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BISMUTH REMOVAL FROM COPPER ELECTROLYTIC SOLUTION BY CHEMICAL REACTION WITH BARIUM CARBONATE

Joshi Dilip kumar Rameshchandra ,*Jyoti Singh, **R. K. Singh

*B.N.C.E.T ,Sitapur Road, Lucknow, Uttar Pradesh, India
** Sardar Bhagwan Singh University, Balawala,Dehradun – 248001 ,Uttarakhand,India

****Address for Correspondence :** Dr. R. K. Singh, Vice chancellor, Sardar Bhagwan Singh University, Balawala, Dehradun – 248001,Uttarakhand, India; Email ID : rktox@gmail.com, singhprofrk@gmail.com

ABSTRACT

Bismuth removal from electrolyte by chemical reaction using barium carbonate takes 4 hour to complete the reaction and required amount of barium carbonate is 30 times higher than the calculation as per chemical reaction.

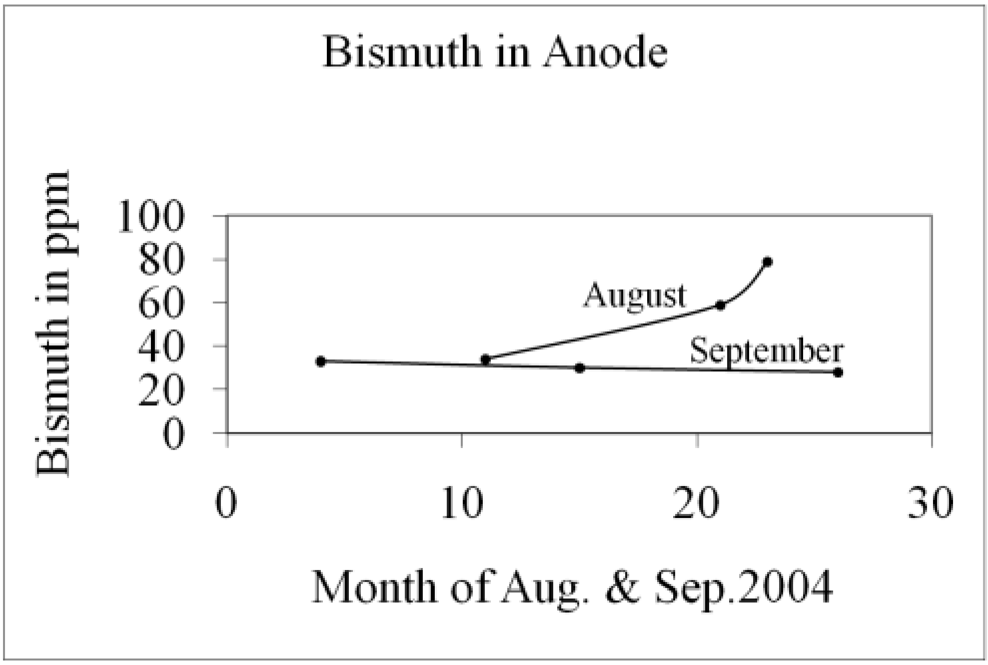
Key Words: Bismuth removal ; Copper electrolyte

