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Metal values extraction from Copper Bismuth slag of Silver refinery

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Abstract: *Slags as a byproduct, are the indispensable tools for extraction of valuable metals at competitive prices and are promising options to conserve natural resources. Adhering to the aforesaid statement, in order to establish the recovery of silver from slag, extraction of impure metals followed by recycling of Ag enriched slag was investigated. The corresponding raw material was rich in Cu (8-10%), Bi (6-8%), Pb (14-16%), Ag (3-4%), and Sb (8-10%). Upon XRD and microscopic examination, major phases like Bismuth Antimony oxide, Cuprite, Silver coupled with Copper, Litharge and a minor phase, lead iron antimony oxides were found. The extraction of metal values from slag sample for copper followed by bismuth was done with sulphuric acid and hydrochloric acid respectively. Effect of various parameters viz., temperature, agitation, pulp density, acidity and retention time on leaching was determined for Cu leaching. Leaching kinetics was determined based on shrinking core model. Chemical reaction was found to be the rate determining step and the activation energy was found to be 30 KJ/mol. The residue that is left over after copper extraction is processed for chloride ion leaching followed by a series of impurity removal steps. Finally, impurity free bismuth chloride solution is hydrolyzed and bismuth oxychloride is produced with a grade of 77% Bi.*

Keywords: *Leaching; Kinetics; chemical reaction; metals; hydrolyzing*

1. INTRODUCTION

Pyro-electro winning processing of lead concentrates results in generation of bottom mud, termed as “Anode Slime” rich in precious group metals (Ag rich) along with other impurities. A separate schema has been allotted to extract the silver as in most refined form, leaving behind other impurities to the slag, termed as oxidation prophase slag. About 250 MT of CBslag generated annually, contains Cu,Bi,Sb, Pb, Ag as the major constituents and to recycle this byproduct (to recover Ag) in to the process, removal of impurities is obligatory since there are fair chances of final product contamination. In the quest of recycling silver rich CB in lead smelting operations, a pretreatment scheme has been designed, developed and validated at pilot scale in R&D for over a period of four months. This article demonstrates the procedures adopted for extracting the metal values from CB and their advantages over other routes of extraction.

For extraction of copper, several methods were attempted and adopted globally. These can be characterized in to Pyrometallurgical methods involving roasting in presence of oxygen, soda ash process and hydrometallurgical routes involving chloride, sulphates, nitrates, ammonia as lixiviates in ambient and enforced conditions [1][2][3].

Pyrometallurgical treatment methods are not chosen since they involve treatment of downstream processing of gases which is an added cost. Hence hydrometallurgical treatment has been chosen, as less involvement of capital costs, air pollution can be mitigated and process can be easily handled. Ammonia based lixiviates are better systems for copper extraction but involvement of capital expenses enthused towards sulfate based leaching, since the handsome availability of sulphuric acid. Here the leachibility of other metals from the slag viz., Sb, Bi, Pb, Ag is completely negligible and hence using sulphuric acid as lixiviant can be justified and the reactions are as follows. [4]

$$Cu_2O + H_2SO_4 \rightarrow Cu + CuSO_4 + H_2O \qquad [1]$$

$$Cu_2O + 2H_2SO_4 + ½\ O_2 \rightarrow 2CuSO_4 + 2H_2O \qquad [2]$$

As per Eq. [1] cuprite reacts with sulphuric acid to form copper sulphate and residual amount of metallic copper however in presence of oxidizing agents it is also converted to copper sulphate eq. [2].Native copper is not reactive to the free hydrogen ion present in the dilute acid. Hence an external aid like temperature will enhance the reaction as per Eq. [3]. While in presence of an oxidizing agent extraction of native copper is good. Eq. [4]. [6]

$$Cu + 2H_2SO_4 + 3\ H_2O \rightarrow CuSO_4.5H_2O + SO_2 \qquad [3]$$

$$2Cu + 2H_2SO_4 + O_2 + 8\ H_2O \rightarrow CuSO_4.5H_2O \qquad [4]$$

From this information, it is possible to evaluate the effects that certain variables, such as the level of oxygen saturation, concentration of sulfuric acid and percentage of solids, may have on the extraction behavior of copper. Although copper is extracted handsomely, there are all chances of impurities like zinc and iron getting digested in to the sulphate solutions, hence metal displacement or cementation method being one of the most effective and economic ways can be employed for attaining copper from impure solutions by a more active metal, likezinc as per reaction Eq. [5]

$$Cu^{2+} + Zn^{o} \rightarrow Cu^{o} + Zn^{2+} \qquad [5]$$

Bismuth, Antimony and lead are the other three main constituents of slag. Bismuth considered as green metal Bismuth is considered “green and ecologicallyclean” metal and used in cosmetics and pharmaceuticals [4]. However, very little bismuth directly comes from the primary processing of bismuth minerals. Mostbismuth is obtained as a by-product in other metallurgical process for copper, silver, tin, lead and gold where it is usually present in sludge or in acidic liquorscan be easily extracted by mechanically activated concentrates using sodium chloride, sulphuric acid, sodium thiosulphate and hydrochloric acid. electrode position, sol-gel process, plasma-chemical method, flame spray pyrolysis,laser vaporization-controlled condensation technique, polyol mediated synthesis, and hydro-thermal methodetc.[5]

