Occurrence of Sesquioxide in a Mid-Low Grade Collophane-Sedimentary Apatite Ore from Guizhou, China

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Abstract: Checking the presence of sesquioxide (Fe$_2$O$_3$, Al$_2$O$_3$) is helpful for its removal in advance. Therefore, the occurrence of sesquioxide in a mid-low grade calcareous-siliceous collophane ore (massive carbonate-apatite, also known as francolite) from Guizhou, China was determined by X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), field emission scanning electron microscope-energy dispersive X-ray spectrometry (FESEM-EDX) and Mineral Liberation Analyzer (MLA). The results show that iron mainly occurs as pyrite Fe$_2$S$_2$, goethite FeO(OH) and as substitution within dolomite Ca(Mg,Fe)(CO$_3$)$_2$, while aluminum is enriched in muscovite KAl$_2$(AlSi$_3$O$_10$)(OH)$_2$ and also found in apatite (F,CO$_3$)CaPO$_4$ and calcite CaCO$_3$ due to isomorphism or adsorption. All these minerals are fine-grained, among which pyrite and goethite tend to be enriched in larger particles. Intergrowth is predominant in the six minerals’ locking. Pyrite is mainly intergrown with calcite, biotite and also included in apatite and muscovite, while the monomer pyrite appears as semi-automorphic fine grain with the liberation of 56.1%. Apatite particles are mainly intergrown with quartz and calcite. Most of goethite, dolomite, muscovite and calcite form intergrowth with apatite, with contents of 21.7%, 11.1%, 19.5% and 41%, respectively. The removal of pyrite, goethite, dolomite, muscovite and calcite in the ore is the key to reduce the contents of Fe$_2$O$_3$ and Al$_2$O$_3$. In the subsequent beneficiation, the ore must be fully ground. In addition to flotation, magnetic separation can also be considered to remove part of iron in ore. For the removal of aluminum from apatite, leaching method can be considered.

Keywords: mid-low grade collophane ore; iron; aluminum; sesquioxide; occurrence

1. Introduction

Phosphate ore is an essential raw material for manufacturing phosphoric industrial products, which is nonrenewable, nonrecyclable and irreplaceable. The world’s phosphate reserves in 2019 are 70 billion tons. Morocco has the largest phosphate reserves, which are 50 billion tons accounting for 71.43% of the total. China, Morocco, the United States and Russia are the leading phosphate
producing countries with a proportion of 79% [1]. According to mineralization, phosphate ore can be divided into three major types: igneous deposits, sedimentary deposits and biological deposits (guano accumulations). About 75% of phosphate resources are sedimentary [2].

The common gangue minerals (impurities) in phosphate rock include silicate minerals (quartz, mica), carbonate minerals (calcite, dolomite) and clay [3]. Most of phosphate rock in the world cannot be directly used in the production of phosphorus products, it must be through mineral processing to obtain economic utilization [4]. Due to the complex metallogenic environment, there are variable amounts of carbonates (calcite or dolomite) and silicates in sedimentary phosphate rock [5]. This makes it difficult to beneficiate from carbonate rich sedimentary phosphate deposits [6]. At present, phosphate ore processing can be different simple or complex combinations of the following processes: crushing, grinding, screening, scrubbing and desliming, heavy medium separation, washing, roasting, calcination and flotation [4,5]. Among these processes, flotation is the most widely used method and more than 60% of the commercial phosphate in the world is produced by flotation [2,7]. Before flotation, phosphate ores are usually subjected to other processes such as scrubbing and desliming, screening or classification. Scrubbing and desliming techniques are used to remove silicates (clays) [5]. Separating carbonate minerals from phosphates by flotation can be an ineffective process due to their similar physicochemical properties [5,8]. Calcination is an effective method to separate carbonate and phosphate minerals. During calcination, carbonates decompose to form free calcium and magnesium oxides, which can be removed by washing or slaking the thermally treated ore [9–11]. Tiit Kaljuvee et al. [12] studied the possibility of calcination-separation enrichment of carbonate-phosphorite ores from Karatau area. The content of P₂O₅ in carbonate phosphate ores increased from 21–23% to more than 28% and the recovery of P₂O₅ was not less than 85% by calcining phosphate ores in fluidized bed kiln, grinding the calcinated ores in a centrifugal impact mill and classifying the ground material in a non-rotary air separator. However, calcination is used for ores with low or average carbonate content and there are some problems in this method, such as low efficiency, high cost, excessive water consumption and extensive stages of grinding, washing, classification and so forth [5,12].