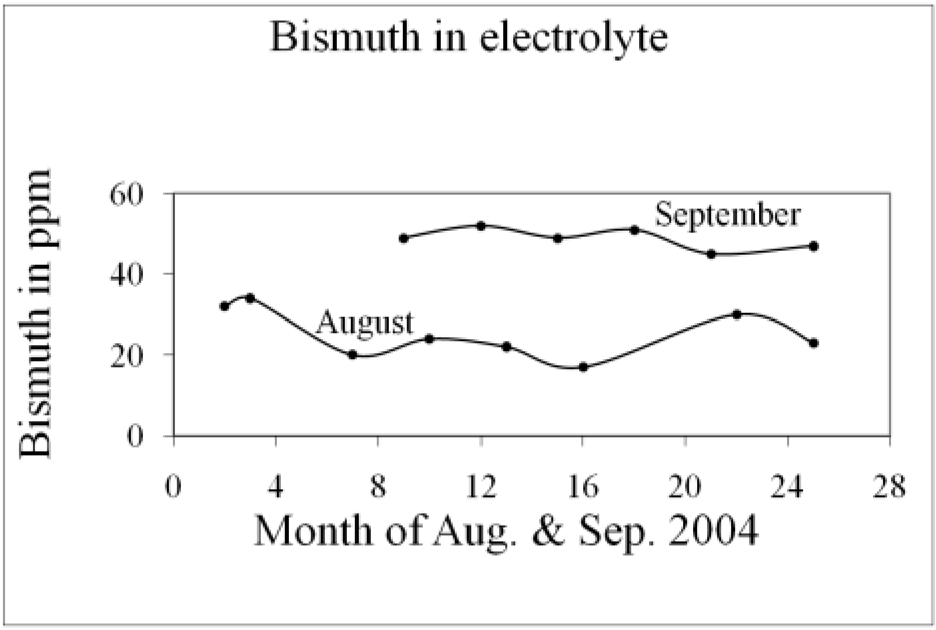
INTRODUCTION

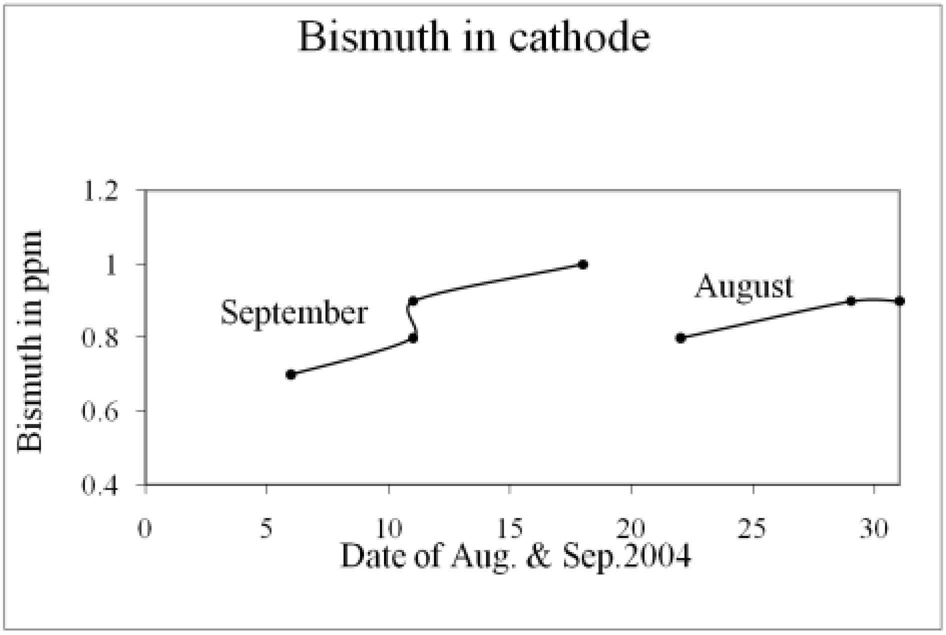
The quality of copper cathode has always been a matter of great concern to its end user i.e. manufacturer of cables, winding wires, strips, flats, power cables, tubes, copper rod etc. Swil Limited is one of the largest secondary copper cathode producers in India approximately 50,000 MT/Yr. At present cathode quality is critical, it's controlled by various parameter like cathode alignment, electrolyte composition & temperature, current density as well as the addition reagents. Understanding the impact of various impurities & combination of impurities in high purity copper is a challenge. In fact for the end user, the impurity levels present in copper is the predominant importance. This paper describes the impact of Bismuth on various applications. Bismuth can cause problems with bar cracking, usually micro cracks during the casting and rolling of rod at one part per million. In copper refinery day-by-day impurities are increased in copper electrolyte from impure copper anode during electrolysis, to minimise the impurities from electrolytes the industries are taking different methods like adsorption, ion-exchange separation using resin and chemical reaction. In the production of copper these anodes are purified to high-purity copper cathodes by electrolysis in a solution of copper sulphate and sulphuric acid whose nominal composition is 40-45 g/l copper and 160-180 g/l sulphuric acid. In electrolytes anode impurities behave in three ways. Impurity those are more electronegative than copper dissolve in the electrolytes e.g., Nickel, Zinc, Iron and Cobalt. Second type of impurities is more electropositive than copper and goes to slime, e.g., Gold, Silver, Selenium, Tellurium, Lead and Tin. Third type of impurities having similar electro-potential as copper, e.g., Antimony, Bismuth and Arsenic. These impurities are most harmful, as they tend to deposit with copper cathode. Although smelting, converting and fire refining greatly reduce