Vinyl chloride monomer... What you should know

This survey of the VCM (vinyl chloride monomer) industry, commercial developments, chemistry, commercial processes and new developments indicates that VCM can remain competitive with rising crude costs

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DEVELOPMENT OF THE VINYL chloride monomer (VCM) industry has been closely interrelated with the polyvinyl chloride (PVC) industry. Effectively 96 percent of the VCM production goes into the manufacture of PVC. Therefore, technological advances in one area have significant impacts upon the other, producing a domino effect. This, in conjunction with increasingly tighter environmental regulations, has insured a continuing evolution of VCM technology. It is timely to review the state of the art.

INDUSTRY PROFILE

The commercial significance of vinyl chloride monomer (VCM) can be highlighted by the statistical ranking of the 19th largest chemical commodity in the United States. Turning our view upstream, we realize the significance VCM plays in wedding the petrochemical and chloro-alkali industries. Fig. 1 schematically depicts the U.S. market integration surrounding VCM. Pondering the posture individual companies present to the market (Table 1), one can muse as to the motivational forces behind their respective business strategies.

It holds that, if 96 percent of the VCM demand in this country is derived from PVC, then VCM's future is inescapably tied to that of PVC's. Within the scope of known-unknowns, one basic fact attests to its longevity. On an energy-equivalent basis, PVC is one of the most energy-efficient construction materials available (Table 2). This follows even after weighing the socioeconomics of health and environment.

Looking at the two principal components of the PVC

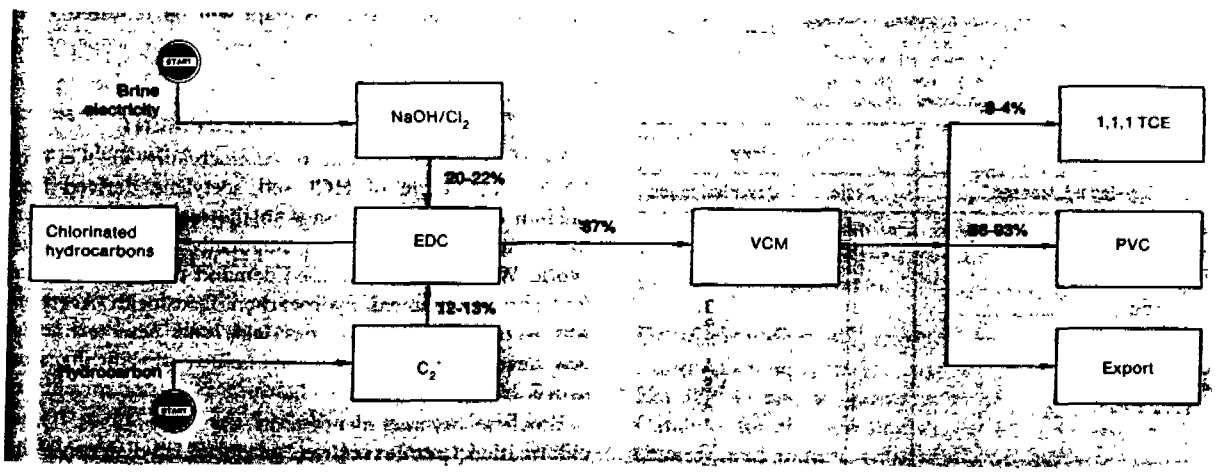

Fig. 1—Shows the U.S. market integration surrounding vinyl chloride industry.

market, flexible or plasticized products, of which fabric for automobile interiors and electrical wiring insulation are examples, and rigid products, including sewer and water pipes, electrical conduits and shoe soles, we find the rigid aggregate growing at 9 percent per year, as opposed to the flexible area which is increasing at a rate of approximately 5 percent. Within the past few years, the rigid aggregate has surpassed the size of the flexible market which can be witnessed by the creeping seasonal response the VCM industry has to construction, the major end-use outlet for rigid products.

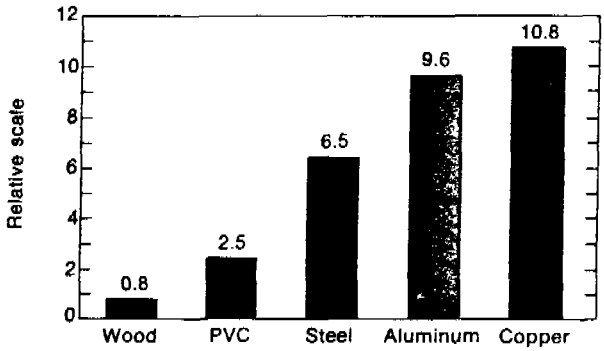

Fig. 2—Relative energy content of various construction materials.

TABLE 1—Nameplate capacities (MM pounds)

	PVC	VCM	Ethylene	Chlorine
Borden	550	300	None	None
Conoco	550	700	650	None
Diamond	None	1,000	None	2,500
Dow	None	2,250	4,800	8,400
Ethyl	175	300	None	500
B. F. Goodrich	1,100	1,100	350	250
ICI	None	300	None	300
Monochem	None	300	None	None
PPG	None	900	None	2,900
Shell	None	1,540	2,700	200
Stauffer	420	170	None	780

TABLE 2—Commercial types of VCM technology

I. High Purity Acetylene Feedstock
II. Dilute or Mixed Gas Feedstock
III. Balanced Ethylene Feedstock
A. Air-Based Oxychlorination
B. Oxygen-Based Oxychlorination

Developer/Licensor	Technology	
	Basic	Oxychlorination
Dow	III	A
Ethyl, ICI, Solvay	III	A
B. F. Goodrich	III	A,B
Kureha	II	—
Mitsui Toatsu	III	B
Monsanto	III	A,B
PPG	III	B
Rhone Poulenc	III	A
Stauffer	III	A,B
Tokuyama Soda	III	A
Toyo Soda	III	A
Hoechst	I	—
ICI	I	—

Over the course of the past ten years, VCM has become a major item of international commerce, with the United States the architect of this business. Between 1975 and 1977, eight percent of the VCM produced was carried offshore, making it third only to styrene monomer and toluene in the generation of trade dollars by a chemical commodity. This factor has tended to fill in the valleys in demand brought about by construction. More significantly, it has permitted the VCM industry to consistently operate near capacity levels by exporting domestic surpluses into the world arena. Looking at the global VCM market, we view forces at work changing the disposition of trade. Beginning within the past five years, Europe as a whole has swung from a net importer to exporter of VCM. With ten billion pounds of VCM capacity integrated to where there is less than 15 percent merchantly derived PVC demand, producers are now challenging U.S. material for a share of the remaining world exports.

Japan, whose five billion pound VCM industry was built to serve the whole of the Asian-South Pacific market, first in PVC and then later in VCM, has witnessed a major influx of U.S. and now European monomer producers into their domain.

The present situation in the U.S. is manifested by cheaper feedstocks, vis-a-vis energy, and an undervalued currency that together are able to offset logistical costs and remain competitive in the consuming markets. Eventually, merging energy parity and emission cost pass-throughs will leave U.S. VCM no more competitive than that of any other nation. We conclude, therefore, that exports will continue as developing third world markets seek to establish a plastics industry in advance of petrochemicals. Conversely, the major market imbalances of the past have gone by the wayside, and market growth will come from the domestic sector. Fig. 3 depicts the longer term outlook for VCM. In making our projections, we assume that the growing capital commitment required to make VCM will not force PVC to become uncompetitive with alternative products. Secondly, we foresee no major technological innovation on the horizon that could radically alter the economics of production. We do see, however, technological improvements of degree that directionally level out the inflationary trend of plant construction. Within the U.S., we project a 700 to 1,000 MM lb. per year grass roots plant will be required every two years to meet demand. It is within the scope of this time frame that innovation will be tested.

COMMERCIAL DEVELOPMENT

VCM was first produced commercially in the early 1900s via reaction of HCl and acetylene derived from calcium carbide. VCM usage in the manufacture of synthetic rubber accelerated dramatically during and after World War II. This increased demand prompted searches for more economical hydrocarbon feedstocks. Acetylene was recovered from refining steps, and new technology was developed to produce acetylene specifically from hydrocarbon cracking.

Ethylene became plentiful in the early 1950s. Direct chlorination processes to produce 1,2-dichloroethane (EDC) from chlorine and ethylene were developed in

conjunction with EDC cracking technology to yield VCM. This process yielded byproduct HCl and did not proliferate immediately, except in conjunction with acetylene-based technology which needed HCl to produce VCM.

In the U.S., ethylene production from abundant supplies of low cost LPG began to predominate. In Europe, ethylene prices also continued to drop, though not to the same degree since higher priced naphtha and gas oil were the primary feedstocks. Therefore, while European producers continued to use acetylene-based VCM technology, American companies moved rapidly to ethylene-based technology. With the startup in 1958 of the first large scale oxychlorination process to yield EDC from HCl and ethylene, a new era in VCM technology began. This "balanced" process allowed production of VCM from two commodity chemicals, chlorine and ethylene, without voluminous byproduct HCl.

VINYL CHLORIDE CHEMISTRY

Large scale production of vinyl chloride was first done by addition of hydrogen chloride to acetylene:

Hydrochlorination of acetylene

$$HCl + HC \equiv CH \xrightarrow{\text{Catalyst}} H_2C = CHCl \quad (1)$$

However, much lower costs for production of ethylene than acetylene and the discovery that 1,2-dichloroethane (EDC) thermally decomposes to vinyl chloride in excellent yield led to the following reaction sequence as the predominant manufacturing method for VCM:

Direct chlorination of ethylene

$$CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$$

EDC cracking to VCM

$$ClCH_2CH_2Cl \xrightarrow{\text{Heat}} CH_2 = CHCl + HCl$$

This method was especially advantageous for those producers having a use for the HCl by product, particularly so if acetylene were available; since then, a balanced VCM process with no coproducts could be operated.

Later, the discovery that oxychlorination technology could be applied to ethylene to give 1,2-dichloroethane in high selectivity now allowed a completely balanced process based only on ethylene and chlorine as feedstocks.

Oxychlorination of ethylene

$$CH_2 = CH_2 + 2HCl + 1/2O_2 \xrightarrow{\text{Catalyst}} ClCH_2CH_2Cl + H_2O$$

At present, about 92 percent of the vinyl chloride produced in the United States is from plants that use the balanced process based on ethylene via chlorination, oxychlorination, and thermal cracking of EDC.[1] These three separate steps are described in greater detail below. Additionally, the hydrochlorination of acetylene is also discussed below since plants using this chemistry are still

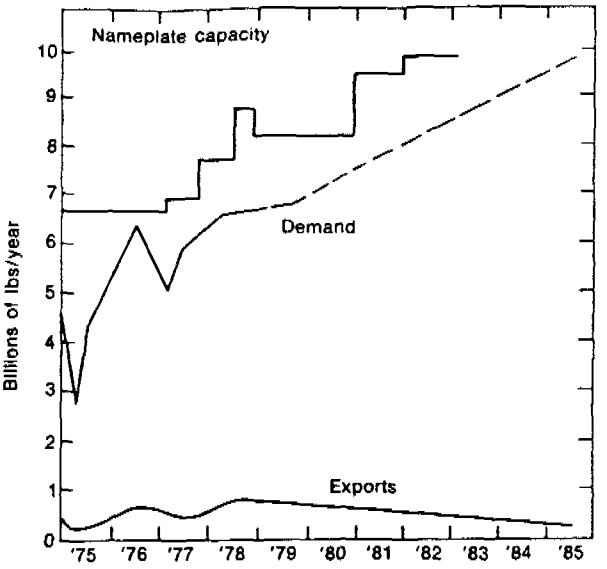

Fig. 3—U.S. vinyl chloride nameplate capacity versus demand

in operation. Moreover, some recent crude oil cracking technology may narrow the cost gap between acetylene and ethylene with consequent revival of interest in VCM from acetylene. Some chemistry on direct preparation of VCM from ethane is also briefly outlined.

