〒Fundamental Study on Processing of Tin Ore of the Huanuni Ore Deposit,Bolivia(ボリビア国ワヌニ鉱床の錫鉱石処理に関する基礎的研究)〒

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論文内容要旨

CHAPTER 1 INTRODUCTION

Bolivia is one of the leading metallic producers in the world. Presently tin represents about 70% total metal exprorts and 40% of total income of the Bolivian economy.

The Huanuni is one of the most productive tin mines in Bolivia, however due to the extraction of enriched ores in the past, it became as an impoverished deposit, which are increasingly difficult in regards to beneficiation. The ore is composed of cassiterite, being intimately associated with quartz, tourmaline and rutile.

The aim of the present study is to develop and utilize the low grade ore. It was based on the examination of the mineralogical characters such as grain sizes, textures and associations of minerals to determine the forming conditions of the ore deposit; the optimal liberation degree of cassiterite to reduce its overgrinding, thus the cost of comminution which is very expensive in lode mining; and to establish the optimum operational conditions of ore processing methods to design an adequate flow sheet for this mine. The ore processing methods such as gravity, magnetic and electrostatic separations, and flotation, have been applied in close connection with the mineral behaviors, forming condition and liberation properties of the ore.

CHAPTER 2 GEOLOGY AND ORE DEPOSIT

The Huanuni mine area is characterized by deep valleys striking to NE-SW. The rivers show dendritic and crossed drainages in interbeddings between competent and incompetent rocks.

The rocks in the vicinity of the mine are aged as the Silurian. They are partially covered by Tertiary lava flows. The most receptive host rock of mineralization is the LLallagua formati on, which is composed of quartzite and slate.

The rock fracturing corresponds to thrust type and it is closely related to the time of mineralization. The minerals are generally fine due to the super saturation of the ore farming fluid, and they show frequentry some ductile deformation due to the tectonism that affected the whole area.

The ore of the Huanuni mine is composed of cassiterite as the economic mineral, being associated mainly with quartz, tourmaline, rutile and pyrite. Other minerals are pyrrhotite, sphalerite, galena, stannite, chalcopyrite, marcasite, siderite, etc.

The sequence of mineralization can be divided into four phases.

The first phase as the initial growth stage of the veins is represented by cassiterite, which appears associated with quartz, tourmaline, pyrite and rutile.

The second phase is marked by the deposition of arsenopyrite and pyrrhotite.

The third phase is represented by stannite, sphalerite and chalcopyrite, which from complex intergrowths and associations.

The forth phase is composed principally of clay minerals as of the group of kaolinite; carbonates and phosphates. They were probably formed by an alteration process, however, the distinction between late hypogene and supergene deposition of ores is still not well defined in this mine. The types of alteration were discriminated as silicification, sericitization and advanced argillic alteration.

CHAPTER 3 FLUID INCLUSION STUDY

Fluid inclusions contained in quartz and in cassiterite may provide clues for interpreting the forming conditions of the Huanuni ore deposit. There minerals show abundant healed cracks, which are generally outlined by secondary fluid inclusions. Primary inclusions were indentified by their solitary location and alignment along visible group planes. Secondary inclusions were indentified as those occurring in close proximity along healed cracks and showing a varied gas /liquid ratios; these inclusions also showed extremely varied degrees of filling temperatures though narrow range of salinities. Such occurrence suggest that they were formed in a short ti me and were originated by necking down process or boiling of the fluids. Under boiling conditions those inclusions would trapped the liquid phase and the gaseous phase in various ratios. Other evidences that may support the origin of those inclusions by boiling, are based on the

presence of a colloidal texture in pyrite, and on the results obtained of an experiment in which synthetic fluid inclusions were formed under boiling condition. They occurred along cracks, in close proximity and showing a variety of gas/liquid ratios.

Thus, it may be concluded that the ore forming fluid responsible for the Huanuni ore deposit was mainly affected by boiling, which could favored the ore formation under conditions of super saturation.

Results of measurements of filling and freezing temperatures showed that the forming temperatures were about 350℃ in the early vein stage and 100℃ in the waning stages of the mineralization, and fluid salinities ranged from 12 wt% NaCl equivalent to pure water.

CHAPTER 4 MINERAL LIBERATION STUDY

Liberation is usually achieved by grinding the rock into small particles. In lode mining, which processes large amounts of mineral ores, the achievement of optimum liberation of valuable minerals is indispensable and since comminution is an expensive operation, great attention should be paid to the subject when the ores are investigated from an economic point of view. In the present study, the economic liberation size was determined though characterizations of grain sizes, types of intergrowth, composition of grains and amounts from composite minerals of the raw ore.

The raw material used in this study, as well as for the ore processing, was collected from the feed to the ball mill at the beneficiation plant of the Huanuni mine. It was composed of particles of about 10 mm in size.

