# Electrolyte impurity control at Chinchpada Refinery of Sterlite Industries (India) Limited

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## ABSTRACT

Sterlite Industries operates copper refinery at Silvassa, India using ISA PROCESS with a capacity of 1,80,000 TPA. The anodes are received from its custom Smelter at Tuticorin, Southern India. The impurities in anode vary substantially especially bismuth, which has varied from 10 ppm to 150 ppm over the last few years.

This paper discusses the various operating practices and technologies adopted at Sterlite copper refinery for electrolyte impurity management. The main emphasis is given for controlling bismuth, antimony, nickel and iron in the electrolyte. The paper discusses the control of bismuth and antimony in electrolyte by progressively increasing arsenic level in electrolyte. It was observed that at a critical arsenic level in the electrolyte, bismuth and antimony reports to anode slime.

Considerable importance is given in controlling nickel and iron content in electrolyte by adopting latest low cost acid purification system. This novel method coupled with an effluent treatment plant ensures recovery of sulfuric acid, removal of nickel and iron from electrolyte, production of disposable nickel sludge besides ensuring zero discharge to environment. With a more suitable impurity management system, Sterlite is able to achieve and sustain the cathode quality superior to ASTM standard.

## INTRODUCTION

To meet the stringent demand of customers, the copper producers are giving prime importance to produce high quality copper cathodes superior than ASTM standards. The major challenge for refinery is to improve cathode quality and appearance despite fluctuating anode impurity levels. The backbone in achieving good quality cathode includes the control of electrolyte impurity.

Sterlite Copper is an ISA process licensed copper refinery located in Chinchpada, Silvassa near Mumbai, India. The refinery was commissioned in 1997 with the installed capacity of 60000 MTA of copper cathodes. The process adopted for refining is the ISA permanent cathode technology. Over the past Six years the company has undergone aggressive expansions along with the de-bottlenecking to reach the present capacity of 180000 MTA. The greatest challenge for Sterlite is produce cathode quality at efficiency at par with the international producers irrespective of the rapid expansion. The continuous quality improvement plan has helped the plant to produce copper cathode as per ASTM standards and establish itself in the international market.

The copper refinery receives anode by trucks from the smelter situated in southern India, which is 2000 kms away from the refinery. The smelter is a custom smelter processing concentrates having wide variation in impurity levels. The impurity levels have varied in wide range in last six years of operation. With the progressive expansion and due to wide variation in anode impurities, the impurity levels in electrolyte have increased over the years.

The refinery operates at relatively higher current density of 320 Amps/m2. At this high current density operation, the control of electrolyte impurity is a prime factor in determining the cathode quality. Sterlite has given utmost attention in controlling the impurity levels within the specified limits. The paper discusses strategies adopted with the purpose of revamping and modernizing the electrolyte impurity management system.

**Anode Composition**

Being a custom feed smelter, the Sterlite receives concentrates both from its own mine situated in Australia and also purchased concentrates. The variation in concentrate composition, to some extent is nullified by blending the concentrates thus enabling to have a uniform composition feed to the smelter. However sometimes this is limited by wide variation of impurity levels in concentrates. This variation in impurity levels in purchased concentrates has a significant affect on the overall impurity balance.

The Fig - 1 & Fig- 2 shows the monthly average levels of impurities in anodes for the last three years.

