Oxidative Chlorination Leaching of Stibnite Using Acidic Ferric Chloride Lixiviant

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Summary: A hydrometallurgical process was developed for the preparation of commercial grade antimony trioxide (Sb_2O_3) from indigenous antimony ore. The developed process includes oxidative chlorination leaching of stibnite (Sb_2S_3) concentrate assaying 64.86% Sb prepared from indigenous low-grade ore containing 20.16% Sb using ferric chloride ($FeCl_3$) solution in acidic medium as lixiviant followed by purification, precipitation and crystallization of antimony trioxide as end product. An effort was made to investigate the effect of all the important variables encountered in leaching of metallic sulphide minerals in order to establish the best process conditions for the extraction of antimony and subsequent preparation of antimony trioxide. The experiments were carried out on laboratory scale and the effect of various process variables on the dissolution of antimony from stibnite concentrate was studied by single factor variation method arranged in a sequential manner. An industrial grade antimony trioxide having 99.70% purity with 90.72% yield has been prepared. The developed process is technically feasible and environmentally friendly.

Keywords: Stibnite ore, Flotation, Leaching, Ferric chloride, Extraction, Antimony trioxide.

Introduction

Antimony trioxide Sb_2O_3 is one of the most important antimony compounds which has a large number of industrial applications. It is found in nature as the mineral valentinite (rhombic) and senarmontite (octahedral). The most abundant antimony mineral in the earth crust is stibnite (Sb_2S_3) which is converted to various oxide minerals on weathering. Synthetic antimony trioxide in powder form contains Sb_2O_3 content ranging from 99.5% - 99.9% with minor impurities of lead, iron and arsenic. It is an intermediate compound from which a large number of other antimony compounds are prepared [1].

Antimony trioxide (Sb_2O_3) is commonly used in flame retardant applications. It is used as a synergist containing 2-10% Sb_2O_3 along with halogenated compounds. Such flame retardants find applications in plastics, polymers, rubber, heavy textiles etc. It is used as a catalyst in the preparation of polyethylene terephthalate (PET) plastic. It is primarily used as heat and ultraviolet radiation stabilizer for polyvinyl chloride (PVC) plastic [2, 3]. It is also used as white pigment in weather resistant exterior paints, in special oil based paints and colour fastener in yellow paint. It is used as opacifier in vitreous enamel frits and glazes for sanitary ware. It is used as a degasser, decolourizer and antisolarant in a small amount ranging from 0.1-2% especially for television tube glass, optical glass, ruby glass and in fluorescent light bulb glass [4, 5].

General pyrochemical processes used industrially for the preparation of antimony trioxide from sulphide ores involve roasting of the high grade ore or concentrate. The resultant impure volatilized antimony trioxide is either purified in reverberatory furnace to produce pure antimony oxide or reduced with some carbon source by smelting at high temperature (1150ºC to 1350ºC) to produce antimony metal. The metal is re-volatilized to produce pure antimony trioxide. Roasting and smelting of antimony ores under high temperature creates serious environmental pollution problems. Low boiling point valuable metals associated with antimony such as lead, cadmium, arsenic, mercury etc along with toxic gases generated such as SO_2 are emitted in to the atmosphere. The loss of valuable by-product makes the process un-economical. These are the major concerns associated with pyrometallurgical processes [6].

The development of hydrometallurgical processes for the extraction of antimony from low-grade stibnite ores without emitting SO_2 gas to atmosphere has received considerable attention in recent years. Hydrometallurgical processes may be applied successfully for simple as well as complex antimony ores. Two general solvent systems with some modification are introduced in hydrometallurgical processing of antimony ores. These include the alkaline sulfide system and the acidic chloride system [7]. The alkaline sulfide system dominates the acidic chloride system and many industrial plants have employed it. It consists of two steps i.e. leaching and electrowinning. The leaching operation uses a mixture of sodium hydroxide and sodium sulphide and the reactions

involved in the leaching operation are quite complicated. The second electrowinning step requires an ample supply of electrical energy that makes the process uneconomical. Therefore, a lot of research has been undertaken to utilize the acidic chloride system (8).

Several hydrometallurgical processes using acidic media have been proposed for the treatment of low grade antimony ores by different researchers. Various leaching agents alone as well as in combination have been applied for leaching. These include: the dissolution of antimony sulphide in an aqueous solution of hydrochloric acid saturated with chlorine gas; in a mixture of hydrochloric and tartaric acid; in a mixture of nitric and tartaric acid; in water and hydrogen sulphide and so on [9]. However, the use of acidic ferric chloride to extract metals from complex sulphide ores has received great attention recently [10]. This is because the reaction of sulphides with ferric chloride proceeds very rapidly. Secondly, it produces elemental sulphur as by product instead of poisonous SO_2 gas. Increasing interest due to the advantages of this reaction has stimulated a number of experimental studies for commercial applications [11].

Experimental

Sample Preparation

The antimony ore used in this investigation was obtained from Krinj area; district Chitral, Khyber Pukhtoon Khwa (KPK) province, Pakistan. A representative sample of run-of-mine ore weighing about 100 Kg was collected by random sampling from a bulk sample of the ore weighing about 10 tones. The ore sample consisted of lumps ranging in sizes from 100-250 mm (4-10″). It was subjected to crushing, grinding and screening steps in order to reduce the particle size. Large lumps of ore were fed to a jaw crusher for primary crushing to reduce the size below 10-12 mm (~1/2″). The jaw crusher product was charged to a roll crusher for secondary crushing to attain the particle size below 4-6 mm (~1/4"). A head sample for chemical analysis and X-ray Diffraction studies was obtained by riffling of the crushed ore. It was pulverized separately in a disc pulverizer (Denver, USA) to pass 200 mesh sieves (75μm) for chemical analysis and XRD studies. The rest of crushed ore was kept for leaching studies. It was further ground in a laboratory rod mill to get the required feed size. The grinding time was adjusted accordingly to achieve the desired feed size of the sample where ore minerals were liberated from associated gangue minerals. The ground ore was fed to a vibrating screen fitted with sieve No. 100 mesh

size (75μm) for screening. Oversize ore sample was returned to the rod mill to achieve the undersize product. Finally a feed of 100% passing 100 mesh size (minus 150 μm) was prepared by sieving for the leaching tests.