Basing on the microscopic pictographs and XRD reports, it has been decided to treat the first stage residue with hydrochloric acid at ambient temperatures without any involvement of an oxidizing agent. Further hydrolytic precipitation of bismuth has been performed, instead of solvent extraction as it might attract some capital expenditures. Leaching and hydrolysis (pH make up by caustic) reactions are as follows.

$$Bi_2O_3 + 6HCl \rightarrow 2BiCl_3 + 3H_2O \qquad [6]$$

$$BiCl_3 + 2H_2O \rightarrow BiOCl\downarrow + H_2O + 2HCl \qquad [7]$$

For filtrate quality affected by elements like antimony, a differential pH, precipitation followed by reagents addition has been performed for selective removal of impurities.

2. MATERIALS AND METHODS

2.1 Materials

Copper Bismuth (CB) slag sample has been received from Pantnagar was used in the test work with sizes varying from 20 to 25 mm. These slag particles were grinded in a hammer type pulverizer as to make it acquiescent for leaching. The size fractions and complete assay for the pulverized product are mentioned in tables I and II.

Table I: *Sieve Fractions and chemical distribution*

Sieve Characteristics		Input 100 gms	Chemical Assay %		
Mesh No #	**Particle size µm**	**Weight retained**	**Cu**	**Bi**	**Ag**
+100	147	1.5	**6.95**	**6.38**	**2.2**
+120	125	2.2	**6.85**	**6.2**	**2.3**
+150	105	2.6	**7.25**	**6.5**	**2.6**
+200	74	4.4	**6.95**	**6.54**	**2.04**
+300	53	89.3	7.01	**7.15**	**5.3**

Table II: *Chemical assay of the received CB samples*

Elements	Cu	Bi	Sb	Zn	Fe	Ag	Pb
% composition	12-14	9-10	8-10	4-5	7-8	3-5	20-25

Sulphuric acid 98% and Hydrochloric acid 35% pure of Merck make GR grade, Triple distilled water from Infusil make apparatus and compressed air were used in the preparation of leaching media. The optical microscopy of polished sample was done with Leitz Wetzlar Ortholux II pol-BK universal optical microscope and mineralogical analysis with Bruker make AXS E4 EndeavourX Ray diffractometer. pH values were monitored with Eutech pH 700 using a refillable glass double junction electrode.

X ray diffractogram for the CB sample received is mentioned in **Figure I**. Pattern of diffractogram clearly confirms that copper is majorly present in the form of cuprite and delafossite, bismuth and antimony in the form of their oxides but lead is coupled as lead iron antimony oxide.Further, optical microscopy image of the polished bulk sample in Figure II was recorded using a Leitz Wetzlar Ortholux IIpol-BK universal microscope under plain polarized reflective light. The images give a clear glimpse and denoted the existence of silver, copper, lead (litharge) and traces of bismuth metal in ex solution blebs, dendritic texture, and individual specks.

Figure IIa denotes Cu-Ag-Pb metal association snapped under20x10 magnification. Copper yellow to bronze brown in color, silver bright white with tints of oxidations (pink and brownish white) and indigo – violet/purple grains showing IR are litharge (PbO). Rest blackish grey is siliceous gangue or detrimental mass. **Figure IIb** denotes grains of bismuth reported in slag, showing polysynthetic twinning and rapid oxidation.

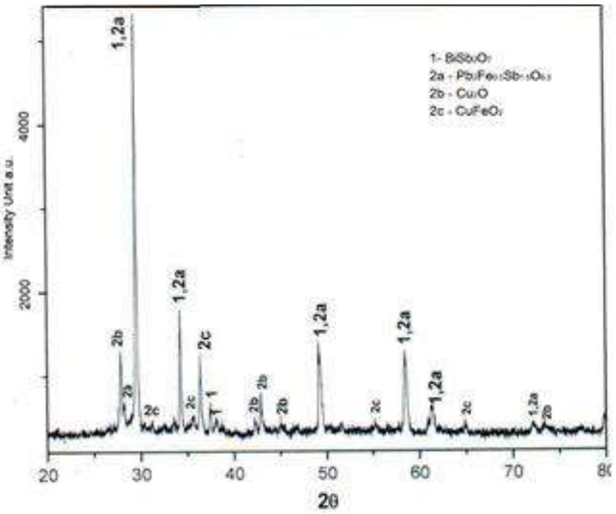


Figure I: XRD study for CB sample.