Phosphate ores also contain other metal impurities, such as iron, aluminum, titanium, manganese and even rare earth elements (such as La, Ce, Nd) in addition to the gangue minerals like silicates and carbonates [18]. The metal concentration in phosphate rock varies with origin, such that igneous rocks have lower concentrations whereas sedimentary rocks have higher concentrations [19]. Iron and aluminum are common impurity elements, which mainly exist in sedimentary phosphate ore as independent minerals and isomorphism. In nature, the major independent iron minerals include magnetite, hematite, limonite, pyrite, siderite and so forth, while aluminum minerals mainly involve diaspare, boehmite and gibbsite. These iron and aluminum minerals are often regarded as associated minerals of phosphate ores. Moreover, iron and aluminum can also be hosted in gangue minerals in the form of isomorphism, such as iron dolomite formed when Fe²⁺ is more than Mg²⁺, fayalite, aluminosilicate minerals (like feldspar and mica). The contamination of iron emanating from limonite in phosphate concentrates has been a problem in phosphate ore flotation. The reason is that being similar floatability, limonite easily turns into flotation concentrates, then reducing the grade of concentrates. Therefore, increasing the surface hydrophilic of limonite to avoid the adhesion of air bubbles is one critical process in this separation process [20]. For high-iron phosphate ores, starch and its derivatives are usually used as depressant to depress the iron minerals in hematite based iron beneficiation [21,22]. However, flotation practice indicates that their separation effect is not ideal in the treatment of high-limonite phosphate ores with complex nature and fine dissemination [20]. Meanwhile, guar gum is extensively applied in the process of many oxides ores acting as depressant of iron oxide.
minerals [23]. However, the high cost limits the application of guar gum in industrial flotation [24]. In view of this problem, Jun Yu et al. [20] studied the depression effect of sodium lignosulfonate on limonite in high iron collophane flotation, so as to improve the separation efficiency of collophane and limonite. The results showed that sodium lignosulfonate displayed a good depression effect toward limonite but had little depression effect on collophane flotation.

Iron and aluminum elements not only have an impact on phosphate ores beneficiation but also influence the subsequent phosphorus chemical production. Generally, the oxides of iron and aluminum are collectively referred to as sesquioxides (expressed as $R_2O_3$, $Fe_2O_3 + Al_2O_3$) [25]. The sesquioxide makes difficult the production process of phosphoric acid and phosphate fertilizer and degrading the quality of products. When $R_2O_3$ in phosphate ore is introduced into the system of phosphoric acid production, the consumption of sulfuric acid increases significantly, the growth of calcium sulfate crystal is interfered and phosphoric acid can be converted to sludge, resulting in a great loss of $P_2O_5$. In addition, iron and aluminum can form fine-crystal complexes with phosphate, which increases the viscosity of solution and slurry, easily blocks the pores of filter cloth and cake and also causes a difficulty to concentrate and dry phosphoric acid, which leads to undesirable quality of products [25, 26]. Therefore, there are strict restrictions on the contents of iron and aluminum minerals in phosphate concentrate. For instance, $Fe_2O_3/P_2O_5$ in concentrate is required to be less than 8% in the production of calcium superphosphate or phosphoric acid [27]. Thus, in order to obtain high-quality phosphate concentrate, the removal of sesquioxide from phosphate ore is necessary except the traditional de-magnesium and de-silicon, which requires more rational and effective beneficiation process and may increase the difficulty and cost of beneficiation.