Chemical Analysis

The chemical analysis of head sample of the antimony ore was performed according to conventional gravimetric and volumetric methods as well as instrumental methods. The constituents such as silica, alumina, antimony, lead, barium and sulphur were estimated by gravimetric methods [11, 12]. Iron was determined by redox titration using standard solution of potassium dichromate [14]. Alkaline earth metals such as calcium and magnesium were estimated by complexometric titration, as well as by Atomic Absorption Spectrometer (Model: Z-8000, Hitachi, Japan) [15]. Alkali metals such as sodium and potassium were determined by Flame Photometer (Model: PFP7, Jenway Limited, England) [16]. The complete chemical analysis of head sample is shown in Table-1. Moreover, the chemical analysis of leached solutions was also performed to determine the percent extraction of antimony.

Table-1: The chemical composition of head sample.

Constituents	Percentage (%)
Antimony (Sb)	20.16
Lead (Pb)	1.45
Sulphur (S)	8.28
Silicon oxide (SiO_2)	63.07
Iron oxide (Fe_2O_3)	4.10
Barium oxide (BaO)	0.68
Aluminum oxide (Al_2O_3)	0.56
Calcium oxide (CaO)	1.62
Magnesium oxide (MgO)	0.14
Sodium oxide (Na_2O)	0.22
Potassium oxide (K_2O)	0.18

X-ray Diffraction

X-ray powder diffraction (XRD) technique was used to characterize the various types of mineral phases present in this ore. The ground sample of ore was run on an automatic X-ray Diffractometer (Model: D-5000, Siemens, Germany), which is equipped with a continuous scanning device. It has an X-ray tube consisting of a copper target which produces Cu Kα radiations having wave length of 1.5406Aº. The sample, placed in a sample holder, was bombarded with Cu Kα radiation of 40 kV and 30 mA with a sample rotation of 30 rpm. The diffraction patterns for the sample were measured with the scan angle (2-theta) ranging from 0° to 60° to get the main peaks of the minerals present in the ore. X-ray diffraction was done at 0.02 step size per second. The spectrum obtained shown in Fig. 1 was matched with standard data provided with the

instrument to identify the crystalline mineral phases. The mineral phases were identified by a search and match programme of the Joint Committee for Powder Diffraction Standards (JCPDS). The minerals identified are given in Table-2.

Table-2: The mineralogical composition of head sample.

Mineral Phases	Percentage (approx.)
Quartz (SiO_2)	60-64
Stibnite (Sb_2S_3)	19-25
Pyrite (FeS_2)	5-6
Boulangerite ($Pb_5Sb_4S_{11}$)	2-3
Calcite ($CaCO_3$)	2-3
Dolomite [$Ca\,Mg\,(CO_3)_2$]	< 1
Barite ($BaSO_4$)	< 1
Clays	1-2

Flotation Tests

Flotation trials of the antimony ore were performed in a laboratory flotation machine (Model: D-12, Denver, USA) using stainless steel cells of 1 and 2 liters capacity. The surfaces of different minerals were modified by certain chemicals called as flotation reagents. Valuable (worthy) mineral was made hydrophobic while valueless (gangue) minerals hydrophilic with flotation reagents. Air was supplied to float the hydrophobic stibnite in the form of froth. Stibnite concentrate was removed from the surface of cell with the help of scraper and collected in a tray. It was dried in an electric oven at 110ºC for subsequent

chemical analysis. Flotation tests were performed to investigate the important flotation variables. The optimum conditions of flotation parameters and material balance of typical test are recorded in Table-3 and 4 separately.

Table-3: The flotation parameters and the optimized conditions.

