

# Producing Copper Powder from Copper Bleed Solution by Hydrogen Reduction

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## Abstract

This paper deals with the bench scale investigation on the hydrogen reduction of a highly acidic copper bleed solution (CBS), generated in an Indian copper smelter, to produce highly pure copper powder. A titanium-lined autoclave of 1 L capacity was used for this study. After the optimization of the parameters for the recovery of copper powder, hydrogen reduction of copper was done in a larger autoclave to validate the results.

The effect of various parameters viz, time of reduction, temperature of reduction, pressure variation, iron dose, volume of copper solution etc was studied. Experiments were performed with synthetic and actual solution obtained from the copper plant. A 99% copper powder recovery is achieved by hydrogen reduction at a pressure of about 24kg/cm<sup>2</sup>, reaction temperature of 180°C, stirring speed of 400rpm for a reaction time of 2h. The fine copper powder thus obtained had good metallic luster. Kinetics of reduction of copper was examined by drawing the samples at different interval of time and analyzing the percent copper reduction. The copper depleted solution could be further purified with respect to the residual copper and processed for the recovery of nickel powder by hydrogen reduction.

Properties of the copper powder obtained from the large-scale experiments from actual plant and synthetic solutions have been evaluated for P/M applications. Compaction, green density, flow ability, particle size and purity were determined for the as produced and the annealed powder obtained from the synthetic copper solution and was found to have an apparent density of 3.50 g/cc, flow rate 35.6g/min, hydrogen loss 0.195 %, purity 99.785% and green density of 8.57 g/cc while the powder from actual plant solution has apparent density of 3.49 g/cc, flow rate 46.0 g/min, hydrogen loss 0.598 %, purity 99.398% and green density 8.57 g/cc. Thus, the copper powder produced by hydrogen reduction was found suitable for the P/M application.

## INTRODUCTION

Copper powder occupies a premier position in powder metallurgy and is produced almost all over the world by different techniques. Having various applications such as manufacture of self-lubricating bearing, electrical and electronic components and different mechanical parts, it is one of the most useful products because of its unique combination of high electrical and thermal conductivity. Copper powder has no substitute in the manufacture of iron base bearings; 5-15% copper powder is added as an alloying element to enhance the mechanical properties and control the dimensional changes during sintering, it is largely used in the production of printing inks, as a constituent for welding electrode, dispersion strengthened alloys and infiltrates. It is also used in the chemical & pharmaceutical industries. The copper powder is produced mainly by four methods viz. reduction of copper oxide, atomization of molten metal, chemical precipitation and electrolytic deposition.

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Various low-grade materials are used for the production of copper powder by reduction method. They are mainly copper oxide obtained by the oxidation of chemical precipitate or, finely divided electrolytic copper. In the process, the oxides are ground and reduced to the metal by treatment in continuous reduction temperature ranges from 400 to 600°C. The reducing atmosphere is a combustion gas containing chiefly CO, H<sub>2</sub>, N<sub>2</sub>, hydrocarbons and CO<sub>2</sub>, while oxygen and water vapour are kept at a minimum, since they impede the reduction cycle purity and particle size of the initial metal oxides on the reduction temperature and nature of reducing agent.

Other sources of copper are the solid and liquid wastes generated during the processing of various primary ores. Copper bleed stream is one such rich source of copper and nickel, which is generated during the electrorefining of copper anode wherein various impurities present in anode, dissolve and /or settle as sludge in the cell. The dissolved impurities (Nickel, Iron, Antimony, Bismuth, Manganese) build up in the electrolyte solution with the recycling of the electrolyte. Since these impurities degrade the quality of the deposited copper cathode, the electrolyte solution is required to be purified to control the purity of metal. This is done by various methods depending on the nature and extent of impurities. Discarding a part of the electrolyte as copper bleed stream (C.B.S.) and replenishing it with the pure solution is the practice in vogue world over. Recovery of valuable metals like copper and nickel from the C.B.S. is followed using different methods: some of important processes are discussed below.