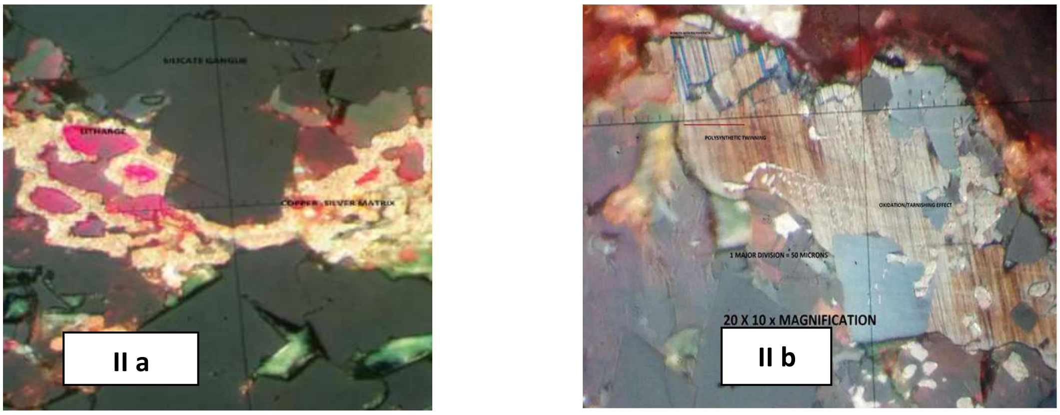


Figure II a & IIb Optical microscopy photographs for polished CB sample

2.2 Methods.

For copper extraction, leaching experiments were carried in a specially designed compact, two-liter glass reactor with a top driven agitator and a lid to control evaporation losses in temperature based trials. Total volume of one liter was arranged with distilled water and sulphuric acid as per desired acidity. Temperature was monitored with a digital magnetic stirrer hot plate provided with a PID controller. Once the platform was set for reaction, calculated quantity of CB sample ground in a hammer type pulverizer from 25 mm to 37 µm was added to the solution for desired solid liquid ratio. Air purging was done through a sparger for fine dispersed bubbling and flow rate was managed with a rotameter. Samples were withdrawn regularly to monitor the acidity. Aliquots of 5 ml samples of solution were collected periodically, filtered and analyzed to know the copper leaching trend. For bismuth a special SS reactor with rubber lined has been used instead of a glass made, keeping all other procedure same. Final leaching recovery has been calculated based upon the remaining individual element content in leached residue on dry weight basis. Recovery calculation is as follows.

% element recovery = (element present in leached and dried cake) x100 / (element in input cake)

3. RESULTS & DISCUSSION

For leaching of solid particles in fluid media, kinetic studies search for the factors that influence the rate of reaction. Variables such as temperature, agitation speed, and particle size, solid to liquid ratio (pulp density), acidity (grams of free acid in a liter of solution) and retention time, are the key, for these kinds of studies. Here selection of model should be as such that it should closely represent what is taking in reality without too many mathematical complexities and hence liquid solid heterogeneous models (shrinking core model) is chosen for predicting rate controlling steps. [7,8]

3.1 Effect of particle size

Particle size plays a predominant role in determining the rate control step. The extraction rate is the function of surface area and the surface area available depends on the particle size and it increases with fineness of the material. Based on some preliminary tests, solid to liquid ratio and acidic concentration optimized at 150 g/l and 70g/l. Keeping temperature, air and RPM constant at 75°C, 1.5 LPM and 110; a correlation between Cu extraction efficiencies and average particle size ranging from 147 to 53 µm, has been plotted against the retention time. From figure III it is evident that copper recoveries increase with a decrease in particle size from 147 to 53 µm. nearly 90% copper extracted when average particle size is 53µm and it was only 31% when avg. particle size is about 147µm.

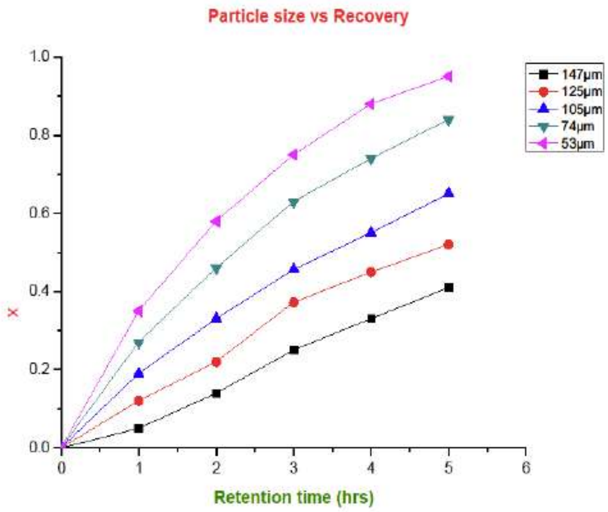


Figure III: Effect of particle size on Cu leaching

3.2 Effect of Temperature.

All though the mode of approach is different, all the theories, Arrhenius rate equation, collision theory and transition state theory states one and the same that reactions are temperature dependent.