Rougher Flotation Parameters	Optimum Conditions
Grind size	80% passing 100 mesh #
Agitation speed	1200 rpm
Pulp density	25%
Pulp pH	~8.5
Lead nitrate	300 g/ton
Potassium amyl xanthate	120 g/ton
Pine oil	30 g/ton
Sodium silicate	200 g/ton
Sodium cyanide	50 g/ton
Conditioning Time	15 min
Cleaning Flotation Parameters	**Optimum Conditions**
Grind size	100% passing 100 mesh #
Agitation speed	1000 rpm
Pulp density	15%
Pulp pH	~8.5
Lead nitrate	200 g/ton
Potassium amyl xanthate	80 g/ton
Pine oil	20 g/ton
Sodium silicate	100 g/ton
Sodium cyanide	30 g/ton
Conditioning time	12 min
Re-Cleaning Flotation Parameters	**Optimum Conditions**
Grind size	100% passing 100 mesh #
Agitation speed	900 rpm
Pulp density	10%
Pulp pH	~8.5
Conditioning time	10 min
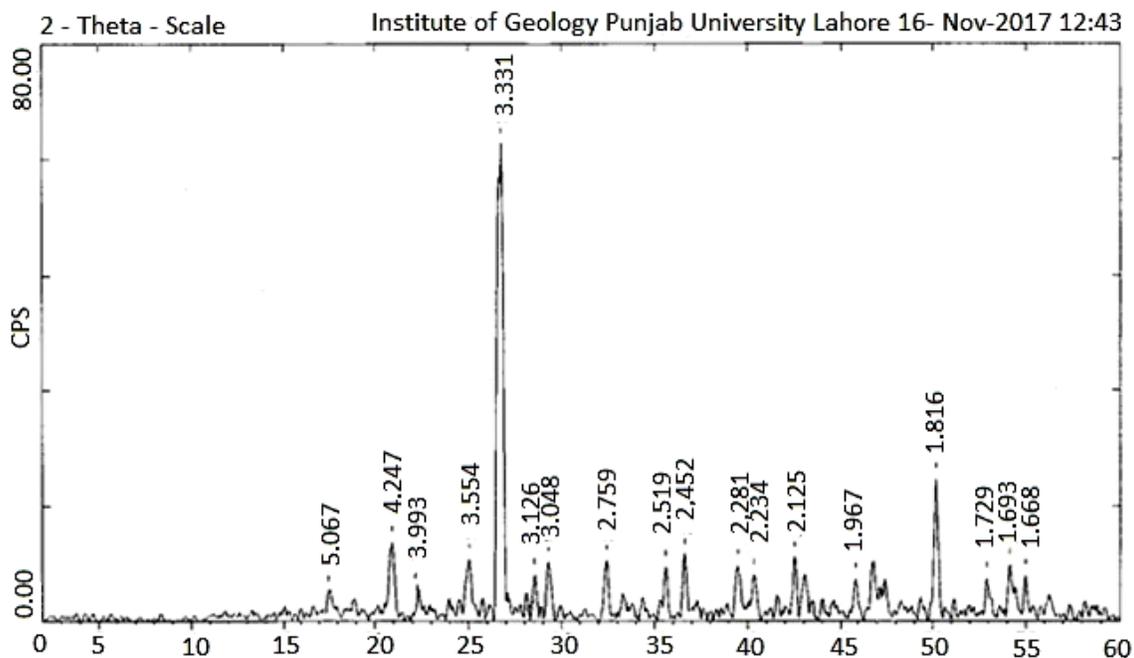
Fig. 1:   X-Ray Diffractogram (XRD) of antimony ore of Krinj, district Chitral, KPK.

Table-4: Metallurgical balance calculations for flotation of antimony ore.

Flotation Products	Weight (%)	Grade Sb (%)	Recovery Sb (%)
Re-cleaner concentrate	27.15	64. 86	87.34
Re-cleaner tailings	3.47	22.31	3.84
(Cleaner concentrate)	30.62	60.04	91.18
Cleaner tailings	6.41	12.26	3.90
(Rougher concentrate)	37.03	51.76	95.08
Rougher tailings	62.97	1.57	4.92
Head sample (ore)	100	20.16	100

Preparation of Ferric chloride

Ferric chloride ($FeCl_3.6H_2O$) in association with HCl was used as lixiviant in the present study. It was prepared in the Mineral Processing Laboratory by reacting a stochiometric quantity of iron scale and commercial hydrochloric acid (37%). The solution of ferrous chloride ($FeCl_2$) thus obtained was filtered. Chlorine gas (Cl_2) was passed through it in order to convert ferrous chloride into ferric chloride. It was evaporated on a sand bath until a solution of about 1.8 g/cm^3 specific gravity was obtained. This was cooled in a desiccator to crystallize ferric chloride hexahydrate salt. Its purity was determined and found to be more than 98%.

Leaching Tests

Stibnite concentrate (Sb $\geq$ 60%) was leached using commercial grade ferric chloride ($FeCl_3 \geq$ 95%). The leaching experiments were performed in batch-wise mode in order to determine the optimum leaching conditions for extraction of antimony from stibnite. Leaching tests were carried out in a Pyrex glass beaker (500 ml) placed on hot plate (made by PCSIR, Pakistan). The solution was stirred with a magnetic stirrer and heated on an automatic regulated hot plate with controlled heating. The leaching solution of ferric chloride (40%) was transferred to the beaker. Accurately weighed 10.00 g of stibnite concentrate was added in it. Water was added to maintain the desired L/S ratio. The pulp slurry was continuously stirred with the help of a magnetic stirrer and heated to attain the desired temperature. The important parameters of leaching such as particle size of concentrate, liquid to solid ratio, $FeCl_3$ concentration, HCl concentration, stirring speed, reaction time, reaction temperature were investigated in order to find the best conditions for dissolution of antimony from stibnite mineral in leached liquor. The results obtained are presented in graphical form in Figs 2-8.
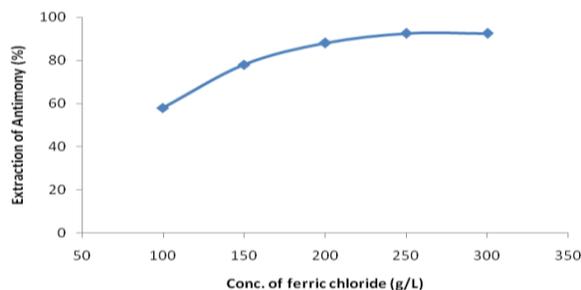
Fig. 2: Effect of ferric chloride concentration on the extraction of antimony from stibnite concentrate.

Experimental conditions:		
Particle size of conc.	=	85% minus 200 mesh
HCl concentration	=	10g/L
Stirring speed	=	500 rpm
Liquid to solid ratio	=	10
Reaction temperature	=	90°C
Retention time	=	60 min
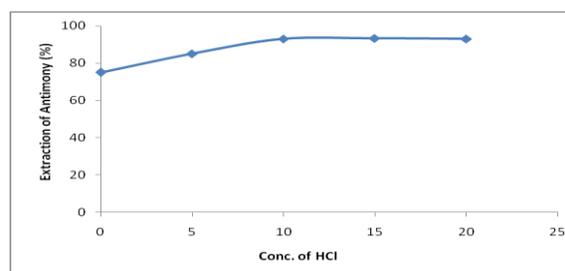
Fig. 3: Effect of HCl concentration on the extraction of antimony from stibnite concentrate.

