Characteristics of electrolytic cells

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SYNOPSIS

The characteristics of electrolytic cells for production of zinc from zinc sulphate solution are discussed with special reference to the variable factors with a view to maintaining productivity and controlling the purity of the product.

THE electrolysis section of zinc smelter, at Debari, is designed for a low current density process taking into consideration the ambient temperature of the region. The cells are made of reinforced concrete with lead lining and contain 28 anodes of lead (alloyed with 0·5—1·0% silver) and 27 cathodes of high purity aluminium sheet. Current density is maintained around 300 amps/m^2 and the cells are operated between 9 000 and 10 000 amperes per hour per cell. There are 240 cells distributed in 20 cascades of 12 cells each. Each cascade has two rows of six cells. The temperature in cells is maintained by removing excess heat with the help of lead cooling coils. The normal working temperature varies between 38 and 45°C. Purified zinc sulphate solution, termed neutral solution, is fed to individual cells through a small feeder pipe with provision for regulating the flow. The rated capacity of the plant is 55·5 tons of zinc cathodes per day.

Factors influencing capacity

There are several factors which need careful control in order to attain the optimum working conditions in the electrolytic cells. They are classified into three groups :

(a) Design aspects.
(b) Control at purification.
(c) Efficiency of operation.

The last aspect can be sub-divided into : (1) skill of strippers and (2) skill of operators. The above factors are now discussed in detail.

Design aspects

Many factors related to design aspects are not clearly understood. This is partly due to lack of experimental facility in the actual production unit. In general, the points which affect design are (a) current density, (b) acidity, (c) distance between anode and cathode, (d) concentration of zinc in neutral solution.

Current density

Current density is the strength of electrical current used per unit cross section of cathode. In practice it is expressed as amp/m^2 or amp/ft^2 of surface of cathode. The electrolytic cell is designed for a current density of 300 amp/m^2. At this current density the voltage drop across each cell is 3·3 V. The theoretical decomposition voltage is 2·35 for zinc sulphate solution. The extra voltage is due to ohmic drop through the electrolyte and discharge voltage at the cathode. Added to this, there is formation of a thin film of MnO_2 in the anodes and a thin film of oxygen which act as additional resistance in the system and consume extra voltage. The energy efficiency of electrolysis is 60% and for a greater current density the heat dissipated will be higher increasing the temperature of the solution in cells, which is undesirable.

Temperature

The optimum temperature of solution in cells varies between 35 and 40°C. Higher temperatures give trouble in stripping due to sticky deposit. The purity of the product is also affected mainly due to improper deposit of manganese. This in turn exposes the surface of anodes. It has been observed that manganese deposit has a flaky form even at 35°C. The ambient temperature varies between 17 and 33°C during the year. This restricts the efficiency of heat removal by cooling water. The cooling water temperature varies between 14 and 25°C and that of the neutral solution between 19 and 35°C. At full load (around 320 amp/m^2 current density) the temperature rise of the solution varies between 7 and 15°C. The 15°C rise is generally after a full deposit of zinc and also when the anodes are not polished. With the design for neutral solution feed at temperature of 25°C, the optimum cell temperature comes to 40°C. Too low a cell feed temperature around 14 to 16°C will increase the resistance of the solution increasing power consumption per ton of zinc. This needs efficient vacuum cooling and a sufficient quantity of steam.

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Circulation rate

The designed circulation rate for the cell is 14 m^3/ton. This works out to 2·6 l/mt/cell. This rate is applicable only when the neutral solution is processed. In case of acidic solution i.e. spent electrolyte the flow rate is around 12–16 l/mt/cell. The circulation rate is very closely related to acidity maintained in cells. The design requirement is 120 g/l of acidity in spent electrolyte with the feed at 120 g/l of zinc. The actual flow characteristic is that the neutral solution flows down the cell by higher density and moves up as zinc gets deposited. The controlling factors being rate of ionisation, rate of diffusion through electrolyte film, and final deposition. At the present moment it is not yet clear which of these factors is the controlling step. The rate is also related to the amount of manganese, deposited in the cells.

Cell characteristics

The detailed sketch of cell with anodes, cathodes and cooling coils is given in Fig. 1. It may be observed that distance between anode and cathode is 31·4 mm. Allowing for thickness of zinc sheet and deposit of manganese on anodes the clear space amounts to 25 mm. A closer spacing will have the added advantage of lower resistance and therefore lower energy but this may lead to short circuiting resulting in a sharp rise of temperature in cells ; this would also affect the purity of zinc cathode.