Guizhou Province has abundant phosphate resources and the identified reserves rank the second in China [27]. Most of phosphate ore in Guizhou are marine sedimentary deposits, which is of various types, rich in small shelled animal fossils and algae and associated with other available resources such as rare earth elements, uranium [28–30]. Wu et al. [31] classified phosphate ore in Guizhou into 12 basic types through detailed study and investigation (Table 1). With the continuous depletion of phosphate ore, phosphate resources in the whole province are facing dilution problem. A great quantity of low-grade collophane (carbonate-rich fluorapatite) ore have become the main mining and utilization objects.

| Texture Type | Ore Type | Origin |
|--------------|----------|--------|
| Arenaceous   |          |        |
| Granular     |          |        |
| Massive      | Massive arenaceous phosphorite | Abnormal chemical conditions |
| Laminated    | Laminated arenaceous phosphorite | |
| Striped/banded | Striped/banded (dolomitic or clayey) arenaceous phosphorite | |
| Detrital     | Gravel phosphorite | |
| Oolitic      | Brecciated detrital phosphorite | |
| Coagulum     | Oolitic phosphorite | |
| Agglomerate  | Agglomerated arenaceous phosphorite | |
| Gelatinous   | Gel layered phosphorite | Authigene |
| Biogenetic   |          |        |
| Stromatolite | Cylindric stromatolite phosphorite | Biological |
| Algae        | Algal arenaceous phosphorite | |
| Shell        | Bioclastic (containing small shell fossils) arenaceous phosphorite | |

Table 1. Classification of phosphorite in Guizhou according to Wu et al. [31].
Checking the occurrence accurately and comprehensively is an important step in sesquioxide removal from collophane ore. This can provide theoretical basis for beneficiation process selection and optimization index control and is of great significance for the effective utilization of phosphate resources. However, most of the current works are about the removal of silicon and magnesium from Guizhou phosphate rock and the research on sesquioxide in Guizhou phosphate rock has not been done on industrial scale. In this study, X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), field emission scanning electron microscope-energy dispersive X-ray spectrometry (FESEM-EDX) and Mineral Liberation Analyzer (MLA) were used to characterize a collophane ore in Guizhou. Therefore, the main objective of this work is to determine the mineral species, particle size distribution and embedded characteristics of sesquioxide ($R_2O_3$) in collophane.

2. Materials and Methods

2.1. Site Description

The sample for this study was collected from Kaiyang phosphate mining area located in Jinzhong Town, 86 km north of Guiyang City, Guizhou Province, 29 km away from Kaiyang County [32]. It starts from Wenquan Town in the north and ends at Yongshaba Town in the south. This mining area is famous for its large output and high grade (the average grade of $P_2O_5$ is 33.32%) [33]. And it is composed of six sections, namely, Maluping, Niuanchong, Yongshaba, Jile, Liangchahe and Shabatu [34]. The potential in this area is high in the south and low in the north. The elevation of the highest point is 1713 m and the lowest point is at the junction of Yangshui river and Liangchahe river, with an elevation of 722 m. The basin terrain in the area is ridge valley with width of about 3–5 km. The ridges on both sides of the valley face each other. In the valley, the mountains are high and steep with relative elevation difference of 300–500 m and the gullies are developed, of which the density reaches 1.4 km/km². The terrain gradient is steep, generally 30–50° [32]. Kaiyang phosphate deposit is located on the Yangshui anticline which is asymmetric and the axis of the anticline is 25° NE, the dip angle of the east side is 25–45° and the west side is 45–75°. The specific situation of Kaiyang phosphate mining area is shown in Figure 1 [33].

Figure 1. Map of Kaiyang phosphate mining area in Guizhou Province, China [33]
2.2. Sampling

The ore sample was collected from No. 3 ore heap and the sampling point was about 1 m away from the bottom of the ore heap. The collophane ore sample (about 500 kg) was first crushed to about 1 mm particle size by jaw crusher (model PEW760, Shanghai Shibang Machine (SBM) Group, Shanghai, China) -cone crusher (model HPC300-F2, Zhengzhou Great Wall Heavy Industry Machinery Co. Ltd., Zhengzhou, China) -roller mill (model MPG-ϕ200 × 75, Wuhan Exploring Machinery Factory, Wuhan, China). The samples within 1 mm particle size were divided by the sample splitter (model XSHF2-3, Wuhan Exploring Machinery Factory, China). The grinding of the divided subsamples was done in a laboratory bar mill (model HLXMB-ϕ240 × 300, Wuhan Hengle Mineral Engineering Machinery Co. Ltd., Wuhan, China) to ensure that the particle size of 90% of the subsamples was less than 0.075 mm and then a certain amount of representative samples were reduced. The ore sample for analysis was taken by spinning sample rifflers (model XSHF2-3, Wuhan Exploring Machinery Factory, Wuhan, China) and dried put into for use.

