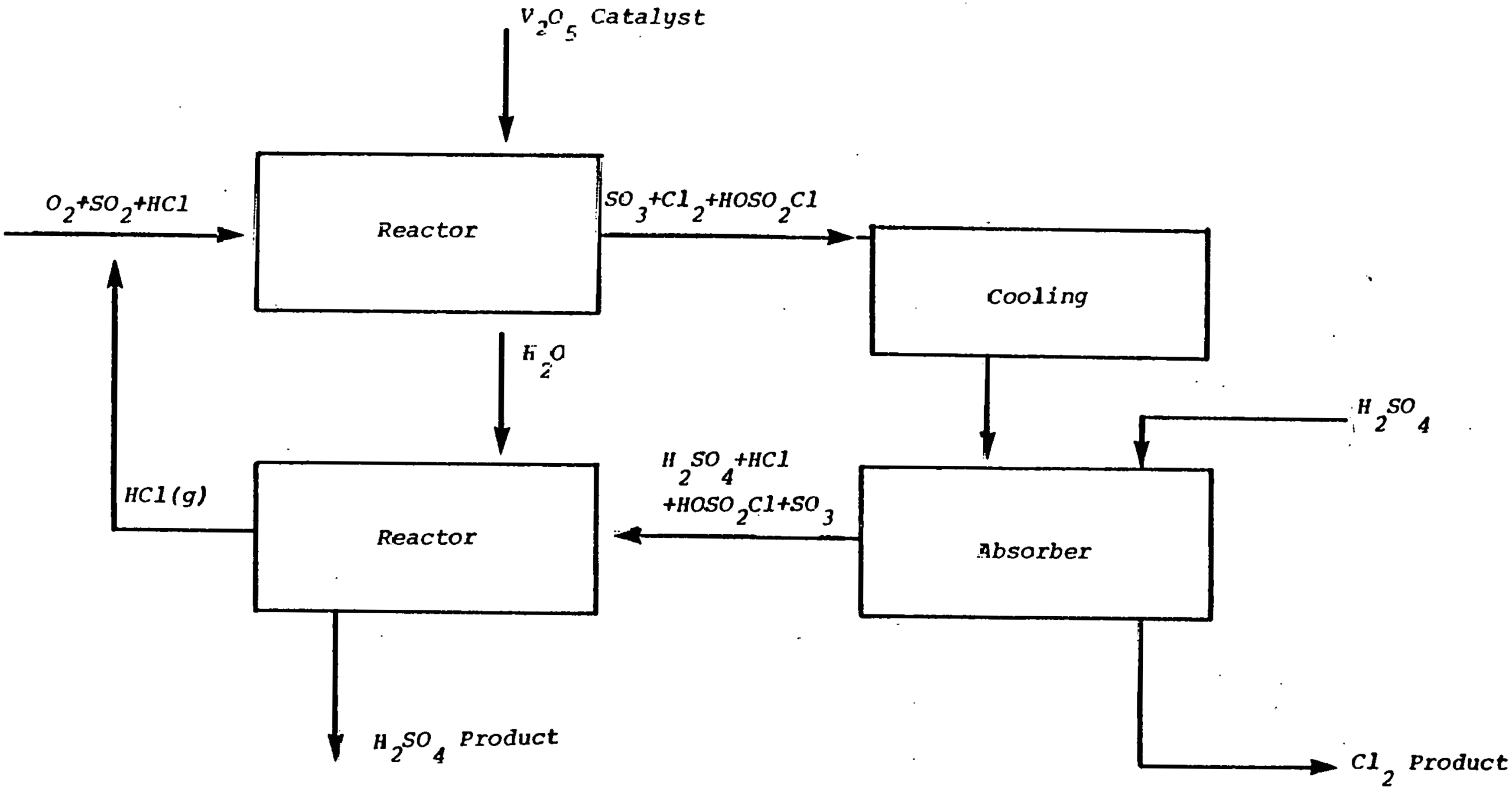
4.13.2.3 Engineering

The conceptual method of operation for this process involves a two-stage process: heating, then cooling. In the heating state an equilibrium is reached between the reactants (i.e., SO_2, O_2 and HCl) and the products (i.e., H_2SO_4 and Cl_2).

The temperature at atmospheric pressure must be between 400° and 600°C. These high temperature ranges must be maintained; however, the pressure level may vary from below atmospheric up to 10 atmospheres.

The obtained equilibrium, however, does not permit a complete conversion of hydrogen chloride to chlorine. This requires a cooling stage in which the reaction of the hydrogen chloride and sulfur trioxide is completed. In the cooling stage chlorosulfonic acid is formed from the hydrogen chloride and the sulfur trioxide. The reaction temperatures present in this zone are between 100° and 120°C.

Figure 25. Flow Diagram For Kuhlmann Process



Under the above operating conditions, the contact times between the gaseous starting mixture and the catalytic mass should range between 1 and 20 seconds. Optimal contact time is between 3 and 10 seconds. Catalytic contact can be made on either a fixed or fluidized bed, which promotes continuous process operation.

4.13.2.4 Economics

No economic assessment or cost data are available.

4.13.2.5 Conclusion

The advantages of this process are that 95 percent yields are attainable and continuous operation is easily achieved. The major problems are: (1) the process is based on hydrogen chloride, so raw material supplies are limited; (2) materials involved are of a highly corrosive nature; and (3) high process temperatures are required.

The overall conclusion is that the costs and raw material shortages outweigh the yield and operating advantages, so this process will be excluded from further study.

4.14 Oxidation of Hydrogen Chloride with Hydrogen Peroxide

4.14.1 Process History

In this process hydrogen chloride is reacted with hydrogen peroxide and calcium chloride. The principal developers of the process are Hans Klebe, Alfred Meffert, and Albert Logenfeld.[116] The process patent was assigned to the Deutsche Gold- and Silver-Scheideanstalt-vormals Roessler of Frankfurt, Germany. The original patent was filed on July 5, 1972, and granted on April 23, 1974. The patent is an improvement on earlier work performed by Klebe in 1970. The main refinement to the original patent work is the addition of dissolved calcium chloride to the reactant mixture to improve yields. The complete process operation was only carried out on a bench scale and commercial feasibility was not explored. Currently, process development is inactive.

4.14.2 Scientific Basis

The basic equation for this technique is:

$$H_2O_2 + 2HCl \rightarrow 2H_2O + Cl_2$$

As an additive to this equation, calcium chloride is used. This is added in the amount of 100-500 grams of calcium chloride per liter of reaction solution. The aqueous hydrogen chloride solution concentration ranges from 20-40 percent by weight with a preferred range of 25-35 percent. The aqueous hydrogen peroxide solution has a preferred concentration range from 40-70 percent, with a maximum value of 90 percent. During solution preparation hydrogen peroxide is usually added in the ratio of 0.8 to 0.9 moles for every 2 moles of hydrogen chloride. The temperatures at which the various components react depend on the particular procedural mechanism used.

The reaction can occur either at the temperature provided for the absorption agent of 27°-40°C or at the temperature provided by the oxidation reaction activation temperature, which is below 60°C. Operating pressures of 0.2 to 0.95 atmospheres enhance chlorine liberation. Chlorine can also be liberated by using a rinsing gas that strips the chlorine from the reaction chamber. A combination of low pressure and a rinsing gas often is used.

4.14.3 Engineering

The process can be carried out by batch or continuous operations. With a continuous operation, water must be constantly removed to maintain adequate hydrochloric acid concentrations. Water formed during reaction can be withdrawn in the form of dilute hydrochloric acid. Hydrogen chloride gas is added to maintain hydrochloric acid concentrations.

The overall process can be accomplished using any of three separate sub-processes which differ in how the hydrogen chloride is extracted from the hydrogen chloride-containing gas.

The first method uses a multi-step countercurrent wash with hydrochloric acid to separate the hydrogen chloride, steam, and air mixture and remove heat prior to reaction with hydrogen peroxide. The cooled product flows concurrently to the hydrogen peroxide through a packed tower to form the chlorine gas. One advantage of this technique is that chlorine can be obtained from gas mixtures having a low concentration of hydrogen chloride.

The second technique uses the same multi-step wash, except that the resultant solution is heated until enough hydrogen chloride is removed to form an azeotrope. The desorbed hydrogen chloride is then contacted countercurrently with concentrated hydrochloric acid and hydrogen peroxide. Chlorine is formed in the reaction tower and removed. Excess water is discharged in the form of azeotropic hydrochloric acid.

The third alternative sub-process does not separate the gaseous mixture. The hydrogen chloride is introduced immediately into the aqueous medium and reacts with the hydrogen peroxide. The product chlorine gas must be reconcentrated, however, because it is mixed with accompanying gases of the hydrogen chloride mixture. Regardless of the procedure used, the yields are good, in excess of a 90 percent conversion. Table 11 contains information obtained from the patent.

An advantage of this process is that no special equipment is needed to perform the operation. Standard reactions such as the desorption of hydrogen chloride from hydrochloric acid to form the azeotrope can be accomplished by existing commercial processes.

Table 11

Yields from the Hydrogen Peroxide-Hydrogen Chloride Process

HCl Reaction	
Hydrogen chloride brought in as hydrochloric acid	128.5 kg/hr
Theoretical chlorine yield	125 kg/hr
Chlorine obtained.	103 kg/hr
(a yield of about 83 percent)	
H_2O_2 Reaction	
H_2O_2 (100 percent added)	52.5 kg/hr
Theoretical chlorine yield	109.5 kg/hr
(a yield of about 94 percent)	

4.14.4 Conclusion

Although this process has low energy requirements and high yields, it is ruled out as a viable means of commercial chlorine production because of the high cost and low availability of hydrogen peroxide. Hydrogen peroxide producers have no incentive to increase production without an increase in price. Precise economic data were not available in the patent.

4.15 Chlorine from Alkali Metal Chlorides and Nitrogen Oxide Compounds

4.15.1 Vicksburg Process

4.15.1.1 Process History

The concept of producing alkali metal nitrates and a chlorine co-product from alkali metal chloride and nitric acid and/or nitrogen dioxide is quite old. As early as the 1930's, Allied Chemical worked on a process for co-production of sodium nitrate and chlorine. A facility was built before World War II at Hopewell, Virginia, and was operated until the mid-1960's when it was shut down due to a lack of demand for sodium nitrate. Also in the 1930's, the U.S. Department of Agriculture developed a process for potassium nitrate (KNO_3) production based on the reaction of nitrogen dioxide with potassium chloride. This process, however, was never commercialized.[117]

In the late 1950's interest developed in a process based on the reaction of nitric acid with potassium chloride to yield a potassium nitrate by-product usable for fertilizer applications. At least three organizations performed independent work in this area. In 1962 a patent was granted to J. L. Chadwick of Delhi-Taylor Oil for this process, however, this patent was not commercialized due to corrosion problems.[118] Almost at the same time another patent was granted to H. A. Beekhuis (unassigned) for a similar process.[119,120] This work also saw no commercial application.

In 1961, the Southwest Potash Division of American Metal Climax Corporation (AMAX) began work on a process for converting potassium chloride to potassium nitrate and chlorine. After pilot plant evaluation, a plant was opened in 1965 at Vicksburg, Mississippi to produce 63,000 TPY of potassium nitrate and 22,000 TPY of chlorine by-product.[121] This facility was operated by AMAX for several years, then was sold to Vicksburg Chemical Company in 1973.[122] Vicksburg Chemical Company has continued to operate the facility to the present date and has made a number of minor modifications, mostly in construction materials to reduce corrosion problems. No other facilities using this process have been constructed or are planned.

4.15.1.2 Scientific Basis

In this process, 64 percent nitric acid is first reacted with potassium chloride according to the equation:

$$3KCl + 4HNO_3 \rightarrow 3KNO_3 + NOCl\uparrow + Cl_2\uparrow + H_2\uparrow$$

This initial reaction is generally conducted below 10°C to avoid corrosion problems involved in handling hot nitric acid-chloride based mixtures. From this reaction both gaseous nitrosyl chloride and chlorine are liberated.

Next, the liberated gases are passed through a gas column reactor where they are contacted with nitric acid vapors at elevated temperatures to oxidize the nitrosyl chloride present according to the equations:

$$NOCl + 2HNO_3 \rightarrow NO_2Cl + 2NO_2 + H_2O \tag{1}$$

$$H_2O + 3NO_2 \rightarrow 2HNO_3 + NO \tag{2}$$

$$NO_2Cl + NO \rightarrow NO_2 + NOCl \tag{3}$$

$$2NO_2Cl \rightleftarrows 2NO_2 + Cl_2 \tag{4}$$

For these reactions, nitric acid in excess of 70 percent is required.

The product mixture of nitric acid vapors, nitric oxide, nitrogen dioxide, nitrosyl chloride and chlorine is separated by fractional distillation. The chlorine fraction is compressed, liquefied and prepared for shipment as product. The other separated materials (NO, NO_2, NOCl and HNO_3 vapors) are fed to a nitrogen dioxide fractionating column, where nitrogen dioxide and nitric acid vapors are separated from the other components. The nitric oxide and nitrosyl chloride are collected and recycled to the second process. The gas column reactor and the nitric acid and nitrogen dioxide are then reconverted to 65 percent nitric acid for recycle back to the initial reaction step.

Further processing is needed for the initial reaction step solutions which, after release of nitrosyl chloride and chlorine, still contain the potassium nitrate co-product and unreacted 65 percent nitric acid. These solutions are stripped of excess water by heating and are then cooled and fed to a series of vacuum crystallizers, where 81 percent nitric acid is removed as vapor. This acid gas is then recondensed, converted back to 65 percent nitric acid and recycled to the initial process step. The potassium nitrate recovered in this evaporative process is further separated from residual nitric acid by centrifugation and is then dried, melted, prilled, cooled and marketed. Nitric acid separated during centrifugation is recovered and recycled.

Some key aspects of this process are:

(1) A shift in the composition of the nitric acid-water azeotrope from about 70 percent nitric acid to over 80 percent in the presence of high concentrations of potassium nitrate. It has been found that only the nitrates of the alkali metals heavier than sodium shift the nitric acid azeotrope to higher concentrates. The nitrates of the lighter alkali metals (i.e., lithium and sodium) have the reverse effect of shifting the azeotrope to lower nitric acid contents, which was no problem with the old Allied sodium nitrate process.