Direct chlorination of ethylene. Direct chlorination of ethylene to 1,2-dichloroethane is almost always conducted in a liquid phase reactor by intimately mixing ethylene and chlorine in liquid EDC. Ferric chloride, a highly efficient and selective catalyst for this reaction, is normally used in commercial processes. Amides, such as n,n-dimethylformamide, have been reported to increase PVC selectivity.[2] Oxygen, frequently present as an impurity in chlorine, likewise increases EDC selectivity in direct chlorination of ethylene by inhibition of free radical reactions that give 1,1,2-trichloroethane.

Direct chlorination reactions may be run rich in either ethylene or chlorine, depending on the methods available to the plant for handling offgases from this reactor. Conversion of the lean component is usually 100 percent, and selectivity to EDC is greater than 99 percent.

1,2-Dichloroethane, as it comes from the direct chlorination reactor, is frequently of sufficient purity for cracking, except that it may contain ferric chloride, which would lead to rapid fouling of the cracking reactor. To avoid expensive purification of this already pure EDC, one may remove $FeCl_3$ by adsorption on activated carbon[3] or other solids.[4] Alternately, one may operate the direct chlorinator at the boiling point of EDC, taking pure EDC overhead and using the heat of reaction to supply the heat for vaporization.[5,6,7,8]

Oxychlorination of ethylene to EDC. Ethylene oxychlorination is normally conducted at temperatures of 225-325° C and at pressures of one to 15 atmospheres. Catalysts for this reaction almost always contain copper chloride and sodium or potassium chloride deposited on alumina or other suitable support. The detailed mech-

anism of the catalyst's activity is not known, but it is recognized that cupric chloride is the active chlorinating agent. The cuprous chloride produced is rapidly reconverted to $CuCl_2$ under the reaction conditions, but the presence of some cuprous chloride is thought to be advantageous because it complexes with ethylene, bringing it into contact with $CuCl_2$ for a long enough time for chlorination to occur. The sodium or potassium chloride serves to increase EDC selectivity, mostly by inhibiting formation of ethyl chloride. Other catalyst components, such as rare earth metal chlorides, sulfate salts, ferric chloride and numerous other additives, have been described in the patent literature.

Good temperature control of the highly exothermic oxy reaction is a key element in successful production of 1,2-dichloroethane. Temperatures higher than about 325°C lead to increased byproduct formation, mostly through increased dehydrochlorination of EDC to vinyl chloride followed by additional oxychlorination to give products having high levels of chlorine substitution. High temperatures also increase the amount of ethylene burned to carbon monoxide and carbon dioxide. Of equal importance, high temperatures deactivate the catalyst by highly accelerated coking and consequent powdering of the catalyst units and by increased sublimation of copper, chloride away from the catalyst.

Temperature control in **fluidized bed reactors** is maintained by the excellent intermixing of the catalyst particles and by use of internal cooling surfaces.[10] Temperature control in **fixed bed reactors** is more difficult since "hot spots" tend to develop. To keep the hot spot temperature below below 325° C, yet get maximum utilization from the reactor, it is common practice to pack the reactor tubes with active catalyst and inert diluent mixtures in proportions of each so adjusted as to have low catalyst activity at the inlet, steadily increasing to maximum activity at the outlet. This grading of the catalyst activity flattens the temperature profile, allowing for good temperature control with high productivity. For example, one patent[9] indicates the use of four zones with 93 percent, 85 percent, 40 percent, and 0 percent, respectively, of the active catalyst pellets replaced by inert graphite. As an alternate to using inert materials in the catalyst bed, catalysts, each with higher levels of $CuCl_2$ and consequently of increasing reactivity, are sometimes used.

Fluid bed oxychlorination of ethylene, operated under good control, results in 94-97 percent ethylene conversion, 95-97 percent HCl conversion, and EDC selectivities in the range of 94-96 percent. Fixed bed oxychlorinations are normally run with excess ethylene relative to HCl, resulting in 93-97 percent ethylene conversion, 94-95 percent HCl conversions, and EDC selectivities of 93-95 percent. These data do not include recovery of excess ethylene in subsequent reaction steps. Excess ethylene in vent gases from oxychlorination is normally converted to EDC by direct chlorination with chlorine,[11,12] although, if oxygen is used rather than air, the excess ethylene may be recycled directly back to oxychlorination.

Byproducts of ethylene oxychlorination are vinyl chloride, ethyl chloride, 1,1-dichloroethane, vinylidene chloride, *cis*- and *trans*-1,2-dichloroethylenes, trichloroethylene, chloroform, carbon tetrachloride, methyl chloride, methylene chloride, chloral and high boiling compounds. All of these byproducts present problems in one way or another, such that their production needs to be minimized to lower raw material costs, to lessen the difficulties of preparing pure EDC, and to prevent fouling in the cracking reactor. Chloral, in particular, needs to be removed since it polymerizes readily in strong acids to give solids which clog and foul operating lines and controls.

One must also take care to see that the feeds to oxychlorination are pure. Normally, the only problem is with low levels (0.1 to 0.5 percent) of acetylene present in the HCl from cracking of EDC. Acetylene in the feed leads to the formation of considerable highly chlorinated byproducts and tars. Selective hydrogenation of this acetylene to ethylene and ethane is practiced by many companies.[15]

Oxychlorination with oxygen instead of air. Use of oxygen instead of air for ethylene oxychlorination has received much attention.[14-19] The outstanding benefits from using oxygen are avoidance of expensive facilities to recover EDC, ethylene and other chemicals from the large nitrogen vent gas stream; a large reduction in the quantity of offgases that will probably need to be incinerated; and the ability to use ethylene as a diluent for oxychlorination, a procedure said to improve heat transfer in tubular reactors.

Purification of EDC for cracking. Great care must be taken to ensure that EDC used for cracking to vinyl chloride is of high purity, normally greater than 99.5 percent, since cracking is exceedingly susceptible to inhibition and fouling by trace amounts of impurities. Additionally, the EDC must be bone dry to prevent excessive corrosion downstream of the cracker. For these purposes, one must consider removal from EDC of byproducts from three sources: EDC from direct chlorination, EDC from oxychlorination, and EDC recovered from the cracking step (see below).

EDC from direct chlorination is usually quite pure, greater than 99.5 percent; and, except for the $FeCl_3$ present, it needs little further purification. As mentioned previously, ferric chloride may be removed by adsorption on a solid, or the EDC may be distilled away from $FeCl_3$ in a boiling reactor. Alternatively, the ferric chloride may be removed by washing with water, usually in conjunction with oxy-EDC.

1,2-Dichloroethane from oxychlorination contains a variety of impurities as listed previously. EDC from this source is usually washed with water and then with caustic solution to remove chloral and other water extractable impurities.[20] Low boiling impurities and water are taken overhead in a first (light ends) distillation column, and then pure dry EDC is taken overhead in a second (heavy ends) column.

EDC recovered from the cracking step contains an

appreciable number of impurities, of which two, chloroprene and trichloroethylene, are not readily removable by distillation, necessitating the use of other treatments. Chloroprene, if not altered by chemical treatment, concentrates in the light ends column where it can polymerize to solid or rubbery materials which seriously foul and upset this column. Trichloroethylene forms an azeotrope with EDC, boiling very close to EDC. If it is not removed in some way, it accumulates in the EDC, leading to reduced cracking rates and increased fouling. Both impurities may be removed by subjecting the recycle EDC stream to chlorination prior to distillation.[21-23] Treatments with HCl[24-26] and by hydrogenation[27] have also been patented as methods for removal of chloroprene.

Cracking of 1,2-dichloroethane to vinyl chloride. At temperatures in the range of 425-550° C, and near atmospheric pressure EDC undergoes clean thermal dehydrochlorination (cracking) to yield vinyl chloride and hydrogen cloride:

$$ClCH_2CH_2Cl \xrightarrow{\text{Heat}} CH_2 = CHCl + HCl$$

The mechanism of this reaction has been extensively investigated[28] and shown to involve a sequence of free radical intermediates.

Use of pressure up to 25 to 30 atmospheres during cracking at temperatures of 500-550° C provides better heat transfer, reduced equipment size and easier separation of HCl from the product by fractional distillation. EDC conversion levels are normally maintained in the range of 50 to 60 percent at residence times of 2 to 30 seconds, with selectivities of VCM ranging from 96 to 99+ percent. Some byproducts generated during cracking act as inhibitors to the free radical sequence so that increasing severity leads to smaller and smaller increases in EDC conversion with correspondingly increasing levels of byproducts. Various materials, such as chlorine, bromine, or oxygen have been shown to be initiators for EDC cracking.[28] Recently, however, exclusion of oxygen is claimed to result in considerable reduction of fouling on the cracker tube walls.[29] A rather spectacular claim has been made that use of nitromethane as an initiator provides EDC conversion levels of up to 92.5 percent at 480° C.[30] An important processing requirement in EDC cracking is rapid cooling or quenching of the reaction mixture. If cooling is done too slowly, substantial yield losses to heavy ends and tars result.[25, 30, 31]

Byproducts from the cracking reaction include acetylene, ethylene, methyl chloride, butadiene, vinyl acetylene, benzene, chloroprene, vinylidene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and other compounds. Most of these impurities remain in the unconverted EDC fraction and are removed when this stream is distilled. Ethylene and acetylene codistill with the HCl and are thus routed back to oxychlorination (after optional hydrogenation of the acetylene to ethylene). Methyl chloride and butadiene more or less codistill with the vinyl chloride, depending on the efficiency of the VCM fractional distillation system. Addition of chlorine or carbon tetrachloride to the cracker feed is claimed to suppress methyl chloride formation.[33] Removal of butadiene, a contaminant which can interfere with polymerization of VCM, has been done by treatment with chlorine,[34] anhydrous HCl,[35] or selective hydrogenation.[36]

HCl addition to acetylene. Recent development of a new crude oil cracking process[37] using very high temperature steam (2,000° C) as a heat transfer fluid produces substantial yield of acetylene along with ethylene. Under some economic and geographic conditions, the use of this cracking process may be advantageous and may, thereby, provide acetylene for vinyl chloride production.

Typical conditions of hydrogen chloride addition to acetylene are total pressures on the order of five to 15 atmospheres, temperatures of 150 to 180° C, and use of a mercuric chloride-on-carbon catalyst.[38] With stoichiometric quantities of reactants, essentially 100 percent conversion is observed with VCM selectivities on the order of 98 percent. It is notable that ethylene does not react under these conditions, thereby allowing the use of mixed ethylene-acetylene streams as feeds. Ethylene, easily recovered from the vinyl chloride product by fractional distillation, is then chlorinated to yield 1,2-dichloroethane.

Other catalysts have been shown to be effective for addition of HCl to acetylene, but $HgCl_2$ is vastly superior.[39] However, in addition to the general toxicity problems involved in working with mercury-containing substances, $HgCl_2$ has appreciable volatility under the above reaction conditions leading to a need for considerable care and control in operation of the reactor. In fixed bed operations, $HgCl_2$ vaporizes from the hot spot of the reactors, condenses at cooler locations downstream and results in continuous movement of the hot spot downstream with eventual loss of catalytic activity. This loss is minimized by periodic reversal of flow through the reactor.

Ethane-based vinyl chloride processes. A number of patents dealing with chemistry for conversion of ethane to EDC and/or VCM have been published in recent years.[40-44] Most of these reactions involve high temperature oxychlorinations, such as

$$CH_3CH_3 + HCl + O_2 \xrightarrow[350\text{-}450^\circ C]{CuCl_2\ Catalyst} CH_2 = CHCl + 2H_2O$$

However, these processes suffer from a number of disadvantages, the most important of which includes low selectivities, low conversions and difficult operating conditions such as $CuCl_2$ sublimation.