**Behaviors of Impurities**

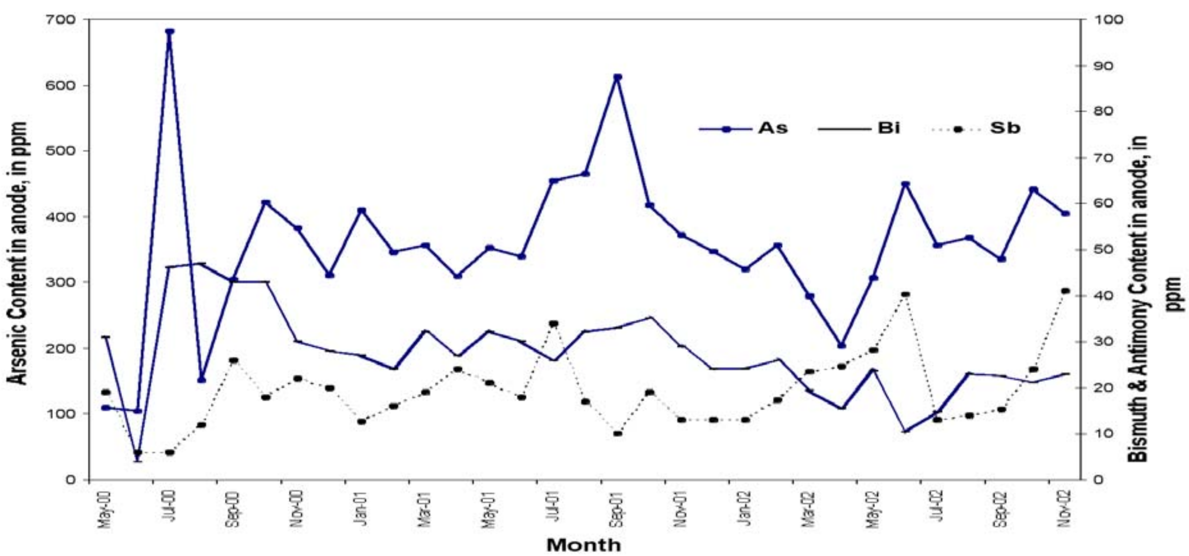



FIG-1 : Arsenic,Bismuth & Antimony in Anodes - Monthly Average

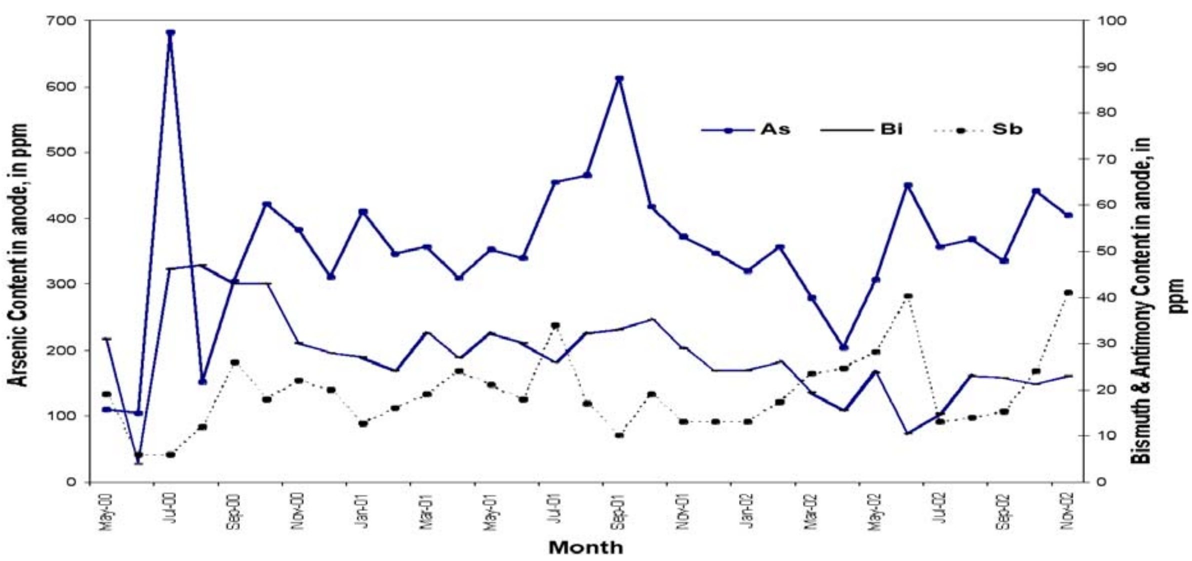



FIG-2 : Arsenic,Bismuth & Antimony in Anodes - Monthly Average

Various elements are present in the anode in different forms/complexes and each of them behaves differently during electrorefining. Primarily during copper electrorefining, anode impurities behave in following ways.

- Elements less noble than the copper such as nickel, iron dissolves in the electrolyte.
- Elements like gold, silver, platinum, selenium, tellurium, which are more noble than the copper remains undissolved and form an anode slime, which gradually drops, to the bottom of tank.
- Arsenic, antimony and bismuth present as impurities in the anode constitute a separate group. Most of the arsenic present in the anode dissolves in electrolyte and is oxidized by atmospheric oxygen from a trivalent to pentavalent state. Only a part of antimony and bismuth dissolves in electrolyte and the rest goes to the slime.

