Elf Atochem a proud survivor in the war on chlorine

The Portland, OR, chlor-alkali plant sets high standards for itself.

DONALD G. MEADOWS

It starts with salt, mounds of it, delivered by ship down the Willamette River and by truck up I-84 from Moab, UT, to Elf Atochem North America's chlor-alkali plant in Portland, OR. Add water, add electricity, and the result is chlorine, plus sodium hydroxide and hydrogen.

The Portland facility was spawned in 1941 to meet the wartime need for chlorate production in the western United States. It was built by Pennsylvania Salt Manufacturing, expanded and operated by Pennwalt Corp., and acquired in recent years by Elf. Elf Atochem North America, headquartered in Philadelphia, PA, is an affiliate of Elf Atochem S.A., which is part of the Paris-based Elf Group in France.

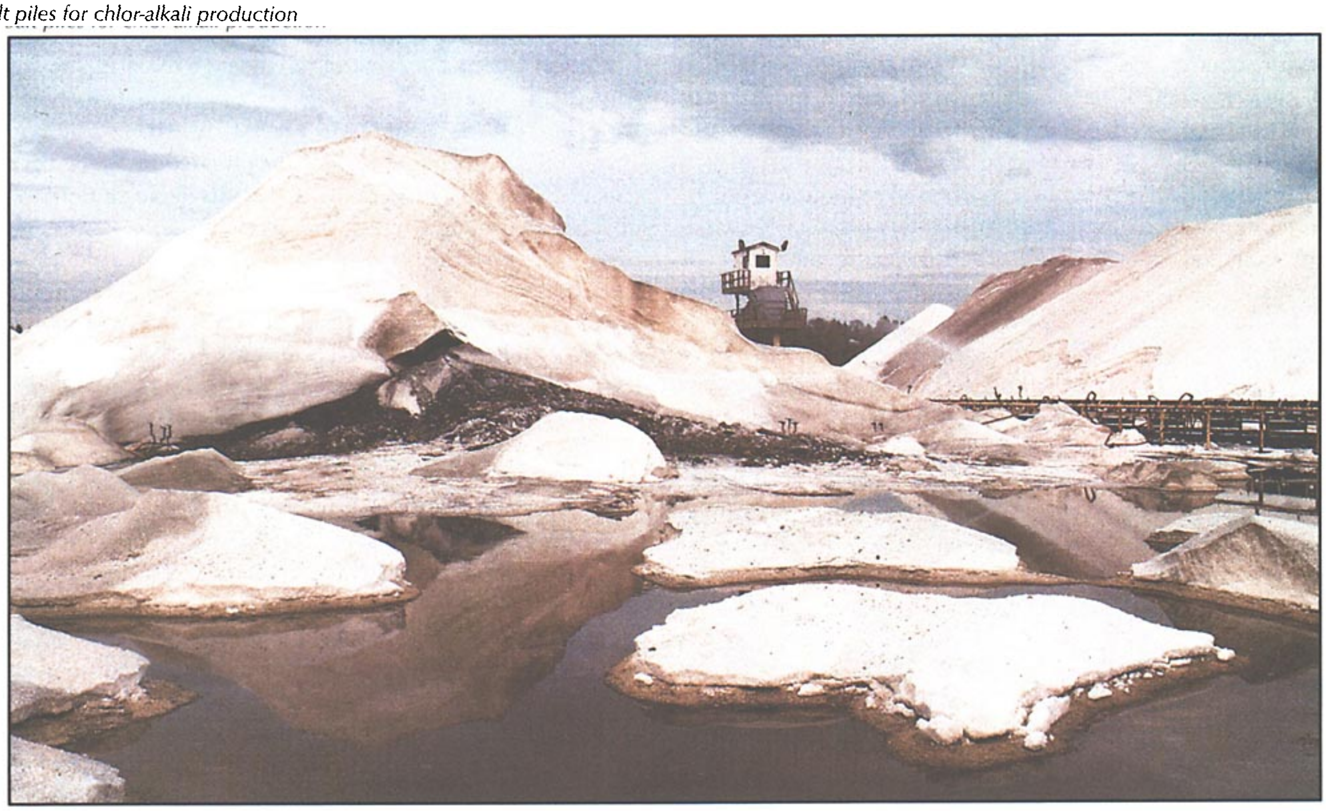
The plant employs 156 people: 47 salaried, 76 hourly, and 33 maintenance, plus some contractors. Production is continuous, throughout the year. Evening and weekend shifts require 13 people, said Bob Theis, operations manager for the company.

