

Responding to a Harsh Business Environment: A New Diaphragm for the Chlor-Alkali Industry

by Sajjad Ahmed and Peter Foller

The last several years have been difficult for producers of U.S. chlor-alkali chemicals. Low prices for chlorine and caustic and escalating fuel costs have resulted in several plant closures and have squeezed the profitability of those that have remained. For those plants operating with diaphragm cell technology, which still comprises a major portion of domestic production, conversion to membrane cells is not a viable option. Replacement of diaphragm cells with membrane cells entails abandonment of existing highly efficient caustic evaporator trains, provision for solid salt to replace solution-mined salt, and significant brine treatment upgrades, along with writing off the original investment in diaphragm cells.

In addition to the direct cost issues, there are indirect costs associated with diaphragm cell production of chlorine. These issues center on the environmental health and safety concerns over asbestos, which is currently used in diaphragm cells as a separator to keep products from mixing. Although the chlorine industry has an excellent track record of using asbestos safely, many businesses have been forced into bankruptcy due to high damage awards resulting from the past sale of asbestos-containing products. A great deal of pressure exists to find alternative diaphragm cell separators, if only to assure continuity of supply of raw materials.

PPG Industries has responded to this difficult period by developing a new separator for its diaphragm cells operating at its plants at Natrium, West Virginia, and Lake Charles, Louisiana. The new separator is asbestos-free, energy efficient, and durable. The new separator, which we have named Tephram, is capable of retrofit to existing diaphragm cell facilities with minimal changes to existing equipment and procedures. Full circuit operation has been under-

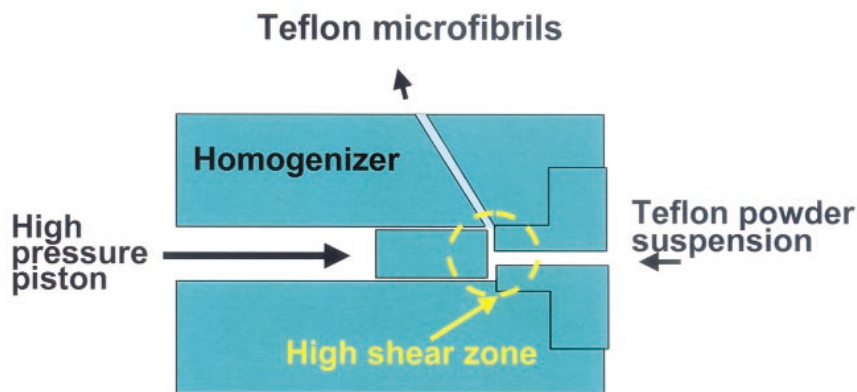


Fig. 1. Manufacture of pTFE Microfibrils.

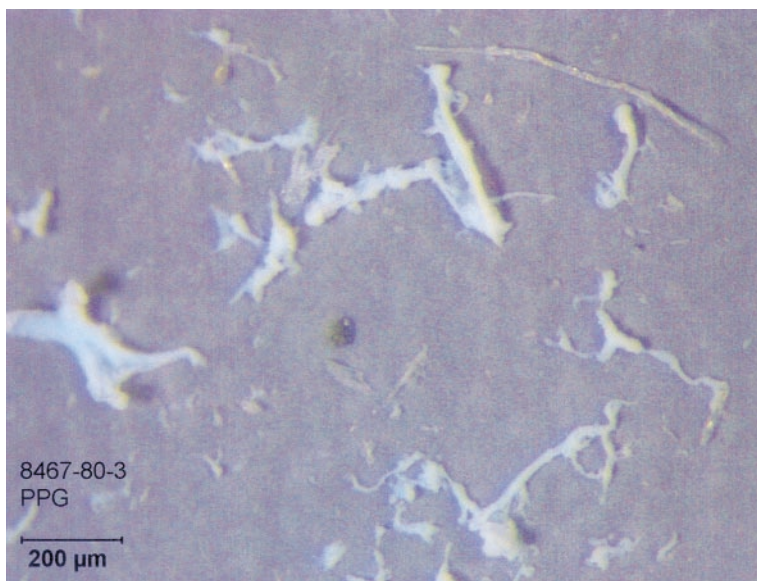


Fig. 2. Typical pTFE Microfibrils.