**Build Up of Impurities in Electrolyte**

The initial increase in the impurity level in electrolyte at Sterlite Copper was compensated by continuous dilution of the electrolyte due to addition of more number of cells as a part of expansion. For initial period there was no need for impurity control due to continuous dilution. As the production capacity increased the impurity levels had shown an increase in levels in electrolyte. The Sterlite had intend to keep its impurities level well below the specified limits, which could help in avoiding the major cathode quality upset due to electrolyte composition upset. The Table–I gives the target electrolyte composition.

Table –I: Target Electrolyte Composition

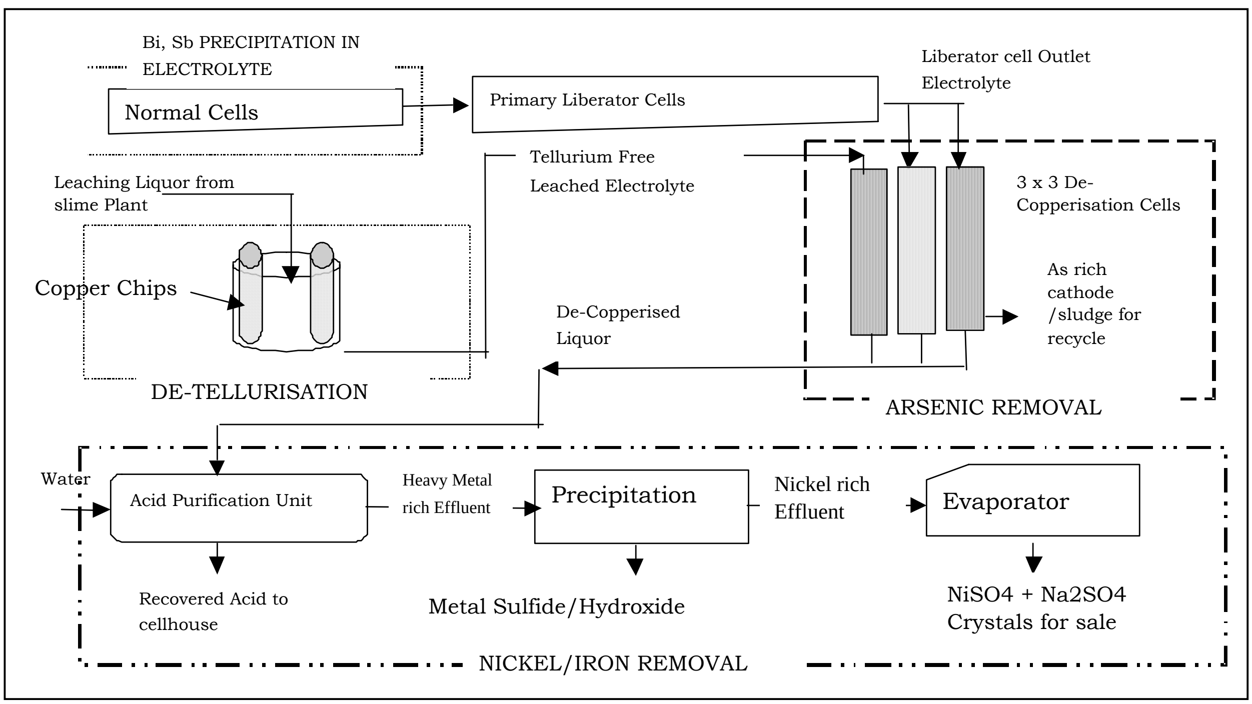
| SL. No. | Component | Concentration gpl |
|---|---|---|
| 1 | Copper | 48 – 52 |
| 2 | Sulfuric Acid | 160-180 |
| 3 | Arsenic | 12-15 |
| 4 | Antimony | < 0.2 |
| 5 | Bismuth | < 0.2 |
| 6 | Nickel | < 15 |
| 7 | Iron | < 3 |

**Electrolyte Impurity Management**

Electrolyte impurity management at Sterlite Copper basically involves following four steps.

1. Control of bismuth and antimony in electrolyte by altering the anode and electrolyte chemistry
2. Control of arsenic by purification cells (Electro-winning)
3. Control of nickel, iron and other soluble impurities by acid purification unit.
4. Control of tellurium by cementation on copper.

Fig - 3 Gives the flowchart for electrolyte impurity control. Each section is discussed in details.