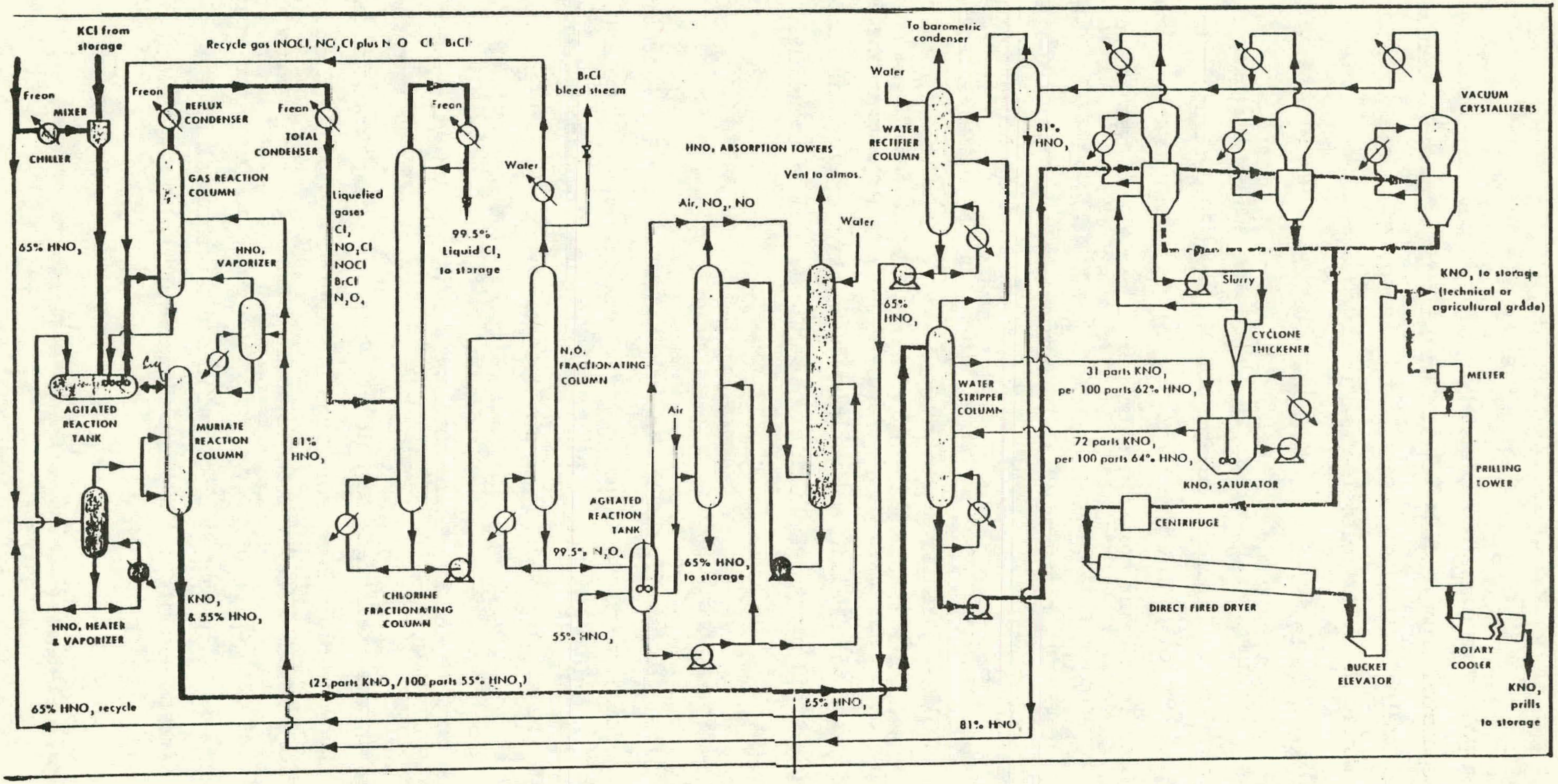
(2) The oxidation of nitrosyl chloride (NOCl) to chlorine and nitrogen dioxide with nitric acid in the 70-80 percent range at temperatures and pressures which are practical from an operational viewpoint.

4.15.1.3 Engineering

A detailed process flow sheet is provided in Figure 26. For the initial digestion reaction, titanium equipment with external ceramic temperature insulation is used. Since the initial digestion is conducted below 10°C, the nitric acid is pre-chilled before mixing with the potassium chloride.

In the muriate column, where continuation valve sieve trays are used, as shown in Figure 26, residual chlorine values are stripped from the nitric acid/potassium nitrate solutions. This stripping protects the equipment through which these solutions are further pressurized to recover nitric acid and recover the potassium nitrate product. Without removal of residual chlorine, severe chloride corrosion problems would be encountered. All subsequent equipment for processing of the potassium nitrate liquors and product is made of stainless steel.

Figure 26. Detailed Vicksburg Process Flow Sheet



The second main reaction, oxidation of nitrosyl chloride, is conducted in gas reactors made of glass-lined stainless steel. A nitric acid content of over 70 percent is required to make this reaction proceed at a practical rate. Even with strong nitric acid, however, the oxidation does not go to completion. After separation by distillation in the nitrogen dioxide fractionator, nitrosyl chloride is recovered and recycled to the gas reaction columns. These columns, using combination valve and sieve trays, perform the dual functions of oxidizing the nitrosyl chloride and removing nitric acid vapor and water almost completely from this gas stream. This is necessary to protect subsequent processing equipment from corrosion. All fractional distillation equipment for the nitrogen dioxide/chlorine is made of Inconel nickel-chromium alloy. Regeneration of nitric acid from nitrogen dioxide is conducted at 100 psig.

Equipment involved in recovery of potassium nitrate from the potassium nitrate-nitric acid solutions is made of Type 304 ELC stainless steel. The Struthers vacuum crystallizers used in potassium nitrate recovery grow relatively large crystals from a 90 parts potassium nitrate/10 parts 82 percent nitric acid fed by circulating large volumes of high density slurry and producing only a small amount of supersaturation per cycle. Purity of the potassium nitrate produced is over 99.3 percent.

Thermodynamic calculations for the overall reaction

$$6KCl + 6HNO_3 + 3/2O_2 \rightarrow 6KNO_3 + 3Cl_2 + 3H_2O$$

show the entire process has a ΔF value at 25°C of +27.1 Kcal/mole of chlorine generated.

4.15.1.4 Economics

Currently, there are two facilities producing potassium nitrate in the United States. These two plants satisfy the entire domestic demand. Of these two, the Vicksburg Chemical plant is by far the larger.[122] The second facility, operated by Mallinckrodt Chemical Company, produces only a small amount of reagent grade material.

As a result of limited markets for potassium nitrate, further expansion of this process is unlikely. Process economics become unfavorable if the potassium nitrate co-product (current sale price $190 per ton) has to be disposed of as a waste at a cost in excess of $10 per ton. For example the Vicksburg facility would annually sustain a $12.5 million decrease in income if it could not sell the potassium nitrate.[122]

Plant construction costs (1965 base) of $8,000,000 have been reported. No operating cost data have yet been provided.

4.15.1.5 Conclusion

While this process is technically viable, limited markets for the potassium nitrate co-product make it unlikely that additional plants of this type will be constructed in the foreseeable future.

4.15.2 Potassium Nitrate Process

The process described below is a forerunner of the present-day Vicksburg process. The process itself was never carried past bench scale and the production of chlorine was not a consideration. The process originated with Donald Reed and K. G. Clark[117] in the mid-1920's. They were working with the Bureau of Chemistry and Soils of the U.S. Department of Agriculture. The main thrust of their work was in the chemical fertilizer industry. They developed a process for the production of potassium nitrate using nitrogen oxides and potassium chloride as follows:

$$2NO_2 + HCl \rightarrow KNO_3 + NOCl$$

No further work was carried out.

Based on the Vicksburg process, however, the technology is known for converting nitrosyl chloride to chlorine. The entire process is shown in Figure 27. Fairly good reaction rates were obtained in this process, but the conversions were poor. Reactions were conducted generally under ambient conditions.

Aside from work on the initial process reaction, no other efforts were expended on this process. However, the thermodynamics and engineering considerations for the reactions of nitrogen dioxide with potassium chloride are similar to those discussed for the Vicksburg process.

In conclusion, this process was a predecessor effort to the now commercialized Vicksburg process. Since the Vicksburg process supplies over 70 percent of U.S. potassium nitrate production, a market does not exist for significant additional amounts of this material.

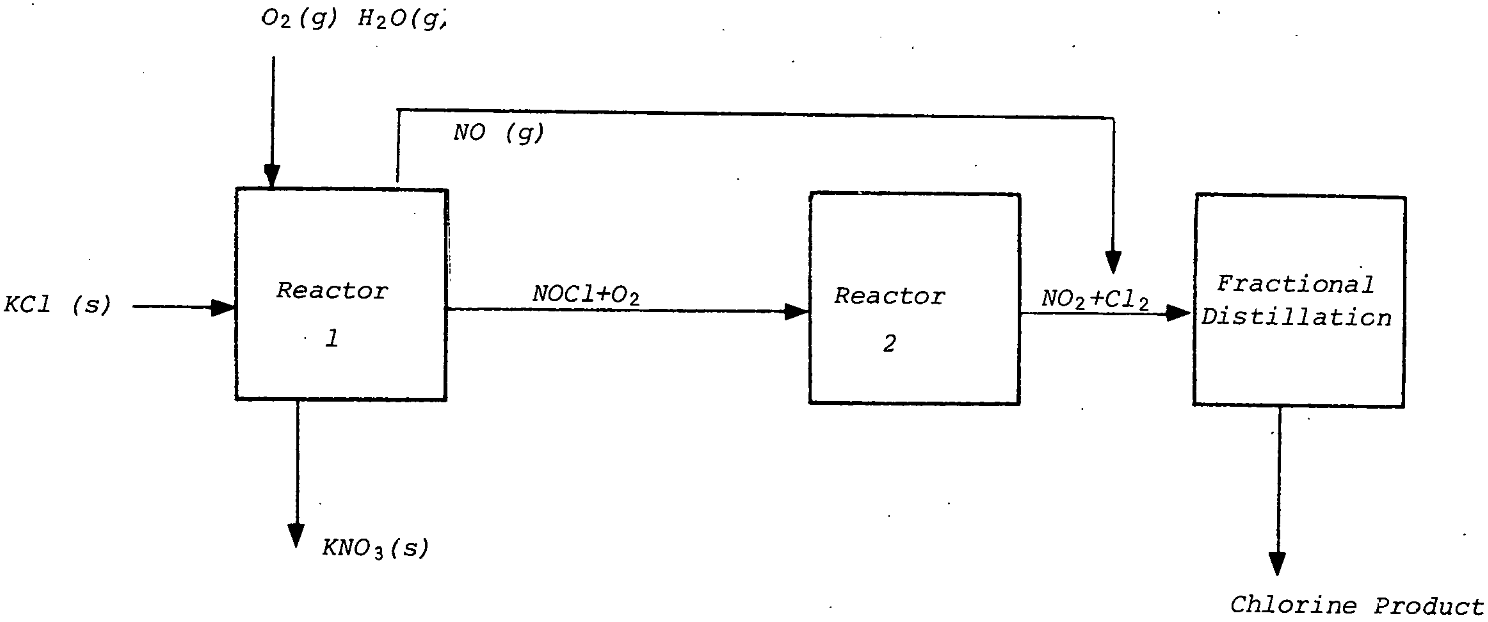


Figure 27. Flow Diagram for the Vicksburg Process

4.16 Allied Chemical Company Salt and Nitric Acid Process

4.16.1 Process History

In 1847, Dunlop Company patented a process using sodium chloride and nitric acid to produce chlorine. Many modifications were made to this basic process until the Allied Chemical Company developed a commercially feasible scheme in the mid-1930's. The first and only commercially successful plant to use this technology was built in Hopewell, Virginia, in 1936. The process continued to be modified and improved until the early 1950's. The last major change converted the by-product nitrosyl chloride to chlorine and sodium nitrate. By the 1960's, however, the Hopewell plant was shut down because of the reduced market for the sodium nitrate co-product. This market had been reduced by the trend away from sodium nitrate-based fertilizers.[1,2,3]

4.16.2 Scientific Basis

The first phase of Allied's method is known as the salt process with nitrosyl chloride neutralization. It converts salt, nitric acid, and sodium carbonate to chlorine and sodium nitrate. The overall chemical reaction including salt digestion, chlorine recovery and nitrosyl chloride oxidation is:

$$6\ NaCl + 12\ HNO_3 + 2\ Na_2CO_3 \rightarrow 3Cl_2 + 10NaNO_3$$
$$+ 2\ CO_2 + 2\ NO + 6\ H_2O$$

Note that for each pound of chlorine produced, four pounds of sodium nitrate are produced.

There is a tendency in the digestion reaction to form nitrosyl chloride (NOCl), reducing the chlorine yield. To increase yields, Allied oxidized the nitrosyl chloride as follows:

$$2NOCl + O_2 \rightarrow N_2O_4 + Cl_2$$

The nitrosyl chloride is first vaporized and oxidized with oxygen. This mixture is then cooled, condensed, and distilled. Nitrogen tetroxide is recoverable as a liquid product that can be stored and sold or recycled to make nitric acid.

4.16.3 Engineering

The salt and nitric acid process flow chart is shown in Figure 28. To initiate the salt process, nitric acid (63 to 66 percent) is mixed with sodium chloride. This mix is thermally digested and the chlorine formation reaction occurs, forming nitrosyl chloride and sodium nitrate. The product solution proceeds down the column where nitrosyl chloride and chlorine are stripped out. This nitrosyl chloride-chlorine mixture with entrained water vapor and nitric acid then enters a drying column and is scrubbed with cooled nitric acid. The nitrosyl chloride is then oxidized.