Experimental conditions:		
Particle size of conc.	=	85% minus 200 mesh
$FeCl_3$ concentration	=	250g/L
Stirring speed	=	500 rpm
Liquid to solid ratio	=	10
Reaction temperature	=	90°C
Retention time	=	60 min
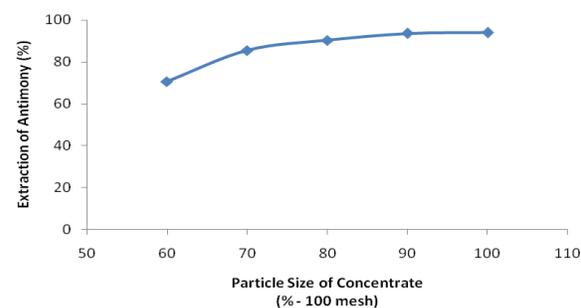
Fig. 4: Effect of particle size on the extraction of antimony from stibnite concentrate.

Experimental conditions:		
$FeCl_3$ concentration	=	250g/L
HCl concentration	=	15g/L
Stirring speed	=	500 rpm
Liquid to solid ratio	=	10
Reaction temperature	=	90°C
Retention time	=	60 min
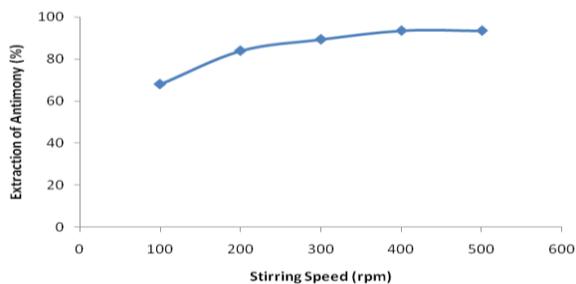
Fig. 5: Effect of agitation (stirring) speed on the extraction of antimony from stibnite concentrate.

Experimental conditions:		
Particle size of conc.	=	100% minus 200 mesh
FeCl₃ concentration	=	250g/L
HCl concentration	=	15g/L
Liquid to solid ratio	=	10
Reaction temperature		90°C
Retention time		60 min
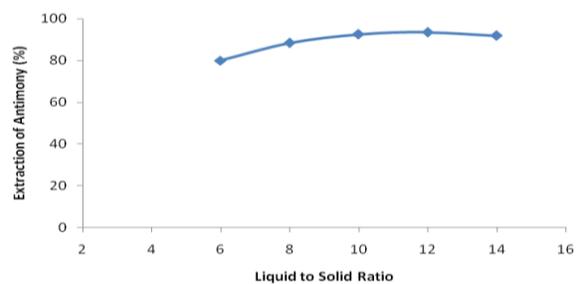
Fig. 6: Effect of liquid to solid ratio on the extraction of antimony from stibnite concentrate.

Experimental conditions:		
Particle size of conc.	=	100% minus 200 mesh
FeCl₃ concentration	=	250g/L
HCl concentration	=	15g/L
Stirring speed	=	400 rpm
Reaction temperature	=	90°C
Retention time	=	60 min
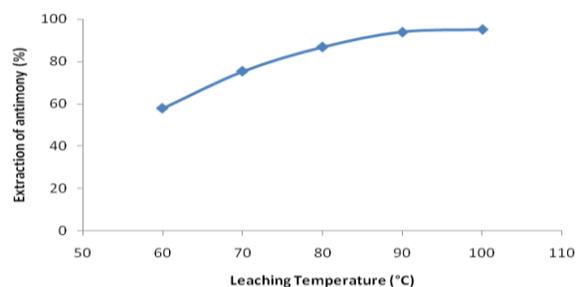
Fig. 7: Effect of leaching temperature (°C) on the extraction of antimony from stibnite concentrate.

Experimental conditions:		
Particle size of conc.	=	100% minus 200 mesh
FeCl₃ concentration	=	250g/L
HCl concentration	=	15g/L
Stirring speed	=	400 rpm
Liquid to solid ratio	=	12
Retention time		60 min
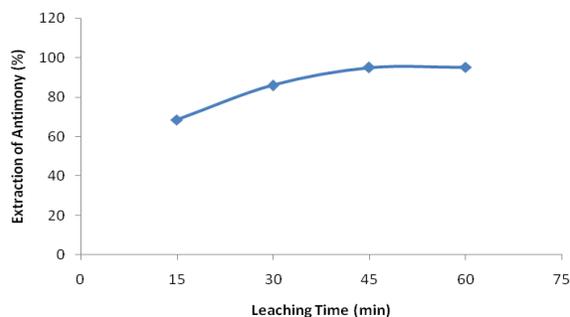
Fig. 8: Effect of leaching time (min) on the extraction of antimony from stibnite concentrate.

Experimental conditions:		
Particle size of conc.	=	100% minus 200 mesh
FeCl₃ concentration	=	250g/L
HCl concentration	=	15g/L
Stirring speed	=	400 rpm
Liquid to solid ratio	=	12
Reaction temperature	=	90°C

Filtration and Washing

The pregnant leached solution (PLS) was filtered from residual matter using a Gooch crucible funnel with the help of vacuum filtration pump for efficient filtration. It was followed by washing with dilute hydrochloric acid (1:10) to make the residual matter free from antimony content. The volume of the solution was made up to mark in 100 ml measuring flasks. An aliquot of 5 mL of leached liquor was taken out with the help of pipette to analyze the metal content dissolved in the leached solution. The concentration of antimony dissolved was used to calculate the recovery of antimony. Remaining leached solution was stored in a polythene bottles for hydrolyzing studies.