way at a small circuit at our Natrium location for over 10 years with the Tephram diaphragm. Just this year, PPG completed conversion of its largest diaphragm cell area at Lake Charles from asbestos to Tephram diaphragms. Currently, conversion of the Natrium plant's largest circuit is underway. The

success seen so far indicates that the diaphragm will be adaptable to a variety of cell designs. The cells to which the Tephram diaphragm has been successfully applied at PPG locations include the Columbia N6, the Glanor V-1244, and the Oxytech MDC-55.



FIG. 3. Tephram Diaphragm on a Glanor V-1244 Electrolyzer Cathode.



FIG. 4. Assembled Glanor V-1144 Electrolyzer at Lake Charles "Plant C."

The requirements for any new chlor-alkali diaphragm are very demanding. Here is a partial list:

- Resistance to chlorine and caustic
- Separation of chlorine and hydrogen
- Permeability sufficient to match the desired brine feed
- High conductivity
- Resistance to brine upsets
- Rapid recovery from outages
- Minimal impact on established plant procedures and existing capital
- Long life

What is a Tephram Diaphragm?

The Tephram diaphragm is a fluoropolymer-based separator comprised

of pTFE (polytetrafluoroethylene) microfibrils and a secondary, longer, pTFE fiber. The longer fiber, DuPont's Teflon Floc pTFE fiber, offers good reinforcement of the diaphragm but is too coarse to be used as the primary fiber. The microfibrils are prepared by a PPG-patented process and comprise the bulk of the diaphragm material. The microfibrils are made by forcing an aqueous suspension of pTFE powder through an orifice at high pressure. The process is depicted in Fig. 1, and the resulting microfibril product is shown in Fig. 2.

The microfibrils prepared by this process become highly entangled in the deposition process so that there is no need for high temperature sintering to assure diaphragm integrity. The fact

that the diaphragm is an entangled mat instead of sintered is thought to play an important part in avoiding hydrogen transfer from the catholyte to anolyte along Teflon pathways during cell operation, a problem commonly associated with perfluorocarbon based diaphragms. To assure that the diaphragm is wettable, DuPont's Nafion solution is used to coat the pTFE so that the normally hydrophobic fibers are permanently wetted.

The pTFE microfibrils and Teflon Floc fiber components are mixed with other deposition aids in a water-based slurry containing 2-4 wt.% suspended solids and vacuum deposited directly onto the cell cathode. Both woven screen and perforated plate cathodes can be used. The diaphragm mat is then dried at low temperature (< 100 °C) to remove water. The fact that drying steps are done at low temperature puts less stress on cell components. A topcoat is next applied by vacuum depositing inert inorganic fillers into the diaphragm to adjust permeability as desired. The fillers typically used are Attapulgit clay and zirconium oxide. Once the topcoat is applied, the diaphragm is dried and is ready for assembly into a cell.

The steps required for Tephram diaphragm manufacture are:

- High shear manufacture of pTFE microfibrils
- Mixing of aqueous slurry (filter aids, surfactants, viscosity modifier, etc.)
- Vacuum deposition of diaphragm onto cathode and drying
- Topcoat application (zirconium oxide & Attapulgit clay)
- Drying
- Cell assembly

Except for the microfibril preparation and some mixing equipment, the diaphragm manufacture uses the same equipment as asbestos diaphragms. This allows for easy transition from asbestos to Tephram diaphragms. The final Tephram diaphragm is typically about 0.10 inch thick and has an area density of about 0.4 lb/ft². A photo of a completed Tephram diaphragm on one of 12 cathode elements of a bipolar Glanor V-1244 electrolyzer is shown as Fig. 3.

A fully assembled 25 Ton Cl₂/day Glanor V-1244 Electrolyzer ready to move into place is shown as Fig. 4. Sixty four such electrolyzers were converted to Tephram diaphragms in the conversion of Lake Charles' Plant C.

