

Mineralogical and Liberation Characteristics of Antimony Ore of Chitral, NWFP, Pakistan

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Summary: An investigation was carried out to identify the various types of minerals present in antimony ore of Chitral, North West Frontier Province (NWFP), Pakistan and to determine the suitability of the method for its concentration. Ore has been evaluated and characterized by ore microscopy, X-ray diffraction technique and chemical analysis. The major and minor minerals present in the ore were identified. The textural characteristics such as grain size, grain shape and their arrangement in the ore body were also investigated. The degree of liberation of antimony bearing mineral was studied by particles counting method. Based on the mineral assemblage and the textural characteristics, the antimony ore of Chitral is amenable to beneficiation by froth flotation technique.

Introduction

Antimony rarely occurs in native form in nature. It usually combines with other elements to form different minerals. Among, over 100 known minerals of antimony, the main source of antimony metal and its compounds is stibnite (Sb_2S_3). Therefore, it is the principal ore mineral of antimony and is also known as antimonite and antimony glance [1]. Antimony minerals are pre-concentrated, either directly from the ore or as by-product from base metal beneficiation, to obtain saleable concentrate. Generally low-grade ores are beneficiated as concentrates containing 25-65 % Sb content [2].

Selection of the beneficiation technique depends upon the mineralogical composition and texture of the particular ore. Mineralogical composition gives knowledge about the nature of valuable and gangue minerals and their proportion in the ore whereas the texture refers to the aggregation, dissemination and shape of the minerals within the ore. Depending upon the nature, various gravity and flotation techniques are used for beneficiation of lean ores. Gravity concentration methods are mostly used for oxide and coarse-grained ores. While on the other hand, sulphide and fine-grained ores are beneficiated economically by froth flotation technique [3]. Liberation of valuable minerals from gangue minerals is one of the most important factors affecting all mineral separation processes. Ore is ground to a size at which maximum mineral grains are liberated at the coarsest possible size [4].

The antimony content of either the ore or the concentrates determines the method of treatment for the recovery of metal. Ore or concentrates containing 5-25 % Sb are volatilized, 25-45 % Sb products are smelted in a blast furnace while those containing 45-65 % Sb are liquated or treated by iron precipitation. The metal is further purified by fire refining or by electrolytic process [5].

Many researchers on account of its importance have been engaged to study the antimony mineralization and assemblage of associated minerals in the ores. Dianfen and Shuqiong [6] on the basis of research on Chashan antimony ore deposit of China found that it includes ore minerals such as stibnite, berthierite, galena, sphalerite, arsenopyrite, pyrite, wolframite, scheelite and sulphosalts. While on the other hand, Dinh and Leon [7] identified the Sb mineralization of Cam Pha deposit of Vietnam as quartz, stibnite, pyrite, and cinnabar. Similarly, Rodolfo [8] in his study on Fuoco antimoniferous mine of Italy described that it contains useful minerals such as stibnite often altered to stibiconite, valentinite and metastibnite as well as quartz and dolomite.

Stibnite deposits usually occur as veins in fissures, shears and joints or as regular replacement deposits. Stibnite is often found in veins with quartz and occasionally with various antimony minerals resulting from the decomposition of stibnite. Stibnite-

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quartz deposits are hosted dominantly by shale, marl and carbonate rocks. Most replacement deposits form lenticular bodies of quartz and stibnite within limestone at contacts with overlying shale and near high-angle faults. Stibnite deposits are generated by crystallization of magma in fractures to form hydrothermal veins or by hot-spring activity. Deposition of antimony minerals takes place in impermeable host rocks producing complex systems of veins, stockworks and impregnations [9-11].

Antimony deposits have been reported to exist at various localities in Pakistan. The large deposits of antimony occur at Lutkho valley (Chitral), Shekran in Jhalevan area (Kalat), Zaimukht hills in Kurram valley (Peshawar), Qilla Abdulla and Qilla Viala areas (Quetta) and Karangli hill in Salt Range (Jhelum). However, economically important reserves of antimony ore are found at Krinj and Partson about 21 and 24 km to the North of Chitral district of NWFP. These deposits contain stibnite-quartz veins which occur in high mountains in the Paleozoic slates, 150-300 feet below its contact with the overlying Cretaceous limestone [12]. Recently, some small but rich veins of stibnite have been found in the Cretaceous limestone, also in the same region. The average reserves of antimony ore of Chitral areas have been estimated to be 0.03 million tonnes [13].