Hydrolysis and Precipitation of Antimony Trioxide

After optimizing the leaching parameters, all the stored pregnant leached solutions were mixed to make a bulk solution. It was hydrolyzed with 1 N NaOH solution to precipitate antimony oxychloride/ antimony oxide chloride. The hydrolysis of antimony chloride solution was studied by varying the pH from 1 to 6 at 25°C by adjusting with NaOH solution and holding for different period of time. The white precipitates formed were filtered off using a glass funnel and washed with distilled water to remove the attached impurities. The washed precipitates were then dissolved in aqueous ammonia (NH₄OH) solution to prepare pure antimony trioxide crystals. Finally, the product was dried in a desiccator and then in an electric oven at 105°C. The final antimony trioxide obtained was analyzed for antimony content in order to calculate the parentage purity and yield of

the product. A complete process flow-sheet has been proposed.

Results and Discussion

Chemical Composition of Ore

It is evident from the chemical analysis results of the representative sample of ore (Table-1) that the antimony (Sb) content of the ore under investigation is 20.16%. The undesirable elements determined are silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3), barium oxide (BaO), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O) and potassium oxide (K_2O). It is also clear from this table that silica is the main unwanted impurity being 63.07%.

Mineralogical Composition of Ore

The mineralogical composition of ore (Table-2) obtained by X-ray diffraction analysis confirms the presence of stibnite (Sb_2S_3), quartz (SiO_2), pyrite (FeS_2), boulangerite ($Pb_5Sb_4S_{11}$), calcite ($CaCO_3$), barite ($BaSO_4$) and clay minerals. It was identified by JCP.CAT search & match programme of the X-ray Diffractometer that the d values of the major peaks of the X-ray diffractogram (Fig. 4) of the ore correspond to the standard d values of these minerals. It can be determined easily from the chemical and mineralogical results that silica is present mainly due to quartz mineral and partially by clay minerals. After silica the other major impurity is iron, which is present in the form of pyrite. Calcium oxide is present in the ore due to calcite and barium oxide due to barite, whereas aluminum oxide, sodium oxide and potassium oxide are mainly associated with different clay minerals.

Flotation Results

It is clear from the flotation tests (Table-4) that ore is upgraded by rougher flotation to a rougher concentrate containing 51.76% Sb content with 95.08% recovery. The optimized rougher flotation conditions (Table-3) were: pH of pulp 8.5; grind size of ore 80% passing 100 mesh; the amount of lead nitrate as stibnite activator 300 g/ton; amyl xanthate as a stibnite collector 120 g/ton; pine oil as a frother 30 g/ton; sodium silicate as a gangue depressor 200 g/ton and sodium cyanide as a pyrite depressor 50 g/ton. Microscopic examination of rougher concentrate showed that it still contained some middling particles which needed to be librated. Therefore, the rougher concentrate was further ground in a rod mill to liberate the locked stibnite grains. The ground rougher concentrate was cleaned by cleaning flotation to produce a cleaner concentrate

assaying 60.84% Sb content with 91.18% recovery. Additional amounts of collector and forther were required to float the newly liberated fine stibnite grains. Moreover, an additional amount of sodium silicate depressant was also applied in the cleaning operation to depress the silica and clays. Similarly, sodium cyanide was added to depress the pyrite grains as shown in Table-3. The cleaner concentrate was upgraded to a re-cleaner concentrate assaying 64.86% Sb content with 87.34% recovery by another cleaning flotation, without using additional quantity of flotation reagents. The purpose of re-cleaning was to remove any adhering particles attached to the cleaner concentrate during cleaning flotation and to make the final concentrate as free as possible from gangue particles. The re-circulation of the tailings from the cleaning and re-cleaning stages according to the grade at an appropriate point of addition has improved the overall recovery of the antimony flotation process (Fig. 9).

The chemical analysis of the final concentrate (Table-5) shows that it contains 64.85% Sb content. The antimony content of the ore under investigation is increased by flotation from 20.16% to 64.86%. It is also clear from the results that the silica content of the ore is reduced from 63.07% to 2.08%. The other impurities such as Fe_2O_3, Al_2O_3, Cao, Na_2O and K_2O are also reduced considerably. The flotation process has been found quite successful as it improved the grade of ore significantly by reducing the gangue material of the ore. The results prove the suitability of the process selected for this ore [17].

Table-5: The chemical analysis of final stibnite concentrate.

Constituents	Percentage
Antimony (Sb)	64.86
Lead (Pb)	2.71
Sulphur (S)	28.29
Silicon oxide (SiO_2)	2.08
Iron oxide (Fe_2O_3)	1.10
Aluminum oxide (Al_2O_3)	0.15
Calcium oxide (CaO)	0.32
Magnesium oxide (MgO)	0.10
Sodium oxide (Na_2O)	0.12
Potassium oxide (K_2O)	0.09

