

PRODUCTION OF CAUSTIC POTASH BY BIPOLAR MEMBRANE ELECTROLYSER

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The performance characteristics of a bipolar membrane electrolyser for KOH production designed, fabricated and operated at CECRI are discussed. The bipolar elements have been bonded by a novel technique invented at CECRI. Activated anodes and cathodes developed by CECRI and imported Nafion membranes are being used in this electrolyser. Nafion 961, Nafion 90209 are the different membranes tried. The catholyte concentration, KCl depletion and membrane type on current efficiency, cell voltage and water transport across the membrane are reported.

Keywords: Caustic potash, membrane cell and activated electrodes

INTRODUCTION

Potassium hydroxide - known as caustic potash, is a widely used industrial chemical. So far it has been produced mostly by the mercury cell process, wherein aqueous KCl solution is electrolysed between metal anodes and flowing mercury cathode. Cl_2 is liberated at the anode. Potassium is discharged at the cathode forming potassium amalgam, which flows over to the decomposer where it reacts with water forming KOH solution and H_2 gas. However this process involves the hazardous pollutant, mercury. About 60-90 gms of mercury is lost per tonne of caustic potash. As stringent pollution control regulations are stipulated, caustic potash industry worldwide is switching over to the modern membrane cell process.

Membrane cell process

Membrane cells are pollution free and energy conserving. In membrane cells, a cation exchange membrane (CEM) separates the anode and cathode compartments. CEM does not permit bulk flow of electrolyte but it allows only the transport of K^+ ions with their associated H_2O molecules. Ultra pure KCl solution, fed to the anode compartment is electrolysed to produce Cl_2 which leaves the compartment along with depleted KCl solution. Depleted KCl solution is recycled back to the anode compartment after processing and resaturation. CEM transports K^+ ions from anode to cathode compartment. 28-30 wt % KOH liquor is passed through the cathode compartment. At the cathode, water is reduced to OH^- ions and H_2 is evolved. K^+ ions combine with OH^- ions to form 31-32 wt % KOH solution, which flows out of the cathode compartment. Part of the catholyte stream is

withdrawn as product and part is recycled back to the cathode compartment after dilution.

A number of cell designs are available both in monopolar and bipolar type electrolyses with different operating procedures. All are developed in developed countries and marketed in India by various Indian engineering companies or agencies. The critical components - anodes and catalytic cathodes are either supplied by them or imported from the country of origin of technology.

After analysing the merits and demerits of both mono and bipolar electrolyses, CECRI has decided to concentrate on bipolar cells since bipolar electrolyses avoid electrical contact drops of about 100-200 mV and investment on large quantities of bus bars.

The membrane cell process can be divided into two critical systems viz. (1) the secondary brine purification system and (2) cell hardware and their design.

Secondary brine purification system

The successful and efficient operation of the membrane electrolyser depends on the quality of brine fed into the anode compartment. The membrane suppliers specify the impurity level in feed brine to be

Calcium and magnesium	< 30 ppb
Sulphate as potassium sulphate	10 gpl
Silicate	10 ppm

If the impurity level is not maintained the membrane became inactive and its life is shortened, which means decline in current efficiency and increase in cell voltage. After primary brine purification the brine has the following analysis

Potassium chloride	290-300 gpl
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Calcium	10-12 ppm
Magnesium	1-3 ppm

This calcium and magnesium is more detrimental to membrane performance. Calcium causes decline in current efficiency. Magnesium increases the cell voltage by precipitating as the respective hydroxides in the membrane itself. These divalent metallic impurities will be removed by using chelating ion exchange resin. This resin is manufactured in India and CECRI uses the resin supplied by the Indian manufacturer and its performance is good and CECRI is able to control Ca^{++} and Mg^{++} impurities level within 20-25 ppb, and the operating conditions are stable. CECRI has standardized the procedures both analytical and instrumental methods and successfully monitored the brine quality. This process can be automated to have automatic regeneration and operation as and when the impurity level exceeds the prescribed limit.

Cell hardware

A high performance cell hardware should have the following characteristics:

- Complete metal construction
- Uniform current distribution
- Uniform electrolyte distribution
- Easy escape of gas bubbles from the electrode surface.
- Leak proof cell assembly and operation at higher current density
- Reduced electrolyser down time
- Optimum utilization of membrane area

CECRI uses titanium metal for the fabrication of anode compartment and special grade stainless steel for cathode compartment construction. The electrode structures are expanded mesh for anode and perforated/expanded mesh for cathode with appropriate current distributor from base (Chamber wall) to electrode which will also help in maintaining the electrolyte distribution. Most of the cell hardware suppliers are either explosion bonded Ti/Ni or SS for the fabrication of bipolar cell elements or mechanically press the anode and cathode compartments as in filter press type cell arrangement.

The explosion bonded Ti/Ni or SS is costly but minimises the contact drops (about 5 mV maximum) between anode and cathode compartments. Pressing mechanically these two compartments either directly or through a contact metal plate, Cu/M.S. causes a higher contact drop of about 30 mV which is additive/cumulative in an electrolyser. Hence the energy consumption is more. CECRI uses a unique technique of bonding the anode (Ti) and cathode (SS/Ni) compartments which is very cheaper compared to explosion bonding giving a contact drop equal to explosion bonded metal (5- 7 mV max.). Different cell sizes were designed with different

TABLE I: PERFORMANCE DATA OF CECRI BIPOLAR MEMBRANE ELECTROLYSER

Electrolyser type	Bipolar
Anode	TSIA
Cathode	Coated Cathode
Anode chamber	Titanium
Cathode chamber	Special grade SS
Membrane	Nafion 90209/961
Electrolyser size	1500 x 750 mm
Current rating	3.375 kA
Current density	3 kA.m ⁻²
Electrolyser operating temp.	358 K
Feed brine	
(i) Concentration	300 gpl
(ii) pH	3 to 4
(iii) Hardness	< 30 ppb
Return brine	
(i) Concentration	225 gpl
(ii) pH	2 to 3
Feed KOH concentration	30 wt%
Product KOH concentration	31 to 32 wt%
Electrode spacing	3 to 4 mm
Electrolyser voltage	3.35 to 3.40 V
Current efficiency (%)	94.5 to 95.5
DC energy consumption per tonne of KOH	1680 to 1710 kWh

current distributor and provision for easy gas discharge. For convenience 1.0 M² active area cells were fabricated. The anode coating is developed at CECRI to withstand the specific environment existing in the cells. The anode has a high oxygen overvoltage and low chlorine overvoltage with longer service life. The cathode structure is nickel or stainless steel coated with nickel. This cathode as such possesses a high hydrogen overvoltage (350 - 450 mV) at the membrane cell operating conditions. Hence the operating cell voltage is more. The cathode structure was activated thermally by using a mixed electrocatalyst comprising of transition metal oxide and metaloxide of platinum or gold along with the one or more oxides of precious metals. This cathode during cell operation gave a cell voltage of 3.35 - 3.40 (with 3-4 mm inter electrodes gap) at a c.d. of 3.0 K = AM⁻² and at 358-363 K in 31-32% KOH concentration. The cell was fabricated at CECRI itself and assembled only with 3 cell elements (more elements will create chlorine disposal problem). The electrolyser was operated continuously and data collected is given in Table I. The unique feature of this technology is use of all indigenous machineries and equipments for continuous and successful operation of the plant and supply of anode and cathode coating/recoating whenever needed.