The applied methods were heavy liquid separation and ore microscopy. X-ray diffraction and chmical analysis by ICP were used as complementaly techniques. The degree of liberation was determined by systematic particle counting on polished sections mounted in resin.

The density spectrum obtained for the ore showed two distinct fraction groups, one of + 3.20 g/cm^3 and the other of −2.90 g/cm^3, with lack of intermediate density fractions between them. The heavy group was composed mainly of sulfides-cassiterite, while the light group of quartz and clay. Thus, densities of about 3 would be considered as guide condition of separation of sulfides-cassiterite rich from quatz-clay fractions. Although many particles of cassiterite in −100 + 200 mesh fractions still contained inclusions of tourmaline, pyrite, pyrrhotite and rutile (3 μm to 15 μm in size), the liberation degree of cassiterite obtained in those fractions, that is about 70%, may be considered as metallurgically effective.

CHAPTER 5 ORE PROCESSING

In this study, gravity concentration, magnetic and electrostatic separations, and flotation have been carried out to find economical and adequate mineral processing flow sheet. Average

tin content in run-off-mine is approx. 1.5% Sn. Cassiterite is mid-fine grained with grain size of about 10^{-1} mm.

The raw material was first comminuted using cone crusher, roll crusher and ball mill, and then sieved.

Magnetic Separation. The magnetic separation was not tested to date in ores from the Huanuni mine. In this study, it was applied to investigate the magnetic properties of minerals in the ore, and to find the optimal conditions of separation of magnetic minerals from cassiterite. The magnetic separation was performed using a hand magnet and dry high intensity separator in particles size −100 +150 meth. Magnetizations and the thermo-magnetic characteristics were measured by means of magnetic balance. The magnetic fields used in high intensity magnetic separation ranged from 3.5 to 17 KOe. This separation was useful to remove feebly magnetic minerals such as pyrrhotite, siderite and hematite from diamagnetic such as cassiterite, sphalerite, quartz, tourmaline and clay minerals.

Electrostatic Separation. To date, there is a lack of investigation on the electrostatic separation of cassiterite from quartz-sulfide ores. In this study the electrostatic separation was applied to ascertain the optimum separation condition of cassiterite and the observance of mineral behavior in separated products. The separator utilized was the static field roll type. Two electrodes were used, tube and corona. The optimum condition of electrostatic separation for ores of the Huanuni mine in particles size −100 +150 mesh, was found under an electric fields of 30 kv. Such electric field was applied in tests of fractions with a varied particles size, ranging from −10 mesh to + 325 mesh. The highest tin grades and recoveries were shown by fractions of particles size −48 +65 mesh. Therefore, electrostatic separation would be an effective method in the processing of coarse particles. If applicable, it may be useful to reduce the overgrinding of cassiterite amd to reject a great amount of tails.

Gravity Concentration. The property in which cassiterite differs most widely from the bulk of other associated substances is its density (7 g/cm^3). For this reason, cassiterite processing operations have been based on gravity concentration. In this study the gravity separation was carried out by means of "Wilfley type" shaking table. Tests were carried out in four size fractions ranging from −48 to +200 mesh. Recoveries of tin and iron in finest fractions, −100 +200 mesh, were of about 60% and 10%, respectively. Grades of tin and iron in such particles size were about 25% Sn and 22% Fe, which are considered as operationally effective.

Flotation. In this study the flotation experiment was carried out by means of a laboratory flotation cell in fine particles, −200 +325 and −325 mesh fractions, using k octyl hydroxamate as a collector of cassiterite. Tests on particles size −325 mesh included the use of water glass as a depressant reagent. Flotation tests were carried out to establish an optimum reagent consumption, reagent addition and tin recoveries. The optimal condition of cassiterite

flotation was found at a concentration of 100 g／t of k octyl hydroxamate and at pH of about 5.85, with a small addition of k octyl hydroxamate during the process. The results of flotations on particles −325 mesh have shown tin grades of about 20% and recoveries of about 70%, which are considered as satisfactory, regarding that the fractions tested correspond to particles directly ground flom the raw ore, without a previous treatment.

CGAPTER 6 GENERAL CONCLUSIONS

1. The Ore of the Huanuni ore deposit consists of cassiterite as the economic mineral, being associated mainly with quartz, tourmaline, rutile and pyrite.
2. The mineral sequence in Huanuni mine was divided into four phases.

   The first phase was composed of: cassiterite, quartz, rutile and pyrite.

   The second phase: arsenopyrite, bismuthinite, pyrrhotite, marcasite.

   The third phase: galena, sphalerite, stannite, chalcopyrite.