One reaction system based on ethane, called the "TRANSCAT" process, has been developed on a large pilot plant scale but is not yet in commercial practice.[45-53] The chemistry of this process is a complex series of reactions, generally involving chlorination, dehydrochlorination and oxychlorination. A mixture of ethane, ethylene, ethyl chloride, chlorine and HCl are fed to a melt of cupric oxychloride and potassium chloride, yielding vinyl chloride, water, and cuprous chloride as the main products. The cuprous chloride-potassium chloride product is taken to an oxidation reactor where the cupric oxychloride is regenerated by treatment with air. Vinyl chloride is separated from the organic product and puri-

fied by fractional distillation. Removal of about 0.4 percent butane plus butenes present in the main VCM cut represents a very difficult separation.[45] Ethyl chloride and ethylene can be recycled into the feed. Chlorine values in the chlorinated byproducts can be recovered by incineration and then feeding these gases to the cuprous chloride oxidative regenerator reactor.

Disposal of byproducts. Disposal of byproducts presents special problems for vinyl chloride manufacturing plants, since a variety of gaseous organic liquid, and acqueous streams must be handled, each with its own particular problems.

Vent gas streams from various units may contain small amounts of HCl, chlorine, ethylene, vinyl chloride, methane and carbon monoxide. These streams may sometimes be treated by scrubbing, chemical treatment, sorption, or other methods to recover some chemicals when economically justified. Otherwise, the common cleanup technique is either incineration or catalytic combustion followed by recovery of HCl from the vent gases.

Two organic byproduct streams are produced. The light ends contain mainly ethyl chloride, *cis-* and *trans-*1,2-dichloroethylene, chloroform and carbon tetrachloride. The heavy ends or "tars" contain mostly 1,1,2-trichloroethane, lesser concentrations of tetrachloroethanes, chlorinated butanes, chlorinated aromatics and a large number of other compounds present in small amounts. These streams are normally fractionated to recover useful components, the others incinerated to recover chlorine values either as aqueous or anhydrous HCl.

Process water streams are steam stripped to remove volatile organics followed by neutralization and then treatment in an activated sludge system to remove nonvolatile organics in the water.[46]

COMMERCIAL PROCESSES

Broadly speaking, there are three types of VCM processes in commercial use today. These are categorized as acetylene, ethylene, or mixed gas based on feedstock requirement. Within the "ethylene-type" plants, further classification is desirable to distinguish the type of oxychlorination technology used, i.e., oxygen versus air feedstock (see Table 2). Over 90 percent of the world's listed 35 billion lb. per year VCM capacity currently is based upon the balanced ethylene feedstock route. Of this, just under 90 percent uses air-based oxychlorination. However, of the projected worldwide plant startups for the period 1979-1981, approximately 30 percent of the 7.7 billion lbs. per year VCM will be derived from oxygen-based oxychlorination. Other existing producers will undoubtedly be evaluating the conversion of present air-based plants to the use of oxygen during this time frame.

Table 3 presents a summary of the technology sources in use today. It is thought that the technology currently licensed by ICI and Solvay is similar to the process normally attributed to Ethyl. Therefore, all are listed under Ethyl's technology. It is interesting to note that several plants exist where the oxychlorination process

TABLE 3—Curr nt VCM technology sources

Technology Source	Existing		Planned (1979-1981)	
	Plants	VCM, MM Lbs./Yr.	Plants	VCM, MM Lbs./Yr.
1. B. F. Goodrich	18	5,840	4	2,160
2. Hoechst/BFG*	11	4,290	2	580
3. Stauffer/BFG*	5	2,360	—	—
4. Stauffer	19	6,390	2	350
5. Ethyl, Solvay, ICI	14	5,000	1	260
6. Dow	7	3,040	3	1,050
7. PPG	5	1,700	3	1,780
8. Rhone-Poulene	5	1,330	1	500
9. Monsanto	4	1,110	1	250
10. Toyo Soda	3	400	1	330
11. Tokuyama Soda	2	660	—	—
12. Mitsui Toatsu	3	610	1	90
13. Kureha	2	410	—	—
14. Miscellaneous	10	2,400	1	330
	107	35,540	20	7,680

*Oxychlorination process provided by BFG

of one licensor, B. F. Goodrich, has been combined with direct chlorination and VCM technologies of others, i.e., Hoechst and Stauffer. Table 4 presents a tabulation of worldwide VCM producers. This summary was prepared from scores of literature sources, some of which were contradictory. However, the authors have exercised their best judgment in the absence of specific information from the listed licensors.

The reader is referred to Leonard,[54] Gomi,[56] or Sittig[55] for details of the acetylene and mixed gas routes to VCM. The technology discussion herein will be limited to the balanced ethylene feedstock route used overwhelmingly today.

Although each of the major technology licensors has many patents, none has complete coverage of each step of his process. As a result, the sequence and type of operating steps tend to be very similar from process to process. The basic differences stem from the oxychlorination technology and the types of impurities appearing in the crude EDC. The licensor, therefore, provides process know-how primarily, as opposed to patent position. As a result, published literature by major licensors is understandably very sparse and highly simplified, with certain exceptions.[56, 57, 58, 59]

TYPICAL VCM PROCESS

The typical VCM process combines direct and oxychlorination (oxy) processes to provide 1,2-dichloroethane (EDC) feedstock for the EDC pyrolysis unit (see Fig. 4).

The direct chlorination process relative to oxy is characterized by low capital investment, low operating costs and high purity product. However, HCl generated from the EDC pyrolysis unit dictates the use of an oxy unit. With the current pyrolysis yield of approximately 0.55 mol VCM per mol EDC fed, and the HCl yield of 1 mol per mol VCM, the oxy unit size is set at approximately 0.5 mol EDC per mol of VCM desired. This sets the direct chlorination unit size at approximately 0.5 mol EDC per mol VCM.

The combined EDC streams are caustic treated to re-

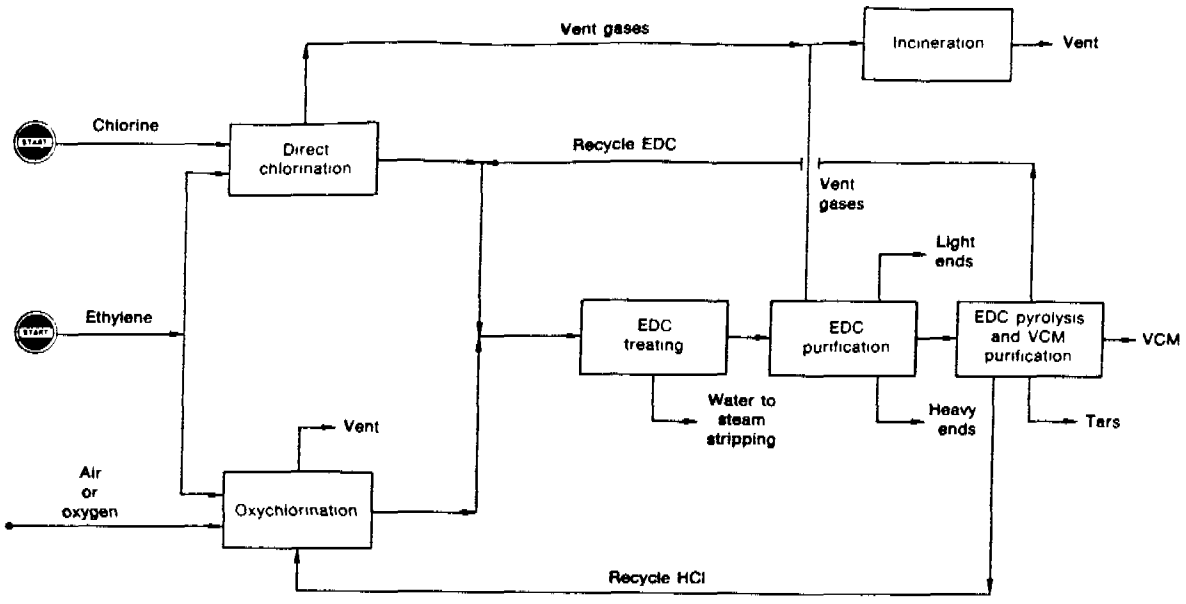

Fig. 4—Typical vinyl chloride monomer block/flow diagram.

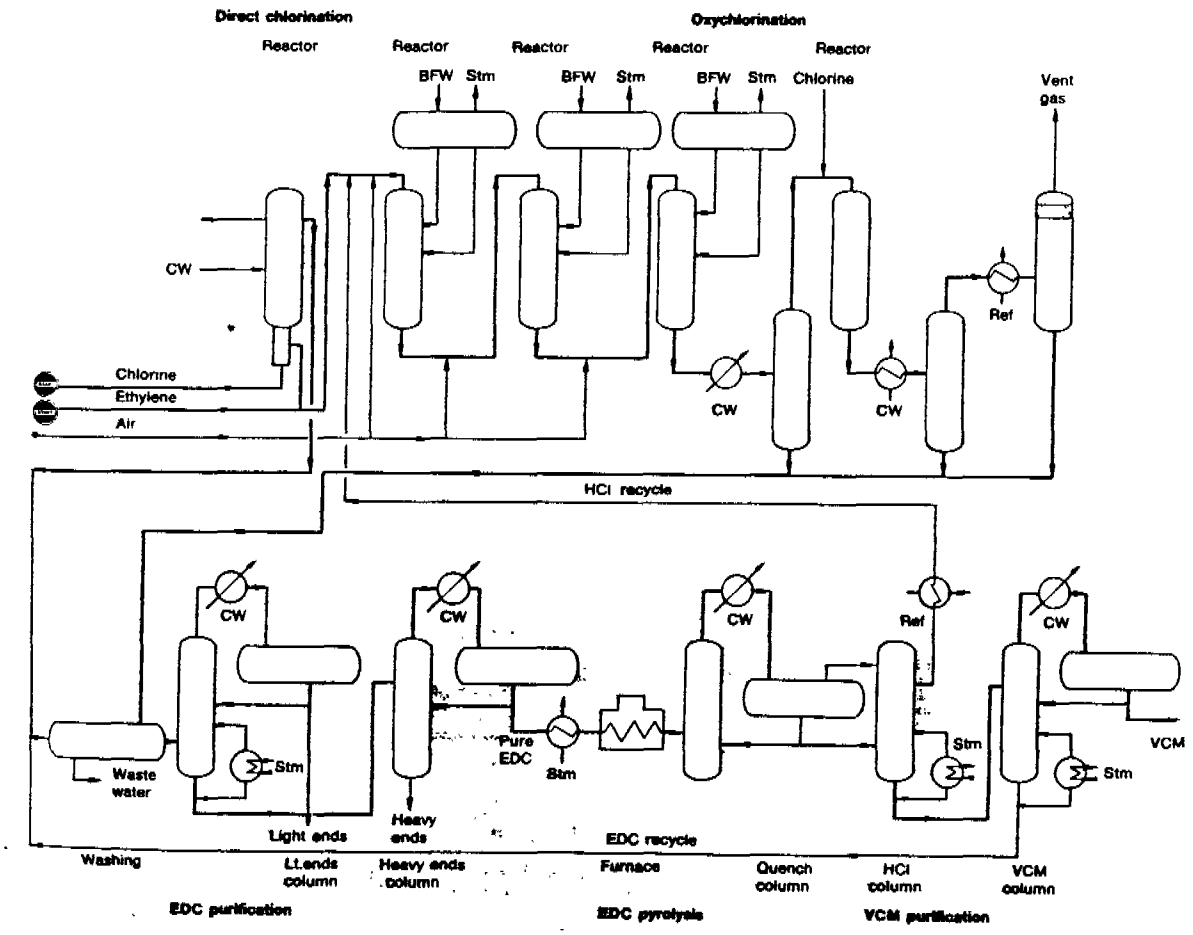

Fig. 5—Schematic of the Stauffer vinyl chloride monomer process.