Start-up and Operating Maintenance of Tephram Diaphragm Cells

Tephram diaphragms are started up and operated much like their asbestos diaphragm counterparts. The diaphragm is flushed with water to remove surfactants and to wet the diaphragm. This gives a low start-up voltage and avoids excessive foaming from surfactant residue. Following the water flush, the cell is filled with hot brine and started at full operating load. The cell is monitored closely during the first several hours of operation to judge diaphragm permeability. The Tephram diaphragm is initially more permeable than required for high strength caustic operation. This allows for the addition of materials to the brine feed to adjust the permeability of the diaphragm to match circuit requirements. The higher permeability also gives a built in cushion for the occasional brine upset, which typically adds an additional burden of magnesium and calcium.

Materials used for permeability trimming include primarily Attapulgitic clay and magnesium hydroxide. The clay particles act by filtration and they swell within the diaphragm matrix. The magnesium forms a gelatinous hydroxide precipitate upon contact with hydroxide diffusion or leakage from the catholyte. Careful attention to amounts of materials added, flow rates, and pH allow for permeability control with good efficiency. Overdosing with magnesium hydroxide can result in excess plugging and lower efficiency, just as with asbestos. However, the magnesium will generally be dissolved from Tephram diaphragms with continued operation, and the occasional circuit outage, so that the efficiency loss is not irreversible. Uneven magnesium hydroxide precipitation is, nevertheless, the most common cause of longer term decline in efficiency with Tephram diaphragms.

Operating Experience with Tephram Diaphragm Cells

Operating results in the smaller Columbia N6 circuit at Natrium have been described earlier.¹⁻⁴ Typically in this smaller (160 T Cl₂/day) circuit, the power requirements were slightly better or equal to those obtained with asbestos diaphragms. The smaller cir-

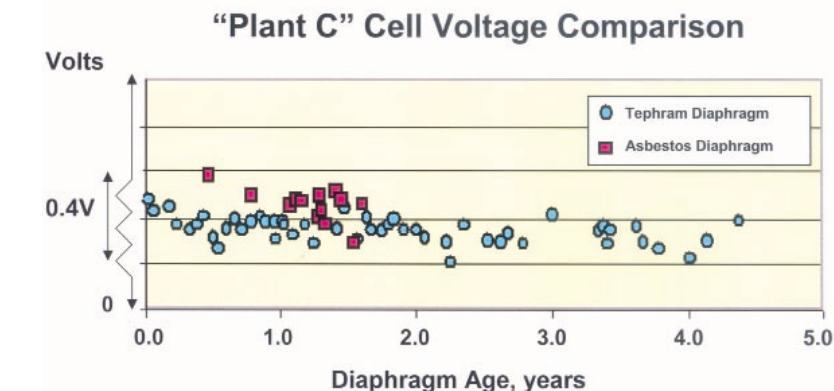


Fig. 5. Glanor V-1244 Cell Voltage Comparison.

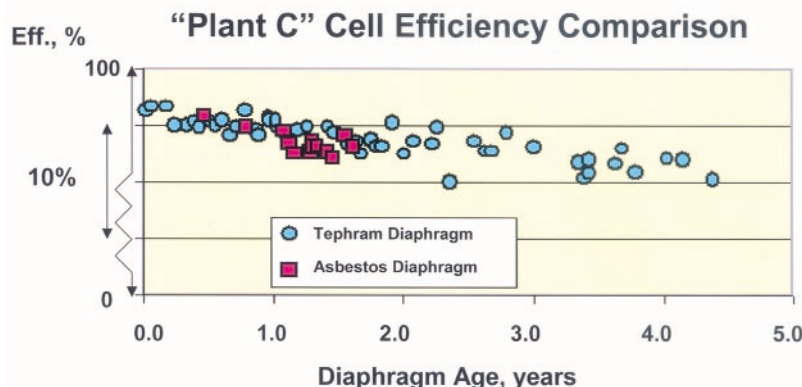


Fig. 6. Glanor V-1244 Cell Efficiency Comparison.