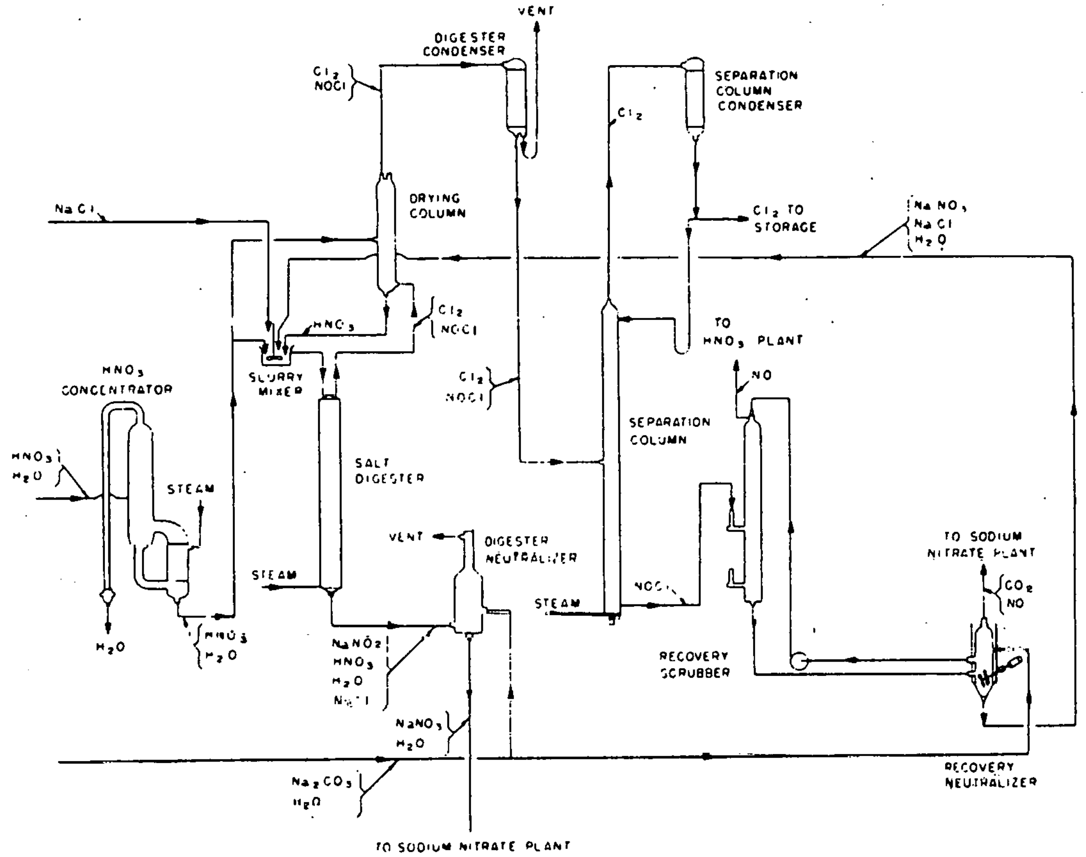
In the oxidation scheme, the nitrosyl chloride is drawn through a separation column, then vaporized and heated. The vaporization, which converts nitrosyl chloride to chlorine and nitrogen tetroxide, occurs in an oxidation interchanger and oxidizer at temperatures of 100° to 200°C. The resultant reaction-product mixture at about 200° to 300°C goes to the oxidation cooler where its temperature is reduced to about 25° to 35°C. The product mixture is sent to an oxidation liquefier where it is condensed at a temperature of -10° to -20°C to facilitate separation of nitrogen tetroxide and chlorine. The operating temperatures in the separation columns are about 15° to 60°C. Nitrogen tetroxide exits from the bottom of the column, while chlorine comes off the top. The entire oxidation system operates at pressures up to 8 atmospheres.

Table 12 gives a raw material product relationship for this process in terms of the overall equation to produce one ton of chlorine.

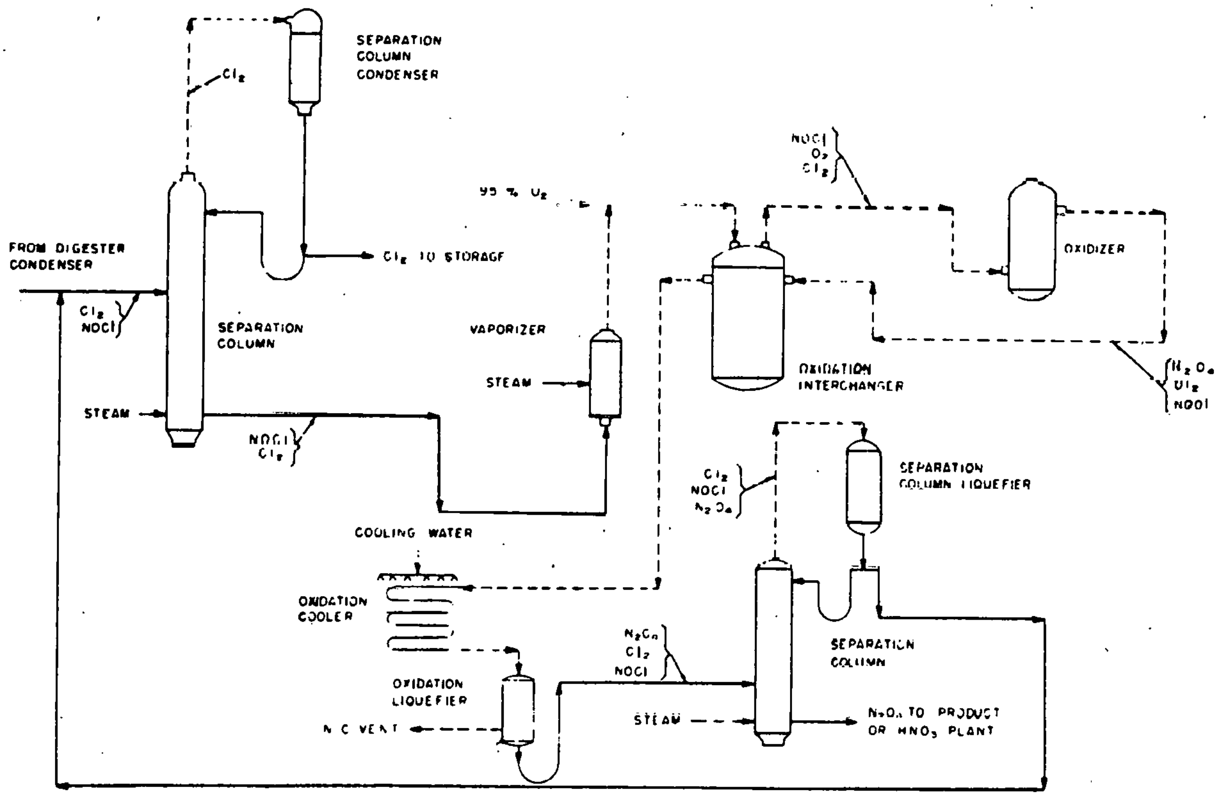
A major operating difficulty for this process is excessive corrosion. The equipment used for this process must be corrosion resistant and fluid-tight. Construction materials, such as metal alloys and corrosion-resistant cement, are needed.

4.16.4 Conclusion

This process is not industrially feasible because of the lack of a viable market for the tremendous quantities of sodium nitrate generated. If none of the sodium nitrate can be sold, disposal costs would be prohibitive from both an economic and environmental standpoint. Combining these problems with those of the corrosion potentials, this process appears infeasible for the large scale commercial production of chlorine.



Chlorine by Salt Process with Nitrosyl Chloride Neutralization



NOCl oxidation

Figure 28. Flow Diagram for Salt + Nitric Acid (Allied) Process

Table 12

Material Balance for Allied Process

Component		Tons of Component		% of Component
Raw Material				
NaCl		1.65		40
HNO_3		2.37		57
O_2		0.15		3
	TOTAL	4.17	TOTAL	100
Products				
$NaNO_3$		2.40		58
Cl_2		1.00		24
N_2O_4		0.43		10
H_2O		0.34		8
	TOTAL	4.17	TOTAL	100

4.17 French Salt - Kaolin Process

4.17.1 Process History

In 1886, A. Goyeu found that heating a mixture of salt and kaolin with oxygen to a temperature of 1,000°C led to the formation of elemental chlorine. Little further work was done with this reaction for over sixty years. In 1948, Briner and Roth performed a more extensive kinetic study of this reaction and corroborated the original findings.[124] Further verification was soon reported by Dodson in 1957.[125] In 1966, after further laboratory studies, F. Trombe, M. Foex, P. Courty and G. Hulbt obtained a patent on a proposed process using this scheme.[126,127] No further efforts in this area have been reported since.

4.17.2 Scientific Basis

According to the patent of Trombe, et al., this process involves the following steps:

(1) Kaolin and salt are precalcined to remove water at 800°C. For the kaolin the following dehydration reaction occurs:

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O \rightarrow 2H_2O + 2SiO_2 \cdot Al_2O_3$$

(2) The hot salt and kaolin are mixed at a temperature of 850°C to create a bed of hot dehydrated kaolin particles covered by a film of molten salt.

(3) Air is passed through the bed forming the co-products sodium aluminosilicate and chlorine, as follows:

$$2NaCl + 2SiO_2 \cdot Al_2O_3 + 1/2O_2 \rightarrow Na_2O \cdot 2SiO_2 \cdot Al_2O_3 + Cl_2$$

(4) The product chlorine exits the process with unreacted oxygen and is recovered by selective absorption in a solvent, such as carbon tetrachloride.

(5) The chlorine is recovered from the carbon tetrachloride by heating.

No specific discussion is made of further processing of the sodium aluminosilicate co-product, although recovery of this co-product may be required to develop a viable process. Aside from the Trombe, et al., patent, no other recent work has been reported in this area.

4.17.3 Engineering

The complete process is outlined in Figure 29. The initial portion of the process is from the Trombe patent; the remaining steps needed to recover a preliminary product are based on engineering estimates. The process equipment needs for this operation are as follows:

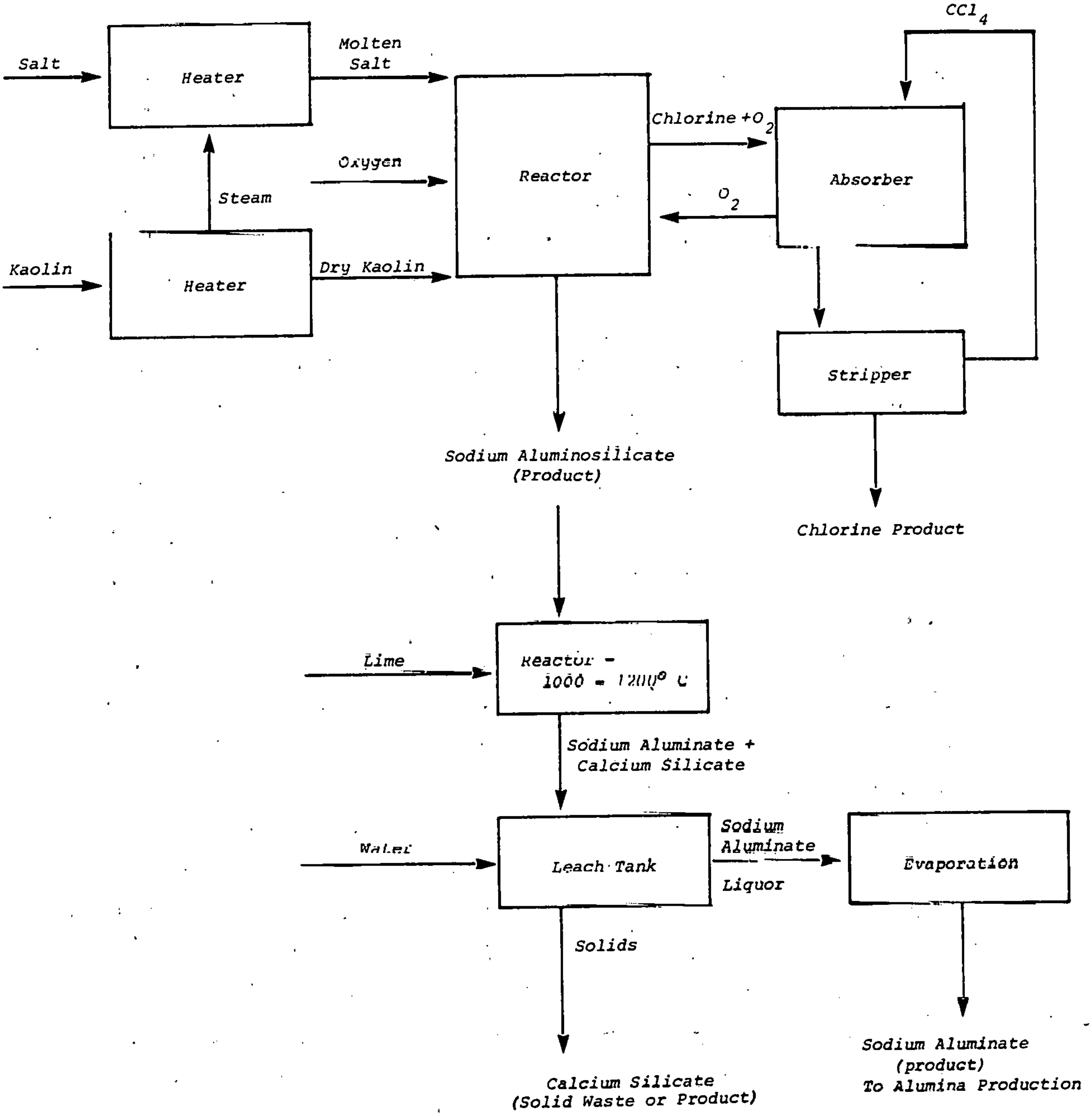
(1) For the initial heating of the salt and kaolin, two calcination chambers are required;

(2) For the reaction of calcined salt and kaolin with oxygen, a specialized high temperature reactor will be required. The liquid sodium chloride must be introduced so as to coat the calcined kaolin particles prior to their reaction with oxygen. Since the process was never developed past the bench scale laboratory stage, no specifications for reactor design are available;

(3) The absorber for recovery of chlorine from the oxygen-chlorine mixture leaving the reactor consists of a countercurrent scrubbing system with carbon tetrachloride as the liquid. The gas is first cooled and then passed through the scrubber where the chlorine is removed by the carbon tetrachloride. The oxygen passes unabsorbed through the scrubber and is returned to the reactor for further process use. The carbon tetrachloride-containing chlorine then flows into a heated chamber where chlorine is expelled into the gas phase and the carbon tetrachloride is recirculated to the scrubber. No data have been presented on concentrations of chlorine in the reactor exit gases or on recovery of chlorine from these dilute gas streams;

(4) The sodium aluminosilicate co-product from the high temperature reaction must also be further processed. This material must be conveyed to a second reactor (furnace) where it is mixed with lime and held at about 1,200°C to convert the sodium aluminosilicate-lime mixture into sodium aluminate and calcium silicate. This product mixture must then be cooled prior to further processing; and

Figure 29. Salt Kaolin Process



(5) The cooled sodium aluminate-calcium silicate product mixture is leached with water to dissolve the sodium aluminate. The resultant slurry is then filtered to remove the solid calcium silicate, which is discarded as a process waste. The resultant clear sodium aluminate liquor is evaporated to recover a solid product suitable for use in the Bayer alumina production process.