TABLE 4—VCM plants—worldwide—(cont'd)

Operator	Location	Process	Startup Year**	Licensor	Engineer/ Contractor	VCM Capacity, MM Lbs/Yr**
Italy						
Anic	Ravenna	A/-/-	1971	Stauffer	Foster Wheeler	165
Montedison	Brindisi	M/A/O	1969	BFG		400
	Porto Marghera	M/A/O	1970	BFG		400
Rumianca Sud	Cagliari	E/-/D	1965	PPG	Opt, Selas	350
	Cagliari	E/A/O	1976	PPG	Euteco	350
SARP	Termini Imersee	..				(110)
Sincat	Priolo			Ethyl		290
Solvic	Rayamino			Solvay	Solvay	110
Sir Consorzio Industries	Porto Torres			Sir	Euteco	310
Japan						
Asahi Penn	Chiba	AE/-/O	1967	PPG		99
Chiba VCM	Chiba	E/A/B	1971	Stauffer	Sumitomo	350
Chisso	Minimota			Toyo Soda	Hitachi	220
Denki Kagaku	Chiba			Denki Kagaku		(330)
Japanese Geon	Takaoka	M/-/D	1967	Japanese Geon		257
Kanegafuchi	Takasaga	E/A/B	1969	Stauffer	Sumitomo	331
Kanegafuchi	Takasaga	E/A/B	1970	Stauffer	Kanegafuchi	331
Kashima VCM	Kashima	E/A/B	1970	BFG		770
Kureha	Nishiki	M/-/D	1964	Kureha	Chiyoda	265
Mitsubishi-Monsanto	Yokkaichi	AE/A/-	1970	Monsanto		130
Mitsui Toatsu	Nagoya	AE/A/O	1964	Mitsui Toatsu	Toyo Engineering	130
	Osaka	E/A/B	1970	Mitsui Toatsu	Toyo Engineering	130
Nissan	Chiba	AE/A/O	1968	Toyo Soda	Hitachi	73
Ryo-Nichi Co., Ltd.	Mizushima	E/A/B	1970	BFG		440
Sanyo Monomer	Mizushima	AE/A/O	1970	BFG		238
Shunan Petrochemicals	Tokuyama	A/-/-		Tokuyama Soda		440
Sumitomo	Niihama	E/A/B	1968	Stauffer		180
Sun Arrow Chemical	Tokuyama	E/A/O	1967	Tokuyama Soda		220
Toyo Gosei	Tokushima	M/-/D		Toyo Gosei		88
Toyo Soda	Tokuyama City	E/A/B	1966	Toyo Soda	Hitachi	110
	Yokkaichi			Toyo Soda		220
Korea						
Korea Pacific	Yeo-Su		(1979)	Dow	Fluor/Daelim	(330)
Korea Pacific	Ulsan			Dow	Procon	132
Libya						
GNOI	Abu Kammash		(1980)	BFG, Hoechst	F. Uhde, Salzgitter	(136)
Mexico						
Pemex	Pajaritos	E/A/B		Monsanto	Lummus	155
	Pajaritos	E/A/B	1978	BFG	Butete	440
Morocco						
SNEP	Mohammadia		1976	Stauffer	Krebs	59
Norway						
Norsk Hydro	Rafnes	E/A/B	1978	BFG, Hoechst	Badger	660
Peru						
Sociedad Paramonga LTDA	Paramonga	E/A/O		Vulcan		17
Poland						
Polimex-Cekop	Wloclawek	E/O/B	(1979)	PPG	Petrocarbon, Davy-Powergas	(450)
Portugal						
CNP	Sines	Planned	(1981)			(330)
Rumania						
Industrial Import	Rimnicu Vilcea			Dow	Klock	88
State Authority	Rimnicu Vilcea	E/O/B		Mitsui Toatsu	Toyo Engineering	350
South Africa						
Africa Explosives and Chemicals	Sasolburg	E/-/D	1968	ICI, Solvay	Humphries & Glasgow	60
	Sasolburg	A/-/-	1978	Tenneco	Crawford-Russel	440
Spain						
Monsanto	Tarragona			Monsanto	Lummus	176-330
	Tarragona			Monsanto	McKee, CTIP	(250)
	Tarragona			Monsanto		530
	Tarragona			Monsanto	McKee, CTIP	220
	Huelva		(1980)	Rhone-Progil		(500)
Rio Rodano	Martonell	E/A/B	1970	Solvay	McKee, CTIP	265
Vinicior	Huelva		(1981)	Dow		(770)
Dow						
Sweden						
Kemanobel	Stenungsund	E/A/B	1967	Stauffer	Lurgi	180
Switzerland						
Lonza	Laiden	A/-/-				44
Taiwan						
Formosa Plastic	Kaohsiung	E/A/B	1973	Stauffer		530
Chung Tai (?)	Toufen	E/O/B/		Mitsui Toatsu		(530)
Turkey						
Petkim	Yarimca Izmit			Solvay	Humphreys and Glasgow	119
Petkim	Aliaga-Ismir	E/-/D	(1981)	ICI, Solvay	CTIP	(257)
United Kingdom						
British Petroleum	Baglan Bay, Wales	AE/A/O	1971	BFG		573
ICI	Hillhouse			Solvay	C. F. Braun	
	Runcorn	A/-/-		Solvay	C. F. Braun	
USSR						
Techmashimport	Djerjinsk			Rhone-Progil	Speichim	66
	Gorki	E/A/B	1970	Stauffer	Speichim	73
	Gorki			Rhone-Progil	Speichim	68
	Kalush	E/A/B/	1974	BFG, Hoechst	F. Uhde	550
	Volgograd	EA/-/D		Kureha	Chiyoda	145
	Zima	E/A/B	(1979)	BFG, Hoechst	F. Uhde	(595)
Venezuela						
Petroplas	El Tablazo	E/A/B	1977	BFG		110
Yugoslavia						
Ork. Kem. Ind	Skopje			Rhone-Progil		110
Hemijska Ind.	Pancevo	E/A/B	(1979)	Stauffer	Foster Wheeler	(220)
Dow/Ina	KRK		(1981)	Dow		(440)

* Information tabulated from many sources. In cases (several) of contradictory reports, authors have exercised their best judgment.
** Parentheses denote that plant is thought to be in engineering and/or construction stage and has not reached an operational status.

Legend:

Hydrocarbon Feedstock	/ Oxy Basis	/ Process
(E)thylene	(A)ir	(B)alanced
(A)cetylene	(O)xygen	(O)xy
(M)ixed Gas		(D)irect

TABLE 4—VCM plants—worldwide

Operator	Location	Process	Startup Year**	Licensor	Engineer/ Contractor	VCM Capacity, MM Lbs/Yr**
United States						
ICI America	Baton Rouge, Louisiana	E/A/B	1968	BFG		300
Conoco Chemicals	Lake Charles, Louisiana	E/A/B	1968	Stauffer	R. M. Parsons	700
Dow	Freeport, Texas			Dow		200
	Oyster Creek, Texas	E/A/O	1969	Dow		700
	Plaquemine, Louisiana		1978	Dow		1,150
Ethyl Corp	Baton Rouge, Louisiana			Ethyl		300
	Houston, Texas			Ethyl		150
B. F. Goodrich	Calvert City, Kentucky	E/A/O	1964	BFG		1,050
Monochem	Geismar, Louisiana	A/–/				300
PPG	Lake Charles, Louisiana	E/O/B	1960	PPG	Ford, Bacon & Davis	400
	Lake Charles, Louisiana	E/O/B	(1980)	PPG	R. M. Parsons	(1,000)
	Guayanilla, Puerto Rico	E/O/B	1971	PPG	Fluor	500
Shell Chemical	Deer Park, Texas	E/A/B/	1972	Stauffer	R. M. Parsons	840
	Norco, Louisiana	E/A/B	1972	Stauffer	R. M. Parsons	700
Stauffer	Long Beach, California	E/A/B	1957	Stauffer	C. F. Braun	175
Borden Chemical	Geismar, Louisiana	E/A/B		Stauffer	R. M. Parsons	330
Georgia Pacific	Plaquemine, Louisiana	E/O/B	(1980)	PPG	Brown and Root	(1,000)
Diamond Shamrock	Deer Park, Texas	E/A/B	1978	Stauffer, BFG	Lummus, Badger, Brown & Root	1,000
Algeria						
Sonatrach	Skikda	E/O/B	(1979)	Mitsui Toatsu	Toyo Engineering	(88)
Argentina						
Dow Quimica	Bahia Blanca			Dow	Chemico	110
Electroclor	Capitan, Bermudez	E/A/B		ICI		73
	Bahia Blanca			BFG	Badger	287
Australia						
Icianz	Boforry	A/–/D		ICI		?
Belgium						
BASF	Anvers	E/A/B	1967	Stauffer	BASF	240
Libechem	Feluy			BFG		(1,100)
Limburgse (LVM)	Tessenderlo	E/A/B	1972	Hoechst, BFG	Badger	440
		E/A/B	1976	Hoechst, BFG	Badger	440
Solvic	Jemeppe-Sur	E/A/B	1968	Ethyl	Solvay	550
Brazil						
Copamo	Elctor	E/A/B	1972	Solvay, ICI	McKee, CTIP	220
Monomers Vinilicos	Bahia Blanca			BFG	Badger	(286)
Petroquim Camacari	Camacari		(1979)	BFG	Badger/Promon	(330)
Bulgaria						
Technocomplekt	Burgas Devnya	E/O/B	(1979)	PPG	Technip/TPL	(330)
Canada						
Dow	Sarnia, Ontario			Dow		?
	Fort Saskatchewan		(1979)	Dow		(660)
Shawinigan	Varennes, Quebec	E/A/B	1967	BFG	Badger	126
	Shawinigan, Quebec	A/A/O	1969	BFG		126
Chile						
Petroquimica	Concepcion				Fish Engineering	35
Dow/ENAP	Concepcion			Dow		35
China						
Technical Import Corp	Peking	E/A/O	1978	B. F. Goodrich	F. Uhde	176
Colombia						
Petroquimica Columbiana		E/A/B	1973	Stauffer		
Czechoslovakia						
Chemopetrol	Neratorice	E/A/B	1972	Stauffer	R. M. Parsons, Voest, Alpine	265
Chemickezavody W. Piecka	Novaky, Slovakia	M/–/D	1972	BFG, Hoechst	F. Uhde	240
Finland						
Pekema Oy	Porvoo		1971	Solvay	CTIP	88
France						
AKZO	Gonfreville					
Chomie	Le Havre					
EMC/DSM	Ottmarsheim					
Daufac	Jarrie	E/A/B	1967	Stauffer, BFG, Hoechst		440
Rhone-Poulenc	Lavera	M/–/D		Rhone-Progil	Rhone-Progil	795
	St. Auban	E/A/B	1970	Rhone-Progil	Rhone-Progil	291
	St. Fons		1965	BFG, Hoechst		440
Solvic	Tavaux	E/A/B		Solvay, Ethyl	Solvay	440
PCUK/Shell Chemie	FosSurMer	E/A/B	(1980)	BFG	Badger	(440)
East Germany						
Industrie Anlagen Import	Schkopau		(1979)	Hoechst	F. Uhde	(440)
West Germany						
Alusuisse	Wilhelmshaven					(660)
Huls	Marl	AE/–/D		Huls		700-770
BASF	Ludwigshaven	AE/–/D		Stauffer		160-320
Solvay	Rheinberg	E/A/B	1973	Solvay	Solvay	440
Dynamit Nobel	Lutsdorf	E/A/O	1966	Stauffer, BFG	C. F. Braun	130
Hoechst	Gendorf	E/A/O	1972	BFG, Hoechst	Uhde	375
	Knapsack	EA/A/O	1963	BFG, Hoechst	Badger, Uhde	220
	Vlissingen					(440)
Knapsack, AG	Knapsack			BFG	Badger, Uhde	220
	Knapsack			BFG	Badger, Knapsack	330
Wacker	Burghausen	E/A/O	1971	Stauffer/Stauffer	R. M. Parsons	176
	Burghausen	E/A/B		Wacker	R. M. Parsons	350
ICI	Wilhelmshaven		(1980)	ICI	Fluor	(680)
Greece						
Ethyl Hallas	Thessalonika	E/–/D		Ethyl		33
Holland						
AKZO	Botlek	E/A/B	1971	Stauffer/BFG	Comprimo-Lurgi	660
	Botlek (Expansion)		(1979)		AKZO Engineering	(330)
Hoechst	Vlissingen		(1981)	Hoechst		(350)
Shell?	Pernis					
Hungary						
Chemokomplex	Berente			Hoechst	Uhde	79
	Berente	E/A/B		BFG, Hoechst	Badger	350
Bososodi Vegyi Kombinat	Kazincbarcika	E/A/B	1978	BFG, Hoechst	Badger	350
India						
C&P India	Madras	E/–/D	1967	BFG		33
National Organic Chemistry	Bombay	A/–/–		Shell, BASF		45
Iran						
Abadan Petrochemical	Abadan	E/A/B	1969	BFG	Badger, Lummus	130
Iran-Japan J.V.	Bandar	E/A/B	(1979)	Toyo Soda	Hitachi	(330)
Iraq						
State	Basra		(1980)	Stauffer	Lummus, Thyssen	145
Israel						
Electrochemical Industries	Haifa	E/A/B		Monsanto		29
	Akko		(1979)			(220)