In the conventional method followed, a portion of the electrolyte between the electrolytic cell and circulation tank is bled from the circulation tank to the liberator where decopperisation, purification and electrolysis takes place. In the decopperisation section the copper contained in the electrolyte is deposited on the cathode up to a concentration level of 10-15 g/l. The decopperised solution containing impurities is sent to the purification section, where the impurities co-deposit on the cathode with remaining copper. The purified solution is then crystallised to recover NiSO<sub>4</sub> · xH<sub>2</sub>O and black acid recovered is recycled back the circulation tank. Alternative to the decopperisation, copper sulphate powder (CuSO<sub>4</sub> · 5H<sub>2</sub>O) could be produced which could be recycled to circulation tank to maintain the copper content and quality of the electrolyte solution. The process is difficult to operate due to higher cost as reported by Shibata et al. Purification of crude nickel sulphate by precipitation methods has recently been reported by Havlik et al involving cumbersome procedure. Various new processes have been worked upon due to the presence of different kinds and level of impurities in the bleed streams. A few of them are highlighted below.

In the Sumitomo Nihama Copper Refining (SNCR) Process at SNCR[1], the electrolyte solution is mainly contaminated with arsenic, antimony, bismuth and nickel. A process involving, selective adsorption of antimony from electrolyte with activated carbon, removal of arsenic in the liberator tank during the decopperisation process and evaporation and crystallisation of nickel sulphate has been developed. Shibata et al[2] has developed two processes for removing the impurities such as arsenic, antimony and bismuth from copper electrolyte solution at Tamano Refinery, Japan. In one process electrolyte from the outer most layer is discarded after the removal of lesser amount of metal and in another process antimony and bismuth are adsorbed from the electrolyte by using chelating resin.

Shibasaki et al[3] reported a two-step liberation to completely depress copper and impurity ions followed by neutralization and solvent extraction. Sherritt process[4] is yet another process wherein free ammonia in the mixed amine sulphate solution is first boiled off to the precipitate most of copper as copper sulphide and removing small amounts of residual copper with hydrogen sulphide. The pure nickel diammine sulphate solution is reduced with hydrogen gas under pressure to produce nickel powder. Hydrogen reduction[5] of aqueous metal salts at elevated temperature and pressure in autoclave from the leach liquors of ores/concentrates has been reported. Tagashi and Nagai[6] reported hydrogen reduction of copper from CBS at 190°C temperature and 20 atmosphere pressure.

A new approach on selective reduction of copper and nickel powder is being reported here to obtain value added product from such solutions, besides the recovery of the metal from CBS by other methods. The hydrogen reduction of aqueous copper solutions has been studied by many investigators and, in fact the production of copper powder has been applied on a commercial scale. It can be seen from a potential-pH diagram for the Cu-H<sub>2</sub>O system, that the thermodynamic driving force for the reduction of copper salt with hydrogen is smaller at high acidity of the aqueous solution. However, no experiment has been reported dealing with such highly acidic solutions like copper electrolyte or the mother liquor from a copper sulfate plant.

The paper presents the study on the development of a process based on hydrogen reduction as a useful method to reduce the total energy requirement for purifying spent copper electrolyte and to permit the recovery of copper as powders.