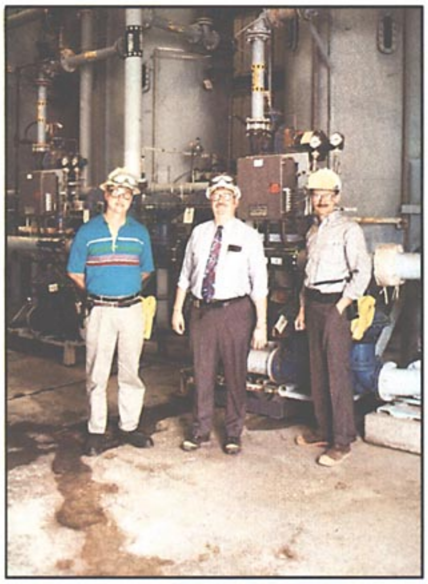
Current production at Elf's Portland facility is 180,000 tons/year of chlorine and 198,000 tons/year of caustic soda. Its sodium chlorate production capacity was increased by 25,000 tons/year in 1991 to 51,000 tons/year.

Since about 1930, elemental chlorine ruled as the preferred bleaching agent for pulp and paper. Since 1989, its use in the pulp and paper industry has steadily declined, primarily in response to concerns over the health risks from dioxin and other by-products of chlorine use.

In 1993, chlorine accounted for 40% of the pulp bleaching chemicals used in the United States, falling second to chlorine

Salt piles for chlor-alkali production





Bob Theis, Norman Hanson, *and* **Larry Patterson**

Diaphragm cells

dioxide.[1] By the end of this century, chlorine's share of the market will likely fall to about 30% and by 2010 to below 20%.

Even so, chlorine continues to be an important bleaching agent and disinfecting agent. It's also used as a raw material for producing such materials as polyvinyl chloride (PVC). And, while chlorine production may be on the decline, demand for caustic is strong and demand for sodium chlorate for chlorine-dioxide bleaching is steadily increasing.

About 95% of all sodium chlorate produced in the United States goes to make chlorine dioxide for pulp bleaching. Caustic soda, on the other hand, has a much wider range of use.

Of about three dozen pulp mills from California to Alaska, Elf serves about 23. They include Boise Cascade, James River, Potlatch, Pope & Talbot, Fletcher Challenge, and others, said A. E. Gene Spina, manufacturing manager.

The company maintains a fleet of 409 chlorine rail cars. Two double-hulled, seagoing barges—one based in Portland, the other in Tacoma, WA—can carry up to 3000 tons of caustic.

The Portland plant ships chlorine to places as far away as Michigan, Nebraska, Minnesota, and elsewhere in the Midwest and East. "That's something that's changed in the last few years because of the declining use of chlorine in the pulp industry, so we have to look to other areas for customers for chlorine," said Spina.

Because of environmental pressures on chlorine bleaching, there's been a dramatic reduction in the amount of chlorine Elf sends to the pulp and paper industry today compared with five years ago. In April, Elf discontinued chlor-alkali production at its plant in Tacoma, WA. The facility produced about 77,000 tons/year of chlorine for use within the company and 85,000 tons/year of caustic. The plant will continue to produce sodium chlorate (26,000 tons/year) and will serve as a caustic soda and hydrochloric acid terminal. The Portland plant and one in Granger, WY, will handle production of chlorine and caustic.