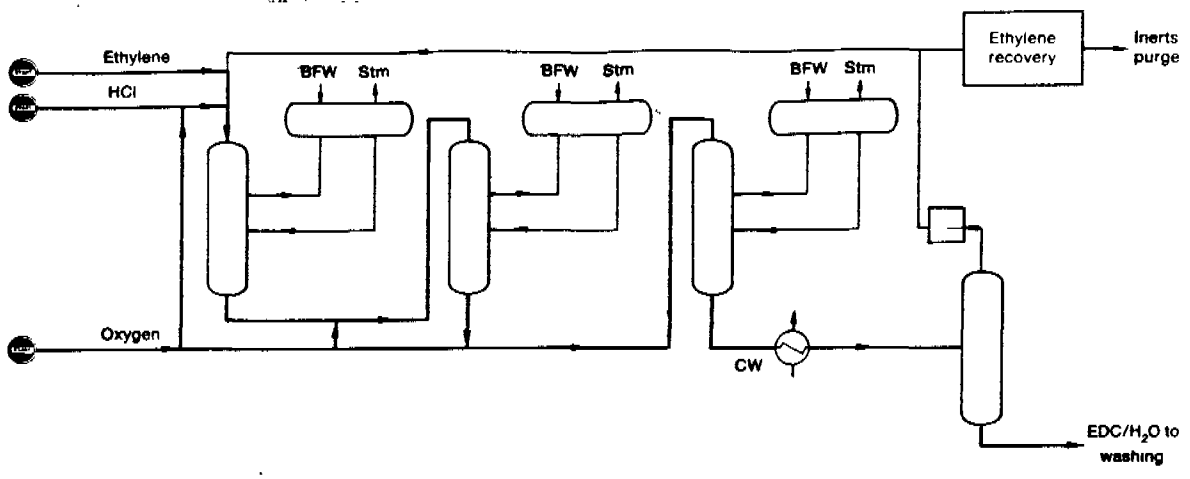

Fig. 6—Modifications used in the Stauffer oxygen-based oxychlorination process.

move HCl and certain clorinated byproducts which otherwise would hinder fractionation or pyrolysis. The "clean" EDC is subjected to distillation steps in which water and other light components are removed, as well as heavy components typically labeled tars. The dry product EDC, generally of 99.5 percent or greater purity, is thermally cracked to yield HCl and VCM in an EDC carrier stream. Further distillation equipment separates EDC and HCl for recycle and yields product VCM for final treating.

The typical VCM plant includes VCM treating, offgas treating, light ends/tars handling and waste treating facilities. It will also include incineration units for reclaiming waste chlorinated hydrocarbons from offgas or liquid streams.[1]

Stauffer technology.[60,61] In the Stauffer direct chlorination process (see Fig. 5), ethylene and chlorine are reacted, in the liquid phase and under controlled conditions, to yield a crude product which analyzes 99.7 percent EDC. The reactor product is then combined with the crude oxy EDC, washed and distilled to remove water, light ends and heavy ends.

Pure EDC is preheated in the economizer of the pyrolysis furnace and then vaporized with steam. EDC vapor is then heated to dissociation temperature in the furnace tubes to yield a mixture of vinyl chloride and hydrogen chloride. Conditions are controlled to maintain EDC conversion at 50 to 55 percent. Following a quench and condensation step, HCl, VCM, and uncracked EDC are separated by distillation. Hydrogen chloride gas is sent to the oxy section. Unreacted EDC is recycled to purification.

The oxy section combines recycle HCl with fresh ethylene and air in tubular fixed-bed catalytic reactors. The ethylene and air are fed in excess of stoichiometric requirements to assure high HCl conversion.[61] Reaction heat is removed by generation of steam on the shell side of each reactor. The final reactor effluent is cooled to condense EDC, and the offgas is contacted/reacted with chlorine to recover ethylene as additional EDC. The offgas stream is cooled versus cooling water and refrigeration to further condense EDC before exiting the process. Residual ethylene concentration in the vent gas is reportedly as low as 10 ppm.[61]

Stauffer also offers an oxygen-based oxy process (Fig. 6) in which the main reactor offgas, following condensation of EDC, is compressed and recycled to the first oxy reactor. An excess of ethylene is used to maximize HCl conversion and minimize byproducts. A small slipstream from the ethylene-rich recycle is purged to an ethylene recovery unit for control of inerts.

Ethyl integrated VCM process.[62] Gaseous chlorine and ethylene are introduced into a direct chlorination reactor in which they combine to form EDC. The very high purity EDC product can be sent directly to (or, after degassing, can bypass) the EDC purification system (see Fig. 7).

Air and gaseous ethylene and HCl are introduced into an oxychlorination reactor in which EDC is produced at an elevated pressure and temperature in the presence of a fluidized catalyst. The reaction products are neutralized and partially condensed to recover EDC which is first sent to a drying column and then to the EDC purification system. A portion of the vent gas, consisting primarily of nitrogen and carbon dioxide is recycled to the reactor for added safety.

The purified EDC stream which contains recycled EDC as well as the EDC from direct and oxychlorination is vaporized and introduced into a furnace. At least half of the EDC stream is cracked to HCl and VCM. The reaction products are cooled rapidly, partially condensed, and then sent to the VCM purification system.

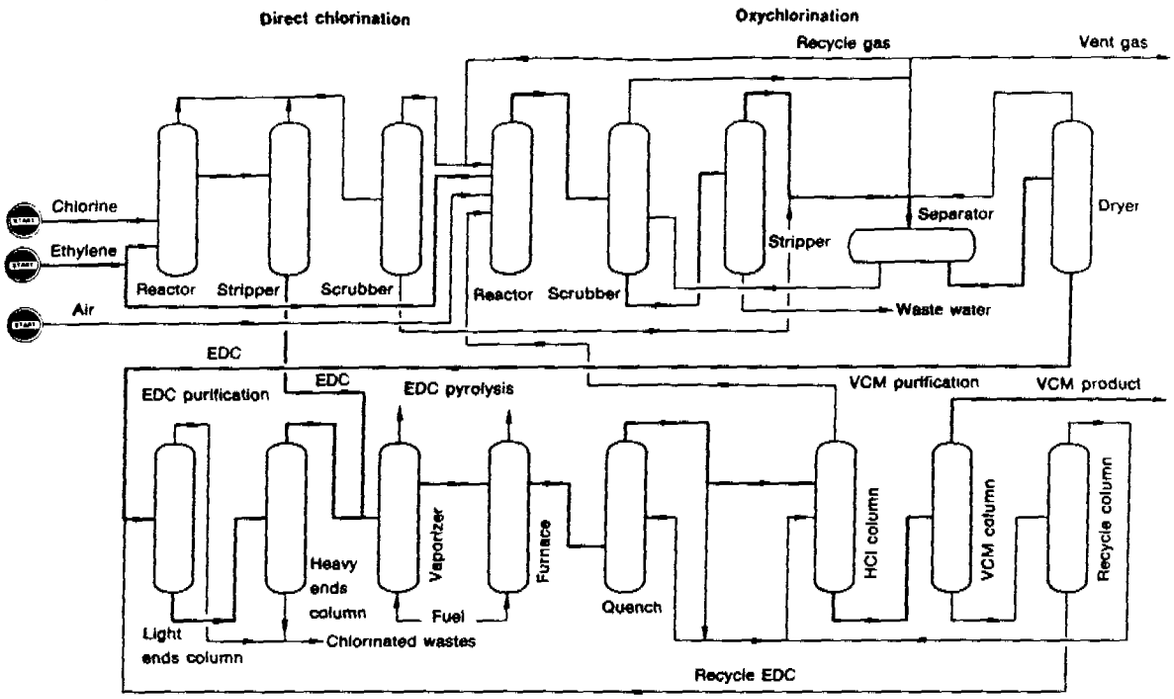

Fig. 7—Ethyl Corp.'s integrated vinyl chloride monomer process.

HCl and VCM are separated by fractional distillation from the unconverted EDC and small amounts of byproducts. The EDC, containing the byproducts, is recycled to the EDC purification system.

Mitsui Toatsu Chemicals technology.[68] The MTC technology utilizes a boiling liquid process for the direct chlorination reaction. Reaction heat is dissipated with the gaseous EDC exit stream which is condensed externally and sent to purification.

The oxychlorination process is characterized by the use of oxygen feedstock and a fluidized bed reactor. The reactor effluent gases are quench cooled with circulating EDC followed by caustic neutralization. The neutralized gas is cooled to condense EDC and water. Uncondensed gases, primarily ethylene, are recycled back to the oxy reactor. A small stream is vented from the recycle gas to allow purging of inerts. EDC liquid is phase separated from water and dehydrated before joining the EDC streams in the purification system.

A conventional EDC purification system splits crude EDC into light ends, heavy residue and pure EDC. The latter is cracked to yield VCM which is purified in a manner similar to that described in the Stauffer technology (see Fig. 8).

PPG technology.[69] The EDC production technology appears very similar to that described for Mitsui Toatsu, particularly in the use of oxygen feedstock and fluidized bed reaction for oxychlorination. However, PPG does not indicate use of a dehydrator to dry crude oxy EDC prior to purification. Also, PPG uses three rather than two towers to obtain the HCl-VCM-EDC separation.

B. F. Goodrich technology.[67,70] Goodrich direct chlorination uses conventional water-cooled technology similar to that shown for Stauffer. The air-based, fluidized bed oxychlorination technology is similar to that shown for Ethyl. Goodrich also utilizes an absorber-stripper system on the oxy vent gas stream to minimize hydrocarbon losses. Goodrich, in conjunction with Badger, Inc., offers complete technology for waste treating of VCM plant effluent streams.

Toyo Soda technology.[59,67] This technology appears very similar to that offered by Stauffer. The principal differences are in the use of an absorber-stripper on the oxy vent gas effluent (as with Goodrich) and the dehydration of crude EDC prior to purification. As with other oxychlorination processes, steam generation is used to remove reaction heat.