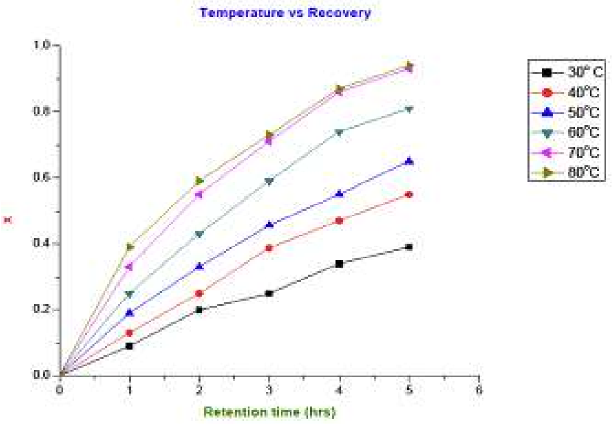
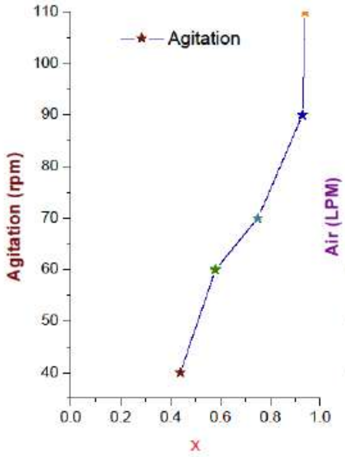


Figure IV: Effect of Temperature on Cu recovery

Hence prediction of temperature impact on the rate of a reaction will play a predominant role in determining the reaction kinetics. Keeping the pulp density, agitation RPM and acidity fixed at 150g/l, 110 and 70 g/l. temperature has been varied from 30° c to 80° c and a correlation between copper extracted vs retention time has been strategized. A clear dependence on temperature for copper extraction can be observed from the figure IV . A maximum recovery of 93% achieved at a temperature range of 70-80ºc, while it confined to 30-65% at lower temperatures

3.3 Effect of Air and Agitation



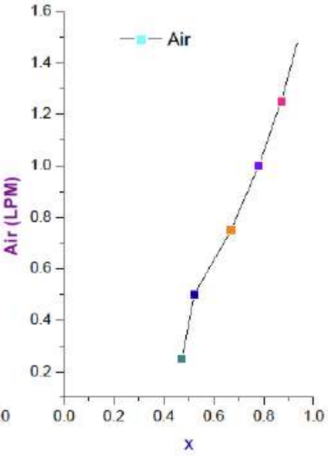


Figure: Va Effect of Agitation on Cu recovery **Figure: Vb** Effect of air on Cu recovery

Agitation speed reduces the liquid film around the solid particles and the diffusion of the reagent through boundary layer towards the external surface of solid particle eases hence the dissolution rate increases. Further, air flow with fine sparging will convert any metallic copper in to copper sulphate as per equations 2 and 4. Keeping temperature, solid to liquid ratio, acidity, retention time fixed at 75° c, 150 g/l, 70 g/l and 5 hours, effect of agitation and air flow rate on copper recovery has been studied in figures 5a and 5b respectively. From figure Va; a linear relation has been observed between agitation and copper extraction. A maximum extraction of ~92% is observed at an RPM of 100 and further increase in agitation speed shown no impact on Cu recovery. Hence agitation speed clearly increases the dissolution rate of the solid particles. Air dispersion in to the system, shown a clear impact on the copper extraction and presence of metallic copper in CB. From figure Vb copper recoveries went up to 40-45% without any air sparging and further no recovery improvement observed in absence of air flow and with the supply of air in to the system, copper recovery enhanced and reached maximum to 91% till 1.4-1.5 LPM and remained still for further increase in air flow rate.

3.4 Reaction Kinetics The reaction occurring between slag particles and the acidic solution is a typical example for heterogeneous solid liquid type reaction. Since these types of reactions are generally non-catalytic, the most common exemplary to predict the rate characteristics would be the shrinking core model. This model assumes that the reaction between solid and liquid reactants occurs on the outer surface of the solid particle. It is considered that the reacting particles are spherical, and their size does not change during reaction. As the reaction proceeds, the unreacted core of the solid particles shrinks toward the center of the solid, and a porous product layer may form around the unreacted core. The rate of the leaching reaction may be controlled by one or more of the following steps: the diffusion through a fluid film, the diffusion through the product layer, or the chemical reaction at the surface of the unreacted core. [9]

Afluid + bB solid → Products. [8]

Limitations for shrinking core model were given below.

a) Diffusion of fluid reactants from bulk fluid to particle surface via fluid film.

b) Diffusion of reactants across the product layer to the unreacted core.

c) Surface reaction between fluid reactant and solid particle on the unreacted core.

The data provided by the leaching tests were analyzed based on the shrinking core model, to determine the rate controlling step and kinetic parameters. When the data was applied to three different types of rate controlling mechanisms, a linear relation was observed with chemical reaction as a rate controlling step for extraction of copper in to the sulphate based solvent.

$$(1-((1-x)^{(1/3)})) = Kt \qquad [9]$$

Plots were figured out for temperature, agitation and particle size impact on copper extraction along different retention intervals. Reaction order with respect to particle size by using the expression in Eq. (9), were plotted to find out the apparentrate constants, *k*, for each parameter. To determine the apparent rate constants, the left side of Eq. (9) was plotted versus the reaction time for each experimental parameter. The slopes of the straight lines obtained were considered to be the rate constants. Table shows the apparent rate constant values and their correlation coefficients calculated by applying Eq. (9). The graphs constructed for the stirring speed, particle size and reaction temperature by using Eq. (9) are given in Figures VI-VIII, respectively. A linear relation between them clearly shows that it is a surface reaction controlled mechanism.