Main purpose of this investigation is to identify the various types of mineral constituents present in the ore and to determine the grain size, shapes, form of association and liberation of valuable minerals from the gangue minerals, which are useful for the evaluation of a suitable process to be adopted for the beneficiation of antimony ore.

Results and Discussion

The analysis of the two samples from this deposit is presented in Table-1. As is evident, the percentage of antimony (Sb) in sample No. 1 is about half of the sample No. 2. On the basis of this preliminary information, it is inferred that percentage of antimony sulphide (stibnite) would widely vary from place to place. Other valuable metal present in the ore is lead (Pb) which is due to presence of boulangerite mineral. It is also clear from the Table-1 that SiO₂ is the major impurity which is present mainly due to quartz mineral. The percentage of silica also shows significant variation and it is expected to increase or decrease with the percentage

Table-1: Chemical composition of the ore samples.

Constituents	Sample 1 (%)	Sample 2 (%)
SiO ₂	64.28	44.65
Sb	18.75	34.09
Pb	1.45	2.09
Fe	3.50	1.70
Zn	0.12	0.31
Al ₂ O ₃	0.25	0.13
CaO	1.20	0.48
BaO	0.10	0.10
MgO	0.14	0.03
Na ₂ O	0.11	0.10
K ₂ O	0.09	0.08
S	8.56	14.86

of antimony sulphide. After SiO₂ the other major impurity is iron which is present in the form of pyrite. Calcium occurs in the analyzed ore as calcite and barium as barite, whereas Al₂O₃, Na₂O and K₂O are mainly associated with clay minerals.

Table-1 indicates that the antimony (Sb) content in the sample No. 1 is around 19 %. This grade is quite feasible to exploit the ore for the recovery of metal but it is better to beneficiate such an ore because it improves the production economics to a great extent. As the percentage recovery of antimony decreases very rapidly with the increase in the proportion of gangue present in the ore, therefore, the direct treatment of low-grade ore is uneconomic [14]. The grade of sample No. 2 is quite rich and can be used as such. However, up-grading undoubtedly has its advantages that must be given due consideration when large volumes of the ore are involved especially on an industrial scale.

Table-2 shows the mineralogical composition of ore, obtained by microscopic examination of thin sections of the ore complemented by chemical and X-ray analysis. Based on ore microscope examination, the main antimony-bearing mineral identified is stibnite that looks lead gray to black with metallic luster. It has modified bladed shapes crystals of stibnite that occur as large grains, veinlets and minute grains (Figs. 1, 3). The specific gravity of separated grains was observed to be 4.5-4.6. Grain habits range from anhedral to euhedral. Boulangerite appears as opaque, bluish black to gray mineral grains with metallic luster (Figs. 2, 6). It has acicular to fibrous crystals. It occurs as large and small grains associated with stibnite. Quartz is present as medium to coarse grained matrix mineral (Figs. 1-6). Pyrite grains are fine, subhedral to anhedral and observed as pale brass yellow as well as partially altered to reddish brown hematite on exposed surface (Fig. 6). Calcite is

Table-2: Mineralogical composition of the ore samples.

Minerals	Sample 1 (%)	Sample 2 (%)
Quartz	64.02	44.52
Stibnite	23.14	46.16
Pyrite	7.50	3.65
Boulangerite	2.63	3.74
Sphalerite	0.18	0.46
Calcite	1.68	0.87
Barite	0.17	0.16
Clay	0.55	0.34

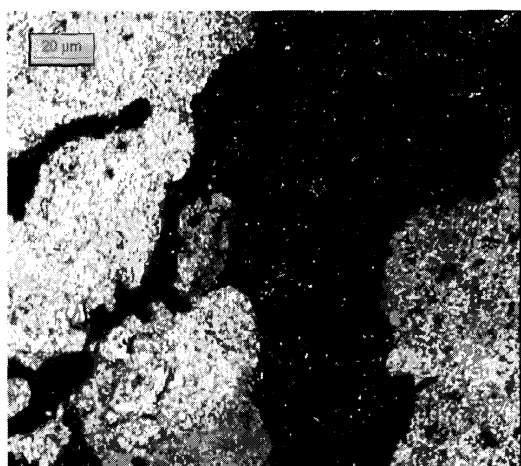


Fig. 1: Coarse-grained stibnite crystals (gray) forming clusters in quartz vein (×200).