## **EXPERIMENTAL**

The hydrogen reduction studies were carried out in a one litre capacity titanium autoclave using around 60%(max.) of the capacity for safety purpose. The autoclave can be operated up to 80bar pressure and 300°C temperature. It has electrical heating system with temperature controller. The solution was mixed in the autoclave with the stirrer. After transferring a known volume of metal sulfate solution and known amount of metal powder seed in the vessel, the pressure and reduction conditions were maintained using hydrogen gas. The reduction was carried out under various operating conditions viz. volume of the solution, reaction temperature, pressure of hydrogen, temperature of reaction, effect of time at constant temperature and pressure and amount of various additives. Samples were taken out after each 20min, and analyzed for the amount of unreduced metal. Thus, effect of various parameters were studied and optimized for the maximum recovery of the metal as powder. After reduction of metal the autoclave was allowed to cool to room temperature and the solution and metal powder were taken out. The powder was properly washed with distilled water followed by sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution to neutralize the acid and finally with distilled water and dried at 100°C. After the optimisation of the parameters experiments large scale were also carried out in a 20L capacity autoclave containing titanium as liner. The powder so formed was treated as described above, dried and stored in a dessicator and analyzed for its purity and other properties. The dried powder was annealed and then properties were evaluated for P/M applications. The spent liquor was also analyzed and recovery of metal during the reduction was calculated on the basis of spent liquor analysis..

## RESULTS AND DISCUSSION

Bench scale experiments for optimizing the parameters for the recovery of copper by hydrogen reduction from the copper bleed stream were performed under different conditions. Synthetic solution containing 40.0 g/L of Cu & 10.43 g/L of Ni as major metallic values along with a high acid concentration (194g/L) was prepared for these studies and the results are discussed in the following text.

### Effect of time on copper reduction

Time for the reduction of copper was varied from 30 min to 120min to see the maximum recovery (Fig 1). It can be seen from the figure that complete reaction takes place between 90 to 120 min. hence further experiments were performed for a time period of 120 min.

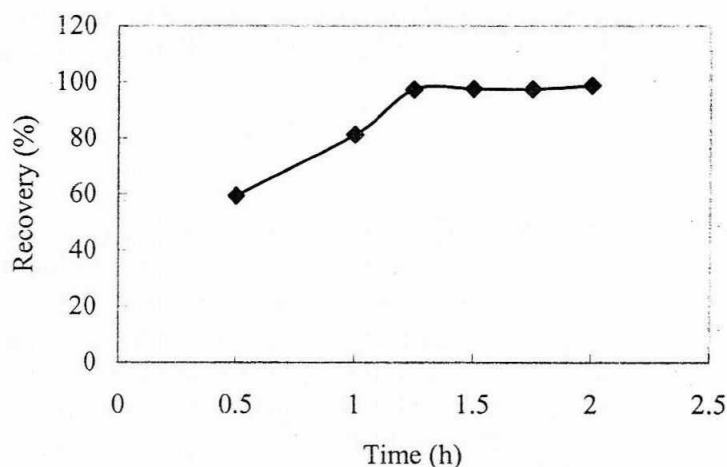


Fig 1: Effect of time on pressure hydrogen reduction of copper from CBS:  $V$ - 0.6L,  $t$ - 2h,  $T$ - 180 °C,  $P$ - 20 kg/sq. cm

### Effect of reaction temperature on reduction

Temperature of reduction was varied from 150°C to 190°C. Fig 2 shows that copper reduction increases with the increase in temperature from 150 to 190°C at the stirring rate of 400rpm and a pressure of 20kg/Cm<sup>2</sup>. Also the recovery of copper at low temperature (150°C) is 92 % that increases to 99.5% at 190°C. Hence the reduction temperature was maintained at 180°C in further experiments.