Fig– 3: Schematic Diagram of Electrolyte Purification & Treatment System at Sterlite

**Control of Bismuth and Antimony in Electrolyte by Altering the Anode and Electrolyte Chemistry**

The increase in the antimony and bismuth in electrolyte observed at the initial stage of refinery operation. Decopperisation cells alone could not take care of the input through anode. Installation of additional decopperisation cells did not help in reducing the bismuth and antimony levels in electrolyte. The level of antimony and bismuth increased above 300 ppm whereas arsenic was still at 3 gpl level. This also associated with the lower level of arsenic in anodes. The cellhouse lost its stability due to this in-balance and following symptoms are observed.

- Heavy top nodulation on cathode &
- Bismuth contamination observed on the cathode
- Lower current efficiency
- Passivation of anodes
- Higher scrap percentage
- Higher power consumption

The electrolyte was found to be very much undersaturated resulting in increasing bismuth and antimony concentration. This together with the lower arsenic in anodes had augmented the problem resulting in deteriorating the cellhouse operations. After a detailed literature survey various technologies were studied for selective removal of bismuth and antimony from electrolyte. However after a thorough analysis and discussion, it was concluded that instead of installing a selective removal system, the bismuth and antimony levels could be brought down and maintained by altering the anode and electrolyte chemistry. Three necessary steps were considered to enable the refinery to come back to normalcy.

- Maintain Minimum As/(Sb+Bi) molar ratio at more than 2 to prevent formation of floating slime and thereby to prevent top nodulation.

- Maintain the minimum absolute arsenic at more than 350 ppm to prevent anode Passivation and reduce nodulation

The arsenic content in the anode plays a vital role in the electro-refining of cathode. The arsenic has a depassivating effect on the anode. It was observed that whenever the absolute arsenic level is less than the 300 PPM, heavy nodulation followed by dip in current efficiency was observed. The scrap anodes were found to be passivated. Few layer of unequal passivation observed on the scrap anodes. The slime on the scrap anode found to be very sticky and difficult to wash.

- Increase arsenic level in electrolyte to more than 12 gpl and precipitate bismuth and antimony in electrolyte.

In order to permanently bring down the bismuth and antimony in electrolyte, after a thorough literature survey, it was decided to intentionally rise the arsenic level in electrolyte and shift the saturation limit of bismuth and antimony. The solubility of these compounds depends on the concentration of these in electrolyte and portion that goes to slime and is influenced by concentration of other impurities in anodes. Antimony and bismuth dissolves in the electrolyte as trivalent ions. They precipitate from the solution as arsanates and so their solubility is determined by the concentration of arsenic in electrolyte.

The arsenic level was increased to more than 12 gpl from the level of 3 gpl deliberately and steadily. With the arsenic level reaching 12 gpl, heavy precipitation of bismuth and antimony observed. The bismuth and antimony level in the electrolyte decreased due to precipitation of bismuth and antimony arsenates as shown in Fig-4.