Leaching Results

Stibnite concentrate contains about 90% Sb_2S_3 content. The remaining 10% portion of the concentrate consists of silica, lead sulphide, iron sulphide, clays and some other minor impurities. $FeCl_3$ has been successfully used as a lixiviant for complex sulphide minerals by many researchers because it is a highly reactive and oxidizing chemical [18, 21]. The present investigation is focused on the study of the role of the ferric ions in leaching of stibnite and to determine the optimum leaching conditions.
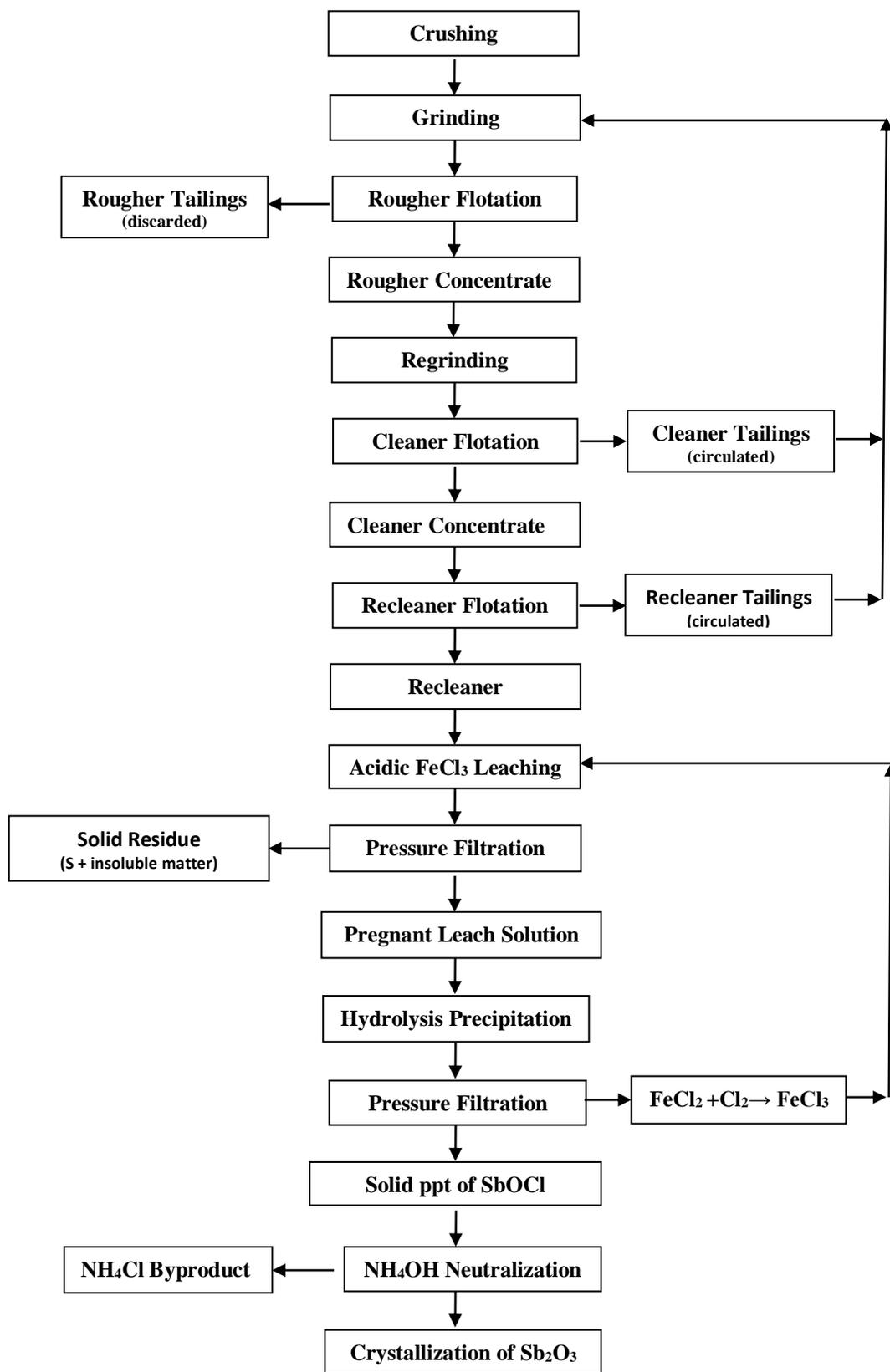
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│ Rougher Tailings │◄─────│ Rougher Flotation│                   │
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                   │  Recleaner  │
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Effect of FeCl₃ Concentration

In present process, ferric chloride reacts with antimony trisulphide to produce an antimony trichloride. The role of ferric chloride concentration on the extraction of antimony chloride from stibnite concentrate was studied by varying the concentration of $FeCl_3$ over a range of 100-300 g/L and keeping other parameters constant at arbitrary selected values. The quantity of concentrate was fixed at 10 g. The results obtained are plotted in Fig. 2. It is apparent from this Fig. that the ferric chloride concentration has a significant influence on the dissolution of stibnite mineral. Under similar leaching conditions, the rate of dissolving antimony from stibnite increases steadily with increasing ferric chloride concentration. Actually, increase in $FeCl_3$ concentration accelerates the dissolution rate at which antimony becomes soluble in the leach solution. At $FeCl_3$ concentration of 250 g/L, the dissolution reaches a maximum value of 92.48% after which it becomes constant. Hence this value was selected for onward study.

Effect of HCl Concentration

Hydrochloric acid (HCl) in conjunction with ferric chloride ($FeCl_3$) was employed for maximum extraction of antimony as chloride from stibnite concentrate. The addition of HCl prevents the hydrolysis of ferric chloride and is necessary to dissolve it in solution [19]. The effect of hydrochloric acid concentration on antimony chloride recovery was studied by varying its concentration over a range of 1 to 20g/L. The results obtained are shown in Fig. 3. It is notable that HCl concentration has an important effect on the dissolution of antimony from stibnite concentrate. Increasing the HCl concentration enhances the rate of leaching of flotation concentrate as shown by the data in Fig. 3. Optimum antimony chloride extraction was achieved at HCl concentration of 15g/L. About 82.51% antimony was dissolved from stibnite concentrate in the absence of HCl, whereas 93.27% was recovered at HCl concentration of 15g/L after that dissolution of antimony was almost the same even at higher acid concentrations.