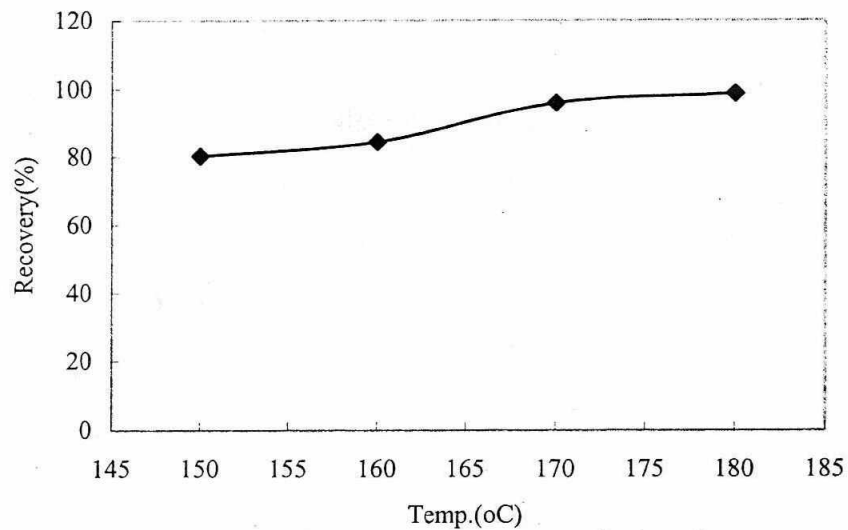


Fig 2 : Effect of temperature on pressure reduction of copper from CBS: *V- 0.6L, t- 120 min., p- 20 kg/ sq. cm, rpm - 400*

### Effect of reaction pressure on reduction

Fig 3 shows that the percent copper reduction increases with the increase in pressure from 10 to 25 kg/cm<sup>2</sup>. However, it becomes constant after 20 kg/cm<sup>2</sup>, hence the optimum pressure for all the experiments being 20kg/cm<sup>2</sup>.

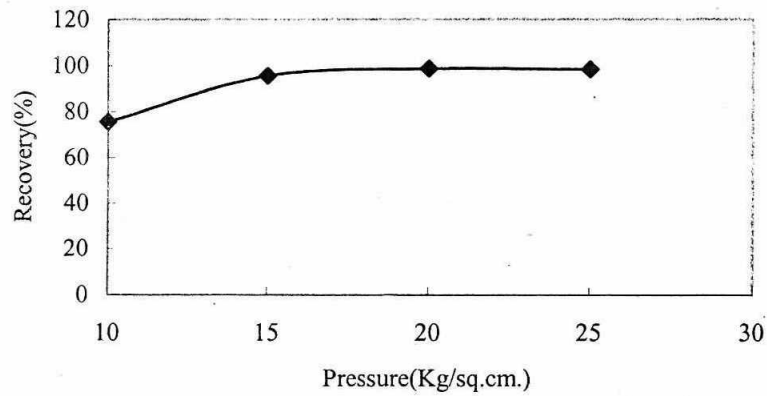


Fig 3 : Effect of pressure on hydrogen reduction of copper from CBS: *V-0.6 L, T- 180 oC, t- 2h, p- 20 kg/ sq.cm, rpm- 400*

### Effect of iron dose

Iron salt was added in the CBS in the range of 0 to 750 ppm. The solutions were taken out after every 20-minute interval and was analyzed for amount of Cu in g/L in the solution. Plot (Fig 4) on percent recovery of copper with time clearly shows that reaction kinetics become faster on addition of 50 ppm Fe(II). The final recovery of copper was found to be same (99.68%) at all Fe(II) doses in two hours.

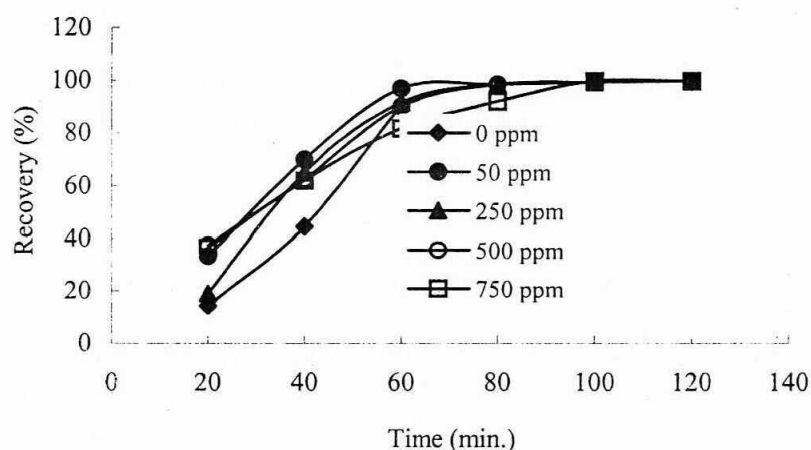


Fig 4 :Effect of iron dose on pressure hydrogen reduction of copper from CBS: *V*- 0.6L, *t*- 120 min., *T*- 180oC, *p*- 20 kg/ sq. cm, rpm - 400