The company has had to broaden its customer base to other markets, such as municipal water treatment and sewage facilities. A plus for Elf is a perceived switch by pulp and paper customers to sodium chlorate and hydrogen peroxide. That's one of the reasons for the 25,000 short tons/year expansion of the Portland facility's sodium chlorate area in 1991, to be able to accommodate an increase in demand. The plant now produces 51,000 tons/year of sodium chlorate.

There has been some talk of building a hydrogen peroxide plant in the Northwest, though for now it's only talk. Elf Atochem S.A. is equal partners with Air Liquide in CHEMPROX Chemical, Inc. for the production of hydrogen peroxide. They operate joint-venture plants in North America, Japan, and Europe, including the largest, in Jarrie, France.

"Our long-term strategy is to supply the pulp and paper market as it evolves from elemental chlorine for bleaching to sodium chlorate, hydrogen peroxide, and other bleaching chemicals," said Robert LeBlanc, the company's executive vice president.

How it's made

Chlorine is produced through an electrochemical process. Basically, direct current is passed through salt brine, releasing chlorine gas at the anode side and hydrogen at the cathode side. The Portland facility uses two similar production technologies, one using diaphragm cells, the other using membrane cells.

Diaphragm cells use a semiporous, polymer-modified asbestos diaphragm to physically separate the chlorine from its co-products. The diaphragm prevents chlorine from passing through but allows brine, water, sodium, and ions to pass

[1] Lucas, A., *Chemical Week* 154(5): 25 (1994).

Membrane cells

through. About 50% of the brine is converted during each pass through the cell. The diaphragms yield 11% caustic, which is then sent to a set of evaporators to concentrate the caustic to a 50% solution. The diaphragm-generated solution contains about 1% salt. Salt is recovered in the evaporators, redissolved, and sent back to the cells.

Membrane cells use a semipermeable membrane to separate a stream of strong brine on one side of the cell from a stream of sodium hydroxide on the other side. The barrier is ion selective, allowing sodium ions and water to pass through. The depleted brine from the chlorine side is resaturated and returned to the cell. Part of the concentrated caustic from the cathode side is diluted with soft water and returned to the cell, the rest is processed for sale.

The Portland plant is equipped with 200 Diamond diaphragm cells and 36 ICI membrane cells. It's also experimenting with asbestos-free diaphragm cells manufactured by OxyTech and PPG.

A key factor in chlorine production is the quality of the brine, especially for membrane cells. The diaphragm process requires brine hardness in the range of <2–3 ppm calcium, compared with <50 ppb calcium for membrane cells. Impurities in the brine can lead to inefficiencies in the chlorine process.

The Portland facility creates brine by dissolving salt with either condensate or soft water. The raw brine is then chemically treated with carbonate and hydroxide to form precipitates of calcium carbonate and magnesium hydroxide. It is then suitable for use in the diaphragm cells. A secondary treatment is required before the brine can be used in membrane cells. That involves passing the processed brine through a three-stage ion-exchange system using a cation-specific resin to lower hardness to about 20 ppb.

Salt used at the plant is either solar salt from Baja, Mexico, or a finer-grade mineral salt mined in Moab, UT. To create brine, water is sprayed on the salt piles using large sprinklers. The saturated brine is pumped to a treatment area where the calcium and magnesium are removed to obtain a purer salt brine. It goes to storage tanks before being transferred to the diaphragm cells. In the diaphragm cells, the sodium chloride is separated into sodium hydroxide (caustic soda) and chlorine. The chlorine at that point is saturated with water vapor. It's cooled and then dried using sulfuric acid and compressed. It's transferred to a liquefaction area where it's refrigerated to turn it into a liquid for transport.

The electrochemical process for making sodium chlorate is the same as the chlorine process. The difference is the absence of a barrier or membrane between the cathode and the anode. The caustic soda and chlorine formed during the process are allowed to mix in the cell. In that mixing, sodium hypochlorite forms. From that comes sodium chlorate for chlorine dioxide bleaching.