$$Cl_2 \text{ Eff} = \frac{\text{vol\% } Cl_2}{\left\{ (\text{vol\% } Cl_2 + 2 \otimes \text{vol\% corr } O_2) + 6 \otimes \left(\frac{\text{gpl NaClO}_3 \text{ catholyte}}{\text{gpl NaOH catholyte}} \right) \otimes \text{vol\% } Cl_2 \right\}}$$

Eq. 1. The Calculation of Oxy "6" Current Efficiency for Chlorine.

cuit demonstrated the ruggedness of the Tephram diaphragm. Generally speaking, cell renewal replacements were due to cell mechanical problems, such as mat leaks or gasket failures, before the diaphragm failed. Operating lives as long as four years were obtained. The ruggedness of the diaphragm has been further demonstrated by empirical evidence: the circuit was mothballed for several months with no special precautions being taken, such as addition of reducing agents or cathodic protection, and restarted with no unusual problems.

At Lake Charles' 1,800 Ton Cl₂/day Glanor V-1244 Plant C circuit, Tephram diaphragms have demonstrated both a longer life and better power efficiency than asbestos diaphragms. Relative comparisons of voltage and efficiency with asbestos are shown in Figs. 5 and 6. Absolute values for efficiency and

voltage are not shown in order to protect company-confidential information. The data shown in the figures are for a period where both types of diaphragms were still in operation so that a same-time, same-circuit comparison could be made.

The chlorine current efficiency values were calculated using the standard Oxy"6" equation which estimates efficiency from caustic concentration, oxygen in chlorine, and sodium chlorate in cell liquor (see Eq. 1 above).

The results for the Lake Charles V-1244 electrolyzers show that the voltage is slightly better and efficiency generally about the same as for the asbestos cells. This gives a power consumption advantage to the Tephram diaphragm cells. It should be noted that the comparison is conservative with respect to the power consumption advantage. This is due to preferential removal of

Table I. Plant C Operating Data with Tephram Diaphragms.

V-1244 Electrolyzers	Diaphragm Age, days	NaOH, gpl	H ₂ , vol.%	O ₂ , vol.%
Average.....	764	137	0.12	2.24

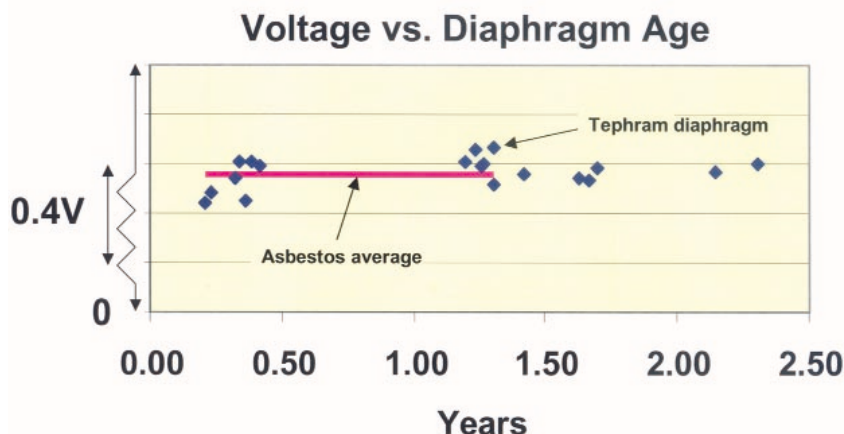


Fig. 7. Sodium MDC-55 Cell Comparison of Voltage.