the concentration of impurities in copper anodes, a small quantity of impurities remains in copper anodes. The quantity of impurities varies depending upon the raw materials composition and the smelting, converting and refining process. Particularly this industry using raw materials in the form of concentrates, copper scrap, reverts, dust, cement. Values are shown in table No- 1 for description of impurities in copper anodes. In adsorption study synthetic zeolites, chelating resins and activated carbons were tested as adsorbents to select the bismuth and antimony for best adsorbent performance, as well as best operating temperature for the process (1). Synthetic zeolites physically cannot resist at high acidic solution and activated carbon is taking 15 days for equilibrium with poor selectivity of bismuth and antimony. Using chelating resin treatment of very bulk electrolyte is very difficult and time-consuming process. In another method for reducing impurities in electrolyte is ion-exchange method in which different types resins are used like SuperLig 83, UR-3300 and MX-2 (2-4). The regeneration of ion-exchange column was carried out by washing with acid then reuses the column so its required interval for column regeneration. Chemical reaction for removing impurity from electrolyte is time saving and non-tedious method, within the hours it can complete with high performance. In reported chemical reaction in electrolyte H_2S gas was passed in electrolyte and converts impurities in sulphide form and precipitated at bottom but Cu also converted in CuS so recovery of Cu is required one more chemical reaction step and process becomes time-consuming and expansive (5). In the proposed chemical reaction only bismuth metal is affected and it is not changing any other composition of electrolyte. In this chemical reaction only physically separation of sludge (barium sulphate and bismuth trioxide) from electrolyte at the end of reaction. In our industry bismuth impurity present in different stage are shown in table no –1 and graphs.