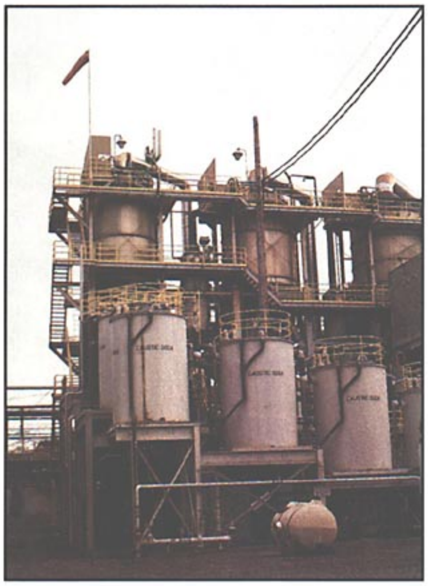
At this point the chlorate solution has sodium dichromate in it, which is used as a corrosion inhibitor and a catalyst in forming the chlorate. This is evaporated some and the chlorate is removed through crystallization, first to 0\F, then to -60\F. The crystals are either redissolved or dried for shipment to pulp mills.

Hydrochloric acid is the other major product of the plant. In both chlorine and chlorate plants, a by-product of the caustic is hydrogen. Some is collected and sold as pure hydrogen, the rest is burned in boilers. Purified chlorine can also be burned with hydrogen together. That releases a hydrogen chloride gas which can be absorbed in water and sold as a 30–33% solution.

Safety gets priority

Safety is the primary concern at the Portland plant. All visitors must complete a safety and health orientation that describes the potential risks of exposure to chlorine, sodium hydroxide (caustic soda), and sodium chlorate. Plant personnel describe emergency procedures and issue a hard hat, safety glasses, and emergency air supply to all visitors to the plant area.

A brief description of sodium chlorate's properties helps explain the company's emphasis on safety. "Dry sodium chlorate creates a flammable or explosive mixture on contact with organic materials, combustible substances, oils, greases, reducing agents or acids," notes a company handling guide. "These mixtures are extremely sensitive to shock, heat, friction, and may explode spontaneously. Materials saturated with chlorate solutions are highly flammable when allowed to dry."



Caustic soda step-down tanks

Loading tank cars for transport

The plant maintains a safety hotline so that any employee who has a safety concern can leave a message. There is also a safety day at the plant devoted to any safety issues employees might want to talk about. Once a quarter, the company brings in a catered lunch for employees as an "appreciation" for continued safe operations.

The safety activities also support team-building, as do the numerous committees at the unionized plant. The safety committee includes the plant's three regular contracting firms. There is also a safety management system consisting of a committee to help run the safety program. The next step in the program is to find additional ways to empower employees to solve safety problems, said Thatcher. "We want it to be, as much as possible, employee driven, using management as a resource," he said.

The safety program is an "evolutionary process" consisting of 15 programs. The programs are used to keep plant safety at an acceptable level and to measure any out-of-compliance problems. The key factor is behavior modification to reach the goal of zero accidents, Thatcher explained.

The plant also works with its industrial neighbors, the local fire department, HazMat teams, and the public to be prepared should an accident occur. "We try not to have secrets," Thatcher said.

Nearly as much emphasis is placed on maintaining an environmentally responsible facility. Consequently, the Portland plant has achieved a 96% reduction in SARA emissions, an 89% reduction in hazardous wastes, and a 92% reduction in use of compounds listed under EPA's voluntary 33/50 program, according to Larry Patterson, the plant's environmental director.

An extensive, five-year asbestos removal program at the plant is 99% complete and all PCB-containing units have been taken out of service.

The plant's goal is "to meet or exceed the environmental expectations of its internal and external customers 100% of the time," said Patterson.

The plant uses tremendous amounts of electricity and ranks first or second in the amount of water it draws from the City of Portland. It is permitted to discharge 25–26 million gal of water—mostly from cooling—back into the Willamette River each day through four outfalls.

Even so, it has reduced its water use by as much as 50% a day. In addition, cooling water returned to the Willamette is only 1–2°F. warmer than the water drawn from the river. Studies have shown essentially no impact outside the discharge mixing zone. TJ

***Meadows is editor of* Tappi Journal.**