Chlor-Alkali Plants

Industry Description and Practices

There are three basic processes for the manufacture of chlorine and caustic soda from brine: the mercury cell, the diaphragm cell, and the membrane cell. The membrane cell is the most modern and has economic and environmental advantages. The other two processes generate hazardous wastes containing mercury or asbestos.

In the membrane process, the chlorine (at the anode) and the hydrogen (at the cathode) are kept apart by a selective polymer membrane that allows the sodium ions to pass into the cathodic compartment and react with the hydroxyl ions to form caustic soda. The depleted brine is dechlorinated and recycled to the input stage. The membrane cell process is the preferred process for new plants. Diaphragm processes may be acceptable, in some circumstances, if nonasbestos diaphragms are used. The energy consumption in a membrane cell process is of the order of 2,200–2,500 kilowatt-hours per metric ton (kWh/t), as against 2,400–2,700 kWh/t of chlorine for a diaphragm cell process. *The World Bank does not finance mercury cell technology.*

Waste Characteristics

The major waste stream from the process consists of brine muds—the sludges from the brine purification step—which may contain magnesium, calcium, iron, and other metal hydroxides, depending on the source and purity of the brines. The muds are normally filtered or settled, the supernatant is recycled, and the mud is dried and landfilled.

Chlorine is a highly toxic gas, and strict precautions are necessary to minimize risk to workers and possible releases during its handling. Major sources of fugitive air emissions of chlorine and hydrogen are vents, seals, and transfer operations. Acid and caustic wastewaters are generated in both the process and the materials recovery stages.

Pollution Prevention and Control

The following pollution prevention measures should be considered:

- Use metal rather than graphite anodes to reduce lead and chlorinated organics.
- Resaturate brine in closed vessels to reduce the generation of salt sprays.
- Use noncontact condensers to reduce the amount of process wastewater.
- Scrub chlorine tail gases to reduce chlorine discharges and to produce hypochlorite.
- Recycle condensates and waste process water to the brine system, if possible.
- Recycle brine wastes, if possible.

For the chlor-alkali industry, an emergency preparedness and response plan is required for potential uncontrolled chlorine and other releases. Carbon tetrachloride is sometimes used to scrub nitrogen trichloride (formed in the process) and to maintain its levels below 4% to avoid explosion. Substitutes for carbon tetrachloride may have to be used, as the use of carbon tetrachloride may be banned in the near future.

Target Pollution Loads

Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The production-related targets presented in Table 1 can be achieved by measures such as those described above. The numbers relate to

Table 1. Target Levels per Unit of Production, Chlor-Alkali Industry

(maximum load/ton chlorine)

Parameter	*Diaphragm process*	*Membrane process*
Lead (kg)	0.04	—
Wastewater (cubic meters)	1.6	0.1

— Not applicable.

the production processes before the addition of pollution control measures.

Treatment Technologies

Caustic scrubber systems should be installed to control chlorine emissions from condensers and at storage and transfer points for liquid chlorine. Sulfuric acid used for drying chlorine should be neutralized before discharge.

Brine muds should be discharged to lined settling ponds (or the equivalent) to prevent contamination of soil and groundwater. Effluents should be controlled for pH by neutralization. Settling and filtration are performed to control total suspended solids. Dechlorination of wastewaters is performed using sulfur dioxide or bisulfite.

Emissions Guidelines

Emissions levels for the design and operation of each project must be established through the environmental assessment (EA) process, on the basis of country legislation and the *Pollution Prevention and Abatement Handbook* as applied to local conditions. The emissions levels selected must be justified in the EA and acceptable to the World Bank Group.

The guidelines given below present emissions levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance. Any deviations from these levels must be described in the World Bank Group project documentation. The emissions levels given here can be consistently achieved by well-designed, well-operated, and well-maintained pollution control systems.

The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unacceptable.

All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

Air Emissions

Chlorine concentration should be less than 3 milligrams per normal cubic meter (mg/Nm^3) for process areas, including chlorine liquefaction.

Liquid Effluents

For membrane cell effluents, pH levels should be in the range 6–9.

For nonasbestos diaphragm plants, the effluents levels presented in Table 2 should be achieved. In some cases, bioassay testing of effluents may be desirable to ensure that effluent toxicity is at acceptable levels, say, toxicity to fish at a dilution factor of 2.

Ambient Noise

Noise abatement measures should achieve either the levels given below or a maximum increase in background levels of 3 decibels (measured on the

Table 2. Effluents from Nonasbestos Diaphragm Plants, Chlor-Alkali Industry

(milligrams per liter, except for pH)

Parameter	*Maximum value*
pH	6–9
TSS	20
COD	150
AOX	0.5
Sulfites	1
Chlorine	0.2

Note: Effluent requirements are for direct discharge to surface waters.

A scale) [dB(A)]. Measurements are to be taken at noise receptors located outside the project property boundary.

Receptor	*Maximum allowable log equivalent (hourly measurements), in dB(A)* Day (07:00–22:00)	Night (22:00–07:00)
Residential, institutional, educational	55	45
Industrial, commercial	70	70

Monitoring and Reporting

Frequent sampling may be required during start-up and upset conditions. Once a record of consistent performance has been established, sampling for the parameters listed in this document should be as described below.

Daily monitoring for parameters other than pH (for effluents from the diaphragm process) is recommended. The pH in the liquid effluent should be monitored continuously. Chlorine monitors should be strategically located within the plant to detect chlorine releases or leaks on a continuous basis.

Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.

Key Issues

The key production and control practices that will lead to compliance with emissions guidelines can be summarized as follows.

Give preference to the membrane process.

Adopt the following pollution prevention measures to minimize emissions:

- Use metal instead of graphite anodes.
- Resaturate brine in closed vessels.
- Recycle brine wastes.
- Scrub chlorine from tail gases to produce hypochlorite.
- Provide lined settling ponds for brine muds.

Sources

Arthur D. Little, Inc. 1975. *Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry.* U.S. Environmental Protection Agency, Contract 68-01-2246. Washington, D.C.: USEPA.

Kirk, Raymond E., and Donald F. Othmer. 1980. *Kirk-Othmer Encyclopedia of Chemical Technology.* 3d ed. New York: John Wiley and Sons.

World Bank. 1996. “Pollution Prevention and Abatement: Chlor-Alkali Industry.” Draft Technical Background Document. Environment Department, Washington, D.C.