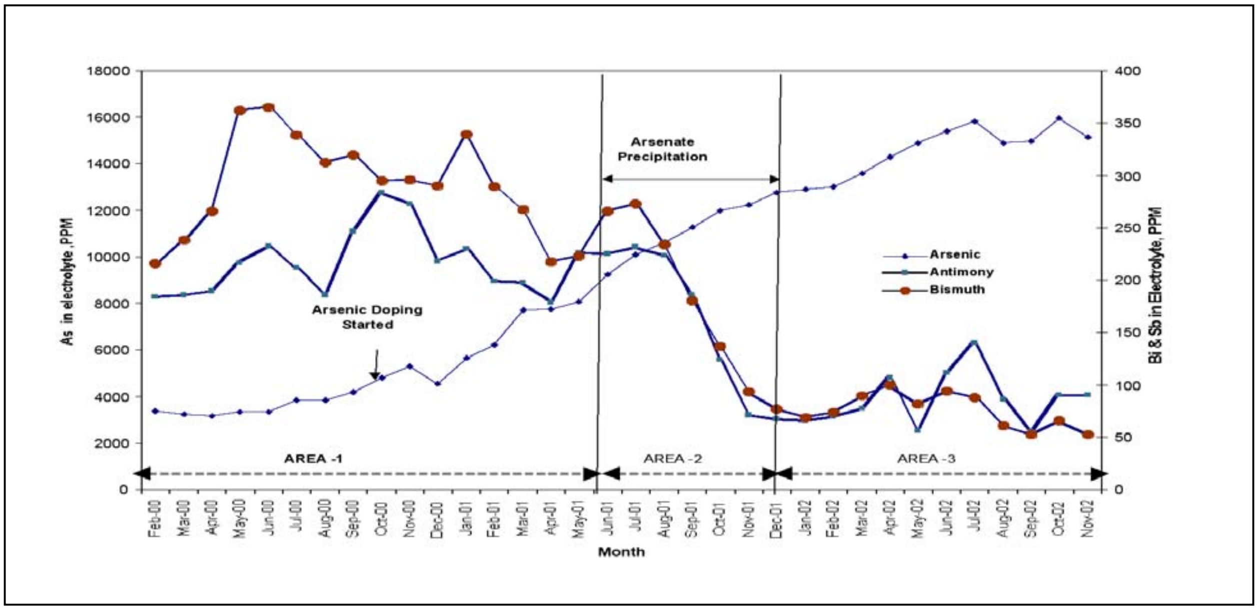



Fig-4: Behavior of bismuth and antimony at various concentration of arsenic in electrolyte

The behavior of impurities in electrolyte is discussed in 3 zones as shown in Fig-4.

**Zone -1:** The Bismuth and antimony were at the range of 200-350 ppm and arsenic at 4 – 6 gpl. The antimony and bismuth were controlled by electrowinning (purification cells). However bismuth and antimony levels could not be brought down below 200 ppm. Arsenic doping started in anode furnace from Oct-00 to increase the arsenic content in anode and ultimately in electrolyte.

**Zone-2:** Arsenic started increasing from Oct-02 steadily and when arsenic level reached 10-12 gpl, the bismuth and antimony level started decreasing drastically as shown in Fig–5. The bismuth and antimony arsenates started precipitating heavily and top nodulation and body nodulation were quite on higher side. Dip in current efficiency is also observed.

**Zone–3:** With Arsenic level consistently above 12 gpl, the bismuth and antimony levels stabilized at below 100 ppm.

Summarizing, the bismuth and antimony levels were undersaturated in zone-1 and concentration was increasing in electrolyte. In Zone-2 they reached their saturation limit and maximum bismuth and antimony in the electrolyte started precipitating out as their arsenates at higher level of arsenic in electrolyte.

In Zone-3, the entire system reached a new equilibrium state with bismuth and antimony levels still undersaturated in electrolyte, but at lower level of bismuth/antimony and higher level of arsenic. Initially due to heavy precipitation of arsentaes, increased body nodulation observed resulting in dip in current efficiency. However with the bismuth and antimony levels reaching steady state of less than 100 ppm, the body nodulation decreased. The cathode contamination by bismuth also reduced. It was very much evident with decreased bismuth levels in cathode as shown in Fig-7.

## Control of arsenic in electrolyte

As discussed earlier, Sterlite had intentionally increased arsenic level in the electrolyte over 12 gpl to facilitate the precipitation of bismuth and antimony and thereby to control concentration of antimony and bismuth in electrolyte. The arsenic level is maintained between 12-16 gpl and totally controlled in Decopperisation/Purification (electrowinning cells).

The input to the purification cells is
1. Leached liquor from Slime plant after detellurisation
2. Normal electrolyte after primary liberator cells in main cellhouse.

Three purification circuits, each having 3 cells in series are utilized. One purification system exclusively serve for treating slime leached liquor. The part of primary liberator cell outlet is taken as feed to other two purification circuits. A current density of 220-250 is maintained in the cells. The slime leached liquor is first filtered to remove any suspended solids and then passed through the purification cells.

A study done in the purification system showed that maximum arsenic removal is between 1-3 gpl and the operation is being done at same range. The Fig –5 shows the % of arsenic and bismuth removed in purification cells.