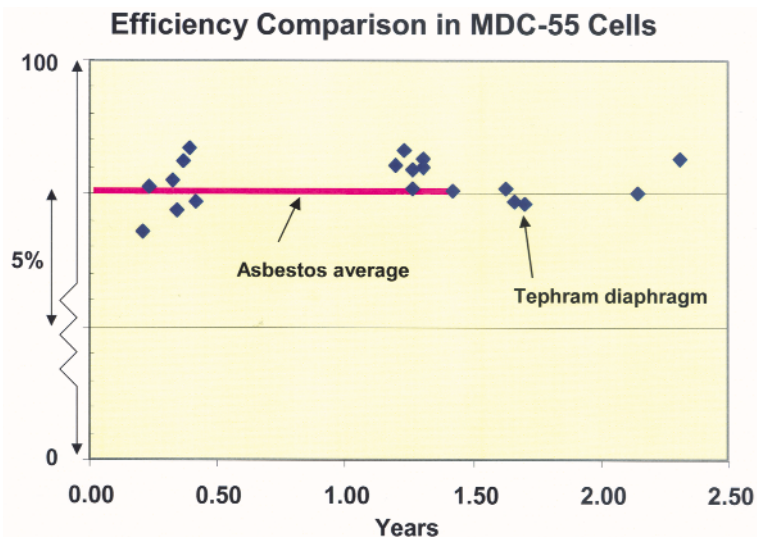


Fig. 8. Comparison of Asbestos and Tephram Diaphragms in Sodium MDC-55 Cells.

Table II. Sodium MDC-55 Cell Operating Data.

	Diaphragm Age, days	NaOH, gpl	H ₂ , vol.%	O ₂ , vol.%
Tephram Diaphragms	398	126	0.10	1.87
Asbestos Diaphragms	299	141	0.15	2.15

the worst-performing shorter lived asbestos diaphragm cells while all Tephram diaphragms were maintained in operation as the conversion proceeded. Also noteworthy is the substantially longer life seen with the Tephram diaphragm cells. The asbestos cells have a life shorter than two years due to the degradation of asbestos from load swings and brine upsets. These factors cause asbestos diaphragms to become less permeable to brine flow. The Tephram diaphragms are much more forgiving, because the fluorocarbon matrix is not chemically attacked as is asbestos. With load swings becoming more common as power costs and chlorine demand fluctuate, the operating stability of Tephram diaphragms becomes an important advantage.

The average caustic strength and anodic byproduct performance of the Lake Charles Plant C diaphragms is listed in Table I. The averages are for 64 electrolyzers, each of which contains 12 bipolar cell units. The data were taken shortly after the plant was fully converted from asbestos to Tephram diaphragms in 2003.

Conversion of the MDC-55 cell circuit at Natrium, WV, has been started. The incentive for this location has been the Tephram diaphragm's durability and recovery from load swings and brine upsets. Of the circuit of monopolar MDC-55 cells, at this writing approximately 15% have been converted to Tephram diaphragms. Because there is a large population of asbestos diaphragm cells still in operation, direct side-by-side comparisons are possible. A plot of recent Tephram diaphragm cell voltages is compared with the average voltage for asbestos diaphragms during the same period in Fig. 7.

A similar plot is given in Fig. 8 for Oxy6 chlorine efficiency. The plot compares efficiency for the two types of diaphragms during the same operating period.

With the MDC-55 cells, voltage and efficiency appear to be generally stable over the test period for the Tephram diaphragms. Again, the asbestos timeline does not extend as far as the Tephram diaphragm timeline due to the shorter life of the asbestos diaphragms.

The data in Table II are for a recent measurement of caustic strength and anodic by-product performance. Note that hydrogen in chlorine is not an issue, being generally less for Tephram

diaphragm cells than for the asbestos diaphragm cells.

The power consumption for the cells with the two types of diaphragm are roughly equivalent, because voltages and efficiency values are very close (power is proportional to voltage/efficiency). Even without a clear power savings, operating advantages such as resistance to load swings and brine upsets and longer diaphragm life have led to the decision to fully convert to the Tephram diaphragm in PPG's MDC-55 circuit.

The current status of the conversion of PPG's diaphragm circuits to Tephram diaphragms is shown in Fig. 9. At this time, over half of PPG's diaphragm cell chlorine capacity utilizes the Tephram diaphragm.

A summary comparison of PPG's experience with the Tephram diaphragm is given as Table III. These conclusions were developed through more than a decade of R&D. Table IV, the U.S. patents for the Tephram diaphragm, shows the program's origins in the 1980s.