Control at purification

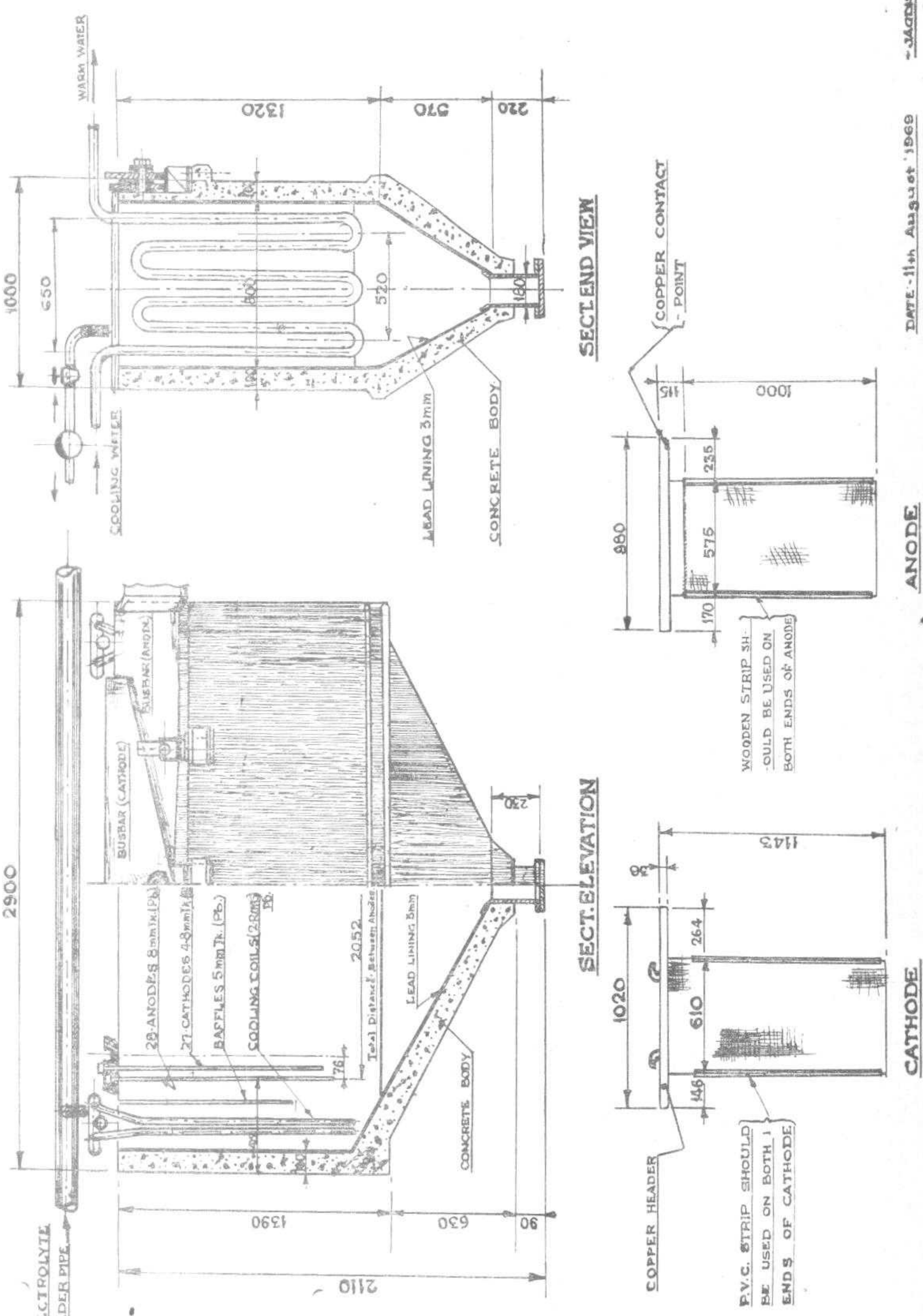
It is well known that for successful electrolysis the zinc sulphate solution must be purified. It is not proposed to discuss here the normal range of purity ; this paper will deal only with some special problems encountered at the smelter. The elements, affecting stripping and thereby production, are cobalt and fluorine directly and sodium nitrate indirectly. The limiting condition for cobalt is 1·5 mg/l and for fluorine 16–17 mg/l. Cobalt above 1·5 mg/l results in black holes on zinc cathodes. Such spots result in etching of aluminium sheet due to sulphuric acid and we usually get uneven deposit on the subsequent day. Cobalt is removed by addition of B-Naphthol and sodium nitrite in the ratio of 2 : 1. The quantity required varies depending on agitation speed in pachucas where purification is carried out. If addition of sodium nitrate is in excess the zinc adheres to cathode tenaciously. There is a possibility that NO_2 is liberated and corrodes the aluminium cathodes, causing difficulty in stripping. For normal good working the value of cobalt should be 0·8–1·2 mg/l. There is no method for removing fluorine at purification except by the roaster. Here again the gas being corrosive attacks the cathodes with the formation of sticky deposit. The effect of fluorine is reduced by addition of aluminium sulphate. Usual addition is 1 kg/ton of cathode expected to be produced.