For the design of this process, the amount of data available on the different process steps varies considerably. From kinetic studies by Briner and Roth, and Dodson, it was found that the reaction rate increases by a factor of 2-2.5 per 100°C in the 700°-850°C range.[125] Further data from Trombe, et al., reveal that the reaction yield passes through a maximum at 850°C and then declines with further temperature increase.[126] At this temperature, reaction times of about 90 minutes would be required to obtain an 80 percent conversion. For the reaction of lime with the sodium aluminosilicate co-product similar rate data have not been presented. Also, no data on the detailed composition of the material leaving the second reactor (where lime is used) have been released. Therefore, further assessment of this process cannot be performed since the amount of unreacted salt and kaolin is unknown. The kaolin, presumably, would exit the process with the calcium silicate waste; however, the sodium aluminate co-product might require removal of residual salt values before it would be acceptable to the aluminum industry. The costs and energy involved in such a purification are at present unknown.

Due to lack of data, overall process energy usages cannot be reliably assessed at this point.

4.17.4 Economics

The detailed economics of this process depend critically on whether or not a marketable sodium aluminate can be recovered as a co-product. If a marketable co-product cannot be recovered, the process must bear the costs of land disposal of about 4 tons of sodium aluminosilicate per ton of chlorine generated. If one assumes a land disposal cost of approximately $10 per ton of material, then a $40 per ton of chlorine waste disposal penalty would result for the process if no marketable co-product is produced. This cost is sufficiently high to make the process uneconomical.

If a recoverable by-product sodium aluminate can be produced, then process economics are likely to depend on the following factors:

(1) The cost of generating sodium aluminate from the aluminosilicate;
(2) The cost of purifying or upgrading the aluminate for sale; and
(3) Waste disposal costs for the unwanted calcium silicate - about 3 tons of this waste will be generated per ton of chlorine produced.

Until further process information is developed on the conversion of sodium aluminosilicate to a marketable sodium aluminate, a reliable economic assessment of the overall process scheme cannot be made.

There are at least four other possible end uses for the sodium aluminosilicate which should also be explored as possible alternatives. In each case by-product cleaning to remove residual unreacted sodium chloride and kaolin would be necessary. These are:

(1) Sodium aluminosilicate is similar to the mineral nepheline syenite which is used as a source of alumina for glass. Further investigation of the aluminosilicate product as a substitute for that material is warranted. The 1970 market for nepheline syenite was about 700,000 kkg per year.

(2) Another possible use for the co-product is as an inert filler for plastic or as a raw material for the manufacture of roofing granules. The selling prices for both of these end uses, however, is expected to be low.

(3) The sodium aluminosilicate may also be convertible into zeolite type materials, which also may be marketable as absorbents, although the market is relatively small.

(4) There are additional processes in the literature for the extraction of sodium aluminate from silicoaluminate minerals. These should be examined to determine if better methods exist for the extraction of a more acceptable material for the aluminum industry.

According to the French inventors, kaolin is the specified raw material. At present, it is not known whether this process would operate with other raw materials such as common clay. Kaolin costs range from $30 per ton for the lowest grade up to $50 per ton for higher grade material. Common clay costs are in the $10-20 per ton range. Use of common clay in place of kaolin could markedly reduce process costs as 3.25 tons of clay are required per ton of chlorine produced.

Tables 13 and 14 show a partial cost analysis for two cases with this process:

(1) The case of no co-product recovery where all solid materials formed are assumed to be waste products.
(2) The case where sodium aluminate is recovered as a co-product in theoretical yield.

In both sets of costs, the following were assumed:

(1) The lowest grade of kaolin would be an acceptable raw material,
(2) Minimum energy usages based on a well-insulated reactor and material transport system,
(3) No cost for oxygen,
(4) No costs were assessed for return on investment, as plant construction materials are uncertain, and
(5) In Table 14, complete recovery of a lowest grade of co-product is assumed.

From these cost analyses, even without return on investment considerations, it can be seen that:

(a) if no co-product is recovered, the process is not competitive at current chlorine prices and
(b) with product recovery, at current prices the process is uneconomic if kaolin is used as the raw material.

If a cheaper clay could be used as a raw material with comparable yields and co-product recovery, the process is marginally viable.

4.17.5 Conclusion

Since complete product recovery and marketability along with the capability to use the cheapest clay is necessary for this process to be marginally economic, we assume this process is less attractive than those to be studied in Section 6.

Table 13

Salt Kaolin Process - No Co-Product

Materials	Cost/ton*	Tons Required	Total Cost
Salt	2.0	1.63	3.26
Kaolin	30.00 (FOBGA)	3.25 (dry basis)	97.50
Oxygen or air	0	---	---
Waste Disposal Penalty**	3.00	4.08	12.24
Total Materials Cost			$113.00

Product	Price/ton	Tons/Product	Revenue
Chlorine	$135.00	1.0	$135.00

Operating Costs/ton Cl

Materials and Waste Disposal	113.00	
Energy (@$2.50/10^6 BTU)	2.60	final calcination
(assuming minimal energy requirement)	2.08	initial calcination
Total Energy	$ 4.68	
Labor @$6.00/hr	$ 6.00	
Labor and Energy and Materials	$123.68	
Overhead and Misc. at 10%	12.37	
Taxes, Insurance at 2%	2.47	
Total Operating Cost	$138.52	

From above minimal costs, process loses $3.52 per ton of chlorine provided co-product is treated as a waste.

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* Prices - Chem. Mark. Rep. September 12, 1977

** Could range from $1-6 ton depending on site.

Note: In costs, no figure of return on investment is listed - if this cost is added, process becomes ever more uneconomical

Table 14

Salt Kaolin Process - Sodium Aluminate Co-Product

Materials	Cost/ton	Tons Required	Total Cost
Salt	2.00	1.63	3.26
Kaolin	30.00	3.25 (dry basis)	97.50
Oxygen	0	-	-
Caustic Soda	140.00	0.46	64.40
Lime	25.00	1.63	40.75
Waste Disposal Penalty	3.00	4.17	12.51
Total Materials Cost	-	-	$226.42

Products	Price/ton	Tons of Product	Revenue
Chlorine	135.00	1.0	135.00
Sod. Aluminate	10.00	2.32	162.40
Total Revenue	-	-	$297.40

Operating Costs/Ton Cl_2		
Materials and Waste Disposal Costs	226.42	
Energy (@ 2.50/10^6 BTU)	2.60	Final Kaolin Salt Reactor calcination
	2.08	Initial Calcinations
	11.35	Water Evaporation; drying, etc.
	4.68	Line Reaction
	20.71	Total Energy Costs
Labor @ 6.00 hr.	18.00	
Labor Energy and Materials	265.13	
Overhead, and Miscellaneous, at 30% and fixed costs	79.54	
Sub Total		
Total	344.67	

Note: In above calculations, no cost was assessed for return on investment. Also, lowest product grade was assumed. Two other assumptions made were: (1) Complete reaction of lime with sodium aluminosilicate and (2) Complete recovery of sodium aluminate.

4.18 DuPont High Temperature Silica and Salt Process

4.18.1 Process History

This high temperature method for preparing chlorine was invented by Wallace Ward of E.I. DuPont de Nemours and Company. The process patent was granted on August 30, 1960. After the patent had been secured the project was terminated. The experience on this process was only laboratory work. No further experimentation has been reported.

4.18.2 Scientific Basis

The reaction mechanism for this process involves the combination of sodium chloride ($NaCl$) and silica (SiO_2), with silicon tetrafluoride (SiF_4) acting as a catalyst to form chlorine. The reaction occurs in the presence of oxygen (O_2) and intense heat. Besides chlorine, the products are sodium silicate (Na_2SiO_3), an alkali metal silicate, and unreacted oxygen. Separation by condensation of the catalytic silicon tetrafluoride allows catalyst recycle. The reaction is as follows:

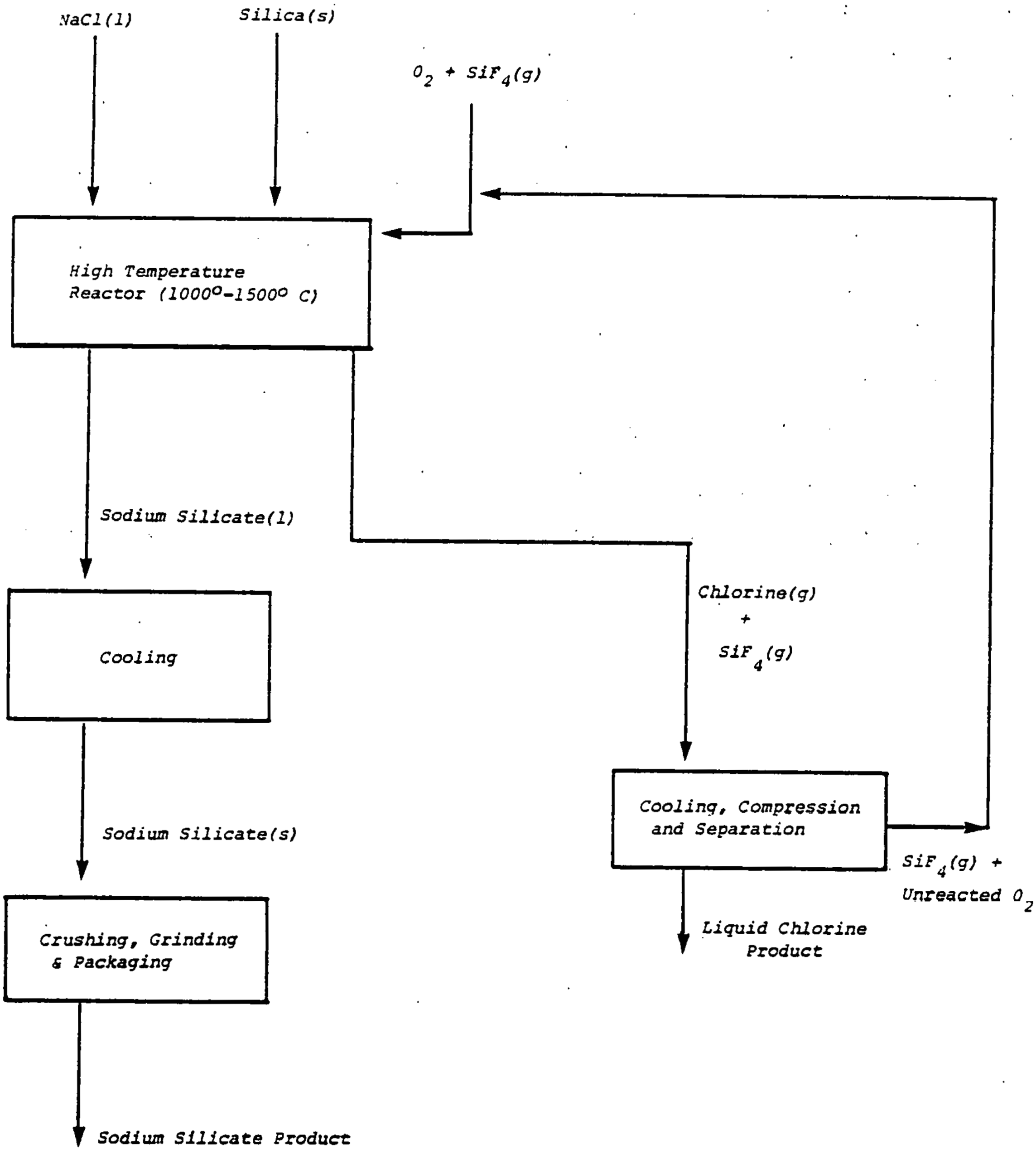
$$2NaCl + SiO_2 + SiF_4 \xrightarrow[1{,}000\text{-}1{,}500°C]{\frac{1}{2}O_2} Na_2SiO_3 + Cl_2 + SiF_4$$

The process thermodynamics show the reaction is endothermic with a ΔF for the reaction equal to 35.0 Kcal/mole at 25°C. Process temperatures necessary for the conversion range from 1,000°C to 1,500°C. The major discovery from this process is that silicon tetrafluoride is a highly active catalyst for chlorine preparation by thermal methods. Process kinetics were not provided in the patent.[128]

4.18.3 Engineering

The actual mechanism for the process, shown in Figure 30, requires a bed of silica particles (in the form of sand) maintained above a molten tank of sodium chloride. The high process temperatures cause not only the molten state, but also considerable vaporization. Silicon tetrafluoride and oxygen (either pure or in air) are then passed through or over the molten sodium chloride. This causes mixing with the vaporized components of the sodium chloride. The entire mixture is then passed through the heated silica bed. Upon completion of this reaction, the silicon tetrafluoride is separated by condensation and recycled.

Figure 30. High Temperature Chlorine Production Using Silicon Tetrafluoride



The sodium silicate by-product formed by the high temperature reaction is a viscous liquid. This liquid is retained in the molten sodium chloride pool and due to density differences and the insolubility of the sodium chloride and the sodium silicate in each other, easy separation of the by-product is achieved.

One advantage of this process is its use of relatively inexpensive raw materials and the formation of a valuable by-product. In addition to the preferred sodium chloride as a raw material, lithium and potassium chloride are possible alternatives. The silica used in the process may also be in both a pure or a combined form. Small particle sizes are usually used to provide the largest surface areas upon which reaction can occur.

Upon completion of a sample laboratory experiment, the yield from this process was found to be between 0 and 48 percent chlorine with the average concentration of chlorine at 28 percent. The reaction period was 220 minutes.

4.18.4 Conclusion

Three factors: (1) low process yield, (2) slow process rates, and (3) high temperature and energy requirements, make this method highly unsuitable for use.

4.19 Israeli Process for Chlorine from Magnesium Chloride

4.19.1 Process History

The Israeli process for chlorine production was originally designed to use the highly concentrated magnesium chloride brines present in the Dead Sea. This process was developed and patented by J. Kiperman and never developed past the laboratory stage.[129]

4.19.2 Scientific Basis

The process as described in the Israeli patent uses a diaphragm-type cell modified by introduction of a membrane prepared from asbestos, cloth and plastic. During electrolysis, the anode section contains a sodium chloride brine and the catholyte is a solution of magnesium chloride. As electrolysis proceeds, chlorine is liberated at the anode and magnesium hydroxide, formed at the cathode, deposits as an insoluble precipitate in the cathode section. This material is periodically recovered by an unspecified method, washed and dried. Thermodynamic requirements for this process are the same as for the diaphragm cell.