PPG is well on the way to becoming asbestos-free at its diaphragm plant facilities. This is being achieved under very difficult business conditions for the chlor-alkali industry. The move to the non-asbestos diaphragm is being driven by two factors, power savings and the operating flexibility to tolerate load swings to match production needs. This does not imply that load swings have no impact on the Tephram diaphragm, only that it will not be destroyed, as will asbestos, and

**PPG Diaphragm Cell
Chlorine Production by Tephram Diaphragm**

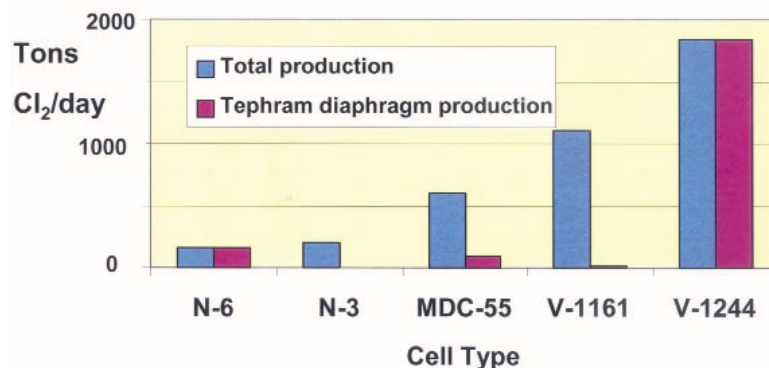


Fig. 9. PPG Tephram Diaphragm Chlorine Production by Cell Type.

Table III. Comparison of Asbestos and Tephram Diaphragms.

Life	Asbestos	Tephram
Life	8-15 months	4 years
Ruggedness	Easily plugged with impurities	Recovers from upsets
Responses to swings	Cycling destroys asbestos may go high level	No long-term effect
Safety	Carcinogen, caustic used in diaphragm preparation	No asbestos, non-hazardous water-base slurry
Materials Cost	Low cost but uncertain supply	Higher than asbestos, secure supply
Electrical Power Use		Lower or equivalent to asbestos

Table IV. Tephram Diaphragm Technology is protected by the following U.S. Patents.

Patent #	Inventor	Title	Year
6,299,939	DuBois, et al.	Method of Preparing a Diaphragm for an Electrolytic Cell	2001
6,296,745	DuBois, et al.	Method of Operating Chlor-alkali Electrolytic Cells	2001
6,059,944	DuBois, et al.	Diaphragm for Electrolytic Cell	2000
5,683,749	DuBois, et al.	Method of Preparing Asbestos-free Chlor-alkali Diaphragm	1997
5,630,930	Maloney	Method of Starting a Chlor-alkali Diaphragm Cell.....	1997
5,612,089	Dilmore, et al.	Method of Preparing Diaphragm for use in Chlor-alkali Cells	1997
5,567,298	DuBois, et al.	Method of Operating Chlor-alkali Cells	1996
5,192,401	DuBois, et al.	Diaphragm for Use in Chlor-alkali Cells	1993
5,188,712	Dilmore, et al.	Diaphragm for Use in Chlor-alkali Cells	1993
5,030,403	Pickens, et al.	Method of Making Polymeric Fibrils.....	1991
4,720,334	DuBois, et al.	Diaphragm for Electrolytic Cell	1988
4,680,101	Darlington, et al.	Electrolyte Permeable Diaphragm including a Polymeric Metal Oxide	1987
4,666,573	DuBois, et al.	Synthetic Diaphragm and Process of Use Thereof.....	1987

that eventual recovery is possible. The longer life of the Tephram diaphragm allows for savings in cell renewal materials and labor, since fewer cell turn-arounds are required. These savings more than offset the higher costs that are unavoidably associated with fluorocarbon materials. ■

Acknowledgments

Teflon, Teflon Floc, and Nafion are registered trademarks of DuPont. Tephram is a registered trademark of PPG Industries, Inc.

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3. P. Foller and D. DuBois, *PPG Technology Journal*, **3**(1), 49 (1995).
4. P. Foller, D. DuBois, and J. Hutchins, PPG's Non-Asbestos Diaphragm, SCI Symposium, London, June 1997.

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