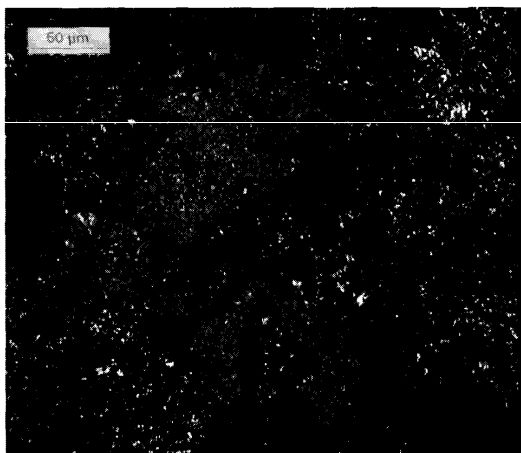


Fig. 2: Boulangerite crystals (bluish gray) associated with stibnite grains (black) (×100).

present as anhedral colorless grains and sphalerite looks as coarse to fine light brown granular aggregates (Fig. 5).

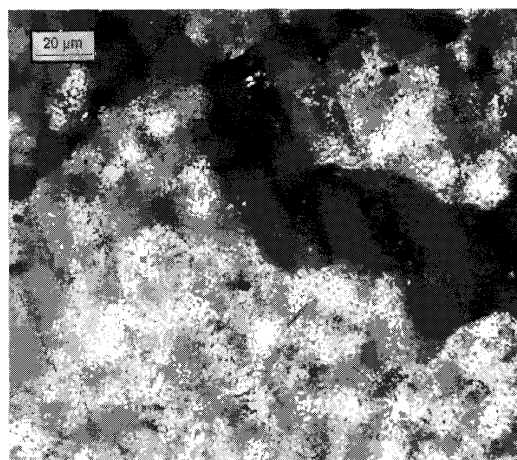


Fig. 3: Stibnite crystals (gray) disseminated in white quartz matrix (×200).

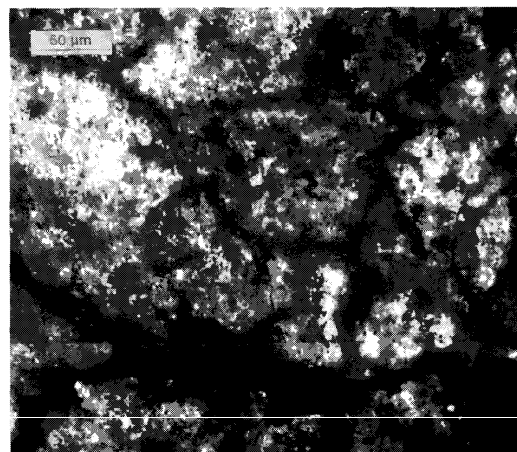


Fig. 4: Sphalerite crystals (brown) disseminated in quartz matrix (×100).

Microscopic studies also indicate that ore occurs in siliceous breccia as fissure filling. Here stibnite has been formed under low temperature hydrothermal conditions in fractures to form fissure filling hydrothermal veins and stockworks in fractures and shear zones. Deposits consist of quartz-stibnite veins in highly metamorphosed fine grained light gray to dark black slate of Precambrian age in contact zones between Paleozoic limestone and underlying slates.

The major peaks of X-ray diffractogram of the ore (Fig. 7) indicate the presence of stibnite

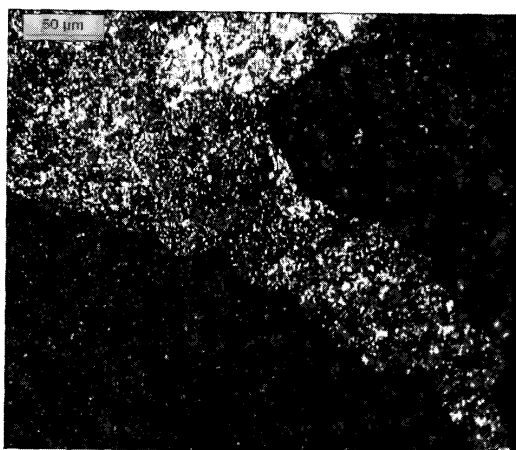


Fig. 5: Calcite grains (colourless) associated with white quartz ($\times 100$).