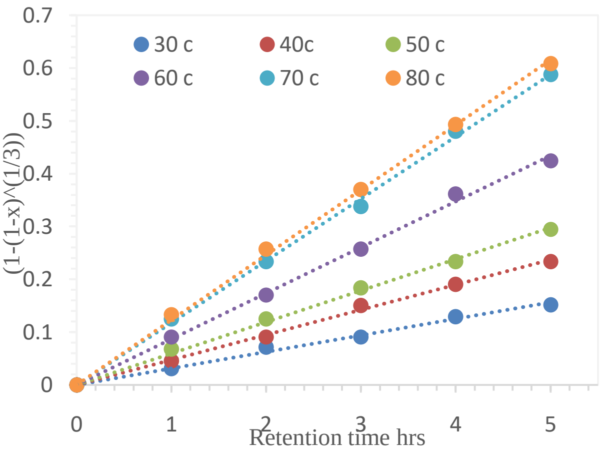


Figure VI. Plot of (1-((1-x) ^ (1/3))) vs retention time at different temperatures

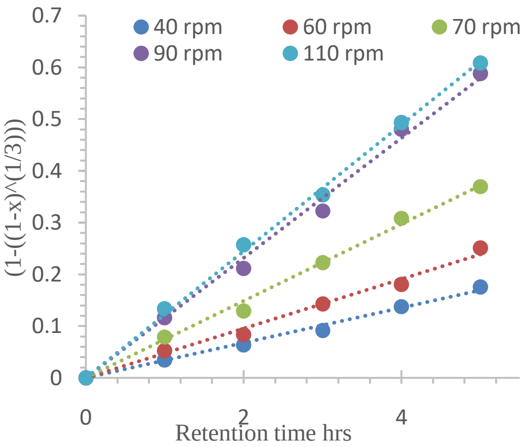


Figure VII. Plot of (1-((1-x) ^ (1/3))) vs retention time at different rpm

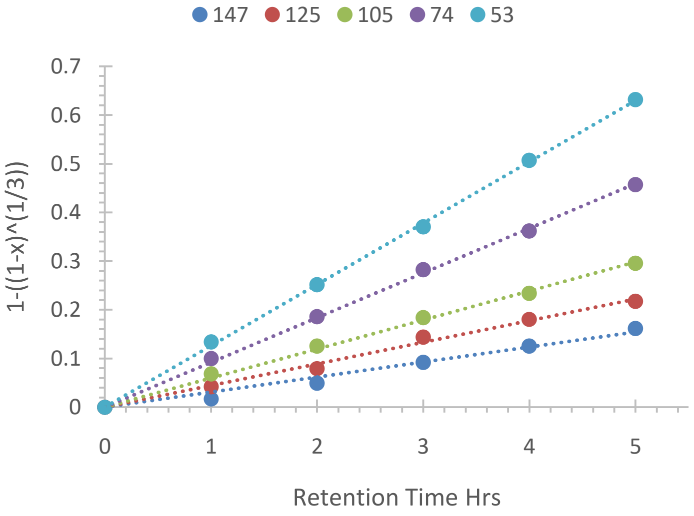


Figure VIII. Plot of (1-((1-x) ^ (1/3))) vs retention time for different particle sizes

The apparent rate constants derived from these plots(slope) play an important role in estimating the activation energy and reaction order. In order to establish the effects of the reaction parameters on the apparent rate constant, the following equation may be suggested.

$K=Ko\ (PS)^a(AS)^b\exp(-Ea/RT)$ [10]

Comparing and combining the equations 9 and 10 a final rate equation can be given as follows.

$(1-((1-x)\ ^\wedge\ (1/3)))=Ko\ (PS)^a(AS)^b\exp(-Ea/RT)\ t$ [11]

a and b are the reaction orders with respect to the particle size and agitation speed. The reaction orders a and b can be determined as the slope of the plot between ln k and ln PS, ln k and ln AS. Activation energy shall be estimated from the plot between ln k and inverse of temperature in kelvin. Figure IX shows the plot between lnk and ln PS. The slope of the straight line gives the reaction order with respect to particle size to the leaching reaction. The reactor order was proportional -1.2026 power of the particle size with a correlation coefficient of 0.9885. Similarly, the reaction order for agitation speed was found to be -1.3932 with a correlation coefficient of .9744.

Figure X shows the plot between ln k and 1/T K (Arrhenius plot). The minimum energy required by the potential reactants to participate in a chemical reaction is termed as Activation energy and it is given by the Arrhenius equation Kr = A exp [-Ea /RT]. Apart from empirical formula, activation energy can also be determined by a plot between logarithmic function of rate constants and the inverse function of temperature denoted in kelvin. From the figure 10, plotted below calculated activation energy is 30 KJ/mol and the intercept 7.65. Consequently, a mathematical expression including the experimental parameters to represent the kinetics of this leaching process may be written as follows:

$(1-((1-x)\ ^\wedge\ (1/3)))=7.65\ (PS)^{-1.2026}(AS)^{-1.3932}\exp(-3000/RT)\ t$ [12]