2.3. Methods of Characterization

Semiquantitative analysis was performed by X-ray fluorescence (XRF) (model Bruker S4 PIONEER, Bruker Corporation, Mannheim, Germany) with a rhodium anode tube, to check the contents of major constituents and trace elements in the sample. The mineral phase composition was identified by X-ray diffraction (XRD) (model Bruker D8 ADVANCE, Bruker Corporation, Mannheim, Germany). The analysis conditions as following: starting and ending angles are 3.000° and 70.008° with a step in angle 0.004°, scanning rate of 2.000° and CuKα1 radiation. A field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectrometry (EDX) detector (model ZEISS GeminiSEM 300, Carl Zeiss AG, Jena, Germany) was used to determine the element distribution on the collophane ore surface. The accelerating voltage was 10 kV. Mineralogy was carried out with Mineral Liberation Analyzer (MLA). The MLA includes a FEI Quanta 650 SEM (FEI Company, Hillsboro, OR, USA) equipped with two Bruker Quantax 200 X-Flash 5010 EDX detectors (Bruker Corporation, Mannheim, Germany) and FEI’s MLA Suite 3.1.4 for automated data acquisition. In order to analyze the loose solid material, it was mounted in an epoxy block and 3 g of the material were mixed with graphite and epoxy resin. Resulting sample block (30 mm in diameter) was ground and polished. The polished sample block was carbon coated using a Leica MED 020 vacuum evaporator (Leica, Wetzlar, Germany) to ensure conductivity of the sample surface.

3. Results

3.1. Properties of Collophane Ore

The chemical and mineralogical composition of the collophane ore are shown in Tables 2 and 3, Figure 2 gives the XRD phase analysis result of the collophane ore and Figure 3 shows the dissemination characteristics of some main mineral particles. The grade of P$_2$O$_5$ is 25.94%, which accords with the characteristic of typical mid-low grade phosphate ore. ω(CaO)/ω(P$_2$O$_5$) is about 1.48 (>1.4) and the content of SiO$_2$ is relatively high, which is 17.14%. All of these indicate that the sample is mid-low grade calcareous-siliceous collophane ore. The content of sesquioxide (Fe$_2$O$_3$, Al$_2$O$_3$) is 7.443%. It can be seen from Table 3 and Figure 2 that mineralogical composition of the ore is complex. Apatite as phosphate mineral is the main useful mineral with a content of 68.42%. Gangue minerals include silicate minerals (quartz, anorthite, muscovite, hornblende, etc.), carbonate minerals (calcite, dolomite) and other traces of orthoclase, kaolinite, pyrite, goethite, barite, biotite and so forth. Quartz, calcite and dolomite make up the most of gangue minerals. It can be seen from Figure 3 that most of apatite present in the shape of hypidiomorphic granular, dense block or strip structure, which is unevenly distributed in gangue minerals. It is also found that the larger apatite particle includes smaller irregular gangue minerals such as hornblende. In addition, some strip apatite and quartz form shell-like intergrowth. Pyrite is mainly scattered in the matrix in irregular granular or clastic granular structure and a small
amount of pyrite is embedded with apatite or other gangue minerals. Due to the low content of magnesium in ore, the main task of flotation is to remove silicon and sesquioxide.

Table 2. Chemical composition of Guizhou collophane ore.

| Component | Content (wt.%) |
|-----------|----------------|
| P\textsubscript{2}O\textsubscript{5} | 25.94          |
| CaO       | 38.45          |
| MgO       | 1.96           |
| SiO\textsubscript{2} | 17.14          |
| Fe\textsubscript{2}O\textsubscript{3} | 1.283          |
| Al\textsubscript{2}O\textsubscript{3} | 6.16           |
| Na\textsubscript{2}O | 0.203          |
| K\textsubscript{2}O | 1.41           |
| MgO       | 1.96           |
| MnO       | 0.0825         |
| SO\textsubscript{3} | 1.56           |
| TiO\textsubscript{2} | 0.269          |
| CuO       | 0.0215         |
| ZnO       | 0.0395         |
| Fe\textsubscript{2}O\textsubscript{3} | 0.015          |
| Rb\textsubscript{2}O | 0.001          |
| BaO       | 0.498          |
| SrO       | 0.083          |
| ZrO\textsubscript{2} | 0.0113         |
| F         | 2.54           |