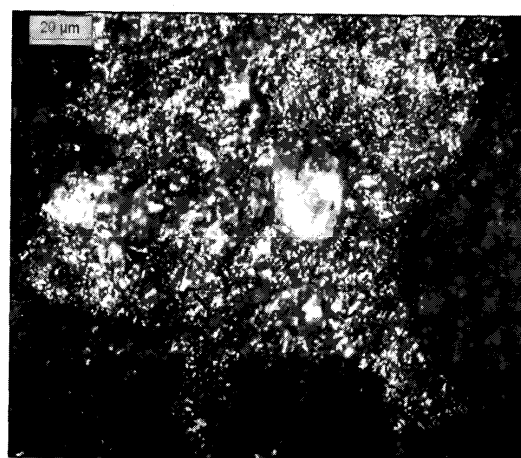


Fig. 6: Pyrite (pale yellow) forming clusters in quartz matrix ($\times 200$).

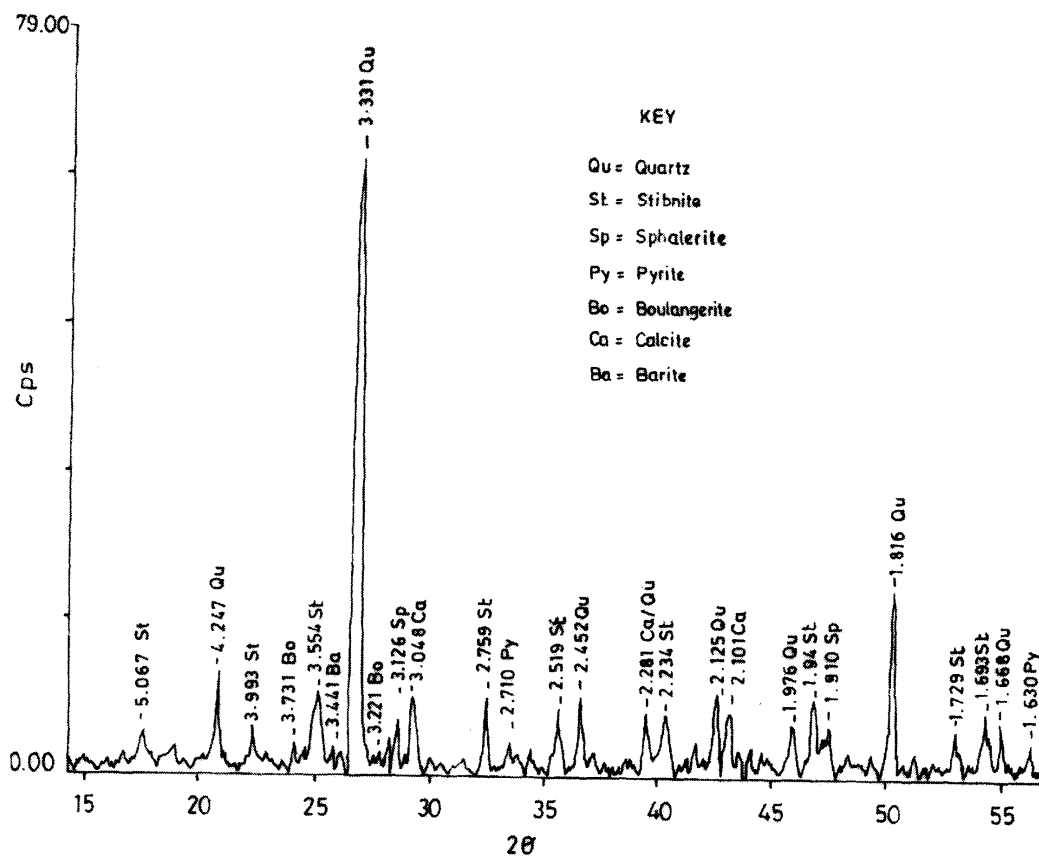


Fig. 7: XRD of Antimony Ore (Bulk Sample) of Chitral, Pakistan.

(Sb₂S₃) and quartz (SiO₂) minerals, as d values of 3.554, 3.048 and 2.759 correspond with the standard d values of stibnite and d values of 4.247, 3.331 and 1.816 correspond with the standard d values of quartz. It was also identified by JCP.CAT search/match programme provided with the X-ray Diffractometer that the other peaks correspond with pyrite (FeS₂), boulangerite (Pb₅Sb₄S₁₁), sphalerite (ZnS) calcite (CaCO₃) and barite (BaSO₄).