### Effect of volume of the aqueous feed

The effect of volume of CBS taken in autoclave was studied keeping other parameters constant. The volume of the solution was varied from 0.4L- 0.6L. The results are presented in Fig 5.

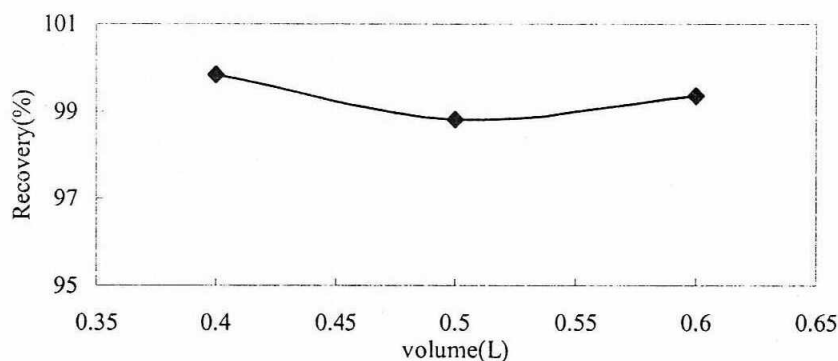


Fig 5 : Effect of volume on pressure hydrogen reduction of copper from CBS: *t*- 120 min., *T*- 180oC, *P*- 20 kg/ sq.cm, rpm - 400

The final recovery of copper also decreases from 99.859% to 99.37% on increasing the volume of bleed stream from 0.4 L to 0.6L (Fig 5). Purity of the copper powder under different conditions before annealing are given in Table 1.

**Table 1 : Chemical analysis of copper powder produced by hydrogen reduction under various experimental conditions on bench scale**

<b>Consti tuents (%)</b>	<b>Temp 180oC Pr 20kg/cm<sup>2</sup> Reduction time 1h</b>	<b>Temp 150oC Pr 20kg/cm<sup>2</sup> Reduction time 2h</b>	<b>Temp 180oC Pr 20kg/cm<sup>2</sup> Reduction time 2h Fe dosage 750ppm</b>	<b>Temp 180oC Pr 20kg/cm<sup>2</sup> Reduction time 2h Fe dosage 500ppm</b>
Ni	NF	NF	NF	Nf
Fe	0.0058	NF	0.0021	NF
Bi	Nf	NF	0.0229	NF
Sb	0.0028	0.0039	0.0022	0.0027
Purity	99.991	99.996	99.97	99.997

**Variables marked in bold are varied**

Thus with the optimization of reaction parameters for the maximum recovery of copper selectively from the synthetic copper bleed stream at bench scale, a few experiments were performed in 20L autoclave to ensure the validity of the small-scale data with the synthetic and actual copper bleed stream.

**Large scale Copper powder synthesis by hydrogen reduction from synthetic CBS**

An autoclave, with a titanium liner, of a capacity of 20L solution was used for the experiments on large scale. Five sets of the experiments with 9.0L solution in the autoclave were conducted. In first three sets of experiments reduction time was varied keeping other variables constant i.e. electrolytic copper powder as seed: 50g, Temperature of reduction: 180°C, pressure applied: 20kg/cm<sup>2</sup>. As can be seen in Fig 6 that with the increase in the reduction time from 0.5h to 2h the percent copper powder recovery increased from 15.8% to 91.87%. Thus the fourth experiment was performed for 2h reduction time keeping other variables same as above, the metal recovery was 95%. Copper powder formed in each set was filtered after cooling the solution in the autoclave upto 50°C after releasing the pressure. The Copper powder formed was washed and treated as described before. Properties of the copper powder were studied after annealing it at 700°C for two hours with a soaking time of 30 min under the hydrogen atmosphere at a flow rate of 10.5L/m. The powder was then cooled for about 5h and was used for properties evaluation.