Table 3. Mineralogical composition of Guizhou collophane ore.

| Mineral             | Content (wt.%) |
|---------------------|----------------|
| Apatite             | 68.42          |
| Orthoclase          | 0.29           |
| Quartz              | 8.41           |
| Kaolinite           | 0.47           |
| Anorthite           | 2.87           |
| Pyrite              | 0.99           |
| Hornblende          | 1.77           |
| Calcite             | 8.32           |
| Goethite            | 0.28           |
| Chlorite            | 0.02           |
| Augite              | 0.05           |
| Albite              | 0.06           |
| Dolomite            | 4.55           |

Figure 2. X-ray diffraction (XRD) phase analysis of Guizhou collophane ore.
Figure 3. Dissemination characteristics of main mineral particles: (a) Apatite mineral; (b) Hornblende was included by apatite; (c) Apatite was included by quartz; (d) Pyrite mineral.

3.2. Distribution of Fe and Al in Collophane Ore

The distribution of Fe and Al in collophane ore are given in Tables 4 and 5. The EDX mapping analysis of collophane ore and pyrite is shown in Figures 4–7. Fe and Al are basically found in gangue minerals. Fe is relatively enriched in pyrite FeS$_2$ and goethite FeO(OH) as independent minerals and also hosted in dolomite Ca(Mg, Fe)(CO$_3$)$_2$ in the form of isomorphism, having proportions of 50.1%, 13.9%, and 16%, respectively. Al mainly occurs as a component element within muscovite KAl$_2$(AlSi$_3$O$_{10}$)(OH)$_2$ and is also found in apatite and calcite in the form of isomorphism or adsorption, which account for 24.9%, 19.7%, and 19.1%, respectively. The EDX elements mapping results of collophane ore show that the distribution of Fe, S, Mg and Ca is consistent, especially Fe and S, which indicates that Fe exists in pyrite and dolomite as FeS$_2$ or Ca(Mg, Fe)(CO$_3$)$_2$; Si and Al have the same distribution characteristics, indicating that most of Al elements are held in silicate minerals. Further analysis of EDX elements mapping and spectrum of pyrite shows that in addition to the main elements S and Fe, there are also a small amount of Si, Al, Ca, Mg, P elements in the pyrite particles, which indicates that some pyrite particles are mixed with a small amount of aluminosilicate minerals and apatite.
Table 4. Distribution of Fe in collophane ore determined by Mineral Liberation Analyzer (MLA) *

| Mineral      | Content (wt.%) | Mineral      | Content (wt.%) |
|--------------|----------------|--------------|----------------|
| Kaolinite    | 1.40           | Dolomite     | 16.00          |
| Anorthite    | 5.56           | Biotite      | 2.79           |
| Pyrite       | 50.12          | Native iron  | 1.67           |
| Hornblende   | 2.55           | Fayalite     | 1.44           |
| Goethite     | 13.89          | (Ca, Fe) silicate | 1.00   |

*: Only minerals with more iron and aluminum are listed, which does not mean that the remaining minerals do not contain iron and aluminum.

Table 5. Distribution of Al in collophane ore determined by MLA *

| Mineral      | Content (wt.%) | Mineral      | Content (wt.%) |
|--------------|----------------|--------------|----------------|
| Apatite      | 19.65          | Hornblende   | 2.67           |
| Orthoclase   | 1.92           | Calcite      | 19.09          |
| Quartz       | 6.76           | Muscovite    | 24.90          |
| Kaolinite    | 5.23           | Biotite      | 3.33           |
| Anorthite    | 14.77          | Albite       | 0.46           |

*: As in Table 4, only minerals with more iron and aluminum are listed, which does not mean that the remaining minerals do not contain iron and aluminum.

Figure 4. Energy dispersive X-ray spectrometry (EDX) elements mapping of collophane ore.
Figure 5. EDX spectra of collophane ore.