Phone-Poulenc technology [58,71] Rhone-Poulenc offers two processes, Chloe I and Chloe II. The former is of a special nature[57] to yield concurrently significant quantities of other chlorinated hydrocarbons such as trichloroethylene and trichloroethane. The Chloe II process is "true" VCM technology using air-based, fluidized bed oxychlorination in combination with boiling liquid direct chlorination.

Monsanto technology.[72] This process appears very similar to that offered by Stauffer.

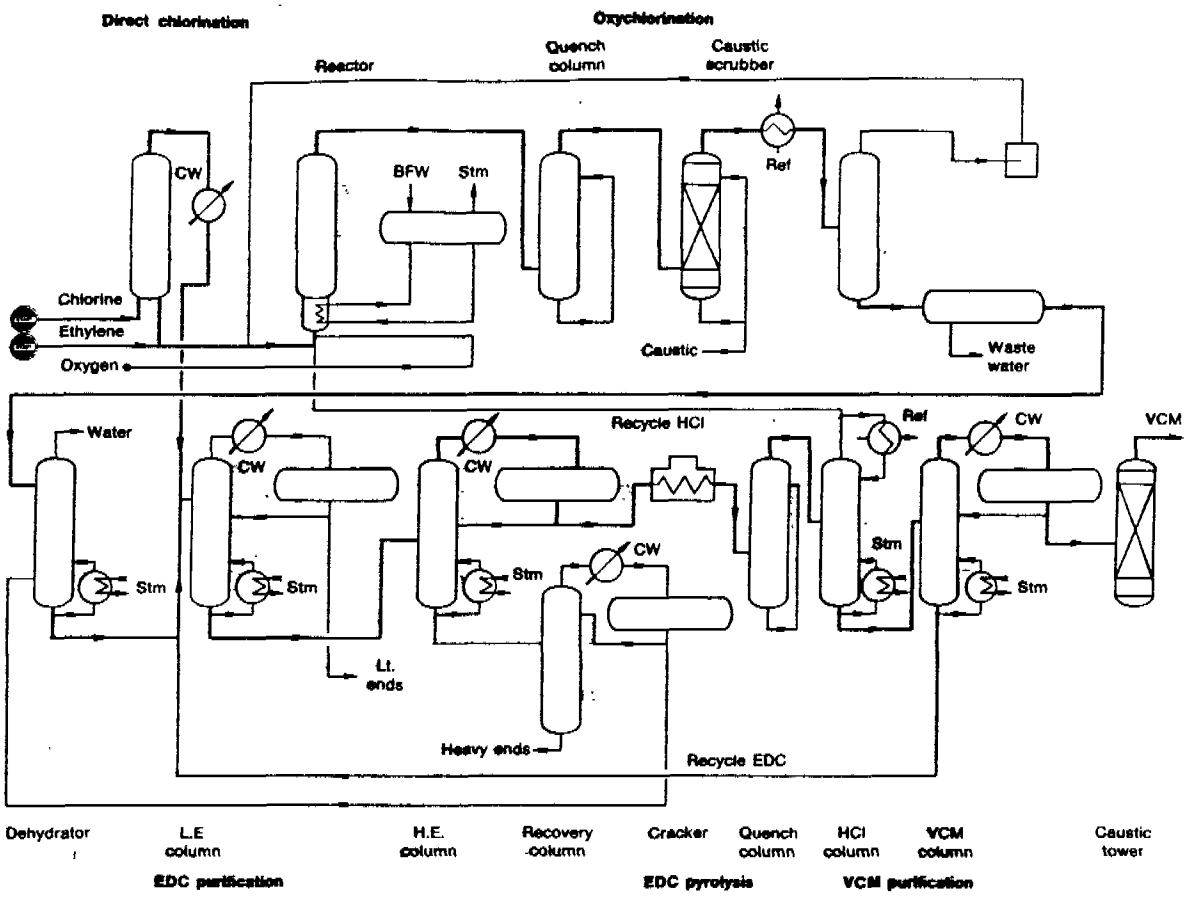

Fig. 8—Mitsui Toatsu uses these modifications in their vinyl chloride monomer process

Dow technology. Dow's technology has not been publicized. It has been used only by Dow and its foreign affiliates.

NEW DEVELOPMENTS

Although it is believed that several VCM producers currently use boiling liquid reactors for direct chlorination, Stauffer has developed a unique application of this concept.[60] Their approach, "High Temperature Chlorination," in effect uses the reactor as a reboiler for the conventional EDC purification system (see Fig. 9) Purified EDC is withdrawn as a side stream from the tower, and any light components formed are removed overhead. Normal feed to the tower consists of treated EDC from oxy and recycle. Small amounts of the normal heavy ends or tars are purged from the base of the reactor. This application eliminates approximately 100,000 lbs. per hour of 150 psig steam consumption for a one billion lb. per year VCM plant. A similar energy savings is achieved in reduction of cooling water usage relative to a conventional reactor and light ends tower. B. F. Goodrich[73] also offers a boiling liquid process in which the heat of reaction is utilized to purify all EDC processed in the purification train.

Increased activity by EPA (U.S. Environmental Protection Agency) and state agencies in regulating hydro-

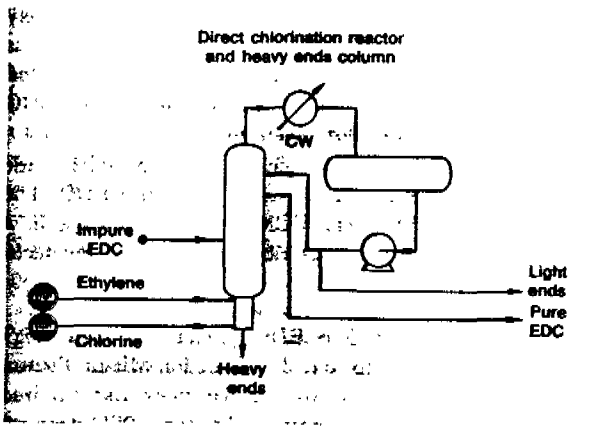

Fig. 9—Stauffer high temperature chlorination and ethylene dichloride purification schematic.

carbon emissions are likely to stimulate further new developments, particularly in oxychlorination processes. These will range from development of new oxygen-based technology to various add-on systems for cleaning up oxy vent gas. The latter may include catalytic oxidation, incineration (of oxygen-based oxy vent gas), solvent absorption, combined refrigeration and absorption techniques and/or other combinations. Several companies not active as VCM producers are involved in developing these add-on systems.

It is expected that companies will continue to devote considerable effort to the development of cracking promoters and inhibitors of side reactions in pyrolysis chemistry. Current cracking practices limit EDC conversion to 50-60 percent. Considerable energy and cost savings could be achieved through increased conversion levels without concurrent losses of EDC to undesirable side reactions.

EPA regulations. EPA's "Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride,"[1] presented the following regulations:

- Emissions from all point sources except oxychlorination would be reduced to 10 ppm VCM by volume
- Emissions from the oxychlorination reactor would be reduced to 0.02 lb. VCM per 100 lbs. EDC product from the oxy process
- Preventable relief valve discharges would not be permitted
- Fugitive emissions would be minimized by requiring enclosure of the emission sources and collection of the emissions.

EPA estimated typical VCM plant emissions in 1974 as follows:

Source	Lbs./VCM/ 100 Lbs. VCM
Fugitive	0.1215
EDC Finishing Column	0.05
VCM Finishing Column	0.24
Oxy Process	0.0364
Process Water	0.0007
Total	0.4479

The regulations were predicated upon reduction of such emissions by 94 percent using best available technology. Compliance testing of these installations was begun in the last quarter of 1978.

Additional EPA and state actions were initiated in mid-1977 to reduce hydrocarbon emissions from VCM plants in non-attainment regions, i.e., much of the Gulf Coast. EDC production is reported to account for 28 percent of the hydrocarbon emissions in the southern Louisiana and East Texas AQCRs.[66] These actions were directed primarily against oxychlorination vent gas from air-based units. The amount of hydrocarbon reduction sought varies from region to region. No published guidelines are currently available to reference.

The net effect of these various regulations has been to increase substantially the scope of add-on technology in VCM plants, such as:

- Installation of primary and redundant incineration facilities for VCM point (ex oxy) source and collected fugitive emissions
- Installation of HCl scrubbing and neutralization or recovery units in conjunction with the incinerators
- Installation of closed process sewers, collection systems and larger or redundant waste water strippers
- Replacement of single mechanical seals on pumps and agitators with double mechanical seals. (In some cases, conventional pumps were replaced with canned or magnetic drive pumps)
- Leak detection systems and portable monitors
- Enclosed sampling and analytical systems
- Vapor recovery systems for VCM loading/unloading and equipment clearing.

The EPA report estimated a maximum capital impact of $0.8 to $1.9 MM (1975 dollars) for a "model" 700 MM lb. per year VCM plant. Recent cost estimates indicate the true impact for these items is nearer $15 MM based on 1978 dollars. Addition of hydrocarbon compliance (proposed regulations) may add another $2-$5 MM.

EPA also has proposed further reductions in VCM emissions.[65] Under consideration at present are regulations which will reduce allowable emissions from 10 ppm to 5 ppm for all point sources, including oxy vent gas. EPA further plans to prohibit emission increases within 8 kilometers of an existing source due to construction of a new emission source. This will effectively prevent expansion of existing facilities or construction of new plants in the vicinity of existing plants. The proposed oxy vent gas regulation will also dictate substantial capital expenditures for add-on facilities and possibly the conversion of air-based to oxygen-based plants to facilitate incineration of tail gases.

ECONOMICS

Table 5 presents a 1981 manufacturing cost buildup for a typical 700 MM lb. per year grass roots VCM plant. Raw materials total 12 cents per lb. VCM or 54 percent of the required FOB plant selling price. Capital-related costs amount to 6.8 cents per lb. VCM or 32 percent. Utilities are only 6.7 percent of the total VCM cost. In perspective, the 1972-1973 reported VCM selling price[67] was only 4-5 cents per lb. By 1981, the capital-related unit costs alone will exceed this by 50 percent.

The obvious major factor in VCM pricing is raw materials cost. Although chlorine price is expected to double between 1973 and 1981, the impact of ethylene price will be even greater (three cents per lb. versus 17 cents per lb.). The real culprit, of course, is crude oil cost. During the late 1960s and early 1970s, plants using inexpensive LNG feedstocks were significant contributors to the low cost U.S. ethylene supply picture. The energy crisis rapidly reversed the low cost feedstock trend. LNG scarcity

dictated construction of naphtha and/or gas oil crackers for present and future ethylene production. This tied VCM prices irreversibly to crude oil prices through ethylene, fuel and power (particularly via its impact on chlorine).

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TABLE 5—Estimated 1981 VCM manufacturing cost

	Lbs/Lb VCM	¢/Unit	Cost, ¢/Lb/ VCM	%
Raw Materials				
Chlorine	0.64	5.6	3.53	16.2
Ethylene	0.49	17.1	8.45	38.8
Catalyst and chemicals			0.39	1.8
Utilities			1.42	6.5
Total variable			13.79	63.3
Labor			1.18	5.4
Miscellaneous			0.98	4.5
Total fixed			2.16	9.9
Total manufacturing cost			15.95	73.2
Capital charges and depreciation			5.85	26.8
Selling price FOB plant			21.79	100.0

Bases:
1. 700 MM Pounds/Year Balanced VCM Plant.
2. 1981 Startup
3. Grass Roots Investment = $140 MM
4. Light and heavy ends incinerated; recovered HCl sold as muriatic acid to break even on incineration costs
5. Fifteen percent DCF rate of return to cover interest charges and profit.
6. Unit values are generalized and are not specific to a particular licensor or technology

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Alloy selection for VCM plants

Data aids engineers in selecting alloys for critical equipment in direct chlorination, xychlorination and EDC pyrolysis sections of vinyl chloride monomer plants

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DESIGN CONDITIONS, alloy selection and operating experience are all part of the proprietary package offered by various VCM process licensors. Therefore, of necessity, this article will be limited to the three separate operating steps that all "balanced ethylene feedstock" plants have in common: direct chlorination, oxychlorination and EDC pyrolysis. We will look into the corrosive effects of chlorine and hydrogen chloride gases as well as that of hydrochloric acid. Aspects of alloy selection are based on published information of various processes, knowledge of corrosion and privileged information on actual sales of large quantities of high-nickel alloys for VCM plants in Europe, Japan and the USA. The data presented, within the limited scope of this article, are intended only for guideline purposes, without any guarantee of performance.