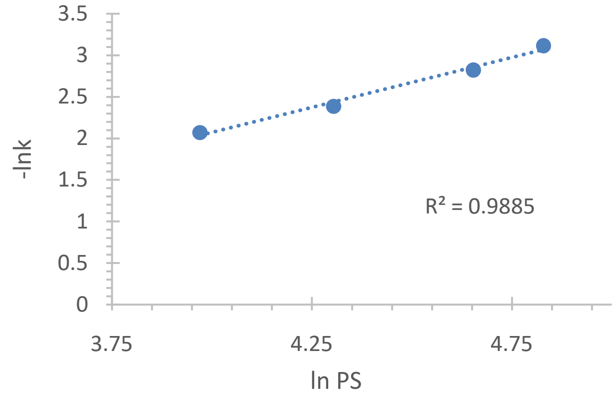


Fig IX: Plot of ln k vs ln PS

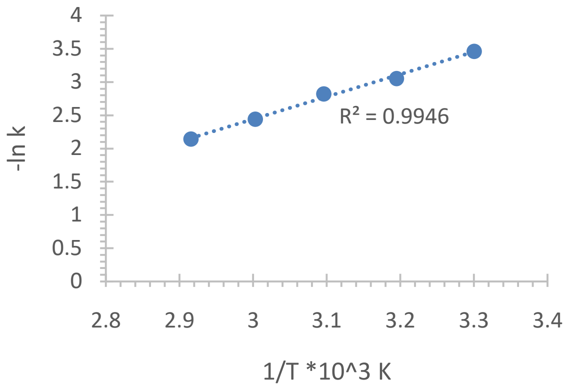


Fig X: Arrhenius plot for leaching plot

The Final filtrate generated containing copper as sulphate is contaminated with Zinc and iron contents. Hence, copper displacement from the solution in the form of metallic copper with Zinc dust (1.1 *Cu) for a retention time of 60 min at an acidity of 15-20 g/l has been performed to produce enriched copper cement with minimal quantities of zinc and iron. **Assay given in table III**

Table III : Composition of Cu cement and filtrate

CuSO4 filtrate	Cu	Zn	Fe	TA
g/l	**56**	**3.2**	**4.1**	**18**
Zn dust filtrate	**0.054**	**54.5**	**4.5**	**11**
Cu cement%	**81**	**2.2**	**1.1**	**------**

The residue generated from the copper extraction, contains antimony, bismuth, silver, lead in enhanced quantities. The assay and size fraction of the residue is given in tables IV and V.

Table IV: Composition of Cu lean residue

Elements	Cu	Bi	Sb	Ag
% composition	1-1.5	8-9	6-7	4-6

Table V: Sieve fractions of Cu lean residue

Sieve Characteristics		Input 100 gms
Mesh No #	**Particle size µm**	Weight retained
+100	147	5.6
+150	105	4.4
+200	74	4.7
+300	53	6.6
-300	< 53	78.7

The residue rich in antimony and bismuth content has been further processed for extracting Sb and Bi values in to the solution. Generally, there are three different routes for the residue treatment like pyrogenic process, pyro-hydrometallurgical process and hydrometallurgical route. When compared to the first two routes, simple hydrometallurgical route is deployed as it has its own advantages like simple chlorate oxidation leaching, less investment, high recovery metal, no augmentation in the existing facilities, high recovery rates, it also prevents hydrolysis of metal ions and promotes the leaching of Bi ion. Chloride based leaching demands special material of construction as the chloride ion is detrimental to the metals [10]. The reactors are perfectly rubber lined and HDPE make piping system have been incorporated for the system in pilot based trials.

The major factors considered, that affect efficiency, during the course of leaching are residence time, pulp density and acidity of the hydrochloric acid. Temperature and oxidizing agents doesn't have much impact, since chloride leaching had yielded very good efficiencies even at ambient conditions and in the absence of oxidizing agents. The leaching of bismuth increased with increase in the pulp density of the cake used initially and reaches up to 85-90% when the concentration is 19-20% of the solution. Retention time of minimum 5hours have been decided evidently. Concentration of chloride ion has been increased from 5% to 15%, and best results were obtained at 15%, further increase in chloride concentration, dose not increased the Bi extraction, instead resulted in the dissolving of un necessary metals like Ag, Pb etc in to the solution. Under the optimum conditions like ambient temperature, pulp density of 20%, retention time of 5 hrs, Chloride concentration of 15%, 92% of Bi has been recovered and the concentration of Ag in the residue is 4-5 %. The composition of enriched lead silver residue is mentioned below.

