# Electrolytic Preparation of Chromium from Chloride Solutions

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ELECTRODEPOSITION of chromium from trivalent baths, yet to be mastered technologically, has great economic prospects for two reasons. The first is that it supplies a product practically free from carbon which is essential for certain high chrome steels of special variety. Moreover, the fast changing techniques of alloy production generally calls for an increasingly large amount of the virgin metal in pure form. The second reason is that it opens out the possibility of using as raw material ores poor in chromium, an important consideration so far as India concerned.

A fairly good amount of work has been done on trivalent sulphate baths, and a pilot plant to produce 70 lbs of the metal per day is described in literature[1]. The study of the chloride bath for winning the chromium metal has not however received the same attention. The early attempts of Cowper-Coles[2], Feree[3] Carveth and Mott[4], and Voisin did not give encouraging results. Britton and Westcott[5] have also made studies on the chloride bath and have discussed some of the theoretical aspects of the problem. More recently Goltz *et al*[6] have attempted to establish the usefulness of chloride bath. They have studied the influence of certain factors in the electrolysis of chromium chloride, and concluded that addition of ammonium chloride to the electrolyte and use of hydrochloric acid as anolyte are essential for satisfactory deposition of chromium.

Electrolysis of chromium chloride solutions for winning the metal is likely to prove advantageous in view of the factors like easy preparation of the electrolyte (even from low grade chromium ores), simpler design of the cell and possibility of development of a cyclic process. Following the lines of earlier work a preliminary study was made in this laboratory to establish the conditions for satisfactory deposition of chromium from chloride bath. For successful deposition of chromium the cathode has to be polarised at a fairly high pH, but this would tend to precipitate the basic matter on the cathode. A compromise must be made between the two factors to get a maximum yield of the product. Addition of neutral salts of alkali metals promotes the stability of the chromium solutions at higher pH. Apart from ammonium chloride, sodium sulphate has been used in our experiments, and the effect of these neutral salts together with the attempts at modifications in the cell set-up are described in this short note.

Chlorination of Indian Chromite ores to prepare chromium chloride has been attempted in this laboratory and the results are encouraging. Alkali fusion of chromite and subsequent reduction with alcohol and hydrochloric acid or sulphur dioxide can also be used to prepare chromium chloride or chromium sulphate-chloride mixtures. Chromium chloride from both sources have been used in these experiments.

The set-up consists of a 400 cc beaker or a trough, a porcelain pot or microporous rubber boxes serving as diaphragm[7], copper strip cathode, and a graphite anode. Chlorine evolved at the anode chamber is removed by suction.

The initial experiments have brought out the necessity of maintaining the bulk pH of catholyte at 1.5 to 2.5 to get satisfactory deposition. Use of sodium chloride as anolyte, while the catholyte is stationery, results in the formation of green basic salts on the cathode very early. It has been found possible to avoid this by using 7-10% hydrochloric acid as anolyte whereby the highly mobile hydrogen ions diffusing into the catholyte serve to maintain the acidity. Temperature has to be kept at not more than 20°C by cooling with ice water, to get a metallic deposit on the cathode. Higher temperatures result in strong hydrogen evolution and the deposit is black and powdery.

## INFLUENCE OF CURRENT DENSITY AND AMMONIUM CHLORIDE CONCENTRATION :

Pure chromium chloride solutions do not give satisfactory results, and among the neutral salts added, ammonium chloride is reported to be the best[6] and a concentration of not less than 1 g. mol. per litre is suggested as suitable. Keeping the concentrations of chromium and ammonium chloride at about 60 g. per litre each, the minimum current density required is found out by the following series of experiments.

**TABLE I**

Temperature: 18–20°C; Cathode: Copper strip; Anode: 7% HCl

| *No.* | *C.D. amp/dm².* | *Current efficiency %* | *Remarks* |
|---|---|---|---|
| 1 | 10 | 5 | Deposit was thin, uneven. No deposit in a few places. |
| 2 | 14 | 7 | |
| 3 | 20 | 11 | |
| 4 | 25 | 18 | Deposit was bright and uniform but peeling off from certain portions. |
| 5 | 30 | 19 | |
| 6 | 40 | 20 | |

In the next series of experiments, the concentration of ammonium choloride is varied and the results tabulated in Table II.

**TABLE II**

Chromium content: 60 g/l;
Anolyte: 7% HCl;
Current Density: 25 amp/dm²;
Temperature: 18—20°C.

| *No.* | *Ratio of Cr : $NH_4Cl$* | *Current efficiency %* | *Remarks* |
|---|---|---|---|
| 1 | 1 : 0.5 | — | Bluish grey. Basic salts deposited. |
| 2 | 1 : 1.0 | 17 | Bright, light cracked deposit. |
| 3 | 1 : 1.5 | 19 | |
| 4 | 1 : 2.0 | 18 | |

A minimum current density of 25 amp/dm² and a chromium, ammonium chloride ratio of not less than 1 : 1 in g. moles are found to be conducive to better yields. These results are in qualitative agreement with that of Goltz[6] though the actual figures are not reproduced in the present experiments.

## INFLUENCE OF SULPHATES:

The influence of sulphates in chromium deposition is well known. To pure solutions of chromium chloride, varying amounts of sodium sulphate have been added and the results are tabulated in Table III. Other conditions were: Current density: 25 amp/dm²; Temperature: 18—50°C; anolyte: 8—10%HCl.

The influence of addition of sodium sulphate is not considerable ordinarily, but on ageing the solution for about 2 weeks after adding sodium sulphate, the current efficiency has been doubled Ammonium sulphate could not be used in place of sodium sulphate as the double salt easily gets precipitated. Chromium sulphate itself has been used in the place of sodium sulphate, and though the current efficiency is only slightly inferior the nature of the deposit is not as good as with sodium sulphate.

Use of hydrochloric acid as anolyte, though satisfactory for maintenance of pH, may be troublesome when electrolysis is done for long durations. Because, as the hydrogen ions get depleted, the anode chambers have to be refilled with hydrochloric acid. This has been overcome by employing sodium chloride itself as the anolyte and circulating acidified catholyte at a rate sufficient to maintain the bulk pH of catholyte at about 1·5. Results are similar to the ones obtained with hydrochloric acid as anolyte.

TABLE III

| *No.* | *Cr. Concn., g/l* | *Concn. of the salt added g/l* | *C. D. amp./dm²* | *C. E. %* | *Remarks* |
|---|---|---|---|---|---|
| 1 | 60 | $Na_2SO_4$ — 50 | 23 | 16 | Deposit was dull, greyish and flaky. |
| 2 | 58 | ,, ,, — 75 | 23 | 18 | |
| 3 | 55 | ,, ,, — 100 | 24 | 22 | Deposit was bright but peeling off. |
| 4 | 57 | ,, ,, — 100 | 25 | 39 | The solution was used after ageing. Deposit was uniform, bright and slightly cracked at the top and edges. |
| 5 | 60 | $Cr_2(SO_4)_3$ — 20 | 23 | 23 | Adherent, bright deposit Treeing at edges. |
| 6 | | ,, ,, 50 | 25 | 31 | Uniform compact and dull deposit. |

These preliminary experiments definitely indicate that further studies on the prepartion of cell feed and operating variables will be worthwhile, for developing the chloride process for the extraction of chromium metal.


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