(**Editor's note.** Alloys 200, 201, 400, 600, 800 and 825 referred to in this article correspond to the VDM trade names shown in Table 1 with which the author has the most recent experience in vinyl chloride monomer plants.)

SELECTING ALLOYS

Nickel and high-nickel alloys are among the few metallic materials having useful resistance to dry chlorine, hydrogen chloride and hydrochloric acid. These alloys are not new to the chlor-alkali industry, being more or less standard selections in caustic, brine and salt processing. We will, in turn, deal with each of the three chief corrosive environments encountered in VCM processes. Table 1 provides a brief description of alloys commonly in use, their ASTM specifications and the tradenames under which they are known.

Chlorine. Gaseous chlorine at low temperatures and in the absence of moisture is not severely corrosive and is commonly handled by carbon steel. Usually a more resistant material such as Alloy 400 is specified for critical parts such as valve trim, instrumentation and orifice plates in chlorine pipe lines. In contrast, wet chlorine is extremely corrosive on steel and nickel alloys, and requires Hastelloy® C or titanium. At elevated temperatures, corrosion rates on steel increase with temperature. The upper limit of usefulness is around 400° F when the protective effects of the corrosion products disappear. Ferric chloride vaporizes at 420° F.

Fig. 1 provides a guide to the selection of various alloys in dry chlorine. The surface coating of chlorides tend to provide protection up to a temperature level

TABLE 1—Alloys commonly used in VCM plants

Materials	Reference in text	Nominal Composition, %					ASTM B number	ASME B number	VDM trade names	Comparable products
		Ni	Cr	Mo	Cu	Fe				
Nickel										
Nickel	Alloy 200	99.6					161-163	161-163	VDM-Nickel 200	Nickel 200
Low Carbon Nickel	Alloy 201	99.6					161-163	161-163	VDM-Nickel 201	Nickel 201
Nickel-copper alloys										
Nickel-Copper Alloy	Alloy 400	67			31	1.5	163-165	163-165	NICORROS 400	Monel 400
Nickel-chromium-iron alloys										
Nickel-Chromium-Iron Alloy	Alloy 600	76	15			8	163-168	163-168	NICROFER 600	Inconel 600
Nickel-Iron-Chromium Alloy	Alloy 800	32	21			46	163-407	163-407	NICROFER 800	Incoloy 800
Nickel-Iron-Chromium-Molybdenum-Copper Alloy	Alloy 825	42	21	3	2.3	30	163-423	163-423	NICROFER 825	Incoloy 825

Note: NICORROS and NICROFER are registered trademarks of Vereinigte Deutsche Metallwerke AG Germany. Monel, Inconel, Incoloy are registered trademarks of The International Nickel Co. Hastelloy is a registered trademark of Cabot-Stellite Division

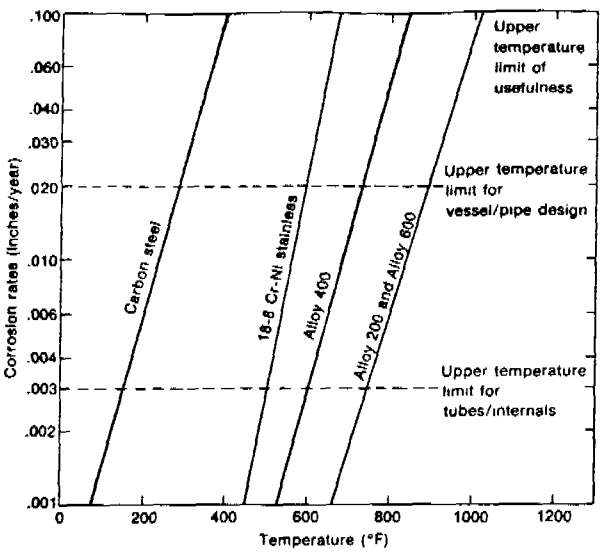

Fig. 1—Chlorine. Alloy selection guide.

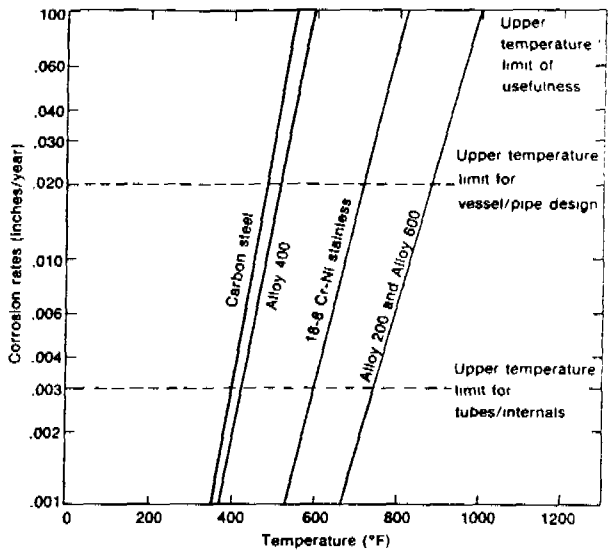

Fig. 2—Hydrogen chloride. Alloy selection guide.

at which melting, vaporization or decomposition removes such films. The corrosion rate appears proportional to the vapor pressure of the metal chlorides. The common design parameter for tubing, valve trim and internals is 0.003 in. per year (IPY) maximum corrosion rate, while for vessels and pipe an upper corrosion rate of 0.020 IPY is frequently adopted with a corrosion allowance of ⅛ to ¼ in.

Alloy 200 and Alloy 600 are the most commonly used alloys for reactors, coils and agitators in the 500 to 1000° F range.

Hydrogen chloride. Dry HCl behaves in a similar manner as chlorine, and carbon steel can suffice up to 450° F above which Alloy 200 is usually specified. Fig. 2 provides a guide to the selection of various alloys in dry HCl gas and the design parameters of 0.003 IPY and 0.020 IPY upper corrosion rates for certain components are shown. The presence of moisture does not appreciably increase corrosion rates above the dewpoint over that by dry gas.

It must be pointed out that there are many variables, and even small amounts of addition agents to control catalyst activity, may exert an influence on the tenacity and vapor pressure of the protective corrosion scales. Therefore, absolute corrosion rates for different temperatures in chlorine and HCl systems are difficult to predict. Even so it is felt that Figs. 1 and 2 are sufficiently accurate to serve as a guide. These figures should be checked against actual experience of each of the different VCM processes.

The performance of Alloy 200 in dry as well as wet hydrogen chloride gas has been consistently good. In cyclic operating conditions, particularly in the presence of air or oxygen, Alloy 600 and Alloy 825 offer good all-round resistance. It is prudent to assume that Types 304 and 316 stainless steels would be subject to chloride stress corrosion cracking conditions during shutdown in spite of various precautions that may be taken.

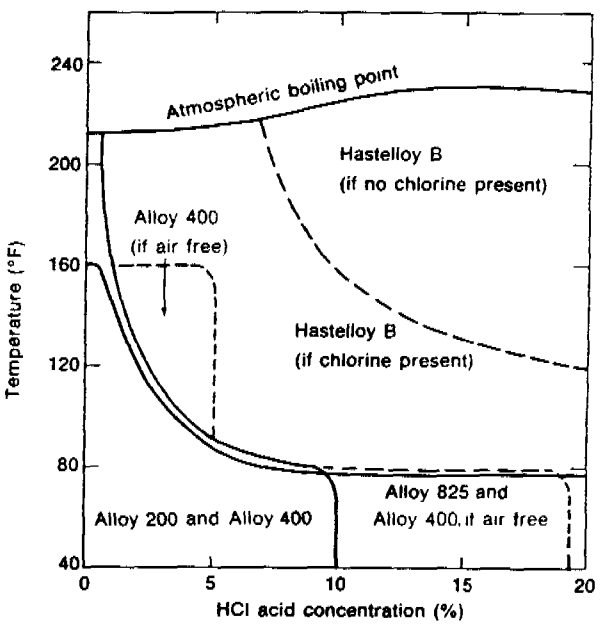

Fig. 3—Hydrochloric acid. Alloy selection guide (Basis: 0.020 IPY max. corrosion rate).

Hydrochloric acid. HCl is a typical reducing acid through its entire concentration range. Its strongly acidic character is harmful to steel. Alloy 200 and Alloy 400 behave similarly and find application at ambient temperature up to 20 percent concentration and at higher temperature below 5 percent concentration. Fig. 3 shows isocorrosion lines for 0.020 IPY which is generally considered the upper design limit of an alloy selection. The graph immediately delineates the conditions suitable for handling with Alloy 400 and those where Hastelloy B is required.

It should be noted that in most cases in which hydrochloric acid is formed as a result of hydrolysis of chlo-

rides or chlorinated hydrocarbons such as EDC, the acid concentrations are less than .5 percent and both Alloy 200 and Alloy 400 can withstand such conditions satisfactorily at temperatures up to 400° F.

Also in hydrogen chloride gaseous processes when cooling takes place near the dewpoint of HCl (that is below 260° F) it is prudent to assume that because of the hygroscopic nature of the chloride on steel that HCl might condense with resultant high corrosion rates. In applications where 18-8 Cr-Ni stainless steel is used at elevated temperatures such condensation can lead to chloride stress cracking. Alloy 800 is highly resistant to chloride stress corrosion cracking while Alloy 600 and Alloy 825 are immune to this phenomena in this application.

Even though with special precautions a system can be kept dry during operation, adequate consideration must also be given to protect equipment during shutdown and when starting up the unit. Purging with inert dry gas prior or during shutdown is helpful in sustaining a dry atmosphere. Alternately one can maintain temperatures above the dewpoint. Also, sludges present in the system absorb chlorides and must be kept dry otherwise aqueous HCl acid is formed from moisture pick-up. Alloy 400 is widely used for handling dilute HCl acid in waterwash solutions and for heat-exchanger tubes in the EDC purification.

VCM PROCESS COMPARISON

The typical VCM process combines direct chlorination and oxychlorination processes to provide ethylene dichloride (EDC) feedstock to the pyrolysis unit. Because of the large amount of hydrogen chloride generated in the cracking of EDC, plant economies dictate the need for an oxy unit. The sequence and three principal operating steps are quite similar from process to process and are shown in Fig. 4. It is not the writer's intention to make a detailed analysis of the entire alloy selection for the various licensed processes, but instead, to comment on the basis of previously provided corrosion data, on alloy considerations applicable to each of the three principal steps.

Direct chlorination. Ethylene is reacted with dry chlorine in the presence of a catalyst, to produce ethylene dichloride. The catalyst usually is a ferric chloride. Liquid EDC is used as a reaction medium to insure intimate mixing. Conventional water cooling removes the exothermic heat of reaction. Temperatures are controlled at 130° F to 150° F. The EDC produced is usually treated for removal of ferric chloride carry-over. In a number of systems lately, the reaction is carried out at the EDC boiling point (approximately 230° F) taking pure EDC overhead and using the heat required to vaporize part of the reactor content, to control the temperature. Fig. 5 shows the direct chlorination process.