Table 1: Bismuth present in anode, electrolyte and cathode

Bi in Anode	Bi in electrolyte	Bi in cathode
28 ppm	46 ppm	< 0.9 ppm







MATERIALS AND METHODS

Materials

Electrolyte composition as per given in table No 2, Barium Carbonate (LR, Qualigens Fine Chemicals), Bismuth metal powder (Loba chemicals Pvt. Ltd. 99.5%).

Experimental

In 2-lit electrolyte add 500 mg Bi powder dissolving in 1:4 HNO_3 stir vigorously then add 5 gm $BaCO_3$ gradually and maintain the temperature of solution 60-65oC during the experiment. Take 20 ml sample for 0, 30, 60, 90, 120, 150 and 180 minute. Analysed all above samples by atomic adsorption spectroscopy (Varian spectra AA 880, Australia) and results are given in below table.

Chemical Reaction

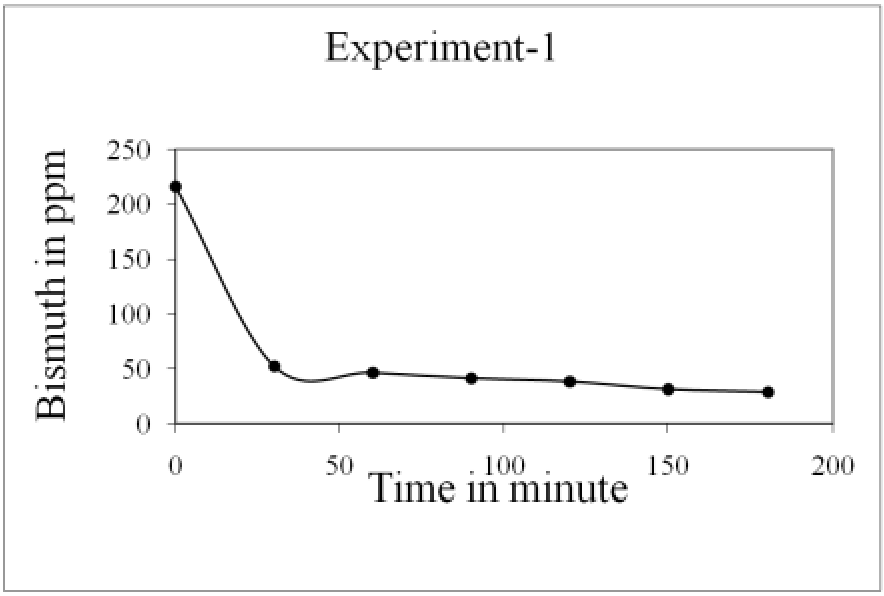
$$2Bi^{+3} + Cu^{+2} + 4SO_4^{-2} + 3BaCO_3 \longrightarrow 3BaSO_4 + Bi_2O_3 + 3CO_2 + SO_4^{-2} + Cu^{+2}$$

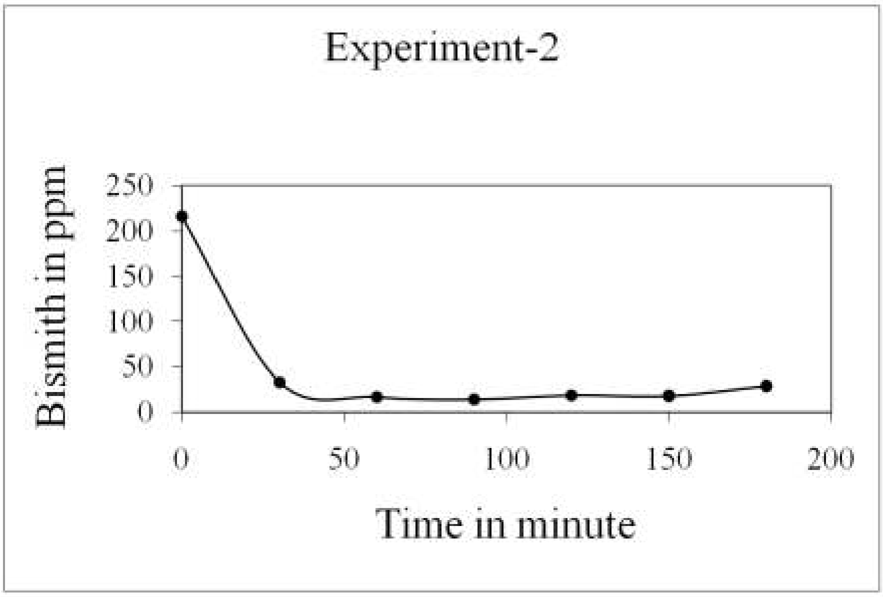
In above reaction barium carbonate reacting with the acid available in electrolyte and immediately liberating carbon dioxide gas in atmosphere and barium is forming barium sulphate and precipitated in bottom. One barium carbonate molecule generating one excess oxygen atom in electrolyte and this oxygen is used to form bismuth trioxide (Bi_2O_3). Bismuth trioxide is insoluble in electrolyte so this also settled at bottom so; this bismuth can reduce by this reaction from electrolyte.

RESULTS

During above reaction we have varied some parameters to optimise the reaction condition are as follows. As per above reaction calculation the required amount of barium carbonate amount is taken different in different experiments like 2 time, 5 time, 10 time and 30 time higher than requirement. Another parameter is time optimisation for reaction completion.

In experiment –1 & 2 both are same composition, in electrolyte 500 ml (320 ppm Bi) add 5 gm $BaCO_3$ and maintain reaction temperature 60-65o C. The both result indicating same trend as shown in Fig. 1 & 2. In these cases Bi is reducing gradually with time.