Effect of Particle Size

After optimizing the above mentioned leaching parameters, the effect of particle size of concentrate on leaching of stibnite was studied. For this purpose, the concentrate was ground in a rod mill and sieved into four size fractions (70%, 80%, 90% and 100% passing 200 mesh size) for antimony extraction experiments. The results obtained are shown graphically in Fig. 4. It was observed from this Fig. that the rate of antimony dissolution increases with decreases in particle size up to 100% passing 200 mesh size. It was found that smaller particle size resulted in higher extraction of antimony from stibnite concentrate in the leached solution as well as increases the rate of antimony leaching by the lixiviant. It can be deduced from these experiments that the rate of dissolution is directly related to particle size. In fact, the rate of antimony dissolution increases with decrease in particle size due to increase in the surface area on grinding. Since fine grinding is an energy intensive process therefore 100% passing 200 mesh size was selected for this investigation and further grinding of the concentrate was avoided [21].

Effect of Stirring Speed

The influence of stirring speed (agitation) on the dissolution of antimony from stibnite concentrate by ferric chloride solution was investigated by varying it at 100, 200, 300, 400 and 500 rpm respectively. A hot plate with magnetic stirrer was used for this study. The results of these tests are presented in Fig. 5, which shows that agitation of the solution during leaching greatly facilitates the reaction of the antimony trisulphide with ferric chloride. This may be due to the reason that with continuous stirring, the rate of collision of stibnite particles with $FeCl_3$ increases [22]. Maximum 93.51% of antimony was dissolved from the stibnite concentrate at an agitation speed of 400 rpm and therefore selected in subsequent experiments. It was found that above 400 rpm, the rate of agitation did not improve the extraction of antimony. It indicates that there was an adequate suspension of the solid particles in the slurry at or above 400 rpm.

Effect of Liquid to Solid Ratio

The effect of liquid to solid ratio upon antimony dissolution in the slurry is another very important factor that needs to be studied. Leaching tests were carried out at different liquid to solid ratio (6, 8, 10, 12 and 14) of solution. To study the influence of liquid to solid ratio on the dissolution of antimony, the amount of sample and concentration of $FeCl_3$ solution were kept constant while volumes of solution were changed by adding distilled water. The results obtained are illustrated in Fig. 6. The Fig. shows that the liquid to solid ratio has a substantial effect on the extraction of antimony from stibnite. It is evident from this Fig. that at a liquid to solid ratio 10, the recovery is 92.45% and at 12, the recovery is slightly higher i.e. 93.48%, after which it decreased.

The results presented in Fig. 6 clearly indicate that maximum antimony extraction took place at liquid to solid ratio of 12. About 93.48% antimony was dissolved from stibnite concentrate at this value and it was adopted for next tests. It is also obvious from this Fig. that further increasing liquid to solid ratio does not increase the rate of dissolution. In fact, it was observed that antimony dissolution in solution decreased with increasing liquid to solid ratio after 12.

Effect of Leaching Temperature

Effect of reaction temperature is another important parameter which is required to be investigated. Five experiments were performed to study the effect of temperature on the extraction of antimony chloride from stibnite concentrate in the range of 60°C to 100 °C. The results of the variation of reaction temperature on the rate of dissolution of antimony from stibnite concentrate are plotted in Fig. 7. It is obvious from this Fig. that the rate of leaching increases gradually with increasing temperature. After one hour leaching time, about 57.84% of antimony was dissolved from stibnite concentrate at a reaction temperature of 60°C, whereas 75.28% of antimony was dissolved at a temperature of 70°C, 86.76% of antimony was dissolved at a temperature of 80°C, 94.97% of antimony was dissolved at a temperature of 90°C and 95.04% of antimony was dissolved at a temperature of 100°C. Antimony dissolution increased with temperature and the highest and fastest dissolution rate of stibnite (94.97%) was obtained at 90°C in 60 min. For all temperature values, there was an increasing effect on antimony leaching recovery with increasing the temperature. It is noticed from Fig. 6 that the optimum result (94.97%) is achieved after 90°C and below that temperature recovery is lower. This was considered as optimum leaching temperature.

Effect of Leaching Time

Reaction time has a significant effect on the yield of product from the concentrate. It permits the surface of the stibnite particles to react with the FeCl$_3$. In order to study the effect of variation of reaction time on the recovery of antimony chloride from stibnite grains, five experiments were carried out for different reaction times (i.e. 15 min, 30 min, 45 min and 60 min). The results obtained are presented in Fig. 8. It is clear from this Fig. that the leaching of stibnite is a direct function of time interval. It is noticed that the dissolution rate of antimony increases with increase in reaction time and optimum result are achieved after 45 min. It was also observed that agitation of the solution during leaching greatly helped the leaching of antimony as chloride. It is obvious from this Fig. that about 68.54% of antimony was dissolved from stibnite concentrate in 15 min, 85.90% dissolved in 30 min, 94.96% dissolved in 45 min, whereas about 95.17% of antimony was dissolved from stibnite concentrate in 60 min at a temperature of 90°C. The reason is that with stirring the rate of collision of iron ions and antimony ions increases with leaching time. It may be pointed out from these results that 45 min leaching time is required to get the optimum result and hence this value was selected.

Filtration of Leached Solution

Ferric chloride (FeCl$_3$) along with hydrochloric acid (HCl) served as the lixiviant to dissolve the antimony from antimony trisulphide. It is supposed that antimony trisulphide and ferric chloride react in the following manner.

$$Sb_2S_3 + 6FeCl_3 \rightarrow 2SbCl_3 + 6FeCl_2 + 3S°$$

The oxide minerals such as senarmontite, valentinite, kermesite and stibiconite, if present, directly react with HCl without requiring FeCl$_3$ during leaching process.

$$Sb_2O_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2O$$
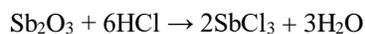
In aqueous medium, ferric chloride (FeCl$_3$) acts as an oxidizing and a chloridizing agent. It converts the antimony sulfide mineral into antimony chloride complex with the production of elemental sulfur. During this reaction ferric chloride is reduced to ferrous chloride and sulphide ions are oxidized into elemental sulfur [23]. The primary reaction takes place as given below.