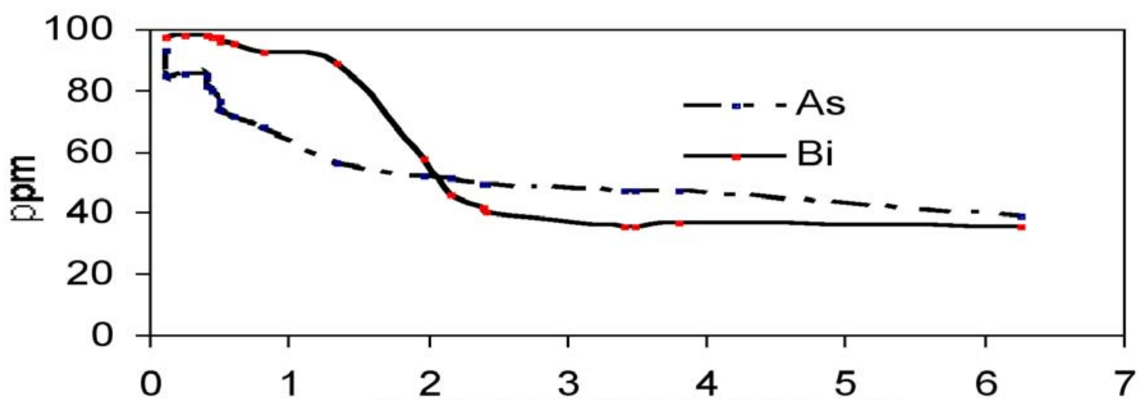



Fig -5 : Purification Removal Efficiencies - As & Bi

Almost 70 % of the arsenic is being removed using electro-winning cells. The purification section is equipped with the all the latest safety requirements to take care of any operational mishaps.

## Control of Nickel, Iron and other soluble impurities

Over the years copper refiners have adopted various technologies for the control of nickel and iron in electrolyte. Most common and conventional systems used are precipitation method or nickel sulfate evaporator system. Though these systems are used in most of the plants, they have their own disadvantages in term of higher capital cost and operating cost.

At Sterlite the necessity of bleeding the electrolyte had come little later due to progressive and continuous expansion carried out in the cellhouse. The nickel and iron were controlled below the specified limits by continuous dilution of electrolyte as a part of electrolyte make up for additional cells.

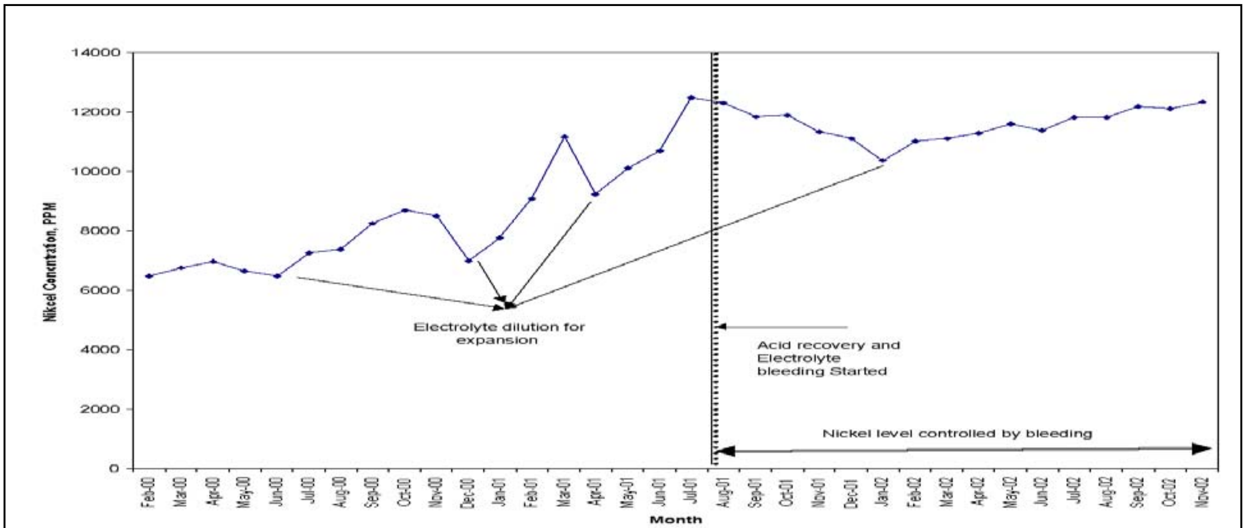



**Fig -6 :Nickel Concentration in Electrolyte**

The electrolyte Nickel/iron control system adopted in Sterlite is a unique one. It is coupled with the acid recovery system. Sterlite had carried out an extensive study of all the systems available for removal of nickel and iron and zeroed in on combination of various technologies. The electrolyte purification method implemented in Sterlite Copper is the latest one and is environmental friendly. The system has many advantages over other available technology. Apart from purifying the electrolyte, the system recovers sulfuric acid from the electrolyte and is more cost-effective in terms of capital cost and operating cost

Following steps are adopted for purification and treatment of bleed electrolyte.

- Acid Purification (Recovery) System
- Precipitation by Sulphidation and Neutralization & Evaporation

Each step is briefly discussed.

