7

Brine Preparation and Treatment

This chapter considers the preparation of brine from solid salt and the design and operation of each of the major units in a brine purification system. The discussion begins with the sources of electrolysis salts (both sodium and potassium chlorides; both natural and refined) and the methods of handling and storing them and then dissolving them to prepare brine. There is also a brief discussion of the storage and handling of brine. The rest of the chapter is then devoted to the treatment of brine to reach the purity demanded by the various types of cell. The sequence of the discussion follows the flow diagrams of Figs. 6.1 and 6.2.

7.1. SOURCES OF SALT

7.1.1. General

The classical work on salt is Kaufmann’s ACS Monograph 145, Sodium Chloride. Although first published in 1960, it is an unmatched overview of all aspects of salt technology and still has much useful material.

Salt is an ubiquitous mineral and perhaps history’s most important mineral. In an age when most of the developed world worries about too much salt intake, it is sometimes hard to remember that salt is an essential component of the human diet and that throughout most of history it has been in short supply. Salt deficiencies that are less than fatal still can interfere seriously with bodily functions. Thousands of Napoleon’s soldiers, faced with a lack of salt in their diet and as a disinfectant, died during the retreat from Moscow because their wounds could not heal. Access to salt or the salt trade has played a large part in shaping the history of nations. The long-lasting alliance between England and Portugal was originally based on trading naval protection for a source of salt [1].

The very word “salary” reflects the importance of salt in the days of the Roman Empire. A soldier’s pay was his salarium argentum, or his salt money. The same origin tells us that a useful man is “worth his salt,” and we say that good people are the “salt of the earth.” Plato referred to salt as “a substance dear to the gods.”

There are large underground deposits of salt, usually in the form of the cubic crystal halite, in many parts of the world, and the oceans themselves contain about 2.7% NaCl. Each cubic kilometer of seawater therefore contains more than 27 million tons of NaCl.
This is enough to meet the world’s demand for salt for seven or eight weeks. Since the seas contain about 1.35 billion cubic kilometers, the present rate of use would consume their chloride in about 180 million years. Solid deposits of salt, measured only in the billions of tons, add very little to this. Since over the course of 180 million years, a very high percentage of the chloride used will have found its way back to the seas, this situation is less alarming than it might appear.

The salt found in underground deposits is usually referred to as rock salt. It is recovered both by classical mechanical mining and by forcing an aqueous stream down into the deposit and back to the surface through a pipe (solution mining). Seawater and saline brines are the other major sources. These are allowed to evaporate in large ponds, precipitating the salt for mechanical recovery. The product is usually referred to as sea salt or solar salt. A relatively minor source is the occasional near-surface pool of brine or low-lying surface deposit. The latter is often in the form of loose particles which can simply be dredged and then washed.

Salt mining is a large-scale specialized activity. Few chlorine producers mine salt or have much control over the process. Section 7.1.2 therefore gives only a brief review of the subject of mechanical mining of rock salt. Solar salt production, on the other hand, is closely tied to chlorine plants in some parts of the world. A fuller description of its production seems appropriate and appears in Section 7.1.3.

While the natural salts predominate in the NaCl market, the chlor-alkali industry also uses quantities of processed and byproduct NaCl. Several techniques, discussed in Section 7.1.5, are used to upgrade both rock and solar salts in order to reduce the cost of on-site treatment. In other cases, byproduct brines are available from chlorine consumers. These usually result from the neutralization of HCl produced in phosgenation or chlorination processes (Section 7.1.4).

KCl is much less plentiful than NaCl. Its molar concentration in seawater is only one fiftieth that of NaCl. It is obtained chiefly from mineral deposits and again is not so widespread as NaCl. Much of the KCl, moreover, exists in mixed ores such as sylvinite, a combination of NaCl and KCl. KCl is discussed separately in Section 7.1.6.

Any chlor-alkali producer whose operation is based on the solid raw material will find it necessary to store salt. Section 7.1.7 addresses this topic.

### 7.1.2. Rock Salt

Rock salts are those formed by evaporation of inland seas over a broad range of geologic time, ranging from the Precambrian through the Quaternary. They abound in many parts of the world and are used extensively in chlor-alkali production. Less than half the total salt used is rock salt. In Canada and the United States, rock salt is the primary source for the chlor-alkali industry, outweighing solar salt by about 5:1. Rock salt is recovered by subsurface mining. Certain applications, including chlor-alkali manufacture, can use the NaCl solution obtained directly from rock salt by forcing water into the deposit to dissolve the salt. This technique, solution mining, is regarded as a brine preparation process and treated in Section 7.2.2.4.

Most rock salt mining involves undercutting of a deposit, drilling, and blasting. Usually, mining advances by undercutting the salt to a distance of about 5 m from the