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Chlor-Alkali Technologies

5.1. INTRODUCTION

About 97% of the chlorine and nearly 100% of the caustic soda in the world are produced electrolytically from sodium chloride, while the rest of the chlorine is manufactured by the electrolysis of KCl, HCl, chlorides of Ti and Mg, and by the chemical oxidation of chlorides [1]. The electrolytic technologies currently used are mercury, diaphragm, and ion-exchange membrane cells. Figures 5.1 and 3.10 show the distribution of these cell technologies in the world and on a regional basis [2]. Mercury cells had a world share of 45% in 1984 and declined to 18% in 2001 because of the health and environmental concerns associated with mercury. However, it is still the leading technology in Europe.

Diaphragm cells held a 67% market share in the United States, vs 37% in the world in 2003. The emerging cell technology is the membrane process, which had a world market share of 30% in 1999 and 40% in 2003.

A wide variety of designs have been developed for each of these three cell processes and have been installed in commercial plants. However, only a few of those cell designs

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FIGURE 5.1. Breakdown of world chlorine market share based on technology [2].
have captured significant shares of the market, withstanding the test of time and market vulnerabilities. This chapter will address those cell technologies that are currently available in the market. Pertinent references are provided for readers interested in prior chlor-alkali cell configurations.

5.2. CELL TYPES—BIPOLAR AND MONOPOLAR

Electrochemical cells, be they for electrolysis to generate products or for producing electricity (e.g., batteries, fuel cells), fall into two broad categories with respect to the electrode configuration, monopolar and bipolar cells. In a monopolar cell, there are typically many anode and cathode assemblies that are electrically in parallel with each other. Thus, a monopolar cell is typically a high current cell compared to most bipolar cells. In the typical DC circuit configuration, monopolar cells are connected in series by intercell conductors.

On the other hand, in bipolar cells, only the terminal cells are connected by intercell conductors, and there are typically many unit cells electrically in series between the terminal cells (Fig. 5.2). The two basic types of bipolar cells are the flat plate cell and the finger type cell. A group of bipolar cells that have a common piping system for the fluids, via manifolds, is referred to as an electrolyzer or sometimes a series or a stack. Within a single bipolar electrolyzer, there are sometimes more than one set of terminal cells. Bipolar electrolyzers can be connected via an external bus within a DC circuit in series or in parallel, but usually not both. Furthermore, in the case of mercury-cell plant conversions to membrane cells, the electrolyzers are connected electrically in parallel as shown in Fig. 5.3.

Historically, the concept of arranging the cells in bipolar and monopolar fashion was known before 1800, when Volta assembled batteries [3]. There are several advantages and disadvantages associated with the construction and operation of monopolar and bipolar cells [4,5]. They are noted in Table 5.1.

One significant difference between the two cell arrangements is the capital cost associated with the cells and the electrical supply system constituting rectifiers and transformers. The most expensive components of the cells are the membranes and electrodes. Therefore, their cost becomes lower as the current density increases and allows the use of less electrode and membrane area. In recent years, membranes that can operate successfully above 4 kA m\(^{-2}\) have been developed. As explained in Section 8.3.1.3, bipolar cells are better suited to take advantage of this development. This explains the current trend favoring bipolar systems. A recent comprehensive cost analysis [6], taking into account the cost of the cells and rectifiers, penalties arising from the lower efficiency of the bipolar cells, and higher downtime production losses compared to monopolar cells, showed (Fig. 5.4) favorable economics for monopolar cells operating below a current density of about 4 kA m\(^{-2}\) and for bipolar cells operating at higher current densities. This critical current density varies with the parameters chosen for the cost calculations. When investment capital is scarce, the choice of bipolar cell technologies makes good economic sense. The structural IR of flat plate type bipolar cells is typically less than for monopolar cells, because the current path through the metal