Table VI: Assay of Bismuth lean residue

Final	**Bi**	**Sb**	**Ag**	**Pb**	**Cu**	**Cl**
Residue %	1.25	2.25	5.25	22	0.6	0.75

3.5 Refining of $BiCl_3$ solution.

Along with Bi other nonferrous metals like Sb has got leached majorly due to its affinity towards chloride ion. But the concentration of the Silver and Lead in the solution is not much appreciable. Hence, a separation/refining step for removal of impurities from the $BiCl_3$ solution is performed at ambient conditions, specific metal precipitation at various acidity ranges has been performed. Pb will mainly exist in the form H_2PbCl_4 and Sb in the form of $SbCl_3$. Upon hydrolysis, these impurities co-precipitate along with bismuth oxy chloride and converted to be $Pb(OH)_2$ or PbO to enter the solid phase of BiOCl when using concentrated NaOH, leading to separation difficult. For this, input filtrate, of Bi 50-55g/l(generated after recycling the solution, since proceeding for higher concentration of Bi resulted in its loss to the residue) has been chosen. The acidity ranges were adjusted with caustic addition. [11]

Table 7: Sb removal at various acidities

$BiCl_3$ g/l	**Bi**	**Sb**	**Ag**	**Pb**	**Zn**	**Fe**	**Cu**	**TA**
Filtrate	**50.3**	**15**	**0.015**	**1.5**	**0.8**	**0.7**	**10**	**70**
Sb filt @ 50 g/l acidity	50.1	7.5	0.01	1.3	0.4	0.3	9.5	50
Sb filt @ 30 g/l acidity	**48.5**	**0.5**	**0.09**	**1.06**	**0.2**	**0.15**	**9.5**	**30**
Sb filt @ 10 g/l acidity	41.5	0.4	0.07	0.9	0.15	0.1	8.8	20
Sb res 50 %	1.06	47.1	---	1.2	2.5	2.6	3.1	---
Sb res 30 %	**1.26**	**86.1**	**---**	**2.8**	**2.8**	**2.6**	**3.0**	**---**
Sb res 10 %	33.5	52.6	---	2.23	2.4	2.4	4.5	---

From the table it is evident that filtrate at 30 g/l acidity, provided a good recovery of 94% and a grade of 86% for $Sb(OH)_3$ precipitate which is pale yellow in colour. Further decrease in acidity result in loss of Bi in to the precipitate there by decreasing the grade of Sb precipitate. The filtrate thus obtained after Sb removal is processed further for the removal of lead and other impurities in minute quantities. Due to the acidic content and chloride ion presence, normal removal methods such as sulphate, phosphate etc. were difficult to meet the requirement. Hence, CB slag has been used to reduce the Pb ions in to the residue. The results show that when ratio of solid to liquid of CB slag to Bi filtrate is 1:8, acidity of 20 g/l, agitation RPM of 250, and a leaching time of 15-20 min, the content of Pb can be reduced to less than 10 ppm. The remaining impurities in the solution like Cu, Ag and Pb present if any, can be reduced with the help of potassium iodide, a reducing agent, for precipitating Cuprous iodide (white precipitate) and the reaction is as follows.

$$2Cu^{2+} + 5KI \longrightarrow 2CuI \downarrow + KI_3. \qquad [13]$$

After the treatment with potassium iodide, with a quantity of 1.3 times of theoretical requirement, for a time period of 1 hr., the copper quantity reduced to less than 20 mg/l and other impurities were reported in between 25-35 mg/l. final assay of the $BiCl_3$ solution is given below in table VIII.

Table: VIII Composition of finalBismuth Trichloride filtrate

$BiCl_3$ g/l	Bi	Sb	Ag	Pb	Zn	Fe	Cu	TA
Filtrate	49.1	0.01	0.003	.004	0.035	0.021	0.018	17

The Bismuth content in the final filtrate can be hydrolyzed easily and precipitated with caustic at 1.5 pH with a water to solution ratio of 1.25:1 and agitation rpm of 200 for a time period of 90 min. The obtained white lustrous Bismuth Oxychloride as per equation 7, is washed, dried and pulverized and bagged. The washings, hydrolyzed water is recycled back to the bismuth leaching. The assay of the obtained bismuth precipitate is as follows.

Table: IX *composition of Bismuth Oxychloride.*

BiOCl	Bi	Sb	Ag	Pb	Zn	Fe	Cu	TA
%	77.5	0.1	0.023	0.015	.018	.02	.05	17

This process has been validated successfully at the pilot scale with a treatment capacity of two tons per day. SS 316 L make reactors and pipelines were used for Copper extraction. Reactors with rubber lining under and HDPE piping systems were used chloride based leaching systems. With all systems in place, around 7-8 lacs of net realization has been achieved for treatment of one metric ton of CB slag @ pilot plant.

The below figure VI gives a glimpse of pilot plant set up arranged and successfully runned for six months. If Zinc and iron abnormalities observed in the copper sulphate filtrate, Copper washing tank is used for zinc dust cementation and where one of the Bi reactor is used for antimony precipitation followed by other impurities removal.