4.19.3 Engineering

According to the Israeli patent, operating conditions are as described below.

(1) The cathode compartment contains a 26 percent solution of magnesium chloride, while the anode section contains a sodium chloride brine of undisclosed concentration.

(2) Electrolysis is conducted at a distance between the steel cathode and membrane of >15 mm to enable the large flakes of magnesium hydroxide formed to settle to the bottom of the cell.

(3) The author claims that high purity magnesium hydroxide can be produced using Dead Sea brine as the catholyte solution if the 260 g/l concentration range is maintained.[129]

(4) Operating temperature is specified as 45°C and an operating voltage drop of 2.8 volts is quoted. Cell current densities are quoted at <0.08 amps/cm^2 and a 95 percent current efficiency is claimed.

4.19.4 Conclusion

This process is merely a modification of the diaphragm cell to enable a magnesium chloride brine to be used. Current densities used are low. A potential problem is continuous recovery of magnesium hydroxide from the cell during operation on a large scale. Also, the availability of high magnesium chloride content brines is limited. Currently in the United States almost all magnesium oxide and hydroxide produced are obtained by chemical treatment of seawater or natural brines. Due to the limited availability of magnesium chloride-based brines, the low current densities used and development of the membrane cell which allows better compartment separation than this diaphragm cell modification, this approach will not be considered in further discussions.

4.20 Hydrogen Chloride-Based High Temperature Arc Process

4.20.1 Process History

In this process chlorine is produced by a high temperature reaction of hydrogen chloride. The principal developer of this method was Irwin B. Margiloff of New York. His patent work was performed for Halcon International, Inc., of Delaware. The original patent claim was filed on September 17, 1962 and granted on June 7, 1966.[130] This process was not developed past the laboratory stage.

4.20.2 Scientific Basis

For the high temperature arc process, heat provided by a plasma generator is used to break down hydrogen chloride into chlorine and water. The plasma generator cracks water by means of an electrical arc. The resulting fragments (or plasma) are then allowed to recombine, thereby generating the high process temperatures. The temperature range for this reaction is 2,200°C to about 4,000°C.

While the reaction is progressing, oxygen is introduced into the system to combine with the hydrogen from the hydrogen chloride to form water. The oxygen can have impurities, although any contaminants will increase power costs. Air may be substituted for oxygen. Besides using water for the plasmas, other suitable substances are argon and nitrogen.

To optimize conversion, pressures range from 1.5 to 7 atmospheres, but yields decrease outside this range.

The products are cooled or quenched upon reaction. Water is preferable but other fluids, including hydrochloric acid, may be used. Quenching should be performed rapidly across the temperature interval between the reaction temperature and 300°C. Beyond this temperature normal cooling is performed. The chlorine product is dried and liquefied.

The process yield is about 45 percent at atmospheric pressure. Increased pressure, hydrogen chloride recycling, and oxygen purification all increased yields somewhat; however, they remained below 75 percent.

4.20.3 Conclusion

This process is not acceptable for commercial chlorine production because of low yields and extremely high temperature requirements. Inherent with high temperature requirements are high energy costs and high material costs. This process, though simple, is not economic.

5.0 ENERGY EFFICIENCIES OF CHLORINE MANUFACTURING PROCESSES

5.1 Energy Requirements

The energy requirement of a constant pressure chemical reaction is a function of enthalpies of raw materials, intermediates, products, co-products and by-products and entropy changes at various stages of the reaction. The total energy required for reaction is defined as the Gibbs free energy (ΔG). The value is calculated by:

$$\Delta G = \Delta H - T\Delta S$$

where

ΔH = enthalpy change (or heat of reaction),
T = temperature at reaction,
ΔS = entropy change.

For reactions in which a phase change does not occur the entropy term is usually quite small compared to the enthalpy term and may be neglected as an initial approximation. Actual industrial conditions (especially with respect to kinetics and conversion) are usually not fully known and energy requirements can only be projected by heat of reaction and entropy change calculations using available thermodynamic data. The situation is further complicated when the raw material needs pretreatment or the product needs post-treatment, thus requiring an additional consumption of energy. The heat of reaction (ΔH) is calculated using the following formulas.

(a) $\Delta H = \Sigma H$ products $- \Sigma H$ reactants

(b) Relative change in ΔH between temperatures T_1 and $T_2 = \int Cp\, dT$, where Cp is the heat capacity at constant pressure.

The actual energy requirement of an electrochemical reaction is more predictable than a non-electrochemical reaction. The inefficiency of an electrochemical reaction results mostly from the overpotential and the current used in generating the useless co-products and by-products. The electrical energy (E), consumption in an electrochemical process is given by

$$E = (v)(i)(t)$$

where a current 'i' flows for a time 't' through a potential gradient of 'v'.

A common pretreatment of raw material or post-treatment of product is the concentration of the solution entering or leaving a reaction. A minimum energy requirement can be computed as reversible process work (W min) under isothermal conditions as:

$$W\ \min = \int_{n_2}^{n_1} (\ RT \ln \frac{P}{P_O}\ )\ dn$$

where P = vapor pressure of dissolved solute of molar strength n

P_O = vapor pressure of pure water

In reality, the process is less than 10 percent efficient; this reflects a high degree of irreversibility and the non-ideal effect of solute in the evaporation process, which cannot be ignored. A practical approach is to use the heat of solution data to calculate the energy requirements. Most data available in the literature are for binary solutions. However, a pseudobinary approximation for a ternary system having a small amount of a third component is found to be quite satisfactory.

The following assumptions are made with respect to recovery and waste of heat.

a. Low grade heat produced by an exothermic reaction cannot be recovered.

b. High grade heat produced by a high temperature reaction (about 1,500°C) can be recovered to a maximum extent of 25 percent, by using a regenerative or a recuperative principle of heat economy.

c. The efficiency of a steam boiler is 80 percent.

d. The fossil fuel equivalent of electrical energy is 3 times the amount of electrical energy delivered to the chlorine process.

The energy requirement as determined from the above considerations does not necessarily reflect the energy-intensity of a process. A more generalized net energy balance that includes energy consumed in producing a raw material, or energy saved by generation of a co-product is more appropriate. Thus, the energy input to a raw material or saved by generating a marketable by-product will change the overall intensity. The energy requirement for producing a material was taken directly from literature sources or was calculated from the heat of combustion data.

5.2 Energy Analysis

In Table 15, net fossil fuel energy requirements are shown for the basic chlorine production processes presented in Section 4. For each process, the energy requirement per kkg of chlorine is projected from the Gibbs free energy calculation or is obtained from actual operating data.

5.2.1 Electrolytic Processes

Energy consumption in an electrolytic process is predominantly electrical. However, fossil fuel energy is assumed for generation of steam.

5.2.1.1 Mercury, Diaphragm and Membrane Cells

The energy requirements for the mercury, diaphragm and membrane cells are quite similar. The values presented in Table 15 are close to some of the values already reported in the literature. Any large variations from reported values are presumably due to the actual experimental conditions. For example, the diaphragm cells used by the Dow Chemical Company are reported to have higher energy efficiency than those used by others. The energy consumption and the energy efficiency of the electrical process in the mercury cell is higher than those in the diaphragm and the membrane cell. The total energy requirements in the membrane process are slightly lower than that in the diaphragm and the mercury processes. Unlike the diaphragm and the mercury processes, the membrane process does not involve any additional step for production of commercial grade sodium hydroxide. This additional step in the diaphragm process involves an additional consumption of energy. The heat generated in the additional step in the mercury process cannot be recovered, thus indirectly reducing the energy efficiency of the total process. Hydrogen obtained in all three processes partially contributes to energy conservation.

5.2.1.2 β-Alumina Membrane

The energy use is high and a large contribution comes from the steam generation step and the brine purification step.

TABLE 15. ENERGY REQUIREMENTS FOR THE BASIC CHLORINE PRODUCTION PROCESSES

Section Number	Process	Useful co-products or by-products	Energy required per kkg of chlorine (joules)	Energy credits for production of useful co-products (joules/kkg)	Energy penalties for production of raw materials (joules/kkg)	Net energy consumption (joules per kkg of product)	Remarks
4.0	Electrolytic Mercury Cell	NaOH, H_2	34.1 x 10^9	21.4 x 10^9	None	12.7 x 10^9	*Base case, current technology.
4.0	Electrolytic Diaphragm cell	NaOH, H_2	34.2 x 10^9	21.4 x 10^9	None	12.8 x 10^9	*Base case, current technology.
4.1	Electrolytic Membrane cell	NaOH, H_2	33.9 x 10^9	21.4 x 10^9	None	12.5 x 10^9	*
4.2	β-alumina Membrane	NaOH, H_2	45.4 x 10^9	21.4 x 10^9	None	24.0 x 10^9	
4.3	Downs Cell	Na	181.3 x 10^9	71.3 x 10^9	None	110.0 x 10^9	*
4.4	Shell HCl Oxidation	None	0.6 x 10^9	None	13.7 x 10^9	14.3 x 10^9	*Energy penalty reflects production of HCl via Hargreaves or Mannheim Process, no penalty should be taken if waste HCl is used. (See Section 6.3).

* Energy requirements presented were obtained from chlorine manufacturers or the literature, rather than calculated from thermodynamic information.

TABLE 15. (Continued)

Section Number	Process	Useful co-products or by-products	Energy required per kkg of chlorine (joules)	Energy credits for production of useful co-products (joules/kkg)	Energy penalties for production of raw materials (joules/kkg)	Net energy consumption (joules per kkg of product)	Remarks
4.5	Catalytic Oxidation of HCl using V_2O_5	None	1.5×10^9	None	13.7×10^9	15.2×10^9	Energy penalty reflects production of HCl via Hargreaves or Mannheim Process, no penalty should be taken if waste HCl is used. (See Section 6.3).
4.6	Kel-Chlor	None	0.4×10^9	None	13.7×10^9	14.1×10^9	*Energy penalty reflects production of HCl via Hargreaves or Mannheim Process, no penalty should be taken if waste HCl is used. (See Section 6.3).
4.7	Catalytic Electrolysis of HCl	H_2	14.5×10^9	3.7×10^9	13.7×10^9	24.6×10^9	Energy penalty reflects production of HCl via Hargreaves or Mannheim Process, no penalty should be taken if waste HCl is used. (See Section 6.3).
4.8	Direct Electrolysis of HCl	H_2	16.7×10^9	3.7×10^9	13.7×10^9	26.7×10^9	*Energy penalty reflects production of HCl via Hargreaves or Mannheim Process, no penalty should be taken if waste HCl is used. (See Section 6.3).

TABLE 15. (Continued)

Section Number	Process	Useful co-products or by-products	Energy required per kkg of chlorine (joules)	Energy credits for production of useful co-products (joules/kkg)	Energy penalties for production of raw materials (joules/kkg)	Net energy consumption (joules per kkg of product)	Remarks
4.9	Oxidation of $FeCl_3$ Salt Complex	None	5.8×10^9	None	None	5.8×10^9	Assumes use of waste ferric chloride and of thermally sealed reactor. Process has operational problems. To produce ferric chloride a penalty of 13.7×10^9 joules/kkg must be added to account for hydrogen chloride consumption.
4.10	ICI NH_4NO_3 Process	NH_4NO_3	-3.3×10^9	-2.0×10^9	4.4×10^9	2.5×10^9	Complex process analysis needed to determine appropriate credits, see Sections 5.3.2.2 and 6.4.
4.11	Modified Metaizeau Process	None	Unknown	None	None	Unknown	Process has operational problems.
4.12	Salt & SO_3	None	Unknown	None	None	Unknown	Process has complex chemistry and operational problems.
4.13	HCl & SO_3	H_2SO_4 (if purifiable)	13.7×10^9	None	13.7×10^9	27.4×10^9	Process thermodynamics, overall should be the same as for the Hargreaves Process (Section 6.3). Mercury contamination makes product sulfuric acid nonsaleable.

TABLE 15. (Continued)

Section Number	Process	Useful co-products or by-products	Energy required per kkg of chlorine (joules)	Energy credits for production of useful co-products (joules/kkg)	Energy penalties for production of raw materials (joules/kkg)	Net energy consumption (joules per kkg of product)	Remarks
4.14	HCl & H_2O_2	None	0.6×10^9	None	30×10^9	30.6×10^9	For peroxide production energy needs see F. A. Lowenheim & M. Moran, Industrial Chemicals, John Wiley & Sons, N.Y., 1975, pp. 487-495.
4.15	Vicksburg	KNO_3	1.5×10^9	0.8×10^9	16.5×10^9 (for NH_3)	17×10^9	*
4.16	Allied Salt & HNO_3	$NaNO_3$	1.9×10^9	None	16.5×10^9 (for NH_3)	18.5×10^9	Assumes sodium nitrate is not saleable.
4.17	Salt & Clay	None	8.4×10^9	None	None	8.4×10^9	Assumes no heat losses in process. Heat losses can be expected to double the value presented. Process has operational and solid waste disposal problems. Energy use for clay processing also excluded.
4.18	Silica & Salt (DuPont)	Na_2SiO_3	12.3×10^9	4.7×10^9	None	7.6×10^9	Assumes negligible heat losses for high temperature processes and excludes produce purification requirements.

TABLE 15. (Continued)

Section Number	Process	Useful co-products or by-products	Energy required per kkg of chlorine (joules)	Energy credits for production of useful co-products (joules/kkg)	Energy penalties for production of raw materials (joules/kkg)	Net energy consumption (joules per kkg of product)	Remarks
4.19	Israeli Process from $MgCl_2$	$Mg(OH)_2$ & H_2	24.1×10^9	18×10^9	None	6×10^9	Limited by availability of $MgCl_2$ brine.
4.20	High Temperature Arc	None	14×10^9	None	13.7×10^9	27.7×10^9	Energy calculations include dissociation energy for HCl, which is required as the initial process step. No process heat losses are assumed.

5.2.1.3 Downs' Cell

The operating voltage is the highest among electrolytic processes for manufacturing chlorine. This fact coupled with the requirement for maintaining the cell at high temperature makes the process energy inefficient.

5.2.1.4 Electrolysis of Hydrogen Chloride

The electrochemical energy requirement in catalytic processes is slightly lower than the direct electrolytic process. However, because of the operating advantages of the direct process, such as no regeneration requirements and ease of automation, this process is preferable to catalytic processes.

5.2.1.5 Israeli Process from Magnesium Chloride

The process appears less energy-intensive; however, major problems like scarcity of raw materials and operating disadvantages must be solved for commercial adaptability of the process. (See Section 4.19.3.)