**Step-1: Acid Purification Unit (APU)**

Sterlite Copper has disadvantage of having copper refinery and smelter at 2000 Kms apart. The make up sulfuric acid needed for the cellhouse is purchased from outside. A thought was given to recover the sulfuric acid in the bleed electrolyte before bleeding it off. The best processes available for this purpose were

1. Ion exchange process
2. Membrane/Electro-dialysis

After studying the pros and cons of these two processes Sterlite adopted Ion-Exchange process due to its easy adaptability and comparatively higher acid recovery, when compared to electro-dialysis. Thus an acid purification unit was incorporated in the treatment system to recover the sulfuric acid in bleed electrolyte rather than neutralizing the acids. The system in known as “Acid purification Unit (APU)” and works on “RECOFLO” technology and is supplied by M/s. Eco-Tec, Canada. The decopperised electrolyte is taken to APU for treatment.

APU is an ion-exchange column. This process works on the principle that the certain ion exchange resins have the capability to sorb strong acids from the solution, while excluding metallic salts of those acids. The process is reversible, in that acid can be readily desorbed from the resin with water. It is thus possible, by alternatively passing contaminated acid and water through a bed of this resin, to separate the free acid from the metal. Fig-7 gives the operational sequence of APU.

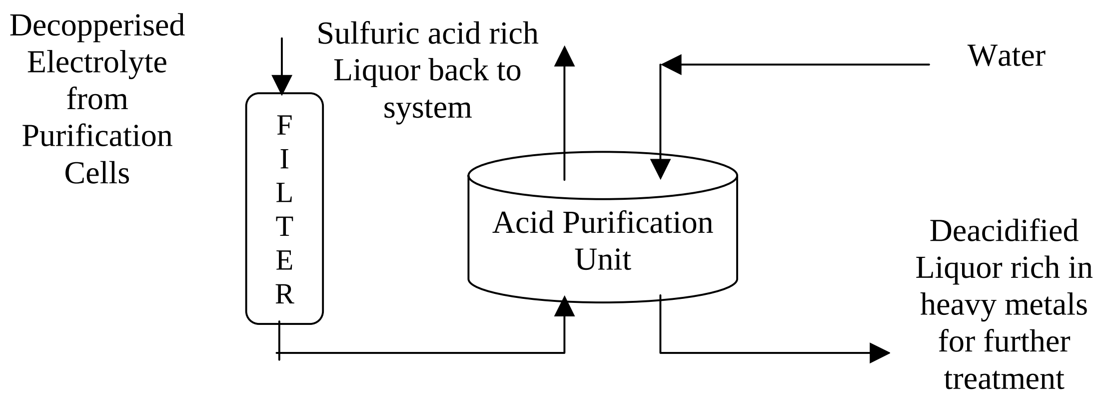



Fig – 7: acid recovery unit operation.

At Sterlite, the bleed electrolyte after decopperising in purification cells is passed through this resin bed. There are basically two basic steps in the APU process. I.e. In the first step the resin adsorbs the sulfuric acid in the electrolyte, whereas the major part of impurities such as Nickel, iron, bismuth, antimony goes in as effluent for further treatment. In the next step, water is passed through the resin, which elutes acid from the resin and the resulting product containing recovered sulfuric acid is sent back to the electrolyte system or used in slime leaching section depending on requirement. The Table –II gives the separation efficiencies of APU. The Table-III gives the typical composition of APU feed, product and byproduct streams.

Table – II: Separation Efficiency for APU

| SL. No | Acid /Impurities | % going to Product (Recycled to system) | % going to waste liquor |
|---|---|---|---|
| 1 | Sulfuric Acid | 85-90 % | 10 –15 % |
| 2 | Copper | 25 % | 75 % |
| 3 | Nickel | 25 % | 75 % |
| 4 | Iron | 34 % | 66 % |
| 5 | Arsenic | 80-85 % | 15-20 % |
| 6 | Antimony | 50 % | 50 % |
| 7 | Bismuth | 50 % | 50 % |

The Table – III gives the typical Composition of Various Streams

| **Streams** | **$H_2SO_4$** | **Cu** | **Ni** | **Fe** | **As** | **Bi** | **Sb** |
|---|---|---|---|---|---|---|---|
| APU Feed | 225-275 | 2.0 | 10 | 3.0 | 4.0 | 0.05 | 0.05 |
| APU Product | 200-240 | 1.0 | 2.5 | 1.0 | 3.0 | 0.025 | 0.025 |
| APU ByProduct | 25-35 | 1.0 | 7.5 | 2.0 | 1.0 | 0.025 | 0.025 |