Selection of the beneficiation technique also depends upon the type of minerals present in the ore. The antimony bearing minerals in the ore *i.e.* stibnite and boulangerite are basically sulphides in nature. They can be easily separated by froth flotation technique because sulphide minerals respond readily to froth flotation treatment [15]. Flotation is a widely utilized unit operation in mineral processing and is based upon the principle that different minerals have different wetting characteristics that can be used as a basis for their separation [2]. It separate the grains of ore minerals from the gangue minerals by making ore minerals hydrophobic and aerophilic and gangue minerals hydrophilic with the help of flotation reagents. Alkyl xanthates are used as collector for sulphide minerals because they are highly selective and produce positively charged ions of alkali metals and negatively charged xanthates which are adsorbed on the surface of the sulphide minerals to form a monomolecular layer of insoluble metal-xanthate complexes which make the mineral grains hydrophobic and aerophilic [3]. The associated gangue minerals such as quartz, pyrite, sphalerite, calcite, barite and clay minerals can be depressed using selective depressants which reduce their flotation tendency by rendering them hydrophilic.

The success and the efficiency of ore processing operation greatly depend upon the grain size and the distribution composition of individual mineral particles in the host rock [16]. Thin sections of the ore reveal that ore is fine-grained. Stibnite occurs as dissemination and vein filling in the matrix of quartz. Some stibnite grains are disseminated in carbonate-altered wall rocks also. The grain size of stibnite shows wide variations under the microscope ranging from coarse crystals of 200 μm to fine disseminated particles of 50 μm. However, the average grain size is about 150 μm. Veins have quartz and quartz-carbonate gangue minerals ranging from fine to coarse grains.

The knowledge of host mineral helps in the possible choice of mineral processing technique [17]. In this ore stibnite is commonly associated and interlocked with the host quartz mineral. Test work to establish both the optimal grind size for stibnite liberation and the best conditions for quartz rejection is therefore mandatory. The results summarized in Table-3 disclose the degree of liberation of stibnite mineral in various size fractions and hence indicate the possibility and extent of its concentration during beneficiation. It is evident from this Table that about 95 % mineral grains of stibnite are liberated when the ore is ground to minus 100 mesh (150 μm) and that finer grind size results in a considerable decrease in stibnite locked with gangue. It is obvious from Table-3 that the liberation increases with a reduction in particle size. In practice, liberation is taken to the point where the economic yield of the process is maximized and particle size is seldom reduced to a point where 100 % liberation is attained not only because of the increasing costs of comminution but also because of losses in efficiency of the particular separation being employed [18]. Therefore, the ore under study should be ground to more than 80 % minus 100 mesh sieve so that it may have a fair proportion of free valuable mineral particles in processing operation.

Table-3: Mesh of liberation of stibnite (Sample 1).

Size Fractions (BSS)	Free Stibnite Grains (%)	Locked Stibnite Grains (%)	Free Gangue Grains (%)	Stibnite Liberation (%)
+30	22.58	27.61	49.81	45.00
-30+50	28.39	16.05	55.56	63.88
-50+70	32.23	8.95	58.82	78.82
-70+100	33.15	5.56	61.29	86.00
-100+150	38.45	1.95	59.06	95.17
-150	40.36	1.02	58.62	97.54

Since gravity methods operate by virtue of differences in density of minerals, the greater the difference in density between the minerals, the more easily they can be separated. Generally, a density difference of more than 2.5 is required for reasonable separation [5]. In this ore, the differences in density of stibnite (sp. gr. = 4.6) and quartz (sp. gr. = 2.6) was found to be 2.0 which is still sufficient for beneficiation by gravity method. But gravity methods work satisfactorily only when the liberation of ore minerals from gangue minerals takes place at coarser size. Because at finer size the density difference of valuable and gangue materials become less effective. Moreover in fine grained ores, the liberation of

valuable minerals from gangue materials require adequate grinding which results substantial losses of valuable minerals in fines produced during grinding, that wash away in tailings leading to severe losses in recovery [18]. As this ore was found to be fine-grained and liberation of stibnite from the host quartz requires adequate grinding therefore this ore is difficult to beneficiate by gravity concentration technique.

