CONTROL OF SULPHATE IN THE PRODUCTION OF CRYSTAL SODIUM CHLORATE

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Chemetics International, as a preferred contractor for ICI’s FM21 chlor-alkali membrane electrolyzer, have in the last 5 years obtained ten contracts for chlor-alkali plants in seven different countries. The future trend for chlorine plants is in the development of small onsite facilities. Today Chemetics is the leader in the supply of such facilities.

Chemetics is also involved in several other chemical industries, and has pioneered the development of high temperature sodium chlorate electrolysers. We now offer to merchant crystal chlorate producers a new process to allow total sodium chlorate production in crystal form without a liquor purge or chemical treatment to control sulphate levels.

Commercial salt, when used as a feedstock for the electrolytic production of chlorate, brings impurities such as calcium, magnesium and sulphate ions into the chlorate plant. These impurities must be removed from the system to minimize precipitation on the electrodes used for sodium chlorate production as the formation of deposits increase the chlorate cell voltage and thus increase the cost of production due to the additional electrical energy consumed.

Techniques for the chemical treatment of salt solutions with sodium carbonate and sodium hydroxide to precipitate calcium and magnesium are well known. In addition, in recent years, with the introduction of membrane electrolysers for the production of chlorine and caustic soda, ion-exchange resins have been developed for the removal of residual calcium and magnesium ions from chemically treated salt solutions. The same ion-exchange technology is now more commonly used in chlorate electrolysers plants.

Sulphate ions in the feed salt solution usually exist at such low levels that it is impractical to use chemical treatment to precipitate sulphate compounds. Thus in a crystal chlorate plant the sulphate accumulates and progressively increases in concentration in the system unless removed. As sulphate has been found to precipitate between the chlorate cell electrodes before saturation concentrations are reached in a standard crystallizer, steps must be taken to control the sulphate concentration. Existing technologies control the sulphate concentration by either
Neither of these two methods is entirely satisfactory for reasons to be explained shortly. Chemetics has patented a third method using co-crystallization of sodium sulphate and sodium chlorate, and this is what will be presented in this chapter.

Referring to Fig. 1, we will quickly review crystal chlorate production technology.

In the process a saturated purified salt brine is introduced into the cell room, where it is electrolyzed with water to produce sodium chlorate and hydrogen. The product electrolyte contains sodium chloride and sodium dichromate, a compound which improves the efficiency of the electrolysis. It is not possible to electrolyze all of the sodium chloride to sodium chlorate because of the increased wear on the precious metal coatings applied to the titanium anodes.

The hot product liquor is treated to destroy residual sodium hypochlorite and is then transferred to an evaporative crystallizer in which water is evaporated, causing subsequent cooling of the liquor and crystallization of sodium chlorate. By selection of the process operating conditions the sodium chloride may be kept in solution so that after subsequent separation of the essentially pure crystal sodium chlorate from the mother liquor the sodium chloride may be recycled back to the electrolytic cells in the mother liquor.

Thus sulphate entering the chlorate plant with the commercial salt and sulphate produced during hypo destruction, if sulphites are used, has no route to exit as it is recycled from the evaporator back to the electrolytic cells in the mother liquor. However, sulphate levels can be controlled by:

1. a chlorate liquor purge;
2. chemical treatment using barium or calcium;
3. co-crystallization of sodium sulphate and sodium chlorate.

The sulphate concentration in liquor leaving the electrolysis section can be controlled by purging a small portion of this liquor. The rate at which liquor is purged will be that required to maintain the sulphate at a maximum acceptable concentration in the electrolyte. Obviously rates higher than the maximum can be employed.

A liquor purge is the most commonly used method of sulphate control. Reference to Tables 1a and 1b shows the effect of varying sulphate concentrations in the raw

![Fig. 1. Simplified flow diagram—crystal sodium chlorate production.](image)