5.2.2 Non-electrolytic Processes

Energy consumption in a non-electrolytic process is mainly in the form of steam or direct heat from fossil fuel combustion, although an amount of electricity is needed for running process accessories.

5.2.2.1 Oxidation of Hydrogen Chloride

Shell Hydrogen Chloride Oxidation and Kel-Chlor

Both processes have a low energy requirement, if waste HCl is available, and have other advantages which make them commercially competitive.

Catalytic Oxidation of Hydrogen Chloride Using Vanadium Pentoxide

Catalyst costs are high, the process is inefficient, and the energy consumption might be much higher than the theoretical value shown in the table because of process inefficiencies.

Hydrogen Chloride and Sulfur Trioxide Process

Although there is an advantage with respect to yield and operation, the energy consumption is high compared to other HCl processes as reflected in the table.

Hydrogen Chloride and Hydrogen Peroxide Process

The process energy requirement is nil; but based on the material cost, one would prefer to run the process backwards i.e., to produce expensive hydrogen chloride and hydrogen peroxide starting from relatively cheap chlorine.

High Temperature Arc Process

Because of high temperature requirements, the actual energy consumption must be higher than the theoretical value by several orders of magnitude. However, this increase cannot be estimated without knowledge of heat losses to the environment. Based on engineering judgment, we estimate that the energy efficiency of this process is only one to three percent.

5.2.2.2 Oxidation of Alkali Metal Chloride

ICI Ammonium Nitrate Process, Vicksburg Process, Salt and Nitric Acid Process

All three processes are similar and their energy consumption is low exclusive of the penalty imposed for using ammonia as a raw material in the ICI and Vicksburg processes. Further, the production of valuable by-products, ammonium nitrate in the ICI process, and potassium nitrate in the Vicksburg process, reduce the energy consumption on a total valuable product basis.

Oxidation of Ferric Chloride - Salt complex, Salt and Sulfur Trioxide process

Operational problems and possible high energy requirements make both processes commercially unacceptable.

Salt and Clay process

The process is marginal from the viewpoint of energy consumption and operational costs.

Silica and Salt process

The theoretically projected value for energy requirements might be misleading, as the conversion is believed to be low.

5.2.2.3 Oxidation of Iron Chloride

The only process known is the Metaizeau process or its modifications.

Metaizeau process

A theoretical projection for energy requirements has not been made since a multiplicity of reactions with unknown equilibrium conversions are involved. The actual energy requirement is believed to be high.

5.3 Critical Review

Based on the above analysis, three electrolytic processes and four non-electrolytic processes merit attention. These are reviewed as follows:

5.3.1 Electrolytic Process

5.3.1.1 Mercury Cell

The main advantage of the mercury cell is the high efficiency of the electrolytic process; the main disadvantage is the use of large amounts of electrical energy. R&D work is needed to recover some of the energy lost during the hydrolysis of sodium amalgam. The energy lost during the latter process could be considered equivalent to the energy lost in short-circuiting an electrochemical cell.

5.3.1.2 Membrane Cell

The membrane cell has the potential of replacing the diaphragm cell because of lower energy consumption and process simplicity. New membranes and electrodes for the cell are developing at such a rate that the values presented may be obsolete within a few years.

5.3.1.3 Israeli Process form Magnesium Chloride

The process looks lucrative from an energy point of view. The questions and answers related to raw materials and operations are the deciding factors for commercial implementation of the process.

5.3.2 Non-electrolytic Process

5.3.2.1 Shell Hydrogen Chloride process, Kel-Chlor process

Both processes are among the least energy-intensive of the processes studied. Further, there is a substantial return on investment with both processes which makes them economically attractive.

5.3.2.2 ICI Ammonium Nitrate process, Vicksburg process

The energy requirements shown in the table reflect no credits or penalties for use of ammonia or nitric acid, since the same amount of these raw materials would be required to produce ammonium nitrate. The energy penalty of 4.4×10^9 joules/metric ton of raw material is attributable to energy use in the Solvay process for production of ammonium chloride. The credit is for production of soda ash equal to the energy requirements to mine and refine the natural trona ore. These debits and credits are assessed because the Solvay process operation would be an integral part of raw material availability. Energy requirements were estimated from A.S. Robertson, Allied Chemical Corporation, "Alkali and Chlorine Production", Kirk-Othmer Encyclopedia of Chlorine Technology, 3rd Edition, John Wiley & Sons, 1978, pp. 866-883.

6.0 SELECTION AND FURTHER STUDY OF PROMISING PROCESSES

6.1 Use of Selection Criteria in Determining Processes for More Extensive Study

For any new chlorine generating process to enjoy widespread application, four criteria must be satisfied. These criteria, which involve technical, energy, environmental and institutional factors, are:

- the required process raw materials must be readily available in significant quantities (i.e., supply 5 percent or more of U.S. chlorine demand).
- the products of the process must be salable. Co-products which are non-marketable impose considerable waste treatment or disposal costs on the operations and probably have major environmental effects.
- energy requirements for the process should be no greater than those incurred with current technology using either the mercury or diaphragm cell processes.
- overall process economics should compare favorably with currently used technology. These economics are considerably affected by the process state-of-development, since RD&D costs and time should be charged against processes that are not presently commercial.

In applying these criteria to the different chlorine generating processes, the viability of each process becomes apparent. This relative viability is shown in Table 16 and is discussed below.

Raw Material Criterion

For any process to be adopted for large scale chlorine production, raw material reserves or production must meet projected demands. Since present U.S. chlorine production is about 9×10^6 metric tons/year, raw material(s) production for a new large scale process must be at least that order of magnitude to have a significant impact on chlorine production energy usage. For processes based on widely available sodium chloride, this criterion is easily complied with. For processes based on iron or ammonium chlorides, however, this criterion highlights a major weakness in the capability of the process to reduce energy usage by the chlorine industry significantly. Presently, the U.S. supply of iron chloride comes as a by-product of either

TABLE 16.

CRITERIA MATRIX FOR CHLORINE PRODUCTION PROCESSES

VALUE SYSTEM

4	▓
2	░
0	≡

CHLORINE PRODUCTION PROCESS	RAW MATERIALS			PRODUCT SALEABILITY			ENERGY USE				STATE-OF-DEVELOPMENT			
	NaCl	OTHER COMMON Cl - KCl & HCl	OTHERS	NaOH H_2 Cl-ALONE H_2SO_4	FREE METALS NO_2, NH_3	MISC. ALUMINO SILICAS Na_2SO_4	ELECTROLYTES	NITRATION/ CATALYTIC	THERMAL > 600°C	THERMAL < 600°C	PRESENT OR FORMERLY COMMERCIAL	PILOT/ DEMO.	LAB / BENCH SCALE	TOTAL POINTS
MEMBRANE CELL WITH OR WITHOUT O_2 CATHODE	▓			▓			░				▓	░		14 - 12
JAPANESE MOLTEN SALT PROCESS	▓			▓			░							10
DOWNS CELL	▓				░				≡		▓			10
HCl OXIDATION ($CuCl_3$ CATALYST)		░		▓				▓				░		12
$CuCl_2$ + RARE EARTH CATALYSTS (BASF & ICI)		░		▓				▓					≡	10
† KEL - CHLOR - MW KELLOG		░		▓				▓			▓			14
WESTVACO PROCESS ($CuCl_2$ ELECTROLYSIS)		░		▓			░							10
SHROEDER PROCESS ($NiCl_2$ ELECTROLYSIS)		░		▓			░						≡	8
SOUTH AFRICAN PROCESS ($MnCl_2$ ELECTROLYSIS)		░		▓			░						≡	8
++ MOBAY - DIRECT ELECTROLYSIS		░		▓			░				▓			12
$FeCl_3$ OXIDATION (DUPONT, CYANAMID)			≡		░					▓		░		8
NH_4Cl + HNO_3 OXIDATION (ICI)	▓		≡		░			▓					≡	10 - 6
NH_4Cl IRON OXIDE CATALYSIS (SOLVAY)			≡		░			▓					≡	6
DUPONT (SO_3 + NaCl)					░					▓			≡	10
ICI (SO_3 + HCl)		░				≡				▓			≡	6
OXIDATION OF HCl WITH PEROXIDE			≡	▓						▓			≡	8
VICKSBURG (HNO_3 + KCl)		░			░			▓			▓			12
U. S. DEPARTMENT OF AGRICULTURE (NO_2 + KCl + O_2)		░			░			▓						8
ALLIED (HNO_3 + NaCl)	▓					≡		▓			▓			12
FRENCH KAOLIN PROCESS	▓					≡			≡				≡	4
DUPONT (SILICA + NaCl + O_2 + SiF_4)	▓					≡			≡				≡	4
ISRAELI - ELECTROLYSIS OF DEAD SEA BRINE			≡		░		░						≡	4
HIGH TEMPERATURE ARC PROCESS		░		▓			░						≡	8

NOTES :

† FOR CATALYTIC HCl CONVERSION THE KEL - CHLOR PROCESS GENERALLY OPERATES AT LOWER TEMPERATURES, WITH HIGHER YEILDS AND HENCE HAS BEEN SOLELY COMMERCIALIZED.

++ OF THE HCl ELECTROLYTIC PROCESS, THE MOBAY PROCESS OFFERS GREATEST EASE OF AUTOMATION AND OPERATION AND HENCE WAS SELECTED FOR COMMERCIALIZATION OVER ITS COMPETITORS.

* MEMBRANE CELL WITHOUT OXYGEN CATHODE.

** MEMBRANE CELL WITH OXYGEN CATHODE.

steel pickling or production of titanium dioxide via the chloride process. Total quantities generated from both sources are only on the order of 200,000 metric tons/year. This represents a chlorine production equivalent of less than two percent of total annual production. Ammonium chloride is recovered as a by-product of the Solvay process soda ash production. The Solvay process is used at only one U.S. site, limiting the amount of ammonium chloride which can be generated to 500,000-700,000 metric tons/year. This also represents a chlorine production equivalent of about five percent of total annual production. Other common chlorine sources, such as concentrated hydrogen chloride and potassium chloride, are readily available in certain local areas and could provide a significant amount of chlorine raw material.

Product Salability

Product marketability can significantly influence wide scale application of certain processes. Co-products such as caustic soda or hydrogen could be marketed in millions of tons per year quantities. However, other proposed co-products such as magnesium and sodium metals, sodium nitrate, sodium aluminosilicate and calcium silicate presently have limited markets. For sodium metal, for example, the available market is saturated by the output of five operating Downs' cell plants. Similarly, current magnesium needs are being met by presently operating electrolytic plants. For sodium nitrate, no markets exist although some fertilizer and fireworks manufacturers use sodium nitrate as a raw material. In fact, one plant generating chlorine with sodium nitrate as a co-product was closed about a dozen years ago due to the lack of a sodium nitrate market. Materials such as sodium aluminosilicate or calcium silicate have limited markets at best. There is some hope that the aluminosilicate might be further processed to recover alumina. No marketable co-product appears to exist for a calcium silicate co-product.

Energy Requirements

Process energy needs and efficiencies will further restrict the number of processes competitive with current technology. Proposed schemes which have high energy requirements such as high temperature processes may not be feasible, particularly if good yields have not been obtained under such conditions. This consideration allows rejection from further consideration of processes which compare unfavorably from an energy-consumption standpoint with current technology (see Section 5). These are:

(a) generation of chlorine by the reaction of salt and silica in the presence of silicon tetrafluoride at temperatures of 1,000-1,500°C. Poor yields have been obtained from this proposed scheme.

(b) generation of chlorine by the reaction of gypsum, salt and oxygen at 1,200°C. Yields are low, energy requirements are high and the co-product, calcium silicate, has a limited, if any, market.

(c) a similar argument can also be made for the French kaolin process, where long residence times at over 1,000°C are required to obtain only 80 percent yields. Also, the product, sodium aluminosilicate, may have marketability problems, although further verification is needed.

(d) high energy requirements and low yields allow rejection of a process based on high temperature (1,200°C) oxidation of magnesium chloride to chlorine and magnesia.

(e) a number of older processes involving oxidation of hydrogen chloride can similarly be dismissed based on poor yields (energy:production ratio). These include:

(1) the old Deacon process and certain predecessor processes all based on the oxidation of hydrogen chloride over iron or copper chloride impregnated solid catalysts.

(2) a German and British modification of the Deacon process which replaced the halide catalysts with a vanadia-based catalytic system. Reported yields were low (<50 percent).

(3) various hydrogen chloride electrolytic type processes which include the Westvaco process, based on the electrolysis of cupric chloride containing hydrochloric acid solutions, a South African process using manganous chloride containing hydrochloric acid solutions, and the Shroeder process, where hydrogen chloride is first reacted with nickel to yield nickel chloride in solution and hydrogen. Electrolysis of this solution then recovers the nickel and generates the chlorine product. All three processes have low conversion efficiency or scale-up and automation difficulties.

Research, Development and Demonstration (RD&D) Economics

Economics are influenced by the process state of development. Research, development and demonstration activities will be charged to a production technique and compared to energy savings provided by the process. If the present value of energy savings is less than RD&D charges, further development of the process is not warranted. In addition, RD&D efforts take considerable time, delaying introduction of commercially-available units that would reduce energy consumption. Conversely, processes presently commercially available can have an immediate impact on energy use in the chlor-alkali industry. No processes, however, will be rejected solely because they have not progressed past laboratory scale.

A detailed economic treatment for each of the processes which could not be rejected based on the first three considerations will be needed to determine which additional schemes can be dismissed on economic grounds alone.

Table 16 summarized how each of the twenty basic processes compares to the four criteria. A numerical rating system was used to rank the processes based on 4 points for a favorable comparison with a criterion, 2 points for an acceptable condition relative to a criterion and 0 points for an unfavorable characteristic. The results are shown in the last column of Table 16. When the rankings were combined with an elimination system for processes which cannot produce significant amounts of chlorine, have energy requirements greater than current technology, or produce unacceptable solid waste streams, the processes which warrant further investigation were revealed. These processes are the membrane cell (with and without hydrogen or oxygen electrodes), the Shell process, Kel-Chlor, Mobay (direct hydrogen chloride electrolysis), and the ammonium chloride/nitrogen dioxide low temperature process.

6.2 Membrane Cell

6.2.1 Introduction

The most promising area described in Section 4 is the development of the membrane cell with or without the additional modifications, such as a catalytic hydrogen or oxygen cathode. In this section we shall consider these three options and their economics.