$$S^{2-} \rightarrow 2e^- + S°$$

$$Fe^{3+} + 1e^- \rightarrow Fe^{2+}$$
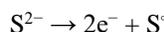
It was found that best yield is achieved when antimony trisuphide and ferric chloride are contacted in leach solution for 45 min. The antimony trichloride and ferrous chloride remain in solution while sulfur particles go in suspension. The aqueous solution comprises of about 250g/L ferric chloride. In order to dissolve this quantity of ferric chloride in aqueous solution it is acidified with hydrochloric acid (HCl) having concentration about 15g/L. When ferric chloride completely reacts with the antimony trisulphide, the resulting reaction mixture consists of antimony trichloride, ferric chloride, ferrous chloride,

lead chloride, sulfur particles and other un-reacted material such as quartz and clay. The sulfur particles in suspension and other insoluble matter are separated by vacuum filtration process from the reaction mixture. The insoluble matter mainly contains quartz, lead chloride and clay particles.

Hydrolysis Precipitation of Leached Solution

The pregnant liquid solution contains antimony trichloride, ferrous chloride and small amount of ferric chloride. Antimony chloride leached out in solution on hydrolysis with water and NaOH solution at pH around 2 immediately produces solid precipitate of antimony oxychloride (SbOCl) whereas ferrous chloride and ferric chloride remain in solution. It was observed that complete precipitation occurs between pH 2-3. Some of the antimony oxychloride may also is converted into antimony oxide chloride ($Sb_4O_5Cl_2$) on further reaction. The reactions occurring during this hydrolysis process are illustrated in following equations [24].

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$

$$4SbOCl + H_2O \rightarrow Sb_4O_5Cl_2 + 2HCl$$
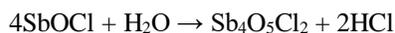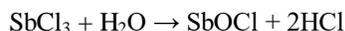
The solid precipitates of antimony oxychloride and antimony oxide chloride on treatment with aqueous ammonia form pure precipitate of antimony trioxide (Sb_2O_3). The reactions occurring during this hydrolysis step are shown below.

$$2SbOCl + 2NH_4OH \rightarrow Sb_2O_3 + 2NH_4Cl + H_2O$$

$$Sb_4O_5Cl_2 + 2NH_4OH \rightarrow 2Sb_2O_3 + 2NH_4Cl + H_2O$$
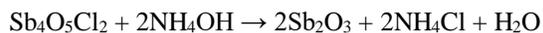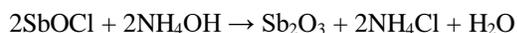
It was observed that maximum precipitation of antimony trioxide occurred when pH of reaction mixture was maintained in the range of 8.0-8.5. The pH controlled by ammonium hydroxide in this range facilitates the production of antimony trioxide with senarmontite crystals [25]. The purity of developed antimony oxide determined on the basis of weight and antimony content was found to be 99. 70% with 90.52% yield.

The ammonium chloride produced as a by-product during hydrolysis may be recycled according to the following reaction:

$$NH_4Cl + NaOH \rightarrow NH_4OH\uparrow + NaCl$$
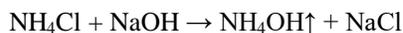
The gaseous ammonium hydroxide produced may be readily dissolved in water to produce an aqueous solution of ammonium hydroxide which may be used in the hydrolysis reaction again. Ferrous chloride produced during reaction is converted into ferric chloride by oxidation process. Chlorine gas (Cl_2) oxidizes Fe (II) ions to Fe (III) ions again. In the chlorination reaction chlorine gas reacts with ferrous chloride pursuant to the following reaction:

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$$
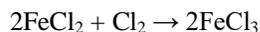
Thus, the chlorination step regenerates ferric chloride, which is then reused to leach stibnite concentrate. The solid waste products produced during leaching such as silica and clay may be disposed of relatively easily. The salts of heavy metal ($PbCl_2$) may be recovered from the residual matter.

The main advantage of the developed process is that it produces the least amount of environmentally hazardous emissions such as SO_2 and H_2S gases. Solid valuable by-products obtained include elemental sulphur and heavy metal salts such as lead chloride which is a great advantage of this process when it is compared with other pyrometallurgical processes. The lixiviant is recycled after proper treatment and reused without disposing it to waste. Hence the process is a closed system and mitigates the cost required for the purchase of new raw material for continuous production. Furthermore, it is economically favorable because it does not require costly equipment used for conventional roasting, smelting and electrolysis and scrubbers to remove emissions of toxic SO_2 gas. Moreover, the process works under atmospheric pressure and at relatively low temperature. The plant based on this process may be established at the mine site. These advantages enable the reduction in overall costs of the process and make it commercially viable for industrial scale implementation. However, the only disadvantage associated with this process is corrosion issues of the chloride system.

Conclusion

The flotation step was found quite suitable for the preparation of high-grade antimony concentrate assaying 64.86% Sb from low-grade stibnite ore containing 20.06% Sb. Leaching experimental results using ferric chloride in acidic medium as lixiviant have shown that particle size of 100% passing 200 mesh of stibnite concentrate, liquid to solid ratio of 12, ferric chloride concentration of 250g/L in solution, HCl concentration of 15g/L, stirring speed of 400 rpm, reaction time of 45 min and reaction temperature of 90°C resulted in higher concentrations of antimony in

the leached solution. A commercial grade antimony trioxide having purity 99.70% with 90.52% yield has been prepared on laboratory scale. The developed process is ideally suitable for utilization of low grade stibnite ore as a starting material. The process is technically feasible and economically favorable as the lixiviant can be recycled. It is environmentally friendly because it produces the least amount of sulphur dioxide (SO_2) gas. A pilot plant study is suggested in order to establish its industrial viability.

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