** All Values in gms/Ltr*

**Step – 2 : Precipitation & Evaporation**

The effluent (rich in metal impurities and with lower acid concentration) is then taken to effluent treatment plant. The effluent is first partially neutralized with caustic/soda ash up to a ph of 3-3.5. This partial neutralization is carried out in order to control the generation of hydrogen sulfide in next step by reducing the sulfuric acid content in the effluent. The partial neutralized liquor is filtered and filtrate is subjected to sulphidation using sodium sulphide. The residual copper, arsenic, bismuth & antimony precipitates as their sulfides due to hydrogen sulfide generated during the process. The slurry is filtered and the filtrate is sent to evaporator. A crystalliser follows the evaporator in order to get mixer of nickel sulfate and sodium sulfate crystals.

This electrolyte purification method implemented in Sterlite Copper is the latest one and is environmental friendly. The system has many advantages over other available technology. Apart from purifying the electrolyte, the system recovers sulfuric acid from the electrolyte and is more cost-effective in terms of capital cost and operating cost.

A comparison of three processes in technology and environmental aspects is given in Table-IV.

Table-IV: Comparison of various electrolyte treatment processes

| Parameter | Direct Neutralization | Evaporation | Sterlite Method |
|---|---|---|---|
| Acid recovery | No | Only 60 % of the black acid is recovered | Yes . 90 % of the sulfuric acid could be recovered. |
| Quality of acid recovered | ---- | Black acid has restricted usage due to higher % of impurities. | Recovered acid with very less impurities. |
| Impurity removal | Removes most of the impurities. | Removes only Nickel and iron. (Precipitates them as their sulfates) | Apart from Nickel and iron, removes certain % of Bi and Sb in APU. Other impurities are removed by precipitation. |
| Caustic/Lime consumption | Very high as all acid has to be neutralized | Periodic neutralization of black acid requires considerable amount of chemicals. | Very low, as only 10 % of the acid has to be neutralized. |
| Sludge Generation | Very high amount of neutralized sludge | NiSO4 will be generated | Only 10 % of the sludge will be generated, when compared to direct neutralization. |
| Capital Cost | Less but cumbersome process | Very high due to evaporator | Less. |
| Operating Cost | Very High due to neutralization chemicals cost | Very High due to power/steam cost.<br>In addition cost of neutralization chemicals for black acid. | Lower cost due to lesser consumption of neutralization chemicals.<br>Cost of steam. |
| Others | Very labor oriented.<br>Gypsum storage and disposal is also a problem. | Due to high temperature operation, the corrosion due to high chloride is very prominent.<br>Occupies space. | Replacement of resin once in every 5 Years.<br>APU operation is fully Automatic with no Manual intervention.<br>Very Compact. |

## Testing and Quality Control

It may be emphasized that in refinery, the problems gets out of the hand over a period of time and it takes equally long time to brig back the operations to normalcy. The initial indications of problems are innocuous, but suddenly they take a turn in the form of poor efficiency, poor quality and high power consumption. To have a better control over process, it is necessary to have strong testing and quality control methods.

Various methods are available for testing cathode purity and other process parameters such as anode quality, electrolyte composition. The database of all the major parameters is maintained and statistical process and quality control methods are used to determine the variation in process. Any abnormality identified is immediately traced back to find out the exact reason and the necessary remedial actions are taken.

## CONCLUSIONS

The various methods of electrolyte impurity management methods have helped M/s. Sterlite to improve the cathode quality to international standards and to make a mark in copper markets. The electrolyte impurity levels especially bismuth and antimony is controlled by altering the anode and electrolyte chemistry. The arsenic level in electrolyte is maintained by operating the de-copperisation section (Electro-winning) efficiently. Adaptation of latest electrolyte purification system, which includes 'Acid Purification System (APU), controls nickel and iron in the electrolyte. This system does a twin job of purifying the electrolyte as well as recovering the sulfuric acid for reuse in the cellhouse. The effluent treatment system ensures production of nickel rich byproduct. The system also ensures zero discharge to the environment. All solid waste produced at the refinery are either recycled or disposed off in an environmentally safe manner. The prime importance is given for protecting the environment by ensuring zero discharge.

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