6.2.2 Economic Considerations

The latest published costs for the membrane cell compared with the diaphragm and mercury cell processes are those released by Asahi Chemical Company in 1977. These are listed in Table 17, along with additional projected costs for the membrane cell using either a catalytic hydrogen or oxygen cathode. Costs for the membrane cell alone are currently competitive with present technology. Use of either an improved hydrogen evolution electrode (saving about 0.3 volts) or an oxygen cathode (saving about 0.8 volts) would provide considerable savings. In these cost estimates, the salt costs used were those for pre-purified evaporated salt. Most U.S. producers currently employ brine as the raw material and then pre-purify this material on-site. This lowers the costs to about the same level. Additional costs of $3.00 per ton were added for licensing fees or additional fixed charges for the capital costs for the improved hydrogen evolution electrodes or oxygen cathodes.

Even with added costs for improved electrodes, improved versions of the membrane cell using either a superior hydrogen evolution electrode or an oxygen cathode could further lower production costs. Even if the fuel value of the hydrogen is considered, these results show that the oxygen cathode is worthy of serious development.

6.2.3 Overall Outlook

Of all the processes investigated in this study, the membrane cell offers the greatest potential for an energy efficient process which can be developed within a short time frame. Further improvements in this scheme, such as the hydrogen generation or oxygen reduction electrodes, can be added to the system without the need for extensive process redesign. In the hydrogen evolution cathode area, some of these improvements could rapidly be achieved by coating the electrodes with films of noble metals, cobalt or nickel. This would considerably lower the hydrogen evolution overvoltages by 0.2-0.3 volts without the need for extensive electrode system redesign. Beyond this, even further improvements can be envisioned. For example, the use of an activated palladium hydrogen diffusion electrode would eliminate most of the remaining hydrogen evolution overvoltage and at the same time allow for direct genera-

Table 17

Cost of Raw Materials and Utilities of Membrane Cell, Mercury Cell and Diaphragm Cell
[Cost per metric ton (m-ton) NaOH (100%) and 0.89 metric ton Cl_2; Japanese base December 1976][1]

Technology		Asahi Chemical's Membrane Process		Membrane Cell W. H_2 Cathode (projected)		Membrane Cell WO_2 Cathode (projected)		Mercury Process (Metal Anode)		Diaphragm Process (Modified Asbestos Expandable Anode)	
Raw Material	Unit price	Consumption	Amount ($/m-ton)	Consumption	Amount ($/m-ton)	Consumption	Amount ($/m-ton)	Consumption	Amount ($/m-ton)	Consumption	Amount ($/m-ton)
Salt	21.34$/m-ton (19.42/ton)	1.495	31.90	1.495	31.90	1.495	31.90	1.495	31.90	1.585	33.82
Electrolysis Power	2.88¢/AC-KWH	2,786 (@3.75v)	80.24	2,563 (@3.45v)	74.33	2,201 (@2.95v)	63.83	3,211 (@4.4v)	92.48	2,371 (@3.5v)	68.28
Other Chemicals			4.00		4.00		4.00		7.46		2.72
Power for Motor	2.88¢/KWH	95	2.74	95	2.74	95	2.74	86	2.48	210	6.05
Steam	7.72$/m-ton (7.02/ton)	0.7	5.40	0.7	5.40	0.7	5.40	0.1	0.77	3.6	27.79
Other Utilities			0.10		0.10		0.10		0.16		0.16
Other cost (Lease, membrane and royalties)			15.00		18.00		18.00		5.32		10.63
Debit for generation of H_2*							.32				
Oxygen @ 20.00 ton						.45 tons	9.00				
Total			139.38		136.47		135.29		140.57		149.45

*Valued at 3.00/10^6 BTU of fuel value tion of atomically pure hydrogen in the cell. The hydrogen so produced and purified by diffusion through palladium or a palladium-rich alloy would contain no entrained salt or caustic. The danger of hydrogen and chlorine mixing in the cells would be completely eliminated. Hydrogen diffusion electrodes have already been developed for use in the alkaline fuel cell area.

If an oxygen cathode is used in place of the hydrogen evolution electrode, further developments are also possible. Recent studies of materials such as lanthanum cobalt oxide-type perovskite materials indicate that it may be possible to develop relatively inexpensive oxygen cathodes, which do not employ noble metals and increase the voltage savings up to 1.0 volts.[2]

In summary, of all the alternative processes studied, the membrane cell and its possible modifications offer the greatest promise for development of a more energy efficient chlor-alkali process suitable for general use. Further reductions in energy usage are possible and should be encouraged. Note that the improved electrode technologies are applicable to the diaphragm cell as well.[3]

6.2.4 Further Assessment Needs

At this stage, a need has developed for a comparative assessment of the benefits of several of the proposed electrode improvement schemes described above. Specifically, it may now be in order to perform a cost-benefit analysis of the following three specific schemes:

(a) The membrane cell with a nickel, cobalt or noble metal coated hydrogen evolution electrode saving 0.2 to 0.3 volts.

(b) The membrane cell with a palladium based hydrogen diffusion electrode saving ∿ 0.4 volts, and

(c) The membrane cell with an oxygen cathode, of the lanthanum cobalt oxide type saving 0.8 volts, but requiring oxygen and not generating hydrogen. Factors such as electrode fabrication costs, anticipated replacement rates and detailed operating characteristics need to be studied and the overall economic benefits of each of the above approaches then need to be compared. Sufficient information on all three approaches should be available from a combination of chlor-alkali industry information and past fuel cell program data to make a meaningful analysis.

6.3 Processes Based on Hydrogen Chloride

The several hydrogen chloride-based processes chosen from Table 16 were previously presented as economically marginal because of the limited supply of hydrogen chloride as a raw material. In this section, the overall economics of generating hydrogen chloride from salt (NaCl) via the Hargreaves and Mannheim processes will be studied for subsequent addition to hydrogen chloride-based processes. The initial discussion will present the overall economics of these hydrogen chloride production processes. The results of the economic study will then be applied to the two most advanced hydrogen chloride processes - Kel-Chlor and the electrolytic Uhde (Mobay) Process.

6.3.1 Conversion of Salt to Hydrogen Chloride

Salt (NaCl) is converted commercially to hydrogen chloride by either the Hargreaves or Mannheim processes. In the Hargreaves process salt, sulfur dioxide, oxygen and water are reacted at about 850°C to yield hydrogen chloride and an impure sodium sulfate co-product. The Mannheim process is similar, except sulfuric acid is used in place of the sulfur dioxide, oxygen and water. The energy requirements for the two processes are about the same. The overall process chemistry for each process is:

(a) Hargreaves

$$2NaCl + SO_2 + H_2O + 1/2\ O_2 \rightarrow 2\ HCl + Ha_2SO_4$$

(b) Mannheim

$$2\ NaCl + H_2SO_4 \rightarrow 2\ HCl + Na_2SO_4$$

Table 18 presents the overall economics for the Mannheim Process. No energy costs were assumed for cleanup of the sodium sulfate product generated. In both processes, the solids product yield is 94 percent sodium sulfate, 3 percent sodium chloride and 3 percent sodium bisulfate. For most purposes, such a product normally would require upgrading by recrystallization from solution. This would add an additional 2×10^6 BTU/ton of product to the energy requirements. It can be seen that these processes are uneconomical for use except in fully depreciated facilities under special circumstances. However, Climax Chemical Company has recently developed a fluidized bed roaster which significantly reduces the energy requirements.[4]

According to the U.S. Bureau of the Census, there are presently three

TABLE 18 Economics For The Mannheim Process[5,6]

Raw Materials	Tons Required/tons Na_2SO_4	Price Per Ton	Cost
Sulfuric acid	0.75	\$ 47	\$ 35.25
Salt	0.835	10.00*	8.35
		Total	\$ 43.60

Products	Amount Produced/ton Na_2SO_4	Value/ton	Total Value
Sodium Sulfate	1	\$ 55.00+	\$ 55.00
HCl (31% aqueous solution)	1.575	35.00**	55.30
			\$ 110.30

Raw Material Costs/ton Na_2SO_4	\$ 43.60
Energy @ 13×10^6 BTU/ton Na_2SO_4	39.00
Subtotal	\$ 82.60
Total Operating and Maintenance Expenses	10.00
Return of investment and interest	10.00
Environmental Costs †	19.60
Subtotal	\$ 122.20
Credits for Products Sold	110.30
Deficit	\$ 11.90/ton Na_2SO_4

* Note \$10 was taken as salt cost instead of the presently quoted \$21.00 per ton assuming the facility had its own brine wells as a source of reasonably pure salt.

\+ Assuming high grade material, lower grades discounted to as low as \$46 per ton.

** Price quoted for 31 percent aqueous HCl.

† For removal of SO_2 and SO_3 from process vent gases and for neutralization of acidic process washwaters prior to discharge. Here, 0.14 tons of 50 percent NaOH @ \$140.00 per ton is required for neutralization purposes. If Na_2SO_4 itself must be disposed of costs will be \$6 per ton higher.

active Hargreaves or Mannheim plants in the United States. The status of these is shown in Table 19.

TABLE 19. Listing of Hargreaves and Mannheim Process Facilities in the United States.

Plant	Process	Capacity HCl (tons)	Year	Status
Morton Salt Weeks Island, Louisana	Hargreaves	68,000	1950	Fully depreciated
Climax Chemicals Monument, New Mexico	Mannheim	54,000	1946	Fully depreciated
Hercules, Inc. Hopewell, Virginia	Mannheim	7,000	1945	Fully depreciated

Two of the existing facilities are in isolated areas, close to cheap sources of salt, and need hydrochloric acid which is not locally available. All of three facilities are also adjacent to sulfuric acid plants or Frasch sulfur operations, providing a cheap source of sulfuric acid or sulfur dioxide.

According to the U.S. Bureau of the Census, in 1976, the total U.S. capacity for sodium sulfate production (all grades) was 1,486,000 TPY.[7,8] Production, however, was only 1,232,000 TPY or 82 percent of capacity. The Hargreaves and Mannheim processes, however, produced only 133,221 tons of sodium sulfate versus potential capacity of 185,000 TPY. This is 72 percent of capacity, and is evidence that the three plants may not be able to dispose of all of the sodium sulfate.

Sodium sulfate, as was discussed in section 4, is generated as a coproduct from a wide variety of chemical processes. Much sodium sulfate is also generated by processing natural brines in West Texas, Utah and California. In addition, other natural sources are known in a number of western states which are currently not exploited due to a lack of markets. Thus, it can easily be understood that a current expansion in production of low grade sodium sulfate would rapidly lead to a situation where the produced material (particularly at lower grades) would be disposed of as a waste. From Table 18, if disposal of sodium sulfate is required, then the manufacture of hydrogen chloride via these processes becomes totally uneconomical since the value of the hydrogen chloride generated cannot compensate for raw material and energy costs. In summary, a large scale use of the Hargreaves or Mannheim Processes for generation of hydrogen chloride as a raw material for chlorine production is not likely to occur for economic reasons.

6.3.2 Hydrogen Chloride Conversion Processes

Section 4 results showed that only two hydrogen chloride-based processes have enjoyed long lived commercial use. These are the Kel-Chlor and Uhde Processes. This section presents further economic information on these processes.

6.3.2.1 Kel-Chlor Economics

For Kel-Chlor, the cost data are provided in Table 20.

Converting power and thermal energy requirements to a common basis, Table 20 provides an equivalent electrical energy need of 118 KWH per ton of chlorine produced.

6.3.2.2 Uhde Process Economics

For the Uhde (Mobay) Process the cost data are provided in Table 21.

6.3.2.3 Economic Comparison of Uhde and Kel-Chlor Processes

Comparison of the cost data in Tables 20 and 21 shows that the energy requirements are much lower for the Kel-Chlor process since it is a non-electrolytic process. However, the Uhde Process capital costs are lower. While full capital costs of both processes have not been released, a simple comparison of the equipment used for both schemes (Table 22) reveals that higher capital costs would be involved for a Kel-Chlor operation. The current Kel-Chlor plant also has major corrosion problems.

6.3.3 Other Hydrogen Chloride-Based Processes

Section 4.4 presented the Shell process, which catalytically converts hydrogen chloride and oxygen into chlorine and water. The cost data presented showed this process to be economically competitive. However, no commercial facility was developed and the only relevant experience was from a small pilot

TABLE 20. Kel-Chlor Process Economics[9]

Feed Materials	Units per Ton of Cl_2 Product
HCl (100 percent)	1.03 ton
Oxygen (99.5 percent)	0.227 ton
NaOH (50 percent)	1 pound
H_2SO_4 (98 percent)	36 pounds
H_2SO_4 (80 percent)	42 pounds
Utilities	
Power	52 KWH
Cooling water (20°F rise)	12,900 gallons
Boiler feed water	24 gallons [2.2×10^5 BTU] energy required
Process water	1 gallon
Other	
Operating Labor	2 men/shift plus supervisor
Maintenance Labor	2 percent capital cost/year
Maintenance Materials	3 percent capital cost/year

TABLE 21. Uhde Process Economics
Operating Costs for the Uhde Process[10]

Raw Materials	Usage per Ton Cl_2
HCl (100 percent)	1.044 tons
Electricity	1600 KWH
Caustic (100 percent NaOH)	36.9 pounds
96 percent H_2SO_4	33 pounds
Utilities	
Plant Water	6.0 gallons
Cooling Water	4,820,000 gallons
Electricity	88 KWH
Nitrogen	0.8517 SCF
Plant Air	0.6417 SCF
Steam	30,000 pounds
Miscellaneous	
Operating Labor (men/shift not including supervisor)	3
Maintenance Labor (percent Capital Investment per year)	2.5
Maintenance Materials (percent Capital Investment per year)	4

In addition to chlorine, the additional products obtained from this operation are:

Product	Amount per ton Cl_2
70 percent H_2SO_4	3.4 gallons
Sodium hypochlorite	254 pounds
Hydrogen @ 99 percent recovery	10,591 SCF

The above figures were presented for a 200 TPD facility currently in operation.

TABLE 22. Major Equipment Needs for Kel-Chlor and Uhde Processes

A. Kel-Chlor (Major items)

1. Absorber and oxidizer columns (nitric acid resistant)
2. Stripper columns (nitric acid resistant)
3. Vacuum distillation system (nitric acid resistant)
4. Fractional distillation hardware
5. Drying tower for chlorine and compressors
6. Process refrigeration units (acid resistant)

B. Uhde

1. Electrolytic cells
2. Drying towers for chlorine and compressors

scale operation still operating in the Netherlands. Compared to Kel-Chlor, this catalytic oxidation process is almost as energy efficient, has lower capital costs and higher operating costs.