It is necessary to insure a dry chlorine feedstock and to properly control the temperature by thorough mixing of the reactants to prevent hot spots and runaway temperatures. With such operating control conditions, carbon steel can be safely used for the reactor and auxiliary equipment. As can be seen from Fig. 1, a suitable corrosion allowance may need to be applied depending

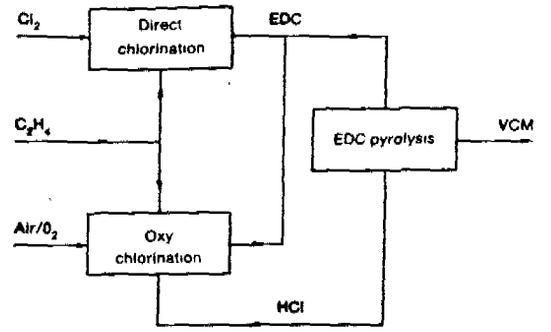

Fig. 4—Principal VCM process steps.

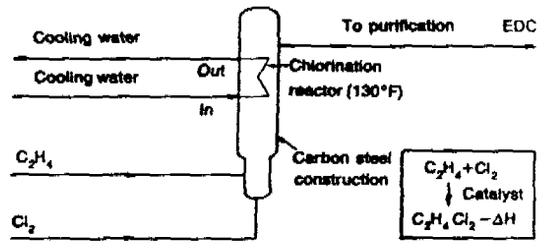

Fig. 5—Direct chlorination.

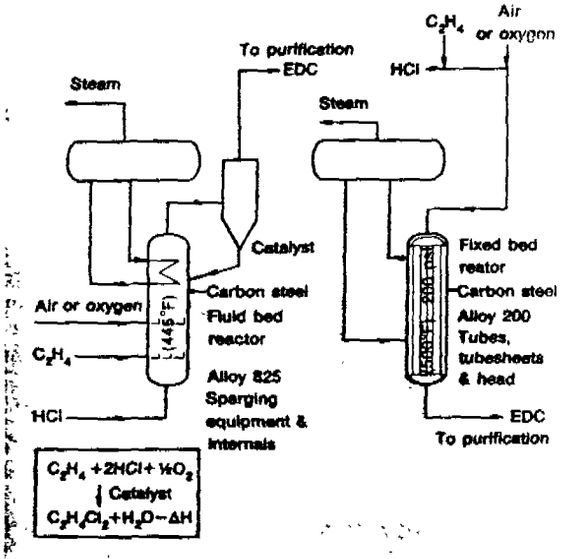

Fig. 6—Oxychlorination.

on temperature and experience. Further, proper shutdown procedures should be employed keeping the unit dry or free from chlorine to prevent attack by wet residual chlorine on the steel when the unit is not in operation.

Oxychlorination. Ethylene is reacted with dry hydrogen chloride and oxygen in the presence of a catalyst to produce EDC and water. The catalyst usually is im-

ALLOY SELECTION

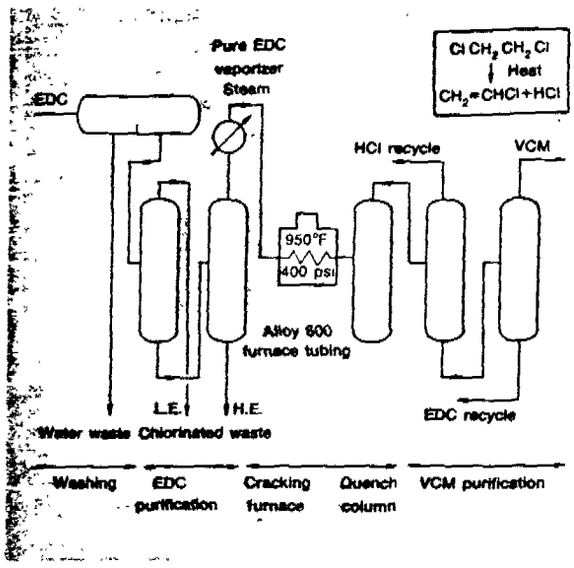

Fig. 7—EDC pyrolysis.

pregnated with copper chloride. The oxychlorination process can be carried out either in a fluid bed of catalyst or in tubular fixed bed catalytic reactors. Further, the reaction of ethylene and HCl can take place either with air or oxygen. Both process systems are shown in Fig. 6.

Fluid bed. Reaction with a fluidized catalyst generally takes place at 435° F to 450° F and atmospheric pressure. The reaction is highly exothermic and the temperature is controlled by good intermixing of reactants and catalyst and by the use of internal cooling surfaces. A carbon steel reactor can be used. Referring to Fig. 2, we can expect corrosion rates in the order of 0.010 IPY which means a corrosion allowance of ⅛ in. or 3/16 in. should be applied. For internals, where corrosion can occur on both sides of the metal, where velocity effects may interfere with protective scales or where a corrosion allowance is not practical or interferes with the rate of heat transfer, a corrosion resistant alloy is commonly specified.

Good service with Alloy 600 and Alloy 825 has been obtained when used for the sparging equipment to introduce the gases in the fluid bed, and for pipe, nozzles and fittings inside the reactor. These alloys are not susceptible to chloride stress corrosion cracking if hydrolysis takes place during shutdown. Occasionally a problem is experienced from the combined effect of corrosion and erosion by the catalyst which removes the protective corrosion products on steel. Also, accumulation of catalyst on the bottom of the reactor can cause localized attack and should be avoided. Because of the carbon steel reactor construction, it is definitely necessary to control temperatures below 500° F. Proper shutdown procedures to prevent corrosion on steel by dilute hydrochloric acid, when the unit is not in operation, is of course most desirable.

High nickel alloys are often restricted to locations in critical equipment. Less expensive materials are then selected as soon as allowed by process conditions.

Fixed bed. Reaction in a fixed-bed catalyst reactor is carried out at temperatures of 450° F to 600° F and pressures from atmospheric up to 200 psi. The catalyst is contained in a number of vertical tubes held in a tubesheet at top and bottom. Reaction heat is removed by the generation of steam on the shell side of the reactor. It is more difficult to control temperatures uniformly than in the fluidized bed, and occasional hot spots tend to develop on the tubes.

As can be seen from Fig. 2 operating conditions require corrosion-resistant alloys. Both Alloy 200 and 600 are preferred alloy selections. Usually Alloy 200 is used for the reactor tubes and has given excellent performance. The tubesheets and heads of the reactor are clad with nickel on steel. The reactor shell which is exposed to water and steam is made of carbon steel. When three or four reactors are required, nickel is also used for the interconnecting piping. Temperatures should be controlled no higher than 600° F to prevent by-product formation and deactivation of the catalyst. Also, when localized hot spots occur on the Alloy 200 tubes we have observed intergranular embrittlement on some tubes. Alloy 201, which has a low carbon level, is resistant to such intergranular attack.

Oxygen versus air. The use of oxygen instead of air in the oxychlorination process improves operating efficiency and product yield. It permits operation at a lower temperature. Even though alloy selection is not affected by this, from a metals standpoint substantially less quantity of alloy is required as the equipment tends to be more compact and smaller. Also capital savings are possible for not having to separate EDC, ethylene and other chemicals from a large nitrogen vent gas stream and burning the vent gas.

EDC pyrolysis. Ethylene dichloride is vaporized and thermally cracked to vinyl chloride yielding volumous by-product hydrogen chloride. Cracking is carried out in a fired furnace at a temperature of 900° F to 1000° F and at an elevated pressure of about 400 psi. The reaction products are cooled rapidly, partially condensed and then sent to a VCM purification system where HCl and VCM are distilled from the unreacted EDC and small amounts of by-products. The cracking process is susceptible to inhibition and fouling by trace amounts of impurities and therefore the crude EDC is purified and the light and heavy ends removed—both of which contain chlorinated waste products. Further, to prevent excessive hydrochloric acid corrosion here and

downstream of the cracker, it is necessary that the crude EDC is washed, neutralized with caustic, and dried. The pure EDC is preheated in an economizer and then vaporized in a steam heated kettle-type reboiler. See Fig. 7 for the EDC pyrolysis process system.

For alloy selection of the pyrolysis furnace tubing we are guided by the fact that hydrogen chloride is formed in the thermal decomposition of EDC, that the furnace requires periodic decoking and that during shutdown conditions hydrolysis of hydrogen chloride is likely to occur. Alloy 600 is the preferred alloy section for this application and has consistently given good reliable performance. In recent years, Alloy 800 has been used with success. It is prudent to assume that the 18-8 Cr-Ni type of stainless steels are subject to chloride stress corrosion cracking below the dew point and during shutdown. One company reported that they had used 5 Cr-½ moly steel without excessive corrosion when insuring a bone-dry feed to the unit and taking the usual special shutdown and start-up precautions of gas-blanketing and keeping the unit dry. Alloy 600 is often specified for the cooling coil where halogen corrosion is the greatest. Also Alloy 600 solid or as clad plate has been used for batch polymerizer reactors in an aqueous medium in the presence of a catalyst and suspending agents, producing PVC resin.

In the purification system, corrosion can be very severe because of the hydrolysis of hydrogen chloride and of various organic chlorides. This can occur at temperatures of 260° F and downwards forming dilute hydrochloric acid. It is extremely difficult to insure a bone-dry system, that is, zero free water and below 10 ppm of total dissolved water. Inadvertent moisture pick-up from sources such as leakage at water coolers and steam heaters and intrusion of humidity at flanges and seals is always a possibility. Also entrained water is frequently carried along in the distillation process. Carbon steel in dry systems usually corrodes less than 0.002 IPY while in the presence of water, dilute HCl acid is formed and corrosion rates are approximately 0.010 to 0.160 IPY depending on the temperature and concentration. In the presence of 2 percent hydrochloric acid, carbon steel corrosion often exceeds one inch per year.

From Fig. 3 we can see that Alloy 400, in most cases, would be the desired economical choice of alloy. It has been used in industry to resist a wide variety of chlorinated hydrocarbons and solvents. Hastelloy B finds use for critical components such as valve trim and pump impellers. Corrosion of steel equipment tends to be the greatest in reboilers, the bottom section of distillation columns, bubble caps, plates, condensers, water separators, valves, pumps and fittings.

It should be pointed out that titanium is *not* a suitable selection in dilute hydrochloric acid, because of its strong reducing nature. Where titanium is used, it has provided useful life under mild conditions with a pH above 1.5. For economic reasons, various coatings and liners are frequently considered and used as an alternate to alloy. The following applications have been reported: a gunnite lined pretreater, glass-lined vessels, polypropylene-lined steel piping, Saran and Kynar-lined pipe, glass-coated pumps, various coatings in accumulators. Even though attractive from a first-cost standpoint, special care is required to maintain such coatings and prevent damage at joints.

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TECHNOLOGY TRENDS

No major changes in the use of established materials of construction is foreseen. Brief mention has already been made of a trend towards higher temperature direct chlorination using the reactor as a reboiler to remove the heavy ends. Also a substantial share of new plants appears to utilize oxygen instead of air in the oxychlorination step. This approach discharges fewer chlorinated hydrocarbons with the vent gases into the atmosphere. For this reason and also to increase existing plant capacity, some VCM plant oxychlorinators are being converted from air to oxygen.

Emission control standards are getting more severe, forcing the scrubbing and neutralization of HCl, use of waste water strippers to remove volatile organics, enclosing and collecting emissions for incineration. Corrosion in parts of this equipment can be very severe and the rate of attack is not always predictable; some of the previously mentioned alloy selection guidelines do apply.

Conclusion. For economic considerations, special high-nickel alloys are often restricted to critical locations from where one downgrades to less expensive materials as soon as process conditions permit. During the final design, the limitations of each material selected must be scrutinized as well as the means used to minimize corrosion by control of process conditions. For example, what will be done to control exothermic reactions, velocity/impingement effects, moisture content, pH/acidic conditions, impurities, sludges and acid concentrations? We have the tools available to do this and particularly in chlorine and HCl processes we should not overlook proper start-up and shutdown procedures, since severe corrosive attack may take place while the unit is not in operation.

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