In experiment –3 electrolytes taken as such (without adding excess Bi, 32.5 ppm Bi) add 1 gm $BaCO_3$ and maintain reaction temperature 60-65o C. In this result Bi is reducing up to 8 ppm with time (Fig.3).

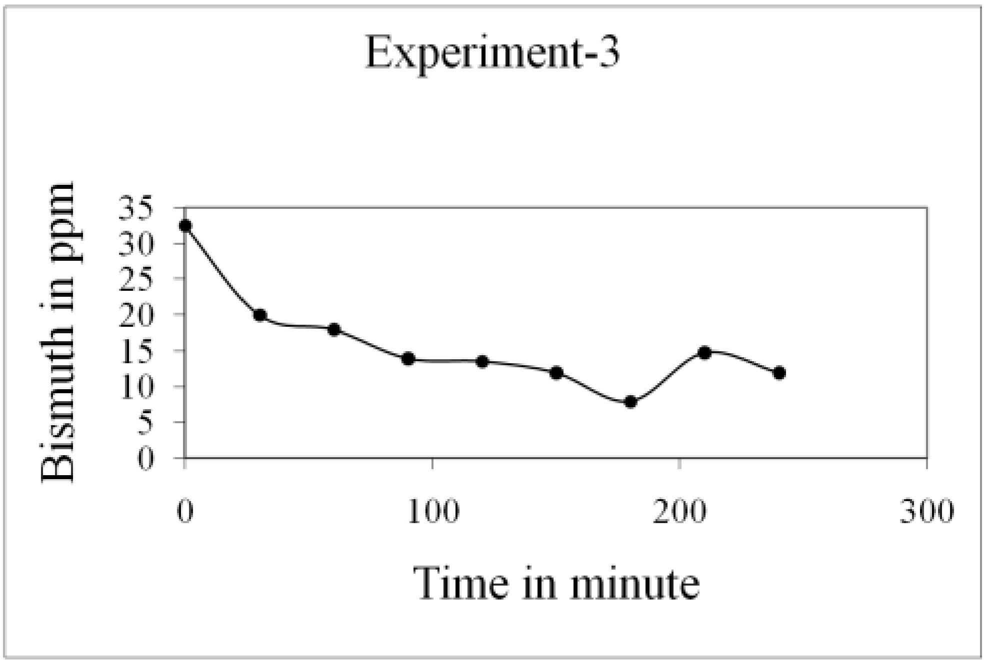
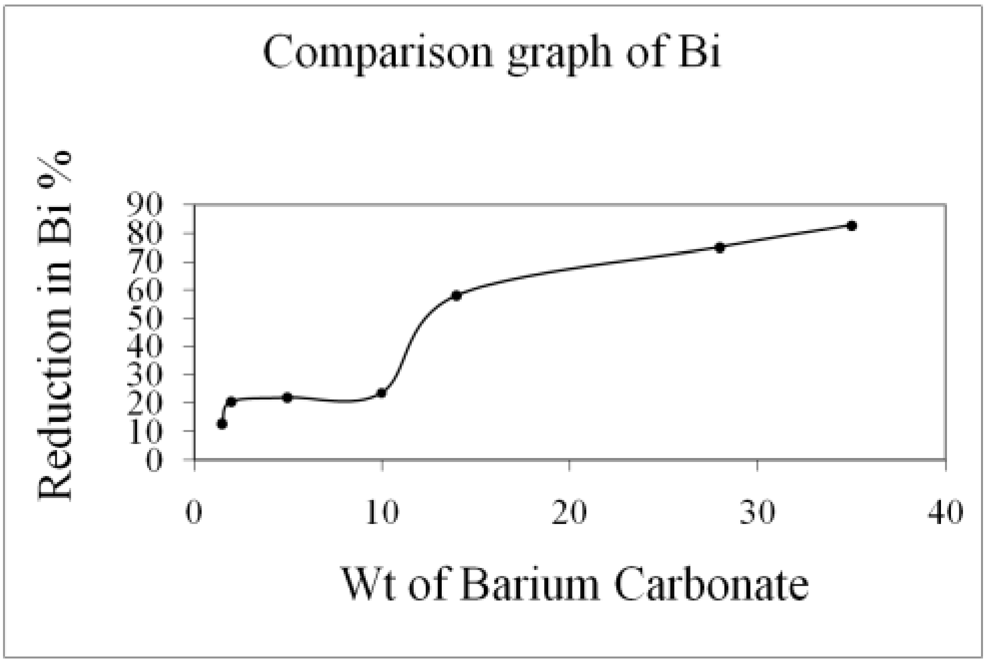
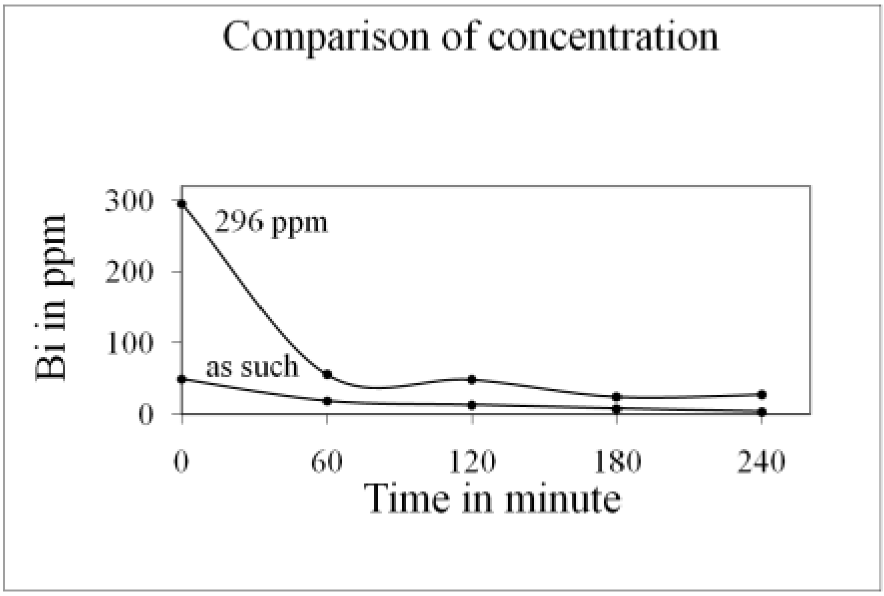