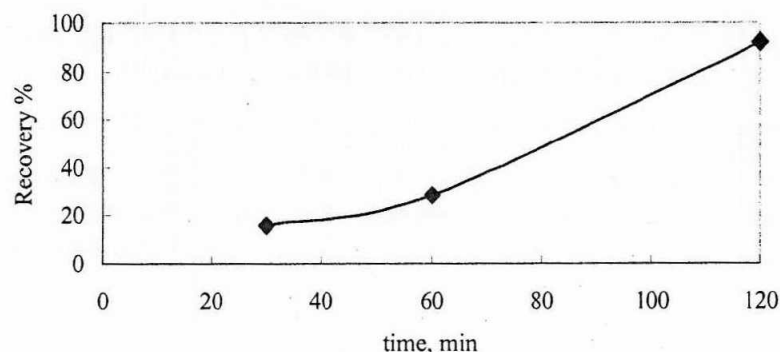


Fig 6 : Effect of time on copper reduction from synthetic CBS in 20L autoclave

After the successful experiment with the synthetic solution, experiments were performed with the actual leach liquor from ICC Ghatsila. 9L of the actual copper bleed solution was taken in the titanium-lined vessel to which 25g of copper powder was added as seed. Temperature and pressure were maintained at 180°C, 24kg/cm<sup>2</sup> and agitated for 2h. After cooling the solution it was filtered and the powder obtained was treated as above. Table 2 shows the experimental conditions followed in four experiments with actual CBS. The dried copper powder was annealed at 700°C for two hours with a soaking time of 30 min under the hydrogen atmosphere at a flow rate of 10.5L/m.

**Table 2: Large scale preparation of the copper powder from actual CBS by hydrogen reduction**

ANALYSIS (G/L) OF THE SYNTHETIC CBS: CU-39.85, NI-9.57, BI-0.108, FE-0.255, H<sub>2</sub>SO<sub>4</sub>-194.04

Parameters	Expt 1	Expt 2	Expt 3	Expt 4
Electrolytic copper powder as seed,g	50	25	25	25
Pressure applied, kg/cm <sup>2</sup>	28	17	24	24
Temperature, °C	180	180	180	180
Time of reduction, min	120	120	150	120
Weight of copper powder obtained , g	407.6	197.88	325.75	350.78
Recovery of copper powder recovered, % (based on spent liquor analysis)	99.21	38.04	99.68	99.36
Nature of copper powder obtained	Lustrous copper powder			



Various properties such as apparent density, acid insoluble, purity of the copper powder, flow rate, hydrogen loss, have been studied and are given in Table 3.

**Table 3: Properties of the annealed copper powder produced from synthetic solution and actual CBS in 20L autoclave**

Parameters	From synthetic CBS	Actual CBS
Acid insoluble (%)	-	-
Apparent density (g/cc)	3.50	3.49
Flow rate (g/min)	35.6	46.0
Hydrogen Loss (%)	0.195	0.598
Chemical analysis of the copper powder (%)	Ni: 0.0055, Fe: 0.0046, Bi 0.0082, Sb 0.0022	Ni: 0.0009, Fe 0.0036, Bi NF, Sb NF
Purity (%)	99.79	99.40

NF-Not found

Size analysis of annealed copper powder produced from synthetic and actual solutions are given in Table 4.