Efficiency of operation

Skill of strippers

The strippers play the most important role in a zinc factory and the production efficiency depends much on their skill. During the stripping operation many points need attention :

1. Contact points between anode, cathode and the respective bus bars, must be regularly cleaned and wetted with water in each sequence of operation. At Debari, each stripper is responsible for six cells giving a production of 1 400 kg or 233 kg per cell ; of the 27 cathodes even if 4 cathodes do not function properly the production is likely to go down by 30 kg. Improper contact will result in deposition and dissolution.
2. Contact between anode and cathode must be avoided while inserting the cathodes in cells after stripping. Such contact would cause short circuiting and localised high temperature which again results in sticky deposit in the particular cell on the next day.
3. The side strips on anode and cathode must be fixed properly. This is to avoid maximum current density effect prevalent on sides and also to minimise the effect of eddy currents. It also helps in releasing zinc cathodes from aluminium plate on hammering.
4. The anodes must be placed straight in the cells. Any twisting cannot be traced from surface and this will result in contact and short circuiting.
5. The anodes do not generally have a uniform manganese deposit and it is in the form of flakes and patches. This develops regions of high current density and high temperature which subsequently result in rough deposit and excess of overgrowth during deposition. Sometimes resolution starts due to high, spot, temperature on a particular cathode. The stripper has to be careful on such cases to remove the anodes after stripping, scrap the manganese and insert it back in cells. While scrapping, care should be taken not to scrap all the manganese as this will expose the surface of anodes resulting in increase of lead in zinc cathodes. To get the best ampere efficiency, consistent with purity there should be a thin coat of manganese on the surface of anodes.
6. Protection of cathode surface from indentation, marks or cavities is very important. While stripping care should be taken to do the minimum hammering in order to avoid formation of cavity. Such spots develop localised corrosion and the deposit tends to be sticky necessitating more hammering. Faulty operation considerably reduces cathode life.
7. Cathodes become inoperative due to salt deposition in the cavity of copper headers, especially near the hooks provided for lifting. The salt deposit being a bad conductor it is observed



1 *Cell arrangement*

that there is very thin deposit and that the adjacent cathodes have more deposit mostly uneven, with projections. This needs periodical cleaning with water spray on the surface of headers; here again care should be taken to put minimum water so that there is no dilution of the solution and the copper sulphate from headers is not carried away in the cells.

Process control

Acidity control

The most important process controls for electrolytic cells are on acidity and temperature. In the cell housing six cells are in series in a row and the solution flows from one cell to the other. Each cell is fed individually by neutral solution. The flow to each cell is periodically controlled to maintain the required acidity in cells. Generally, the flow in the first cell is more than in the last cells. The acidity of each cell is determined by titration against standard alkali and acidities of the first and last cells of a row are usually recorded twice in a shift of 8 hours. For good operation the acidity of the first cells must be kept about 10 gms/l less than that of the last cells. In our working conditions it was observed from experience that the optimum acidity is 105 g/l in the first cells and 115 g/l in the last cells. This range is suitable for a current density of 275–300 amp/m^2 when acidity is above 115 g/l and the zinc deposit was found to be sticky and difficult to strip resulting in loss of production. Another important point is that acidity should be low at the time of initial deposit i.e. when cathodes are inserted after stripping. Once a thin layer of zinc is deposited acidity can be increased, but to avoid wide fluctuation during the day it is maintained between 105 and 115 g/l in the cells.

Temperature conrol

Temperature control is of considerable importance. Every two hours the temperature is checked in each cell; for efficient operation it should be maintained at 50°C. Above this temperature resolution starts. The optimum temperature is around 40°C. When the zinc deposit is stripped, temperature generally drops in the cell. Temperature rises slowly during the day and reaches a maximum on the subsequent day. This variation should be maintained between 3 and 5°C for good operation. If there is an abnormal rise in temperature in a particular cell the flow of cooling water is checked; cathodes and anodes are also checked for short circuits by touching the cathodes. The cathode which is very hot is removed and the adjacent anodes are checked and necessary cleaning of manganese is carried out.

Control on addition agents

The third important control is on addition agents. It is a standard practice in all zinc factories to add glue to form a crystalline zinc deposit with a close structure. This helps in reducing the adhering zinc sulphate to a minimum. It is observed that in the absence of glue, zinc forms a spongy deposit. At the Debari Works glue addition is not favourable and even a minimum addition of 100 gms/ton results in a sticky deposit. Glue addition has therefore been completely stopped and aluminium sulphate is added instead at the rate of 1 kg/ton to reduce the effect of sticky deposit and facilitate stripping.

Conclusion

Optimum working conditions have been established with respect to operating conditions and the data collected during the past six months will be kept in view for the expansion programme and plant design.