6.3.4 Summary of Hydrogen Chloride-based Processes for Chlorine Production

From the preceding sections, several points may be made with respect to generation of chlorine from hydrogen chloride.

- Generation of large quantities of hydrogen chloride from salt via either the Hargreaves or Mannheim Process is not economically viable except perhaps in special circumstances. The major problem is the limited markets for the impure sodium sulfate co-product. Current chlorine selling prices cannot support the $77 per ton hydrogen chloride production costs minimum from either a Hargreaves or Mannheim Process.
- The amount of hydrogen chloride currently available is limited. Most of the hydrogen chloride (about 93 percent) is formed as a by product of organic chlorination reactions. For hydrogen chloride, the current demand-supply situation is as follows:

  Total 1976 Production = 2,495,000 tons
  Amount of product converted to chlorine = 288,000 tons
  Total amount of unconverted hydrogen chloride = 2,208,000 tons

  The remaining 2.2 million tons per year of hydrogen chloride serves the market needs for this material. No more than a small percent of this material is available as a raw material for increased chlorine production. In fact, it is noted that about 74,000 tons of hydrogen chloride were produced directly from chlorine in 1976.
- As a result of the economic non-viability of the processes for hydrogen chloride generation from salt, and the limited supplies of hydrogen chloride available from other sources, it is projected that only a small percentage (<10 percent) of the total U.S. chlorine production could come from hydrogen chloride-based processes. Only significant cost reductions for the generation of hydrogen chloride from salt can increase the contribution of hydrogen chloride processes. No efforts in this area have been noted during this study.

6.4 Chlorine from Ammonium Chloride and Nitrogen Dioxide

6.4.1 Introduction

Section 4.10 presented a process, originally developed by ICI, which reacted nitrogen dioxide with ammonium chloride to yield chlorine and an ammonium nitrate co-product. This process was never carried past the laboratory stage, even though thermodynamic calculations show that the energy requirements for this scheme could be negligible.

The original work performed on the process demonstrated that the reaction of gaseous nitrogen dioxide with solid ammonium chloride under ambient conditions yielded a solid product containing at least 97 percent ammonium nitrate and gaseous nitrosyl chloride (NOCl).[11,12] No work was reported on the subsequent conversion of nitrosyl chloride to chlorine, as would be required in a full scale process.

This lack of reaction kinetics information necessitated that the process be examined from a theoretical viewpoint. A possible process using such a scheme is shown in Figure 31.

In this conceptual process, solid ammonium chloride reacts with nitrogen dioxide under ambient conditions. Solid unrefined ammonium nitrate is recovered, recrystallized to recover pure material, dried, prilled and packaged. Waste liquors from the recrystallization are evaporated with resulting solids returned to the initial reactor.

The nitrosyl chloride co-product from the initial reaction is mixed with oxygen and catalytically oxidized to nitrogen dioxide and chlorine. This product mixture is then fractionally distilled to recover pure nitrogen dioxide, which is recycled to the initial reactor and chlorine. The residual nitrosyl chloride-chlorine mixture is again mixed with oxygen and catalytically oxidized to nitrogen dioxide and chlorine. This mixture is then separated again by fractional distillation, with the nitrogen dioxide recycled to the initial reactor and the purified chlorine compressed and liquified for sale.

6.4.2 Projected Process Economics

Using the process scheme outlined in Figure 31, capital costs for 100 TPD and 1000 TPD chlorine plants were developed. Installed costs were estimated based on the principal pieces of equipment listed in Table 23.

Figure 31. Ammonium Chloride Low Temperature Process

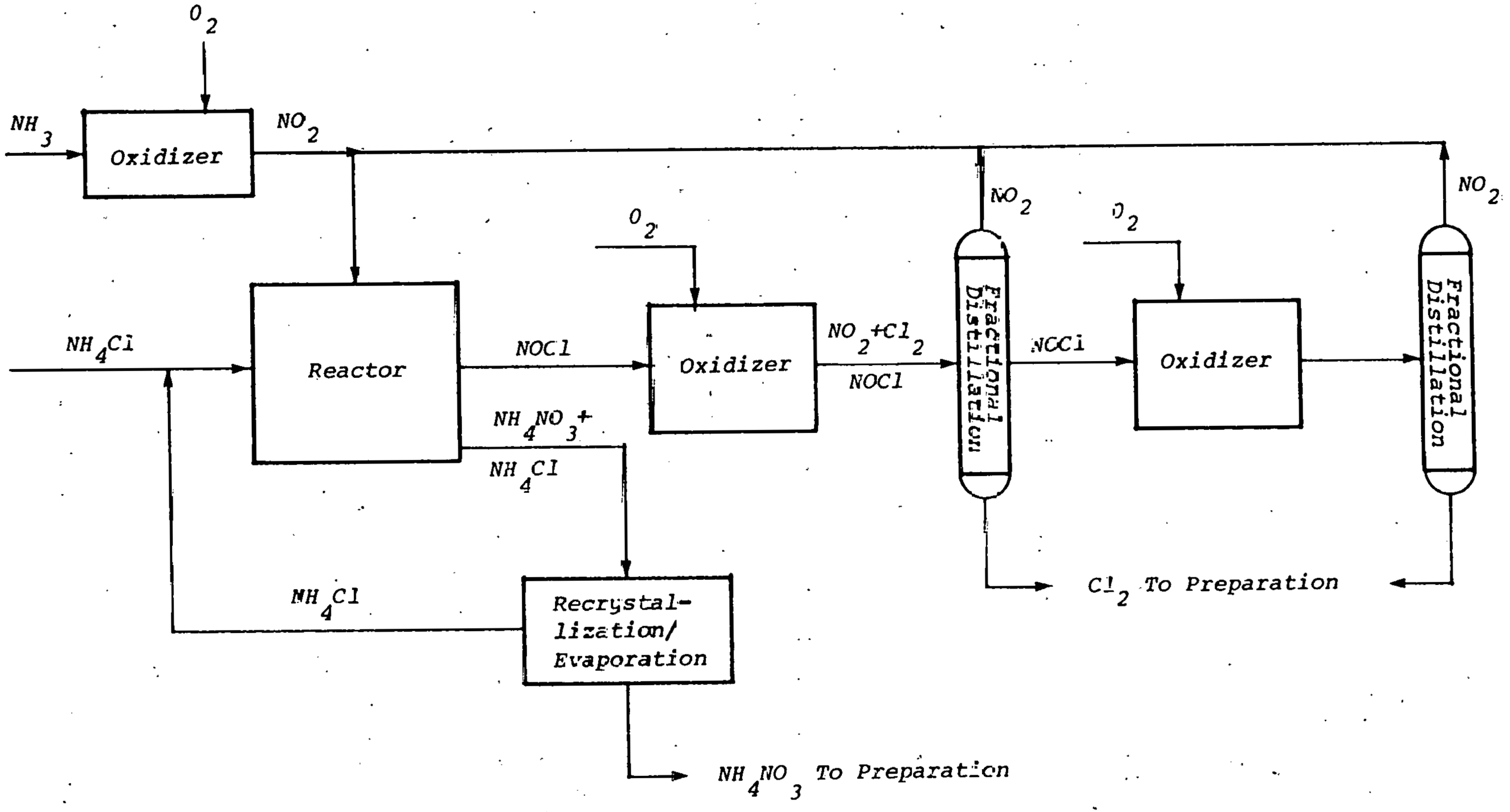


TABLE 23. Equipment Used In Ammonium Chloride Low Temperature Process

(a) One teflon lined gas-solids reactor
(b) One recrystallization system consisting of a dissolving tank, pumps, an evaporator, crystallizer and centrifuge in series.
(c) A second evaporator, crystallizer, centrifuge and pumps needed to recover values from the residual recrystallization liquors.
(d) One drier and prilling tower for the ammonium nitrate product.
(e) Two packed column teflon lined catalytic reactors.
(f) Two teflon lined fractional distillation columns.
(g) The necessary lined (where appropriate) and unlined piping needed to connect the major equipment items.

A capital cost developed for these items (1978 basis) totaled $21 million. Using an exponential scaling factor of 0.90, a capital cost of $167 million was then estimated for a 1000 TPD chlorine plant using such technology. Operating cost information developed for a 100 ton per day is presented in Table 24.

A similar analysis was performed for a 1000 TPD chlorine plant. Under those conditions, with a $90/ton chlorine price, a breakeven point of 84% and a return on investment of 3.7% (90% capacity) were calculated. At $140/ton of chlorine, the breakeven point for a 1000 TPD chlorine plant becomes 57% and the return on investment at 90% capacity becomes 30%.

This analysis shows the process may be marginal at current chlorine prices and it becomes attractive as chlorine prices (and energy costs) rise. Indeed, the process energy requirements estimated here, for product drying and recovery are only about 10 percent of current chlorine production technology.

6.4.3 Availability of Raw Materials

As the projected economics for this process appear favorable, the next matter to resolve is the availability of raw materials. Nitrogen dioxide (NO_2)

Table 24.

Operating Costs (per ton Cl_2) - 100 TPD Plant[13]

Variable Costs (V)		Cost/Ton Cl_2
Raw Materials	NH_4 @ 40.00/Ton	64
	NO_2 @ 110.00/Ton	62
Power @ $.026/KWH		5
Fuel @$3.00/$10^6$ BTu		9
Labor - 4 men/shift @ $6.30/hr		6.30
Supervicion - 1 foreman/shift @$8.50/hr		2.10
Maintenance - 100% Total Labor Costs		8.40
Overhead · 50% Total Labor Costs		4.20
Total Variable Costs		$161.00

Fixed Costs (F)	Costs/Yr
Labor - 2 men/shift @ 7.30/hr	91,000
1 supervisor @ 10.50/hr	22,000
Plant Maintenance - 2% Capital Investment	420,000
Plant Fixed Charge Rate 16% of Capital Investment	3,360,000
Total Fixed Costs	$3,893,000

Revenues (R)	Amount/Ton Cl_2
Chlorine @ 90.00/ton	90.00
NH_4NO_3 @ 90.00/ton	221.00
Total Revenues	$311.00/ton Cl_2

Breakeven Analysis

$$Q\ (R-V) = \text{Fixed cost}$$

$$Q\ \left(\frac{311}{\text{Ton}} - \frac{161}{\text{Ton}}\right) = \$3,893,000$$

$$Q = \frac{\$3,893,000}{150} = 25,950 \text{ TPY of Chlorine}$$

Note: The plant produces 33,000 TPY of chlorine assuming a 90 percent capacity factor. Breakeven point occurs at 78.6 percent of capacity. At 90 percent of capacity, a return of investment is calculated at 5.6 percent If chlorine prices rise to $140.00 per ton, then the above analysis yields a breakeven point of 19,470 TPY and a return on investment at 90 percent capacity of 23 percent, an acceptable rate.

is readily available and can be produced in quantity by oxidation of ammonia. The availability of ammonium chloride, however, deserves further discussion. At present, most of this material is produced as a by-product of the Solvay process. Currently about 25,000 TPY of material are recovered from this source. The remainder of the ammonium chloride is currently discharged as waste calcium chloride after processing to recover ammonia values. However, if full recovery were practiced, enough ammonium chloride could be generated from this source to produce 670,000 TPY of chlorine. The amount of ammonium chloride generated from other sources currently is negligible. The availability of this raw material source is questionable because of the rapid decline of the Solvay process over the last decade.

A second, and possibly expanding, source of this material would be via production from ammonium sulfate produced from coking operations. The amount of this material is expected to increase sharply in the future as coal gasification processes become commercialized on a large scale. The ammonium chloride would be produced via the reaction:

$$(NH_4)_2SO_4(l) + CaCl_2(l) \rightarrow 2NH_4Cl(l) + CaSO_4\downarrow(s)$$

Assuming the ammonium sulfate would be obtained for nominal recovery costs ($5 per ton) the economics of the process are dependent upon the availability and cost of calcium chloride. Calcium chloride (as the hexahydrate) currently sells for $55 per ton. Since about two tons of the hexahydrate are needed to produce one ton of ammonium chloride, this results in an ammonium chloride price of over $110.00 per ton. Use of the anhydrous calcium chloride at $71.00 per ton, excluding conversion costs, lowers raw material costs because only 1.04 tons of this material are needed to produce one ton of ammonium chloride. If conversion costs are included ($10 per ton) the cost of the ammonium chloride generated by this route is $89 per ton. These prices contrast with the $40.00 per ton for ammonium chloride from the Solvay process. Since over 1.5 tons of ammonium chloride are required per ton of chlorine product, the cost of raw materials, even using the Solvay process, are excessively high at current chlorine prices of $90 per ton.

Another possible process for production of large amounts of ammonium chloride from ammonium sulfate is one based on the reaction:

$$(NH_4)_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2NH_4Cl$$

A process using this reaction was commercially operated in Germany as late as the 1930's.[14] The major problem with the process, which involved crystallization of the sodium sulfate from hot solution, was contamination of the product with unrecovered sodium sulfate. To obtain a pure ammonium chloride product, yields were generally limited to about 45 percent, with a considerable amount of product liquors being wasted. A second problem was the low grade of sodium sulfate co-product which in current markets would be unsalable. A third problem was the energy requirements which required about 10 x 10^6 BTU per ton of product for heating and evaporating solutions. Cost calculations made on this process also revealed a breakeven price of over $90 per ton for the ammonium chloride product generated. If this process were used to produce the required ammonium chloride raw material, chlorine prices of $150 per ton would be needed to make the scheme economically viable. Also, there are considerable water pollution problems with such an approach in that about 55 percent of the starting materials would be converted to waterborne wastes, excluding the low grade sodium sulfate product generated.

Aside from the above two processes, no other published methods exist for the economical conversion of waste ammonium sulfate to ammonium chloride. Therefore, aside from the limited Solvay process source, no large-scale economical sources of ammonium chloride exist.

In summary, based on cost considerations, it appears that the ammonium chloride-nitrogen dioxide process is probably limited to the one existing Solvay process soda ash plant still operating. How long the remaining plant remains operational is unknown. Most Solvay plants have closed due to high energy and environmental costs and competition from natural deposits.

6.4.4 Overall Process Outlook

From the above analysis, it appears that this process, if developed, would be useful, at current chlorine prices, only at one location. At all other sites, the availability of ammonium chloride at reasonable cost will limit its applicability. However, this process may become more viable if a cheap, large-scale source of calcium chloride could be found.

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