**Table 4 Partical size analysis of annealed copper powder produced from synthetic and actual CBS on large scale:**

Partical size ( $\mu\text{m}$ )	Annealed copper powder	
	From synthetic CBS	From actual CBS
212	38.48	29.19
212-150	30.42	30.60
150-106	11.75	11.91
106-75	6.82	6.89
75-63	2.22	2.62
63-45	7.64	7.41
45	2.51	11.28
Wt of Cu powder taken(g)	100.02	100.04
Wt of cu powder after sieve analysis	99.84	99.90
% Wt loss during sieve analysis	0.18	0.14

Compactability and green density of annealed copper powder from synthetic and actual CBS were also determined and are given in Table 5.

**Table 5 : Compactibility and green density determination of annealed copper powder from synthetic and actual CBS**

Parameters	Cu powder from synthetic CBS		Cu powder from actual CBS	
	-100mesh	-150mesh	-100mesh	-150mesh
Annealed Copper powder (Purity basis)	99.785	99.785	99.398	99.398
Wt of copper powder (g)	15.20	15.04	15.03	15.05
Wt of the compacted mass(g)	14.98	14.86	14.86	14.86
Length of the compacted mass(mm)	11	10.5	10.5	10.5
Diameter of the compacted mass(mm)	14.5	14.5	14.5	14.5
Green density(g/cm <sup>3</sup> )	8.25	8.57	8.57	8.57

After the complete recovery of copper from the CBS the filtrate or the spent electrolyte was treated with sodium sulphide to remove the residual copper and was processed for the recovery of nickel.

## CONCLUSIONS

The experiments have been performed for optimizing the parameters on bench scale for the production of the copper and nickel powders by hydrogen reduction and were scaled up to 9.0L batch for copper. Bench scale work on the hydrogen reduction of copper from CBS of ICC Ghatsila has also been carried out in autoclave.

Following are the conclusions of the work reported in this report.

1. Experiments were performed with synthetic and actual CBS. A 99% copper powder recovery is achieved by hydrogen reduction at a pressure of 24kg/cm<sup>2</sup>, reaction temperature of 180°C, stirring speed of 400rpm for a reaction time of 2h.. The copper powder thus obtained was lustrous in nature.
2. The annealed powder from synthetic and actual CBS has apparent density of 3.50 g/cc, flow rate 35.6g/min, hydrogen loss 0.195 %, purity 99.785% and green density of 8.57 g/cc and the powder from actual CBS has apparent density of 3.49 g/cc, flow rate 46.0 g/min, hydrogen loss 0.598 %, purity 99.398% and green density 8.57 g/cc
3. CBS with such a high acidity can be used directly for hydrogen reduction of copper and nickel reduction is possible in highly alkaline medium.

## ACKNOWLEDGEMENTS

Thanks are due to the management of ICC, Ghatsila / HCL, Kolkata for providing the copper bleed solution. Financial assistance from Dept of Mines is thankfully acknowledged.

## REFERENCES

1. Toyabe, K., Segawa, C. and Sato, H, In Proc. The Electrorefining and winning of copper, Colorado, AIME., Pennsylvania, Feb. 24-26, p. 117-128, 1987
2. Shibata, T., Hashiuchi, M. and Kato, T.,: In Proc. The Electrorefining and winning of copper, Colorado, AIME., Pennsylvania, p.99-116, 1987
3. Shibasaki, T., Ohsima, E., Ishiwata, S. and Tanaka, H, In Proc. The Electrorefining and winning of copper, Colorado, AIME., Pennsylvania, p 223-237, 1987
4. Mackiw, V. N. and Veltman, H., Recent advances in Sherritts pressure hydrometallurgical technology, Proc. Symposium Nacional de Ingenieria Metalurgica, Nov. 14-19, 1983, Lima, Peru.
5. Schavfelberger, F.A., , Precipitation of metal from salt solution by reduction with hydrogen, J. Metals, 8, p. 695-704, 1956. . Schavfelberger, F.A. and Mc Gauley, P.J., US Patent 2,796,342, June 1957.
6. Togashi, R. and Nagai, T., Hydrometallurgy, 11, 149-163, 1983.