Figure 6. EDX elements mapping of pyrite.
3.3. Grain Size Distribution of Main Fe, Al-Bearing Minerals

Checking the particle size of minerals is helpful to guide the crushing and grinding stages in mineral processing. When the mineral particles are fine and closely associated with each other, it may be regarded as a whole in the beneficiation operation, thus the ore must be fully crushed before it can be dissociated. In addition, the mineral particle size has an effect on the flotation process. Flotation requires not only sufficient liberation of minerals but also suitable particle size. If the ore particle is too coarse, exceeding the floating load capacity of the bubble, it will not float; if the ore particle is too fine, it is unfavorable to flotation. In order to figure out main Fe-bearing (pyrite, goethite, dolomite) and Al-bearing (apatite, muscovite, calcite) minerals distribution in different particle sizes, particle size analysis of several minerals was carried out. The results are shown in Figure 8. Pyrite, goethite and dolomite are all fine-grained with grain sizes within 75 μm. Among the three minerals, both of pyrite and goethite tend to be enriched in larger particles. When the sieve sizes of pyrite, goethite and dolomite are 53–63 μm, 27–32 μm and 38–45 μm, the mass fraction on sieve reaches the maximum, which are 16.3%, 15.6% and 11.6% respectively. The three minerals are mainly concentrated in 16–75 μm, 8.1–32 μm and 8.1–45 μm, accounting for 72.8%, 79.9% and 85.1% of the total respectively.

It can be seen from Figure 8 that the grain sizes of apatite, muscovite and calcite are also relatively small, which in the order of apatite > muscovite > calcite. When the sieve sizes of apatite, muscovite and calcite are 38–45 μm, 11.4–13.5 μm and 8.1–9.6 μm, the mass fraction on sieve is the largest, which are 9.1%, 12.8% and 26.1% respectively. The three minerals are enriched in 22–75 μm, 8.1–32 μm and 6.8–11.4 μm, which account for 60%, 77.1% and 58.4% of the total respectively. Since there are many fine particles in these single minerals, the grinding size must be fine enough to separate them from the useful mineral as much as possible.

Figure 7. EDX spectra of pyrite.
an effect on the flotation process. Flotation with apatite is significant, which is 41%.

According to Figure 9a, most of goethite forms intergrowth with apatite, the content of which is 19.5% and according to Figure 10c, the proportion of calcite intergrown with apatite is significant, which is 41%.

3.4. The Association between Main Fe, Al-Bearing Minerals and Other Minerals

The liberations of pyrite, goethite, dolomite, apatite, muscovite and calcite and their association with other minerals were determined by MLA. The results are given in Figures 9–11. In the figure, binary and tertiary or greater mean that the mineral studied is intergrown with and included by other minerals.

Pyrite is mainly intergrown with calcite, biotite, with contents of 5.1% and 5.4% respectively. The proportion of pyrite included in muscovite and apatite is also relatively large, which is 3.4% and 2.7% respectively (Figure 9a). According to Figure 9b, most of goethite forms intergrowth with apatite, with a content of 21.7%, followed by 8.4% of goethite with (Ca, Fe) silicate. From Figure 9c, it shows that dolomite is associated with apatite and calcite in a larger proportion, especially apatite, with a prominent proportion of 11.1%.

According to Figure 10a, apatite is mainly intergrown with quartz and calcite, with contents of 6.7% and 8.4% respectively. From Figure 10b, it shows that muscovite mainly forms intergrowth with apatite, the content of which is 19.5% and according to Figure 10c, the proportion of calcite intergrown with apatite is significant, which is 41%.
intergrown with apatite, which means that it is difficult to remove Fe and Al from collophane ore and the separation cost is high.

Figure 9. Intergrowth and inclusion contents between the Fe-bearing minerals and other minerals measured by MLA: (a) Pyrite; (b) Goethite; (c) Dolomite.

Figure 10. Intergrowth and inclusion contents between the Al-bearing minerals and other minerals measured by MLA: (a) Apatite; (b) Muscovite; (c) Calcite.