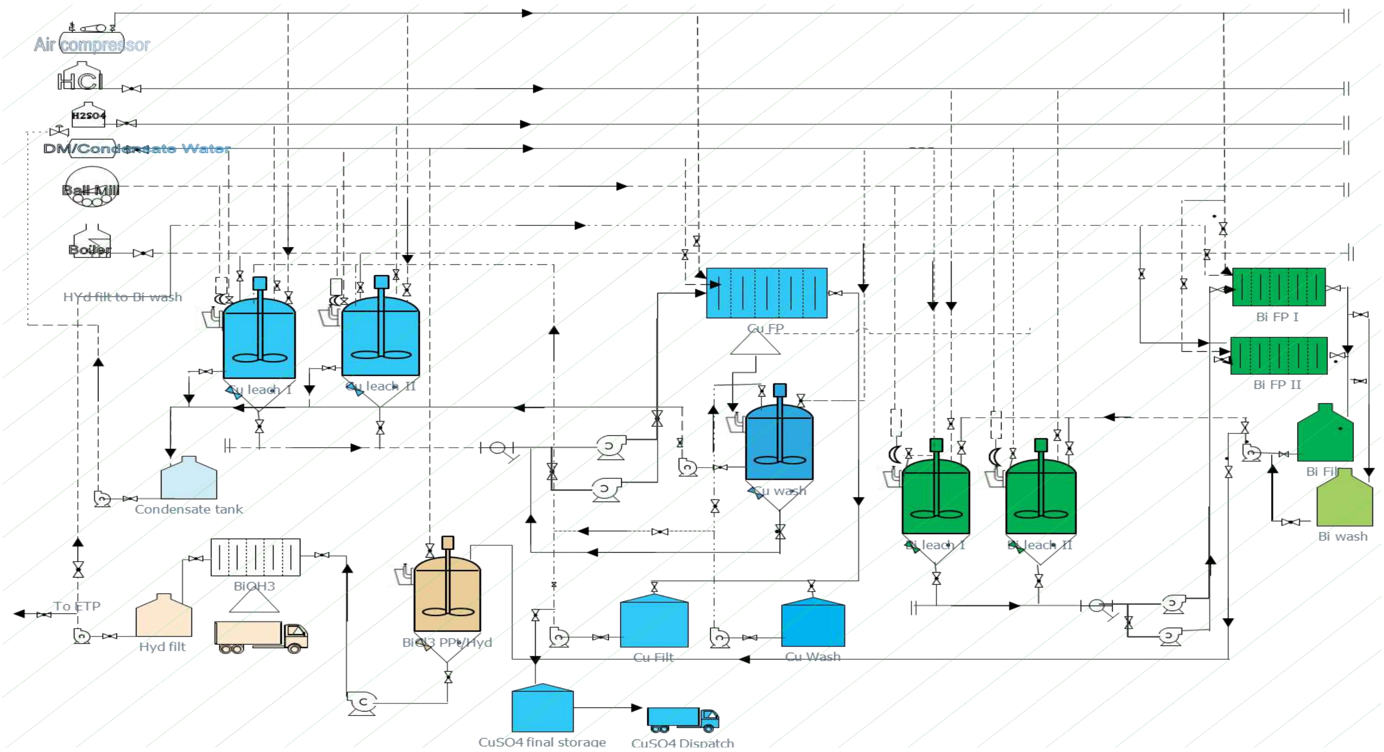


Figure VI: Pilot plant schema for CB slag treatment

4. CONCLUSION

A process has been designed, developed and validated at pilot scale with optimized parameters for the extraction of Copper, bismuth, antimony from CB slag generated in Pyrometallurgical operations. A maximum recovery of 92% for copper has been attained when the temperature, solid to liquid ratio, acidity and agitation RPM are maintained at 75°C, 150g/l, 75 g/l and 100. If the quantities of zinc and iron are appreciable in the filtrate, then the solution is processed for copper cementation with zinc dust with an initial acidity of 15 g/l. the obtained copper cement grade is around 81%. Leaching kinetics for copper extraction is validated through shrinking core model. From the kinetics model, chemical reaction at unreacted core is the rate controlling step which is further confirmed by the activation energy, that is within the range for reaction rate controlling step.

The residue obtained from the copper extraction is treated for Bi extraction with HCl at ambient with a pulp density of 200 g/l, retention time of 5 hrs, acidity of 150 g/l and Chloride concentration of 15%. A maximum recovery of 91% for bismuth is observed. Further to remove the impurities, the bismuth filtrate is treated with caustic to bring down the acidity to 30 g/l so that 94% antimony has been recovered in to the precipitate. The other impurities were diminished from the solution by treating it with CB slag and potassium iodide both acting as reducing agents. Further, the obtained solution is hydrolyzed at a ratio of 1.25:1 and an agitation of 200 rpm, that derives a white lustrous bismuth oxychloride cake with 97%. The process was validated at pilot scale in 2 ton/day capacity which provided a net realization of 8 lacs per ton after the treatment.

Nomenclature

A-Pre-exponential factor in Arrhenius equation

b- Stoichiometric coefficient in eq [8]

c_A Concentration of fluid reactant (mol/m3)

D_e Effective diffusivity (m2/s)

E_a Activation energy (J/mol)

k_c Liquid–solid mass transfer coefficient (m/s)

k_d Apparent rate constant for product layer diffusion (s^{-1})

k_r Apparent rate constant for surface chemical reaction (s^{-1})

k_s Intrinsic reaction rate constant

R Mole gas constant (8.3145 J/(mol·K))

t Time (h or s)

T Temperature (K)/ ° centigrade

x Fraction of extraction

ρ_s Density of solid

r_0 Initial particle radius (m)

CB Cu-Bi Slag

PS Particle Size

AS Agitation speed

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