   The fourth phase: siderite, gibbsite, crandallite, kaolin.
3. The diffent gas／liquid ratios of fluid inclusions, and the colloidal texture in pyrite suggest a boiling of the forming fluid. Boiling, that had probably operated throughout the mineralization, may be also responsible of the fine grain mineration which could be deposited under conditions of super saturation.
4. The density spectrum showed two fractions of different densities. One fraction was of densities +3.20 g／cm³ and the other of −2.90 g／cm³.

   The former one was composed of cassiterite and sulfides rich, and the latter of quartz and clay. Therefore, it mey be concluded that densities of about 3 can be considered as guide condition for the separation of those fractions.
5. The mineral liberation study revealed that the liberation degree in particles size −100 +200 mesh was of about 70%, which is considered as metallurgically effective, though many particles in that fraction contained small inclusions (3 μm to 15 μm) of other minerals.
6. The magnetic separation products were classified as ferromagnetic, paramagnetic and diamagnetic. The ferromagnetic mineral was pyrrhotite, the paramagnetic were siderite, pyrite and marcasite, and the diamagnetics cassiterite and quartz. The optimum condition of the magnetic separation for particles size −100+150 mesh was established under a magnetic field of 15.5 KOe.
7. The optimal electric field found in electrostatic separation tests was 30 kv, and the optimum particles size was of −48 +65 mesh. The electrostatic separation was also effective to reduce the overgrinding of cassiterite, by rejecting about 75% of the ground ore fed to the separator, as tails.
8. The shaking table operation reported high grades and recoveries in particles size −100 +200

mesh. The results are coincident with those obtained in the mineral liberation study.

9. The optimum condition in cassiterite flotation tests was established at a concentration of 100g／t of k octyl hydroxamate. Flotation of particles size −325 mesh showed relatively high tin grade but low tin recovery with respect to flotation of particles −200 +325 mesh in size, due probably to the coagulation of the former particles during the process, thus a previous desliming of the ore fed to flotation is recommended.

10. The final product obtained in laboratory scale ore dressing system was:

Weight of concentrate (%)= 2.01

Tin grade (%)= 48.54

Tin recovery (%)= 76.23

Iron grade (%)= 10.57

Iron recovery (%)= 4.26

審 査 結 果 の 要 旨

世界有数し錫資源保有国であるボリビアの錫鉱床は，大部分が熱水鉱床に属し，その鉱石は，微細な鉱物が共生しているため，通常の処理方式では効率よく錫精鉱を回収することができない。本論文は，ボリビアの代表的な錫鉱床であるワヌニ鉱床を研究対象とし，鉱床の生成環境，鉱石組織，鉱物の共生関係などを明らかにして，これらの鉱物学的特徴と各種処理技術の適用性との関係にいて検討し，新しい処理方式を提案したもので，全編6章よりなる。

第1章は緒論である。

第2章では，ワヌニ鉱床の賦存状態および鉱石の鉱物学的特徴について述べている。鉱石は，主に錫石，黄鉄鉱，磁硫鉄鉱，石英，電気石からなり，その他多種の金属硫化物鉱物，珪酸塩鉱物，炭酸塩鉱物などを伴い，複雑な共生組織を呈すること，錫石は初期に晶出したものであることを明らかにしている。

第3章では，石英および錫石中の流体包有物の研究結果から，鉱化熱水の初期の温度は350℃前後で，しばしば沸騰状態にあり，このような過飽和の程度の大きい鉱化熱水から鉱物の急速な沈殿が生じたため，微細で複雑な組織の鉱石が形成されたことを明らかにしている。これは重要な知見である。

第4章では，砕け易い錫石をできるだけ大きい粒度で単体とし，以後の分離を容易にするために，粉砕産物を粒度別，比重別に区分して鉱物の構成と割合を検討している。各区分の錫品位，鉱石と異種鉱物との共生状態の解析などから，約100 μm が経済的な分離に適当な大きさであることを見いだし，さらにこれより粗粒の段階でも選別方法によっては脈石を除去して，粉砕工程を軽減できることを明らかにしている。

第5章では，種々の選鉱法による錫石と他の鉱物との分離性を粒度別に検討し，分離性と粒度，単体分離粒度ならびに分離条件との関係を明らかにしている。その結果，静電選鉱法により比較的粗い粒度において，錫石をほとんど損失することなく，かなりの量の脈石を廃棄できることを見いだし，微細組織の複雑錫鉱石に対して静電選鉱法を導入し，これにテーブル選鉱，浮選法及び磁選法を組み合わせた新しい処理方式を提案している。これは重要な成果である。

以上要するに本論文は，熱水鉱床産錫鉱石の鉱物学的特徴を明らかにして，複雑な共生組織を有する難処理鉱から，効率よく錫鉱物を分離回収するための新しい処理方式を提案したもので，資源工学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。