Experimental

Sample Preparation

A bulk sample of the ore weighing about 10 tonnes was obtained through the courtesy of Sarhad Development Authority (SDA). It consisted of lumps of various sizes ranging from 100-250 mm in size. About 100 Kg of the ore was collected for present study. Some of the ore was kept for mineralogical study while the remaining ore was comminuted by primary crushing using laboratory jaw crusher set at 20-25 mm and by secondary crushing using roll crusher set at 4-6 mm. A representative sample for chemical analysis and X-ray Diffraction studies was obtained by coning-quartering and riffing of the crushed ore. It was pulverized to 100 % - 200 mesh sieve (74 μm) with the help of disc pulverizer (Denver, USA). Another sample of a small vein in the vicinity of main veins was obtained and its sample was prepared by a similar technique.

Chemical Evaluation

Chemical analysis of bulk sample and hand picked sample were performed in accordance with ASTM and conventional methods of chemical analysis. Silica, Sulphur, Barium and Lead were determined gravimetrically [19-22]. While Antimony was determined by Spectrophotometer (Model: Spectronic-20) using Rhodamine-B [23]. Iron was determined by oxidation-reduction titration using standard solution of potassium dichromate [24]. Alumina and zinc were determined by complexometric titration using standard solution of EDTA [25-26]. Calcium and magnesium were estimated by atomic absorption spectrophotometer (Model: Z-8000, Hitachi, Japan) while sodium and potassium were determined by flame photometer (Model: PFP7, Jenway, England) [27-28]. Chemical analysis of the representative samples are given in Table-1.

Mineralogy

Ore microscope (Nikon, Japan) was used to study the nature of the ore [29]. The rock chips were cut out of the representative samples to the thickness of about 0.1 mm by means of diamond Thin Section Cut-Off Saw. These were then ground on a metal lap wheel to the thickness of about 0.02 mm utilizing progressively decreasing silicon carbide grit abrasives (Nos.120, 240, 320, 400 and 600) followed by final polishing on cloth laps using 7, 3 and 1 micron diamond pastes. The thin rock chips were glued to glass slide with one or two drops of Canada balsam. After grinding down to final thickness (0.03mm), these were covered with cover slip and examined under the ore microscope. The photomicrographs of representative samples are given in Figs. 1-6.

X-ray Diffractometry

The representative ore sample (100 % - 200 mesh size) was run on X-ray Diffractometer (Model: D-5000, Siemens, Germany) to identify the various types of minerals present in the ore. It has an X-ray tube consisting of a copper target which produces ($\text{CuK}\alpha$) radiations of wave length of 1.5406 \AA . The beam of monochromatic X-rays was allowed to fall on finely ground ore sample. X-ray diffraction was done at 0.02 step size per second. Scan angle was ranged from 0-60° to obtain the main peaks of the minerals present in the ore. The spectrum obtained was matched with standard data to identify the mineral phases. X-ray diffractogram of the ore is given in Fig. 7.

Degree of Liberation

Liberation was measured by grain mounts using ore microscope [4]. The product of roll crusher was ground in rod mill (Denver, USA) for 15 minutes and subjected to sieve shaker (International Combustion, England) for separating into number of size fractions using different sieves. The fractions obtained on sieves were analyzed under the ore microscope for measuring the degree of liberation of mineral grains of interest by particles counting method. Grain counting was performed at a magnification of 200 \times . The number of liberated and locked mineral grains in each sieve fraction were noted and the percentage liberation at various size fractions was calculated. The size fractions for counting in the microscope were prepared by placing

a small amount of sample in one or two drops glycerin on a glass slide and covering with a cover slip. About 100 particles were counted for each slide.

Conclusions

1. On the basis of present investigation, it is concluded that antimony ore of Krinj area of Chitral comprises mainly quartz and stibnite as major minerals while pyrite, boulangerite, calcite, sphalerite, barite and clays are minor minerals. Antimony bearing minerals are stibnite and boulangerite while the remaining are associated gangue minerals.
2. Microscopic examination of thin sections of the ore reveals that it is fine-grained in texture and mineral phases are finely disseminated and homogeneously distributed in the host quartz.
3. The distribution of free and locked stibnite grains for each size fraction of the ore shows that it should be ground to more than 80 % minus 100 mesh size to have an economic degree of liberation.
4. Mineralogical and textural observations of the ore indicate that the froth flotation is the most suitable technique for its up-gradation. Gravity concentration technique can not be applied to upgrade this ore of finely disseminated grain texture.
5. On the basis of the findings of this study, it is recommended that lab-scale work should be undertaken in order to develop a suitable froth flotation process and then establish pilot plant parameters for studying the economic feasibility of ore enrichment and metal extraction.

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