Figure –4 indicating the comparison of the amount of barium carbonate used in reaction for decreasing of bismuth amount in electrolyte. It is clearly showing that higher barium carbonate amount(30 times) is giving 80 % reduction in bismuth amount.



In comparison with the bismuth concentration in two different reactions one is having 296 ppm and another is 49.6 ppm Bi. In both adding 30 times higher barium carbonate as per above reaction calculation and results shows the level of bismuth is more reducing in lower concentration that means treatment of electrolyte for bismuth removal is preferred when Bi concentration is low (Fig.-5).



DISCUSSION

Barium carbonate is reacting with electrolyte and relies carbon dioxide in atmosphere. Barium converting in barium sulphate reacting with sulphuric acid present in electrolyte and precipitated in electrolyte. One atom of oxygen is enter in electrolyte from one molecules of barium carbonate so this excess oxygen only playing role in bismuth removal. In literature the following reaction was reported (6).

$$2\,Bi + 3(1/2\,O_2) \longrightarrow Bi_2O_3$$

This bismuth trioxide is insoluble in electrolyte and settled at bottom with barium sulphate precipitated. Conformations of bismuth trioxide is settled in bottom by analysis of sludge by dissolving it into nitric acid and filter the barium sulphate precipitate and analyse the filtrate by atomic adsorption spectrometer. Analysis shows the filtrate containing 122.2 ppm bismuth with barium sulphate. As per the chemical reaction one barium carbonate giving one oxygen but some of them are dissolve in electrolyte and some of them are reacting with bismuth so this reaction is slow and its required 30 time higher barium carbonate then the reaction calculation.

CONCLUSION

Bismuth removal from electrolyte by chemical reaction using barium carbonate takes 4 hour to complete the reaction and required amount of barium carbonate is 30 times higher then the calculation as per chemical reaction.

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