The purpose of ore separation is to effectively enrich and recover useful minerals and the liberation of minerals within the optional particle size range will directly affect the separation effect. Therefore, accurate prediction and determination of the liberation of iron and aluminum bearing minerals will further improve the beneficiation effect of collophane ore. In Figure 11, it can be seen that except for the liberation, intergrowth is predominant in the six minerals’ locking. Among them, calcite has the largest intergrown proportion, accounting for 48.2%, which is also the reason for the lowest liberation of calcite.
Moreover, the content of liberated goethite is also less, which indicates that grinding can only separate a small part of goethite from the ore and the majority must be removed by other means. The contents of liberated apatite and dolomite are relatively high in all the six minerals, which are 73.4% and 78% respectively. Combining Figures 9 and 10, it can be concluded that most of pyrite can be removed from grinding and flotation together with calcite and muscovite that contain aluminum. Although fine-grained goethite, dolomite, muscovite and calcite are slightly different in intergrown and included content with other minerals, they are mainly closely intergrown with apatite, which means that it is difficult to remove Fe and Al from collophane ore and the separation cost is high.

Figure 11. The total contents of each of the six minerals in the state of monomer liberation, intergrowth and inclusion.

4. Discussion

Obviously, the removal of pyrite, goethite, dolomite, muscovite and calcite in the ore is the key to reduce the contents of Fe₂O₃ and Al₂O₃.

Pyrite is an abundant mineral in nature with a chemical formula of FeS₂. It is usually associated with other sulfides (such as sulfide ores containing galena) and oxides [35,36]. Pyrite is rich in the earth’s surface and has been found in the composition of sedimentary and metamorphic rocks, in coal beds and as an alternative mineral in fossils [35]. Sedimentary pyrite generally forms by the reaction of detrital iron minerals with H₂S during the stage of shallow burial [37,38]. Under anoxic conditions, seawater sulfate is reduced to H₂S by bacteria, which reacts with detrital iron minerals and forms pyrite [39–41]. In modern sediments as well as in ancient Phanerozoic, Proterozoic and Archean sedimentary rocks, the dominant textural forms of pyrite are euhedral crystals and framboids [42,43]. Pyrite framboids are dense spherical aggregates, composed of submicron-sized pyrite crystals [43]. There are high crystallinity pyrites in the United States, Peru, China and Spain [35].

As an important mineral, pyrite can be used as a precursor of products, such as sulfur, sulfuric acid, hematite, sulfur dioxide, fertilizers and ferrous sulfate [35]. It has also been widely used in the preparation of smoke agents, rubber, paper, textiles, matches, cathodes for lithium batteries especially for semiconductor materials in the chemical industry [44–47]. Pyrite oxidation produces sulfuric acid and iron oxyhydroxides [48]. When Peter Kraal et al [48] investigated the phosphorus (P) and iron (Fe) fractionation in anoxic sediments, it was found that iron-bound phosphorus accounted for up to 99% of total phosphorus in carbonate-poor samples and its abundance was related to pyrite contents. The phosphorus fractionation in anoxic, carbonate-poor sediments is strongly affected by pyrite oxidation. Pyrite oxidation leads to a conversion of authigenic calcium-phosphorus to iron-bound phosphorus. In more calcareous samples, CaCO₃ can act as an effective buffer against acidic dissolution of Ca–P minerals.

Goethite (α–FeOOH) is a naturally occurring iron oxy-hydroxide mineral, which is a ubiquitous phase in many iron ore types and found in association with several types of mineral deposits including...
iron, manganese and bauxite ores. It is typically the weathering product of iron-bearing minerals formed though inorganic chemical or organic precipitation under oxidation conditions. It has different shapes, sizes and morphology. Goethite is basically composed of Fe, O and OH, distinguished and named according to the differences of the water content. Goethite may contain variable amounts of impurities, such as Al₂O₃, MnO, CaO and SiO₂, which sometimes up to 5% [49]. Goethite processing is difficult because it contains many harmful impurities and it is also the main component of many iron ore plant reject streams [50]. Depending on temperature and reduction conditions, goethite can be transformed to hematite, magnetite and other minerals suitable for magnetic separation [50]. Therefore, there are many studies on the treatment of goethite by reduction roasting followed by magnetic separation [50–53]. Sometimes, goethite contains a high content of phosphorus (P) and the existing phosphorus removal techniques is to thermally roasted the ore with or without alkaline additives followed by chemical or water leaching [54–57]. However, up to date, none of these proposed dephosphorization routes for goethite have been commercialized and current method of utilizing goethite ore in steelmaking remains to be blending with other low-P ore to balance out the overall phosphorus input to the blast furnace [58,59]. Therefore, bio-beneficiation dephosphorization of goethite ore has been studied as a relatively new approach [58]. Williams et al. [60] used some sulfide-oxidizing bacteria to reduce the pH value to \(<1\), in which apatite can selectively dissolve.

Muscovite \([K_2Al_4(SiAl)_2O_{10}(OH,F)]_4\) is typically formed by metamorphism of impure limestones and igneous rocks. It is a 2:1 layered phyllosilicate with an octahedral “O” layer sandwiched between two inward pointing tetrahedral “T” layers, forming “T-O-T” units. Muscovite usually exists in many ores as main gangue components [61,62]. It has a wide range of uses. Sheet mica is traditionally used as an electrical insulation material (such as mica paper), filler in the production of various putties, grout and paints and so forth. In addition, ultrafine muscovite can also be used to produce decorative coatings and cosmetics. The enrichment of muscovite-bearing materials can be carried out by traditional methods, such as gravity (spiral separation, concentration on tables), magnetic separation and flotation [63].

In apatite, the ability of anion to replace phosphate is not limited to \(F^−\), \(CO_3^{2−}\) and \(OH^−\), which exist in different variants of apatite. Silicate, vanadate, aluminate, titanate and arsenate may also occur replacing part of phosphates. The extent to which substitution happen and what the substitute is depend on the prevailing conditions during the formation of apatite and on the effect of subsequent events (such as weathering). In marine sedimentary deposits, phosphates occur in mixtures with detrital materials such as quartz, mica and clay, often with limestone and occasionally with dolomite [4]. For the impurity aluminum in apatite, different elements in the same mineral are difficult to be separated by flotation, so the leaching method can be considered. Dolomite (CaMg(CO₃)₂) and calcite (CaCO₃) are common gangue minerals in sedimentary phosphate ores. Fe substitution often occurs in dolomite. Due to the similar surface properties of dolomite, calcite and apatite, the flotation separation can be a difficult process. However, in this paper, calcite is closely associated with pyrite, so it may be removed along with pyrite to a large extent.

5. Conclusions

After the samples was analyzed by XRD, XRF, FESEM-EDX and MLA, the following conclusions can be drawn:

The collophane ore studied in this paper is mid-low grade calcareous-siliceous, in which apatite is the main useful mineral and quartz, dolomite and calcite make up the most of gangue minerals. The content of sesquioxide (Fe₂O₃, Al₂O₃) in the ore is 7.443%. Iron is relatively enriched in pyrite FeS₂ and goethite FeO(OH) as independent minerals and also occurs as substitution within dolomite Ca(Mg, Fe)(CO₃)₂. Aluminum is mostly hosted in muscovite KAl₂(AlSi₃O₁₀)(OH)₂ and also found in apatite and calcite in the form of isomorphism or adsorption. The six minerals are all fine-grained, among which pyrite and goethite have similar content changes at different grain sizes and both of
them tend to be enriched in larger particles. Pyrite is mainly intergrown with calcite and biotite and also included in muscovite and apatite with a large proportion. The other four minerals (goethite, dolomite, muscovite and calcite) mostly form intergrowth with apatite. Apatite is mainly intergrown with quartz and calcite. Among the six minerals, the liberations of apatite and dolomite are higher, while the liberated calcite and goethite are less.

The removal of pyrite, goethite, dolomite, muscovite and calcite in the ore is the key to reduce the contents of Fe$_2$O$_3$ and Al$_2$O$_3$. In the subsequent beneficiation, the ore must be fully ground. Most of pyrite can be removed from beneficiation together with calcite and muscovite that contain aluminum and magnetic separation can also be considered to remove part of iron in the ore except flotation. Goethite, dolomite, muscovite and calcite are closely intergrown with apatite in fine grain size, therefore, they are difficult to be separated during beneficiation and the separation cost is high. Since different elements in the same mineral are difficult to separate by flotation, leaching can be considered to remove aluminum from apatite.

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